Comets and the Origin and Evolution of Life

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Comets and the Origin and Evolution of Life

Second Edition

With 65 Figures Including 13 Color Figures

Springer

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This volume is dedicated to the memory of
Juan Oró (1923–2004)
and
Carl Sagan (1934–96),
two pioneers in the study of comets and the origins of life.

Picture by Susan Magnolia Houge, 1991. ©The University of Wisconsin System.

Preface

The original volume of *Comets and the Origin and Evolution of Life* was published in 1997 as the product of a conference held on those topics in Eau Claire, WI. The timing of the conference seemed particularly opportune in light of the recent (1986) encounter of the *Giotto* and VEGA spacecraft with Comet Halley, recent improvements in the chemical analysis of interplanetary dust particles (IDPs) and chemical models of organic synthesis in meteorites and comets. In addition, the prospect of new data from spacecraft such as NASA's Comet Rendezvous/Asteroid Flyby mission (CRAF) and the joint ESA/NASA *Rosetta* mission promised exciting progress in our understanding of the nature of comets and their organic materials.

In the 9 years since the publication of the original volume, great progress has been made in this dynamic field. Signature events include the detailed observations of Comet Hyakutake in 1996 and Comet Hale-Bopp in 1997, and new spacecraft encounters with comets: Deep Space 1 with Comet Borrelly in 2001, *Stardust* with Comet Wild 2 in 2004 (with coma samples to be returned to Earth in 2006), and *Deep Impact* with Comet Tempel 1 in 2005. There have also been disappointments: the CRAF mission was canceled, NASA's CONTOUR mission was lost shortly after launch in 2002, and the much-delayed *Rosetta* mission (with mission capabilities now descoped from sample return to Earth to in situ analysis of Comet Churyumov–Gerasimenko in 2014). But the editors agreed with the urging of our publishers that it was now an opportune time to update and rework the original 1997 volume.

As in the original volume, we review the history of our study of comets and the origin of life while describing the current state of the field. Oró, Lazcano, and Ehrenfreund review the historical development of the key idea of this book and its predecessor that comets have played an important role in the origins of life by introducing vital prebiotic organic materials at a very early stage in Earth's history. It seems very likely now that the accumulation of the organic inventory of the Earth was likely a mix of exogenic organics with those endogenically synthesized in the early atmosphere or, perhaps, in other terrestrial or deep-sea locations. Delsemme (in an updated version of an earlier chapter) estimates the volatile inventory brought to the early Earth during its formation by cometary impact.

An important fraction of cometary material has been delivered to the Earth in the form of dust; perhaps the majority of the organic cometary material has been delivered in this way. The analysis of Antarctic Micrometeorites (AMMs), described in detail by Maurette, may provide important information on this cometary material. At the time of publication, however, a conclusive link between AMMs and comets remains to be made.

While less dramatic than spacecraft missions, the continuing progress in discovering complex organic macromolecules in comets, protostars, and interstellar clouds has been spectacular since the publication of the first book. Huebner and Snyder review this active field, in particular, focusing on the discovery of many different organic molecules in the active chemical environments of the hot molecular cores of star forming regions (HMCs). Because synthesis can occur in HMCs at much faster rates than in cold interstellar clouds, they are of particular importance for the study of the organic molecules inside comets.

The inevitable increase in computational power in the last decade has allowed numerical simulations of comet impacts to have increased spatial and temporal resolution. Pierazzo and Chyba present the results of recent simulations that model organic delivery to Mars, Europa, and the Moon, in addition to the Earth. As reported in the previous volume impact shocks, although high, do allow approximately 10% of the incoming organic material to survive the impact process – although many uncertainties in such modeling remain, especially with the applicability of high-temperature pyrolysis data. This survivability is particularly high in the case of oblique impacts. On Mars, with its lower escape speed, higher survivability fractions are possible.

The chapter by Chyba and Hand substantially updates its predecessor chapter in the 1997 volume, coauthored by Chyba and the late Carl Sagan. This chapter places the issue of impact delivery of organics by comets in the broad context of the history of the Heavy Bombardment and the very early history of the Earth. If both exogenous and endogenous sources of organics were present on the early Earth, it is of importance to attempt to compare the amounts of organics produced from either source. (Note that exogenous sources also include the synthesis of organics by impact shock and dust delivery as well as impact delivery.) Although such attempts are necessarily incomplete and limited by necessary assumptions, it seems as though atmospheric UV photolysis and delivery of IDPs probably dominated the origins of organics on the early Earth in roughly equal proportion, with other sources (e.g., hydrothermal vents and impact shocks) playing a smaller quantitative role.

The original volume of *Comets and the Origin and Evolution of Life* also considered the role that comets and asteroids played in the destruction, or frustration, of life on Earth. In the first of three chapters linked by this theme, Zahnle and Sleep analyze the conditions under which life appeared on the Earth. These conditions were shaped by the end of the Heavy Bombardment, and the accompanying shocks and heating events, leading to rock vapor atmospheres with ocean-vaporizing consequences that would have persisted for months to millenia after each large impact. In a companion to the impact delivery analyses of Pierazzo and Chyba, Zahnle and Sleep consider the sterilizing aspect of such events on early Mars as well as on the Earth.

The geological history of the early Earth is preserved only in a few locations on the Earth. Two of them are the Pilbara craton in Western Australia and the Kaapvaal craton in southern Africa. Glikson presents the current results of detailed explorations of both features with a focus on the identification of signatures of events from the early Precambrian. Among the exciting discoveries from this process are the apparent intermittent (perhaps because of impact sterilization events) appearance of stromatolites and possible connections between early impacts and hydrothermal vent activity and iron-rich sediments that may be associated with postimpact volcanism.

In the final chapter liked with the theme of impact destruction of life, Morrison reviews the contemporary hazard of comet impacts. While a significant effort has been made to identify near-Earth asteroids that may pose an impact threat to our civilization, identifying such threats from the comet population (which mostly resides in the outer solar system) is much more difficult. A perpetual survey will be required for such objects. If a comet is identified on an orbit that will likely result in an impact, we have to consider the possibility that a poorly determined orbit may produce a “false alarm.” Finally, the orbital velocities of comets, which are much higher than near-Earth asteroids, present significant problems with interception and orbit change.

If comet nuclei have a significant organic component, how likely is it that, in addition, they may have once contained liquid water? Podolak and Prialnik examine the role that intense internal heating from radioactive ^{26}Al may have played in creating temporary ($\sim 10^5$ y) liquid water environments inside comets of >10 km radius.

Kissel and Krueger, in two concluding chapters, review the history and future of spacecraft missions to comets and the chemistry of interstellar and cometary dust. There are much exciting spacecraft data still to be gathered. The year 2006 will see the recovery of comet dust from the *Stardust* spacecraft and in 2014 *Philae*, the lander portion of *Rosetta*, will make the first soft-landing on a comet nucleus.

In the final chapter, Krueger and Kissel present the results of the analysis of dust from Comet Wild 2, using the CIDA instrument on the *Stardust* spacecraft. The results are compared with a scenario for the synthesis of organic material in cometary dust.

This new volume has taken a long time to compile. The editors decided early in the process of preparation that, given the dynamic nature of this field, a limited rewrite of the previous edition would not suffice. The reader will notice a diversity of views and approaches in the chapters of the book. The editors felt that such a rapidly developing field is best served by conveying differences in ideas, and chose not to impose consensus on the authors. We hope that this book encapsulates the excitement of the study of comets and the origins of life and gives some picture of the great developments in knowledge that surely lie ahead.

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May 2006

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Comets and the Origin and Evolution of Life

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Summary. It is likely that a combination of exogenous and endogenous sources contributed to the synthesis and accumulation of the building blocks of life on the early Earth. It may even have taken several starts before life surpassed the less than ideal conditions at the surface. The importance of comets for the origin of life on the Earth has been strongly advocated for several decades. We review the historical development of this idea, the collisional history of the early solar system, and the role of comets in delivering a large fraction of volatiles and intact carbon compounds onto the early planets.

1.1 Introduction

Did comets play a role in the origin and early evolution of life on the Earth? This possibility, which was suggested independently at least twice during the past century (Chamberlin and Chamberlin, 1908; Oró, 1961), has received considerable attention in the past decade, and has been transformed into a highly interdisciplinary field that includes suggestions on the possibility that cometary impacts may have led to several major biological extinctions (Thomas, 1992). To a considerable extent, this renewed interest in the part that comets and other volatile-rich minor bodies may have played in the origin and evolution of life is one of the outcomes of the space exploration programs, which have provided striking images of the cratered surfaces of planets and their satellites.

A number of discoveries and hypotheses that have also reinforced the interest in this issue include (a) the development of inhomogeneous accretion models for the formation of the Earth (Wetherill, 1990), and the single-impact theory of the origin of the Earth–Moon system (Cameron and Benz, 1989), both of which predict a volatile-depleted young Earth; (b) the ongoing debates on the detailed chemical composition of the prebiotic terrestrial atmosphere (Miller and Lazcano 2002, Kasting and Catling, 2003); (c) the spectrometric observations of comet Halley obtained from Vega and Giotto missions, which

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suggest that many different types of cyclic and acyclic organic compounds may be present in cometary nuclei (Kissel and Krueger, 1987); (d) the possibility that the Cretaceous–Tertiary (K/T) extinction was caused by a large meteorite (Alvarez et al., 1980) or a comet (Davis et al., 1984); and (e) the detection of extraterrestrial nonproteinic amino acids near the K/T 65 million year old boundary, which may be of ultimate cometary origin (Zhao and Bada, 1989; Zahnle and Grinspoon, 1990).

Since the reconstruction of the physical and chemical characteristics of the primitive environment is fraught with problems and pitfalls, it is difficult to evaluate in detail the cometary contribution to prebiological processes. This has led to rather extreme points of view, which range from claims that bacteria and viruses originating in the interstellar medium pass from comets to the Earth (Hoyle and Wickramasinghe, 1984; Ponce de Leon and Lazcano, 2003) to a sobering challenge of the idea that the input of extraterrestrial organic molecules and volatiles played a major part in the origin of terrestrial life (Miller, 1991a, b). As argued throughout this volume, the role that comets may have played in prebiotic and biological evolution probably is important.

As summarized in this introductory chapter, a widely held idea supported by different independent estimates is that cometary impacts represented a rich veneer of volatiles during the early stages of the Earth's history. As the solar system aged, such catastrophic events became increasingly rare, but nonetheless they may have had dramatic implications for the evolution of the biosphere (Steel, 1997), and may represent a potential threat for our own species (Morrison, 1997). The purpose of this chapter is to review the different (and sometimes conflicting) hypothesis on the role of comets in the origin and evolution of life, and to provide a brief summary of the historical background that led to the development of these different ideas.

1.2 Comets and the Origin on Life: An Idea with a Long History

There is an old scientific tradition linking cometary phenomena with the appearance of life. Prompted and funded by Edmund Halley, Isaac Newton published in 1686 his *Principia*, a book that represents a major breakthrough in the development of Western thought. But not even the grave and pompous Sir Isaac, for all his love for mathematical accuracy, was immune to the appeal of popular beliefs, even if they had not been experimentally proven. As summarized by Oparin (1938), more than once Newton expressed his conviction that cometary emanations could lead to the spontaneous generation of plants – a phenomenon neither he nor Halley had the chance to corroborate when the latter's comet returned to perihelion in 1795.

A hundred years later the young field of evolutionary biology faced a major crisis. In 1859, Charles Darwin published the first edition of *The Origin of Species*, but that very same year Louis Pasteur began the experiments that would eventually lead to the discredit of the idea of spontaneous generation, the mechanism implicitly advocated by most 19th-century scientists to explain the emergence of primary forms of life. As Lord Kelvin wrote, "the impossibility of spontaneous generation at any time whatever must be considered as firmly established as the law of universal gravitation." It was not easy to support the concepts of natural selection and common ancestry of all living beings in the absence of a secular explanation for the origin of life – but comets and meteorites came to the rescue. As an attempt to find a way out of this scientific cul de sac, the German physiologist Hermann von Helmholtz (1871) wrote that "who could say whether the comets and meteors which swarm everywhere through space, may not scatter germs wherever a new world has reached the stage in which it is a suitable place for organic beings."

Von Helmholtz's attempts to revive the old idea of panspermia were supported by other distinguished scientists, including Lord Kelvin and Svante Arrhenius. At the beginnings of the 20th-century this hypothesis joined the large list of explanations that were being developed to explain the origin and early evolution of life on the Earth, but not everyone was amused with it (Farley, 1977; Kamminga, 1988; Lazcano, 1992a, b). In 1911, the American geologist Thomas C. Chamberlin wrote against the increasing infatuation of some of his contemporaries with the idea that spores driven by light pressure could travel across the Universe, transporting life from planet to planet (Chamberlin, 1911). Chamberlin was no newcomer to the origin of life issue. A few years before he had published, with his son and colleague Rollin T. Chamberlin, an insightful paper titled "Early terrestrial conditions that may have favored organic synthesis." In their article, the Chamberlins suggested that "planetesimals," i.e., the small-sized bodies from which the planets were formed, may have represented a significant source of organic compounds for the primitive Earth, influencing both synthesis and biological evolution (Chamberlin and Chamberlin, 1908).

What was the driving force behind pioneering ideas of the Chamberlin father-and-son team? The senior Chamberlin studies on glaciations had led him to recognize several different early ice ages (Chamberlin, 1893, 1894, 1896; Alden, 1929) and, eventually, to the rejection of the widely held Laplacian nebular theory (MacMillan, 1929; Fenton and Fenton, 1952). According to the Laplacian orthodoxy, the Earth had originated as a molten hot sphere surrounded with a dense CO_2-rich primordial atmosphere. As the Earth grew older and cooler, the atmosphere became less thick and less moist, leading to a progressive cooling of the environment and to the appearance of longer winters that eventually culminated in an ice age. However, T.C. Chamberlin had found geological evidence of long-term climate fluctuations, i.e., of an alternative periods of warmth and coolness, and this discovery could not be reconciled with the idea of progressively cooling climates implied by Laplace's theory. Chamberlin was forced to look for other explanations (Fenton and Fenton, 1952).

With the help of the American astronomer Forest R. Moulton, T.C. Chamberlin began working on an alternative hypothesis, according to which the young, eruptive Sun had been approached by a smaller star with drew huge tides of solar matter, which eventually condensed into small, organic-rich solid bodies called planetesimals. According to this idea, which was developed independently by James Jeans, the cooling of this solar ejecta eventually led to the formation of a small swarm of small, cold bodies from which the Earth accreted (Moulton and Chamberlin, 1900; Chamberlin, 1904).

The paper that T.C. Chamberlin coauthored with his son in 1908 was the natural outcome of his views on the origin of the Earth. The presence of meteoritic organic compounds had been firmly established since the mid-nineteenth century, when Jöns Jacob Berzelius analyzed the Alais meteorite in 1834, a carbonaceous C1 chondrite, which fell in Alais, France, in 1806, and also when F. Wöhler found organic matter in the Kaba meteorite, a C_2 carbonaceous chondrite (Berzelius, 1834; Wöhler, 1858; Wöhler and Hörnes, 1859). The Chamberlins were obviously well acquainted with such discoveries, and in a bold stroke of chemical insight, they incorporated them in their paper. “The planetesimals are assumed to have contained carbon, sulphur, phosphorus and all other elements found in organic matter,” they argued in a qualitative description that predates contemporary models of the primitive Earth, “and as they impinged more or less violently upon the surface formed of previous accessions of similar matter, there should have been generated various compounds of these elements,” and added that his process would generate “hydrocarbons, ammonia, hydrogen phosphide, and hydrogen sulphide gases mingled with the ordinary gases carried by the planetesimal furnishing rather remarkable conditions for interactions and combinations, among which unusual synthesis would not be improbable.”

This remarkable proposal went unnoticed by those concerned at the time with the study of the origins of life. The Chamberlins had written their paper as part of a larger attempt to understand the origin of the solar system, but at that time very few scientists saw a direct, causal relationship between the Earth’s primitive environment and the origin of life. In fact, by then the nonbiological synthesis of sugars (Butlerow, 1861) and of amino acids (Löb, 1913) had already been reported, but these experiments were not considered a simulation of the early Earth (Bada and Lazcano, 2003). Since it was generally assumed that the first living beings had been autotrophic, plant-like organisms, neither these abiotic synthesis nor an extraterrestrial source of organic material appeared to be a prerequisite for the origin of life. As the Chamberlins themselves wrote

> ... the purpose of this paper is not to meet a geologic necessity, but merely to consider those conditions in the early history of the globe which may be thought to have been specially favorable to organic synthesis, irrespective of the question whether the natural evolution

> of life was wholly dependent upon them or was merely facilitated by them. (Chamberlin and Chamberlin, 1908)

In spite of their geological insight and deep comprehension of evolutionary theory, their ideas soon sank into an 80-year period of scientific oblivion.

1.3 Chemical Evolution of Cometary Nuclei

Nonetheless, comets kept a place in the modern theory of the origins of life. Comets are rich in water and carbon, two key constituents of terrestrial life. Moreover, as realized by Oró (1961) over 40 years ago, they could bring to the Earth reactive C-bearing molecules that might assemble to form amino-acids, purine and pyrimidine bases, and sugars, i.e., the basic building blocks of proteins and nucleic acids. The Halley fly-by mission in 1986 and the appearance of two unusually bright comets in the past century, Hale-Bopp and Hyakutake, have revolutionized our insights into cometary chemistry. Mass spectrometers on board the Vega 1 and 2 and Giotto spacecraft measured *in situ* the chemical composition of cometary grains in comet Halley (Fomenkova 1999, Kissel and Krueger, 1987). Approximately 5,000 grains have been collected, with masses from 5×10^{-17} to 5×10^{-12} g (and sizes from a few hundreds of mm to a few mm). An important discovery of this cometary fly-by mission was the so-called "CHON particles," containing mainly C, H, O, N atoms that are interspersed with silicates on the submicron scale (Jessberger et al., 1988). More than 70% of the dust grains were composed of a mixture of organic and refractory material, the rest of the grains did not contain organic material. Although key prebiotic compounds have been suggested to be present in comet Halley (from measurements of the Giotto and Vega missions, Kissel and Krueger, 1987), they remain highly speculative due to the limited resolution of the mass spectrometers that flew through Halley's coma.

Cometary nuclei are a highly porous agglomerations of grains of ice and dust and they appear stratified in density, porosity, ice phases, and strength (Prialnik 2004). Their composition can be divided into an ice phase dominated by water ice (∼50%), silicates (∼25%), organic refractory material (∼25%), and small carbonaceous molecules (Greenberg, 1998). We can obtain indirect knowledge only on the composition of the cometary nucleus by measuring gases observed in cometary comae that originate from the nuclear ice. Coma molecules can either sublime directly from the nucleus itself or be formed in the coma. They may also appear throughout the coma from an "extended" source, probably because of the decomposition of large organic particles or molecules.

Comet Hale-Bopp and Hyakutake have been observed extensively over a large range of the electromagnetic spectrum. For a most recent discussion on cometary volatiles and coma chemistry the readers are referred to Irvine et al. (2000), Crovisier (2004), Bockelee-Morvan et al. (2004), and Rodgers and Charnley (2004). Molecular ices and the gases released upon sublimation, silicate dust, and solid state carbonaceous materials are the major components of dusty cometary comae that can be studied by astronomical observations in combination with laboratory simulations (Rodgers and Charnley, 2004, Hanner and Bradley, 2004, Colangeli et al., 2004). More than 25 molecules have been identified in the coma. Their abundances in percent relative to water molecules are listed in Table 1.1.

The inventory of cometary species is certainly not yet complete in the range 0.01–1%. Many small reactive molecules important in prebiotic aqueous chemistry are detected: H_2O, CO_2, formaldehyde (H_2CO), ammonia (NH_3), hydrogen cyanide (HCN), acetonitrile (CH_3CN), isocyanic acid (HNCO) and hydrogen sulfide (H_2S). The most complex species identified to date are acetaldehyde (CH_3CHO), methyl formate ($HCOOCH_3$), and formamide (NH_2CHO). Glycine, the simplest amino acid, has not yet been detected in comets; the present upper detection limit is 0.5%. Given the relative high abundance of chemical precursors used in the laboratory synthesis of amino acids, the absence of detectable levels of these biochemical compounds in comets is surprising. However, as argued elsewhere (Oró and Mills, 1989), the final steps of abiotic formation of amino acids require a liquid phase, as in the Strecker-cyanohydrin synthesis (Miller, 1957). If this is the case, only minor amounts of amino acids can be predicted to be present in comets. Interstellar glycine has been recently reported and is likely formed through gas–grain reaction pathways in dense clouds (Kuan et al., 2003).

Apart from a few volatiles measured in the cometary coma, our knowledge on bulk carbonaceous material of comets is rather limited. IR observations of dusty comae ubiquitiously detect a strong near-IR featureless thermal emission that is well-fitted by amorphous carbon. The detection of a polycyclic aromatic hydrocarbons (PAH), phenantrene ($C_{14}H_{10}$), has also been suggested in Halley on the basis of UV spectroscopic data (Moreels et al., 1994). However, no PAHs have been detected in the Infrared Space Observatory (ISO) infrared spectra of C/1995 O1 Hale-Bopp (Crovisier 1997/99), which were taken at larger heliocentric distance. Comet Hale-Bopp has a strong distributed source of CO within the heliocentric range ≤ 1.5 AU, i.e., only 50% of the CO originates from the nucleus (DiSanti et al., 2001). The other 50% of the CO may from the desorption of organic components of the dust. A possible candidate for distributed CO, polyoxymethylene (POM), that is a polymer of formaldehyde was suggested (Boehnhardt et al., 1990, Cottin et al., 2001, 2004).

In the ISM, the distribution of carbon is still an unsolved question. In order to understand the C fraction in the cometary bulk material, we should look into the interstellar precursor material. A large fraction (>50%) of the cosmic carbon is unaccounted for in the interstellar medium. Laboratory simulations in combination with interstellar observations argue that this missing carbon is incorporated into solid state macromolecular (Ehrenfreund and Charnley, 2000; Mennella et al., 1998, Colangeli et al., 2004). The same predominance of

Table 1.1. Molecular abundances of ices for comets Hyakutake and Hale-Bopp (in % with respect to water ice) as deduced from observations of the gas phase coma (taken from Ehrenfreund et al., 2002). The limits on NaCl and NaOH are still uncertain.

Molecule	Hyakutake	Hale-Bopp	Notes
H_2O	100	100	
H_2O_2	<0.04	–	
CO	6–30	20	[a]
CO_2	<7	6	[b]
CH_4	0.7	0.6	
C_2H_2	0.5	0.1	
C_2H_6	0.4	0.1	
CH_3C_2H	–	<0.045	
CH_3OH	2	2.4	
H_2CO	0.2–1	1.1	[a]
HCOOH	–	0.08	
$HCOOCH_3$	–	0.08	
CH_3CHO	–	0.02	
H_2CCO	–	<0.032	
C_2H_5OH	–	<0.05	
CH_3OCH_3	–	<0.45	
NH_3	0.5	0.7	
HCN	0.1	0.25	
HNCO	0.07	0.06	
HNC	0.01	0.04	[a]
CH_3CN	0.01	0.02	
HC_3N	–	0.02	
NH_2CHO	–	0.01	
Glycine	–	<0.5	
CH_2NH	–	<0.032	
HC_5N	–	<0.003	
H2S	0.8	1.5	
OCS	0.1	0.3	[a]
SO	0.1	0.2–0.8	[c]
CS_2	0.1	0.2	
SO_2	–	0.1	
H_2CS	–	0.02	
S_2	0.005	–	
NaCl	–	<0.0008	
NaOH	–	<0.0003	

[a] Extended source - the abundance is model dependent.

[b] Abundance deduced from CS.

[c] Was measured 20% at 2.9 AU by the ISO satellite.

macromolecular carbon is observed in carbonaceous meteorites, where 80% of the carbon are incorporated in such a form (Gardinier et al., 2000). Together with the Halley fly-by data, this strongly suggests that a large macromolecular carbonaceous fraction can also be anticipated in comets, which may be identified by comet rendezvous or sample return missions.

Our knowledge on the cometary mineral composition, in particular the nature of silicate particles, has strongly progressed in the last decade because of a synergy of infrared observations and laboratory data (Wooden, 2002). Laboratory spectra of olivines, pyroxenes, and carbonaceous particles are combined to match cometary spectra. As discussed in Hanner and Bradley (2004), IR spectra of comets and laboratory studies of cometary interplanetary dust particles show that silicates in comets are dominated by two minerals – olivine and pyroxene or $(\mathrm{Mg}_y,\mathrm{Fe}_{(1-y)2})\mathrm{SiO}_4$ and $(\mathrm{Mg}_x,\mathrm{Fe}_{(1-x)})\mathrm{SiO}_3$ – and are in two forms, amorphous and crystalline (Colangeli et al., 2004). The current presence of crystalline silicates is a major puzzle when trying to link cometary and interstellar matter. Studying the silicate mineralogy and crystallinity probes interstellar and nebular processes affecting silicate dust grains prior to their incorporation into comets (Hanner et al., 1996). The current consensus is that cometary amorphous silicates are of probable interstellar origin while crystalline silicates are of probable nebular origin (Hanner and Bradley, 2004; Wooden, 2002). The presence of silicate crystals in comets implies mixing of high-temperature and low-temperature materials in the comet-forming zone and that processed nebular materials were incorporated with volatile-rich icy material.

A comparison with the inventory of interstellar ices, as well as with the gases found in dark molecular clouds and in regions of massive and low-mass star formation, suggests a direct link. However, there are differences in the relative abundances of some cometary species when compared to their interstellar values (Ehrenfreund et al., 2004). Thus, there is circumstantial evidence for processing of the precursor interstellar volatiles; the location, epoch, and source of this processing are yet to be determined. Comets are a mixture of interstellar and nebular components.

1.4 The Collisional History of the Early Solar System

It is generally accepted that the Earth was formed approximately 4.6×10^9 years ago as a result of the gravitational condensation of the solar nebula, a viscous disk of gas and dust circling the protosun. In spite of the many uncertainties haunting current descriptions of the Earth's formation, it is agreed that our planet was formed in a region of the solar nebula from solid material largely devoid of volatiles. The Earth's core formation is constrained by Hf isotope measurements to within 30 million years of the formation of the solar system. Radiometric dating also suggests that the Moon-forming impact occurred within this temporal window (Halliday, 2000). The majority of planetesimals that formed Earth were situated within a few AU, and these may have been relatively water-poor. Larger, water-rich planetesimals located further from the Sun (>2 AU) may have also been incorporated into the agglomerating Earth.

Neon and argon in the atmosphere today are grossly depleted in comparison with solar and cosmic abundances. This might imply the loss of a large fraction of the volatile component of the planet in early history. The Sun's luminosity increases with time, affecting the surface temperature of the planets. 4.6×10^9 years ago, our Sun was approximately 30% less bright; consequently, the Earth's surface temperature might have been colder. In the absence of greenhouse gases (such as CO_2, CH_4) in the Earth atmosphere water oceans would have frozen during this time (Kasting and Catling, 2003). Differentiation of the planet's interior may have occurred rapidly, segregating most of the iron into the Earth's core and leaving behind a more oxidized mantle. Volcanic degassing of this mantle material would have produced a relatively neutral (nonreducing) atmosphere containing water, carbon dioxide, and nitrogen (Selsis, 2004). Prebiotic chemists, however, lean toward more reducing conditions ($CH_4 + N_2$, $NH_3 + H_2O$, or $CO_2 + H_2 + N_2$), under which the abiotic syntheses of amino acids, purines, pyrimidines, and other organic compounds are very efficient. As of today, there is no agreement on the composition of the primitive atmosphere.

Stabilization of the solar system required the "clean-out" of the remaining planetesimals that were not incorporated in planets. Part of this material was ejected in the outer edges of the solar system or far beyond the solar system. In the early history of the solar system many of those planetesimals bombarded the young planets. This heavy bombardment phase lasted about 700 million years. The vestiges of the intense bombardment stage are imprinted in the cratered surfaces of planets and their satellites. Although only three probable impact craters dating from Precambrian times have survived (Grieve and Robertson, 1979), the Earth was obviously not spared from the collisional process that characterized the early history of our solar system, and in which comets may have played a major role (Chyba and Sagan, 1997). It has been argued that the observed terrestrial abundances of water and the so-called biogenic elements, i.e., C, H, O, N, S, P, etc., require an exogenous veneer of volatiles.

1.5 A Cometary Origin for the Terrestrial Volatiles?

Six months before the Chamberlin and Chamberlin (1908) paper was published, the Tunguska explosion took place. Neither event had an impact in the ripening of the different theories that were being developed at the time to explain the origins of life. However, although the possibility that the Tunguska object was of cometary nature or not is still a matter of debate (Brown and Hughes, 1977; Kresák, 1978), the original suggestion that cometary collisions may have played a role in the appearance of life on our planet was based on data from the 1908 Siberian explosion (Oró, 1961). This hypothesis was suggested within the framework of Oparin's (1924, 1938) theory on the origins of life, and followed closely the prebiotic synthesis of adenine, amino acids, and other biochemical monomers from HCN (Oró, 1960), a chemical precursor of more complex molecules. It was thus hypothesized that cometary collisions may have represented an important source of volatiles for the primitive Earth, which may have been the precursors for the nonbiological synthesis of biochemical compounds that preceded the first organisms (Oró, 1961).

Based both on Urey's (1957) collisional probability and on the assumption that cometary nuclei had densities in the range of 0.001–0.5 g cm^{-3} and diameters in the range of 1–10 km, Oró (1961) calculated that during its first 2×10^9 years the Earth had accreted up to 2×10^{18} g of cometary material, which would lead to localized primitive environments in which the high concentrations of chemical precursors facilitated prebiotic synthesis. Other estimates of cometary material trapped by the Earth have been made for different periods of time and under widely different assumptions (Table 1.2). For instance, Whipple (1976) calculated that during the late accretion period our planet captured 10^{25-26} g of cometary material from a short-lived (10^8 years) cometary nebula of mass 10^{29} g, located within Jupiter's orbit (Table 1.2). According to these figures, the secondary atmospheres of Mars, Venus, and the Earth may have accumulated entirely from comets that replenished the gases and volatile compounds lost during the accretion period of these planets (Whipple, 1976). More conservative estimates have been made for this same period of time for our planet, including calculations by Sill and Wilkening (1978), who suggested that during the heavy-bombardment phase of the solar system, the Earth acquired approximately 10^{21} g of cometary material rich in clathrates and other volatiles (Table 1.2). Conservative estimates based on the lower D/H limit observed in water, extracted from meteorites, i.e., $120 \pm 26 \times 10^{-6}$, indicate that 15% of the oceans have been supplied by comets (Ehrenfreund et al., 2002).

An attempt to update Oró's (1961) original calculations by assuming a cometary reservoir of 10^9 random parabolic comets (Everhart, 1969), each of which followed the absolute magnitude–mass relationship (Allen, 1973), led to an estimate that during its first 2×10^9 years the Earth captured 10^{21} g of cometary material. The use of Wetherill's (1975) collisional probability tables to account for the higher impact rate of the early solar system increased this figure a hundred-fold (Table 1.2). In recent years these simple assumptions have been superceded by more complex and detailed models involving a wide range of dynamical parameters, different masses for the Oort cloud, and lunar cratering rates adjusted for the different surface area and gravitational attraction of the planets (Chyba et al., 1990; Chyba and Sagan, 1997). Independent calculations also suggest that carbonaceous chondrites and cometary-derived interplanetary dust particles may have been even more important sources of

Table 1.2. Cometary matter trapped by solar system bodies.

	Trapped cometary matter (g)	Time span	Reference
Venus	4.0×10^{20}	2.0×10^9 years	Lewis (1974)
Moon	2.0×10^{20}	Late-accretion period	Wetherill (1975)
Earth	$2.0 \times 10^{14-18}$	2.0×10^9 years	Oró (1961)
	$1.0 \times 10^{25-26}$	Late-accretion period	Whipple (1976)
	3.5×10^{21}	Late-accretion period	Sill and Wilkening (1978)
	7.0×10^{23}	4.5×10^9 years	Chang (1979)
	2.0×10^{22}	4.5×10^9 years	Pollack and Yung (1980)
	1.0×10^{23}	2.0×10^9 years	Oró et al. (1980)
	$1.0 \times 10^{24-25}$	1.0×10^9 years	Delsemme (1984, 1991)
	$6.0 \times 10^{24-25}$	1.0×10^9 years	Ip and Fernández (1988)
	$1.0 \times 10^{23-26}$	4.5×10^9 years	Chyba et al. (1990)*

*See also Chyba (1991); Chyba and Sagan (1997).

exogenous volatiles than collisions themselves (Anders and Owen, 1977; Anders, 1989; Zahnle and Grinspoon, 1990; Chyba and Sagan, 1992).

Although it is possible that massive comets with high collisional velocities could have eroded as much volatiles as they delivered to the terrestrial planets (Walker, 1986; McKinnon, 1989; Melosh and Vickery, 1989; Hunten, 1993), this phenomenon would not have affected severely the larger worlds of the inner solar system (Chyba, 1990). It is generally accepted that impactors were delivering volatiles and perhaps even some complex organic molecules to the primitive Earth, as a complement of endogenous prebiotic synthesis. The different contributions that comets may have done to the origins of life have been summarized elsewhere (Oró et al., 1995). As argued by Joshua Lederberg (1992), "... I share the idea that cometary fragment infall might account for a substantial part of terrestrial organic matter. This would leave a wider range of possibilities about the primordial chemistry than if we are confined to the early Earth's atmosphere." Current calculations support this eclectic view.

Comets appear to be the best candidates for bridging cosmic phenomena with the origins of life. In fact, comets may be too good. As argued by Miller (1991a,b) and Zhao and Bada (1991), data summarized in Table 1.2 may represent gross overestimates of the cometary influx to the primitive Earth. The idea that comets and meteorites made major contributions of organic material and volatiles to the primitive Earth has been challenged by Miller (1991a, b), who has argued that incoming extraterrestrial organic compounds deposited in the planet would be removed as the hydrosphere underwent periodic $\approx 350°$C passages through hydrothermal submarine vents every 10^7 years. If the rate of volatile influx is increased to compensate for this destructive process, then we are faced with an overabundance of carbon. This has led Miller (1991a, b) to conclude that the amount of extraterrestrial organic material added by comets and meteorites to the primitive Earth was small compared to terrestrial-based synthesis. This criticism is shared by Zhao and Bada (1991), who, on the basis of the concentration of the extraterrestrial amino acids α-amino isobutyric acid (AIB) and racemic isovaline, associated with the K/T boundary clays (Zhao and Bada, 1989), have estimated the efficiency of impact delivery of extraterrestrial organics to the Earth. Their results are not very encouraging: according to their calculations, the estimated concentration of AIB in the primitive oceans would be approximately 2 nM, which suggest that exogenous delivery was an inefficient process when compared to abiotic synthesis occurring on the Earth (Zhao and Bada, 1991).

The efficiency of endogenous prebiotic synthesis is strongly dependent on the reducing state of the primitive atmosphere (Miller and Orgel, 1974). In CH_4-rich primitive atmosphere, the abiotic production of organic matter would have occurred more readily (Miller and Orgel, 1974; Stribling and Miller, 1987), and would have been substantially larger than the exogenous cometary contribution (Miller, 1991a, b; Zhao and Bada, 1991). However, under a CO_2-rich atmosphere the amount of accreted exogenous sources of organic compounds would be comparable to the products of Earth-based, endogenous synthesis (Chyba and Sagan, 1997). Since there is no direct evidence of the composition of the primitive atmosphere, it is difficult to choose between these two opposing points of view. Current model photochemical calculations favor short-lived amounts of prebiotic CH_4, but the actual levels of CO_2 in the primitive atmosphere are still speculative (Kasting, 1993, Kasting and Catling, 2003).

The issue of the relative contribution of endogenous prebiotic sources of organic matter as compared to the cometary contribution is far from solved, and assigning values may be misleading. “Exogenous delivery” refers to the volatiles and organic compounds acquired during the late accretion period, i.e., during the final stages of planetary formation. On the other hand, “endogenous” refers to organic compounds synthesized in the primitive Earth from outgassed volatile precursors injected into the terrestrial paleoatmosphere from the interior, but with an ultimate extraterrestrial origin. It is clear that both cometary collisions (Oró, 1961) and impact shock-waves (Bar-Nun et al., 1970) were more frequent in the primitive Earth and the electric discharges and other free-energy sources also played a major role in the endogenous synthesis of organic compounds (Miller and Urey, 1959). A recent comparision of exogeneously delivered and endogeneously produced organics is summarized in Table 1.3. The primitive Earth may be aptly described by two lines from the roman poet Virgil: “at no other time did more thunderbolts fall in a clear sky nor so often did dread comets blaze” – but additional information on both the thunderbolts and the blazing comets is required to constrain their relative prebiotic significance.”

Table 1.3. Major Sources (in kg/yr) of prebiotic organic compounds in the early Earth.

	kg/year[a]
Terrestrial sources	
UV Photolysis[b]	3×10^8
Electric Discharge[c]	3×10^7
Shocks from impacts[d]	4×10^2
Hydrothermal Vents[e]	1×10^8
Extraterrestrial Sources[f]	
IDPs	2×10^8
Comets	1×10^{11}
Total	10^{11}

Note. From Ehrenfreund et al., 2002, as modified from Chyba and Sagan, 1997.

[a] Assumes intermediate atmosphere, defined as [H2]/[CO_2] = 0.1.

[b] Synthesis of the Miller-Urey type.

[c] Such as that caused by lightning interacting with a volcanic discharge.

[d] An estimate for compounds created from the interaction between infalling objects and the Earth's atmosphere.

[e] Based on present-day estimates for total organic matter in hydrothermal vent effluent.

[f] Conservative estimate based on possible cumulative input calculated assuming flux of 10^{22} kg of cometary material during first Ga (10^9 years) of Earth's history. If comets contain on the order of 15 wt% organic material, and if $\approx$ 10% of this material survives, it will comprise approximately 10^{11} kg year^{-1} average flux via comets during the first 10^9 years.

1.6 Comets and Prebiotic Synthesis

Table 1.2 shows that the flux of organic matter to the Earth via comets and asteroids, averaged over the period of heavy bombardment prior to 3.8 Ga (10^9 year), may have been as high as 10^{11} kg year^{-1} (calculated from data in Chyba et al., 1990, Zahnle and Sleep, 1997, Ehrenfreund et al., 2002). Cometary flux of organic material may overshadow the possible contribution of IDPs, which until recently was perceived as the most efficient mechanism for extraterrestrial delivery (Anders, 1989). This estimate is also larger than the value of 10^{8-10} kg year^{-1}, the best estimate of the terrestrial contribution during that time, assuming that the atmosphere was moderately oxidizing (Chyba and Sagan, 1997).

Despite claims to the contrary, there is no compelling evidence that life may have appeared in comets, or to assume that the emergence of the biosphere was triggered by some unknown substance present only in comets (Bar-Nun et al., 1981; Chyba and Sagan, 1987; Marcus and Olsen, 1991; Oró et al., 1992a, b). However, since the paleontological evidence suggests that accretion period was coeval with the origin and early evolution of life, it is reasonable to ask whether comets may have contributed directly or indirectly to prebiotic synthesis of biochemical compounds.

It has been argued that in some rare cases the soft landing of intact comets or fragments of comets may have occurred (Clark, 1988; Krueger and Kissel, 1989), and the aerodynamic braking and isotropic distribution of the shock energy associated with the collision of small comets may have accumulated relative intact cometary compounds in the Earth's surface (Chyba et al., 1990). However, it is likely that in most cases the transformation of the impactors' kinetic energy into heat would lead to very high temperatures shattering the incoming nuclei and vaporizing and destroying all the organic compounds on board (Oró et al., 1980; Chyba et al., 1990; Thomas and Brookshaw, 1997).

Of course, the large array of amino acids, nitrogen bases, and other organic compounds present in carbonaceous chondrites suggest that a certain amount of the organic molecules present in the nonvolatile fraction of the cometary nuclei could survive collision with the Earth. This conclusion is supported by the discovery of isovaline and of α-amino isobutyric acid, two extraterrestrial amino acids associated with the Danish 65 million years old K/T boundary layer clays (Zhao and Bada, 1989), which shows that incoming organic compounds of biochemical significance can survive a violent impact with the Earth, although the possibility that these amino acids are derived from cometary dust swept up by the Earth prior to and after the collision with a comet has also been suggested (Zahnle and Grinspoon, 1990). It is easier to envisage the survival of simpler compounds: the presence of H_2O, OH, NO, N_2, NH, C_2, CN, CO, and other small carbon-bearing species on the surface of the Sun and of the C_3 and C_5 molecules in hot, circumstellar envelopes (Hinkle et al., 1988; Bernath et al., 1989), shows that these are resilient compounds with string possibilities of surviving a cometary collision and eventually becoming the starting point for further secondary abiotic synthesis (Oró et al., 1992b).

Indeed, it has been suggested that the collisions would produce highly reducing transient atmospheric environments rich in reactive chemical species. Upon quenching to low temperatures due to the subsequent expansion and cooling of the resulting gas ball, chemical recombination would lead to the synthesis of a great variety of organic compounds (Lazcano and Oró, 1991). This possibility has been questioned since theoretical modeling predicts that the rapid chemical destruction of atmospheric CH_4, NH_3, and H_2S and other reduced molecules due to the rapid influx of cometary water (Levine et al., 1980) as well as an oxidation of the cometary carbon due to mixing of gases from a CO_2-rich atmosphere with the vapor plumes of impacting comets (Kasting, 1993; Chyba and Sagan, 1992).

However, the lack of existence of these transient atmospheric environments where abiotic synthesis may have taken place is far from proven. As shown by Barak and Bar-Nun (1975), amino acid abiotic synthesis is feasible in shock-wave tube experiments even in the presence of air and Mukhin et al. (1989) have demonstrated that a number of organic synthesis precursors can be formed using laser-pulse heating of terrestrial rocks and carbonaceous chondrites. These results reinforced the idea that recombination among chemical species formed after the vaporization of volatile-rich impactors would lead to compounds of biochemical significance. These experiments are supported by theoretical studies using the thermochemical model, which predicts efficient synthesis of reduced carbon-bearing compounds during shocking of reactants with the cometary components (McKay et al., 1989).

Using measurements of physical parameters and chemical abundances of Halley's comet, Oberbeck et al. (1989) and Oberbeck and Aggarwal (1992) have argued that during the expansive, cooling stages of such collisional gaseous environments created by the impact of cometary nuclei larger than 150 m, the excited species would recombine and give rise to compounds of biological significance. Cometary collisions may have provided the Earth not only with volatiles but also with an important free-energy source.

1.7 Cometary Collisions and Biological Evolution

The oldest direct evidence for life on the Earth comes from microfossils in stromatolites from coetaneous sedimentary deposits in Pilbara (Australia) and Barberton (S. Africa) dating $3.5 - 3.3 \times 10^9$ years. Indirect evidence based on stable isotope ratios has been used to postulate the existence of life even earlier in the Earth's record (Westall, 2004). For example, low $^{13}C/^{12}C$ ratios in banded iron formations (BIFs) from Greenland might be an indication of life from 3.8×10^9 years ago (Rosing, 1999).

We have reviewed and summarized the evidence, suggesting that comets have contributed to the origins of life. However, it has also been suggested that the intense flux of cometary impactors and other related minor bodies on the primitive Earth may also have created major environmental upheavals that could have delayed or even prevented an earlier appearance of the biosphere. According to this hypothesis, the impact frustration of life was caused by collisions that raised the Earth surface temperature and evaporated the oceans (Maher and Stevenson, 1988; Oberbeck and Fogelman, 1989a, b; Sleep et al., 1989; Zahnle and Sleep, 1997).

Using different assumptions on the lunar cratering record and the size of impactors, Maher and Stevenson (1988) have argued that life emerged and became extinct several times. The arguments presented by Maher and Stevenson (1988) implied the almost absolute unavoidability of life in a planet like the Earth. This is an attractive idea, but far from proven, and fraught with pitfalls. No evidence of such multiple origins is found among extant organisms. Despite some claims on the contrary (Kandler, 1994), the very basic biochemical and genetic unity of life strongly supports the hypothesis of a single origin for all known living beings. Was this common ancestor a heat-loving microbe whose preadaptation to the harsh environmental conditions of deep-sea hydrothermal vents allowed its survival in an early Earth warmed up by cometary impacts to boiling temperatures? The hypothesis of totally annihilating collisions is ridden with major problems, which include the lack of detailed calculations of the energy associated with the lunar and terrestrial cratering record, the difficulties involved in computations of the size of the lunar impactors, and the absence of detailed models of the early Earth (Sleep et al., 1989; Chyba, 1990; Zahnle and Sleep, 1997).

The geological record holds no evidence of catastrophic sterilizing event, but it has been suggested that the memory of such intense heating is found in the phylogenetic distribution of hyperthermophily among extant organisms. Recent attempts to isolate thermophilic organisms have been extremely successful, and have led to the characterization of prokaryotes that can live and reproduce in abyssal environments with temperatures as high as 105–110°C (Huber et al., 1989; Gottschal and Prins, 1991; Daniel, 1992; Johnson et al., 2004). Research on extremophiles is important for providing insights on the habitability of places beyond the Earth and the solar system. However, all the available evidence suggests that the most basic questions pertaining to the origin of life relate to much simpler replicating entities, predating by a long (but not necessarily slow) series of evolutionary events the oldest recognizable lineages (presently hyperthermophiles) represented in molecular phylogenies.

As the solar system matured, leftovers from the accretion period became less abundant and the likelihood of giant collisions negligible. Massive collisions may have delayed the origin of life, but their sterilizing effects were not repeated in later times as shown by the continuity of the fossil record since 3.5×10^9 years ago. Once the Precambrian environment became oxidizing (Holland, 1994), a collision would probably lead to an extended destruction of the reduced chemical species present in the cometary nuclei. However, the conversion of the impactor's kinetic energy into heat would cause major upheavals in the terrestrial environment, and could be the explanation underlying several major Phanerozoic extinctions (Steel, 1997).

The possibility that impacts of extraterrestrial bodies with the Earth may influence biological evolution and led to the extinction of different taxa has been discussed in the scientific literature for some time. As summarized by Raup (1986), in 1970, Dewey M. McLaren suggested that the 365-million-year-old mass extinction that marks the end of the Frasnian stage of the Devonian period could have been caused by a giant meteorite. A few years later, a comparison of tektite ages and geological periods led Urey (1973) to argue that the different major extinctions that have taken place in the past 50 million years could have been caused by cometary impacts, but this bold suggestion went unnoticed. It was not until the discovery of iridium anomalies in different parts of the world where Alvarez et al. (1980) hypothesized that a large asteroid or comet collided with our planet and caused the extinctions that marked the end of the dinosaurs 65 million years ago. According to this idea, the end of the Cretaceous period was due to the impact of an extraterrestrial object that threw large amounts of dust into the upper atmosphere for several months, therefore initiating a chain reaction that began with a darkened world and subsequently led to the cessation of photosynthesis, subfreezing temperatures, and soon to the disappearance of many taxa. The possibility of massive poisoning due to the introduction of cometary HCN to the Cretaceous hydrosphere has also been suggested (Hsü, 1980), but dismissed as somewhat unlikely (Thierstein, 1980).

By the end of the Cretaceous period several major taxa were in decline, but the evidence supporting the impact origin of the K/T boundary extinctions has continued to accumulate. It now includes the presence of extraterrestrial amino acids of possible cometary origin associated with the 65-million-year-old clays (Zhao and Bada, 1989; Zahnle and Grinspoon, 1990). The hypothesis that the disappearance of a Cretaceous dinosaur–dominated biota was caused by a massive impact is still prevalent and has gained many adherents. A number of biologists weary of the standard description of gradual evolution based on panselectionist orthodoxy have greeted with enthusiasm the idea that an unexpected event like a collision with an asteroid or a comet could lead to major extinctions (Gould, 1983). Chance may have played a larger role in biological evolution than is usually acknowledged, and comets and meteorites may have been one of its instruments.

The hypothesis of extraterrestrial-induced unpredictable die-outs took a somewhat different turn when the statistical analysis of a large record of marine extinctions over the past 250 million years led Raup and Sepkoski (1984) to the suggestion that mass extinctions appear to be regularly spaced, and occur with a 26-million-year period. Different astronomical explanations have been developed to account for such periodicity, including the possibility that periodic comet showers were triggered by the Sun's oscillation about the galactic plane (Schwartz and James, 1984; Rampino and Stothers, 1984), or by Nemesis, a hypothetical unseen distant solar companion star (Davis et al., 1984; Alvarez and Muller, 1984; Whitmire and Jackson, 1984; Muller, 1985).

No evidence has been found for Nemesis, and the periodical impact extinction hypothesis has been challenged (Kerr, 1985). The issue has been a controversial one (Raup, 1986, 1988), but the fascination in the role that comets may have played in the origin and evolution of life has not diminished. These traveling chemical fossils of the early solar system come from distant times and faraway places, but they have found a place in contemporary evolutionary theory as the chance agents that may have caused major extinctions. Comets and related minor bodies may have altered the course of subsequent biological events, opening the way for the development of other species, including our own (Gould, 1983). As discussed throughout this book, comets may have been a mixed blessing for the biosphere or, as the Spanish-born Roman philosopher Seneca wrote, "when this rare and strangely shaped fire appears everyone wants to know what it is and, forgetting everything else, seeks information about the strange visitor, uncertain whether it is to marveled at or feared" (Barrett, 1978).

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References

Alden, W.C. (1929), Thomas Chrowder Chamberlin's contributions to glacial geology. *Jour. Geol.*, **37**, 293–319.

Allen, C.S. (1973), *Astrophysical Quantities* (The Athlone Press, London).

Alvarez, W. and Muller, R.A. (1984), Evidence from crater ages for periodic impacts on Earth. *Nature*, **308**, 718–720.

Alvarez, L.W., Alvarez, W., Asaro, F., and Michel, H.V. (1980), Extraterrestrial cause for the Cretaceous-Tertiary extinction, *Science*, **208**, 1095–1108.

Anders, E. (1989), Pre-biotic organic matter from comets and asteroids. *Nature*, **342**, 255–257.

Anders, E., and Owen, T. (1977), Mars and Earth: Origin and abundance of volatiles. *Science*, **198**, 453–465.

Aumann, H.H., Gillett, F.C., Beichmann, C.A., de Jong, T., Houck, J.R., Low, F., Neugebauer, G., Walker, R.G. and Wesselius, P. (1984), Discovery of a shell around Alpha Lyrae. *Astrophys. Jour. Lett.*, **278**, L23-L27.

Bada, J.L. And Lazcano, A. (2003) Perceptions of science. Prebiotic soup- revisiting the Miller experiment. *Science*, **300**, 745–746.

Bailey, M.E., Clube, S.V.M., and Napier, W.M. (1990), *The Origin of Comets* (Pergamon Press, Oxford), p. 452.

Barak, I. And Bar-Nun, A. (1975), The mechanism of amino acid synthesis by high temperature shock waves. *Origins Life*, **6**, 483–506.

Bar-Nun, A., Bar-Nun, N., Bauer, S.H., and Sagan C. (1970), Shock synthesis of amino acids in simulated primitive environments. *Science*, **168**, 470–473.

Bar-Nun, A., Lazcano-Araujo, A., and Oró, J. (1981), could life have originated in cometary nuclei? *Origins Life*, **11**, 387–394.

Barrett, A.A. (1978), *J. Roy. Soc. Can.*, **72**, 81.

Benz, W., Slattery, W.L., and Cameron, A.G.W. (1986), The origin of the Moon and the single impact hypothesis. I. *Icarus*, **66**, 515–535.

Benz, W., Slattery, W.L., and Cameron, A.G.W. (1987), The origin of the Moon and the single impact hypothesis. II. *Icarus*, **71**, 30–45.

Bernath, P.F., Hinkle, K.H., and Keady, J.J. (1989), Detection of C5 in the circumstellar shell of ICR+10216. *Science*, **244**, 562–564.

Berzelius, J.J. (1834), Über Meteorsteine, 4. Meteorstein von Alais. *Ann. Phys. Chem.*, **33**, 113–123.

Beust, H., Lagrange-Henri, A.M., Vidal-Majdar, A., and Ferlet, R. (1990). The β Pictoris circumstellar disk X. Numerical simulations of infalling evaporating bodies. *Astron. Astrophys.*, **236**, 202–216.

Bockelee-Morvan D., Crovisier J., Mumma M. and Weaver H. (2004), The Volatile Composition of Comets. In *Comets II*, M. Festou, H.U. Keller, and H.A. Weaver (eds.), Univ. of Arizona, Tucson.

Boehnhardt H., Fechtig H., and Vanysek V. (1990), The possible role of organic polymers in the structure and fragmentation of dust in the coma of comet P/Halley. *Astron. Astrophys.*, **231**, 543–547.

Briggs, R., Ertem, G., Ferris, J.P., Greenberg, J.M., McCain, P.J., Mendoza-Gómez, X.C., and Schutte, W. (1992), Comet Halley as an aggregate of interstellar dust and further evidence for the photochemical formation of organics in the interstellar medium. *Origins Life*, **22**, 287–307.

Brown, H. (1952), Rare gases and the formation of the Earth's atmosphere. In G.H. Kuiper (ed.), *The Atmospheres of the Earth and Planets* (Chicago University Press, Chicago), pp. 258–266.

Brown, J.C. and Hughes, D.W. (1977), Tunguska's comet and non-thermal ^{14}C production in the atmosphere. *Nature*, **268**, 512–514.

Butlerow, A. (1861), Formation sintetique d'une substance sucreé. *Compt. Rend. Acad. Sci.*, **53**, 145–147.

Cameron, A.G.W. (1988), Origin of the solar system. *Annu. Rev. Astron. Astrophys.*, **26**, 441–472.

Cameron, A.G.W. and Benz, W. (1989), Possible scenarios resulting from the giant impact. *Proc. Lunar Planet. Sci. Conf. XX*, 715.

Chamberlin, T.C. (1893), The diversity of the glacial period. *Am. Jour. Sci.*, **45**, 171–200.

Chamberlin, T.C. (1894), Proposed genetic classification of Pleistocene glacial formations. *Jour. Geol.*, **2**, 517–538.

Chamberlin, T.C. (1904), *Fundamental problems of geology.* Carnegie Institution of Washington Yearbook No. 2: 261–270.

Chamberlin, T.C. (1911), The seeding of planets. *Jour. Geol.*, **19**, 175–178.

Chamberlin, T.C. and Chamberlin, R.T. (1908), Early terrestrial conditions that may have favored organic synthesis. *Science*, **28**, 897–910.

Chang, S. (1979), Comets: Cosmic connections with carbonaceous meteorites, interstellar molecules and the origin of life. In M. Neugebauer, D.K. Yeomands, J.C. Brandt and R.W. Hobs (eds.), *Space Missions to Comets* (NASA CP 2089, Washington, DC), pp. 59–111.

Chyba, C.F. (1987), The cometary contribution to the oceans of the primitife Earth. *Nature*, **330**, 632–635.

Chyba, C.F. (1990), Impact delivery and erosion of planetary oceans in the early inner solar system. *Nature*, **343**, 129–133.

Chyba, C.F. (1991), Terrestrial mantle siderophiles and the linear impact record. *Icarus*, **92**, 217–233.

Chyba, C.F. and Sagan, C. (1987), Cometary organics but no evidence for bacteria. *Nature*, **329**, 208.

Chyba, C.F. and Sagan, C. (1992), Endogenous production, exogenous delivery and impact-shock synthesis of organic molecules; an inventory for the origin of life. *Nature*, **355**, 125–132.

Chyba, C.F. and Sagan, C. (1997) Comets as a source of prebiotic organic molecules for the early Earth. In P.J. Thomas, C.F. Chyba, and C.P. McKay (eds), *Comets and the Origin and Evolution of Life.* (Springer-Verlag, New York), pp. 147–174.

Chyba, C.F., Thomas, P.J., Brookshaw, L., and Sagan, C. (1990), Cometary delivery of organic molecules to the early Earth. *Science*, **249**, 366–373.

Chyba, C.F., Thomas, P.J., and Zahnle, K.J. (1993), The 1908 Tunguska explosion: Atmospheric disruption of a stony asteroid. *Nature*, **361**, 40–44.

Clark, B.C. (1988), Primeval procreative comet pond. *Origins Life*, **18**, 209–238.

Colangeli, L., Bar-Nun, A., Brucato, J.R., Hudson, R.L. and Moore, M. (2004), Laboratory Experiments to Study Cometary Physics and Chemistry. In *Comets II*, M. Festou, H.U. Keller, and H.A. Weaver (eds.), Univ. of Arizona, Tucson, pp. 695–718.

Cottin, H., Gazeau, M.C., Benilan, Y.; Raulin, F. (2001), Polyoxymethylene as Parent Molecule for the Formaldehyde Extended Source in Comet Halley. *Astrophys. Journ.* **556**, 417–420.

Cottin, H., Bénilan, Y., Gazeau, M., Raulin, F. (2004), Origin of cometary extended sources from degradation of refractory organics on grains: polyoxymethylene as formaldehyde parent molecule, *Icarus*, **167**, 397–416.

Crovisier J. (1997) published 1999, Infrared Observations Of Volatile Molecules In Comet Hale-Bopp. *Earth, Moon and Planets*, **79**, 125–143.

Crovisier, J. (2004), The Molecular Complexity of Comets, *In Astrobiology: Future Perspectives*, P. Ehrenfreund et al., (eds.), Kluwer Academic Publisher, Dortdrecht.

Daniel, R.M. (1992), Modern life at high temperatures, *Origins Life*, **22**, 33–42.

Davis, M., Hut, P. and Muller, R.A. (1984), Extinction of species by periodic comet showers. *Nature*, **308**, 715–717.

Delsemme, A.H. (1991), Nature and history of the organic compounds in comets: An astrophysical view. In R.L. Newburn, M. Neugebauer, and J. Rahe (eds.), *Comets in the Post-Halley Era*, Vols. I-II (Dordrecht, Boston), pp. 377–427.

Delsemme, A.H. (1992), Cometary origin of carbon, nitrogen and water on the Earth. *Origins Life*, **21**, 279–298.

DiSanti, M.A., Mumma, M.J., Russo, N.D., Magee-Sauer, K. (2001), Carbon Monoxide Production and Excitation in Comet C/1995 O1 (Hale-Bopp): Isolation of Native and Distributed CO Sources. *Icarus*, **153**, 361–390.

Donn, B.D. (1976), *The Study of Comets* (NASA SP-393, Washington DC).

Eberhardt, P., Krankowski, D., Schutte, W., Dolder, U., Lämmerzahl, P., Berthelier, J.J., Woweries, J., Stubbermann, U., Hodges, R.R., Hoffman, J.H. and Illiano, J.M. (1987), The CO and NH_2 abundance in comet P/Halley. *Astron. Astrophys.*, **187**, 481–487.

Ehrenfreund, P., and Charnley, S.B. (2000), Organic Molecules in the Interstellar Medium, Comets, and Meteorites: A Voyage from Dark Clouds to the Early Earth, *Ann. Rev. Astron. Astrophys.*, **38**, 427–483.

Ehrenfreund, P., Irvine, W.M., Becker, L., Blank, J., Colangeli, L., Derenne, S., Despois, D., Dutrey, A., Fraaije, H., Lazcano, A., Owen, T., and Robert, F. (2002), Astrophysical and astrochemical insights into the origin of life, *Repts. Prog. Physics*, **65**, 1427–1487.

Ehrenfreund, P., Charnley, S.B., Wooden, D.H. (2004), From interstellar material to cometary particles and molecules. In *Comets II*, M. Festou, H.U. Keller, and H.A. Weaver (eds.), Univ. of Arizona, Tucson, pp. 115–136.

Encrenaz, T., and Knacke, R. (1991), Carbonaceous Compounds in Comets. In R.L. Newburn, M. Neugebauer and J. Rahe (eds), *Comets in the Post-Halley Era*, Vols I-II (Dordrecht, Boston), pp. 107–137.

Everhart, E. (1969), Close encounters of comets and planets. *Astrophys. Jour.*, **74**, 735–739.

Farley, J. (1977), *The Spontaneous Generation Controversy: From Descartes to Oparin* (John Hopkins University Press, Baltimore).

Fenton, C.L. and Fenton, M.A. (1952), *Giants of Geology* (Doubleday, New York).

Fomenkova M.N. (1999), On the Organic Refractory Component of Cometary Dust. *Space Science Reviews*, **90**, 109–114.

Forterre, P. (1995), Thermoreduction, a hypothesis for the origin of prokaryotes. *C.R. Acad. Sci. Paris*, **318**, 1–8.

Gardinier A., Derenne S., Robert F., Behar F., Largeau C. and Maquet J. (2000), Solid state CP/MAS ^{13}C NMR of the insoluble organic matter of the Orgueil and Murchison meteorites: quantitative study. *Earth Planet Sci. Letters*, **184**, 9–21.

Gottschal, J.C. and Prins, R.A. (1991), Thermophiles: A life at elevated temperatures. *Trends in Ecol. And Evol.*, **6**, 157–161.

Gould, S.J. (1983), *Hen's Teeth and Horse's Toes: Further Reflections in Natural History* (W.W. Norton, New York).

Greenberg, M.J. (1983), Chemical evolution of interstellar dust - a source of prebiotic material? In C. Ponnamperuma (ed.), *Comets and the Origin of Life* (Reidel, Dordrecht), pp. 111–127.

Greenberg, M.J. and Grim, R. (1986) The origin and evolution of cometary nuclei and comet Halley results. In B. Battrick, E.J. Rolfe and R. Reinhard (eds.), *20th ESLAB Symposium on the Exploration of Halley's Comet* (ESA Report SP-250), pp. 255–263.

Greenberg JM. (1998), Making a comet nucleus. *Astron. Astrophys.*, **330**, 375–380.

Grieve, R.A.F. and Robertson, P.B.: (1979), The terrestrial cratering record I. Current status of observations. *Icarus*, **38**, 212–219.

Grün, E., Bar-Nun, A., Benkhoff, J., Bischoff, A., Düren, H., Hellmann, H., Hesselbarth, P., Hsiung, P., Keller, H.U., Klinger, J., Knölker, J., Kochan, H., Kohl, H., Kölzer, G., Krankowsky, D., Lämmerzahl, P., Mauersberger, K., Neukum, G., Oehler, A., Ratke, L., Roessler, K., Schewm, G., Spohn, G., Stöffler, D. and Thiel, K. (1991), Laboratory simulation of cometary processes: Results from first KOSI experiments. In R.L. Newburn, M. Neugebauer, and J. Rahe (eds.), *Comets in the Post-Halley Era*, vols. I-II (Dordrecht, Boston), pp. 277–297.

Halliday, A. (2000), Terrestrial accretion rates and the origin of the Moon, *Earth and Planetary Science Letters*, **176**, 17–30.

Hän, T.M. and Runnegar, B. (1992) Megascopic eukaryotic algae from the 2.1-billion-year-old Negaunee Iron-Formation, Michigan. *Science*, **257**, 232–235.

Hanner M.S. and Bradley J.P. (2004), Chemical composition of Comet Dust. In *Comets II*, M. Festou, H.U. Keller, and H.A. Weaver (eds.), Univ. of Arizona, Tucson, pp. 555–564.

Hanner, M.S., Lynch, D.K., Russell, R.W., Hackwell, J. A., Kellogg, R., and Blaney D. (1996), Mid-Infrared Spectra of Comets P/Borrelly, P/Faye, and P/Schaumasse. *Icarus*, **124**, 344–351.

Hayashi, C., Nakasawa, K. and Nakasawa, Y. (1985), Formation of the solar system. In D.C. Black and M.S. Matthews (eds.), *Protostars and Planets II* (University of Arizona Press, Tucson), pp. 1100–1153.

Hinkle, K.H., Keady, J.J. and Bernath, P.F. (1988), Detection of C_3 in the interstellar shell of IRC+10216. *Science*, **241**, 1319–1320.

Hobbs, L.M., Vidal-Majdar, A., Ferlet, R., Albert, C.E., and Gry, C. (1985), The gaseous component of the disk around Beta Pictoris. *Astrophys. Jour. Lett.*, **293**, L29–L33.

Holland, H.D. (1994), Early Proterozoic atmospheric change. In S. Bengston (ed.), *Early Life on Earth.* Nobel Symposium No. 84, Columbia University Press, New York, pp. 237–244.

Hollis, J.M., Snyder, L.E., Suenram, R.D. and Lovas, F.J. (1980), A search for the lowest energy conformer of interstellar glycine. *Astrophys. Jour.*, **241**, 1001–1006.

Holm, N.G. (1992), Marine hydrothermal systems and the origin of life. *Origins Life*, **22**. Special Issue.

Hong, J.H. and Becker, R.S. (1979), Hydrogen atom initiated chemistry. *J. Mol. Evol.*, **13**, 15–26.

Hoyle, F. and Wickramasinghe, C. (1994), *From Grains to Bacteria* (University College Cardiff Press, Bristol).

Hsü, K.J. (1980), Terrestrial catastrophe caused by cometary impact at the end of Cretaceous. *Nature*, **285**, 201–203.

Huber, R., Kurr, M., Jannasch, H.W., and Stetter, K.O. (1989), A novel group of abyssal methanogenic archaeabacteria (Methanopyrus) growing at 110 °C. *Nature*, **342**, 833–834.

Huebner, W.F. (1987), First polymer in space identified in comet Halley. *Science*, **237**, 628–630.

Hunten, D.M. (1993), Atmospheric evolution of the terrestrial planets. *Science*, **259**, 915–920.

Ibandov, K.I., Rahmonov, A.A. and Bjasso, A.S. (1991). Laboratory simulation of cometary structures. In R.L. Newburn, M.Neugebauer and R. Rahe (eds.), *Comets in the Post-Halley Era*, Vols. I-II (Dordrecht, Boston), pp. 299–311.

Ip, W.H. and Fernández, J.A. (1988), Exchange of condensed matter among the outer and terrestrial protoplanets and the effect on surface impact and atmospheric accretion. *Icarus*, **74**, 47–61.

Irvine, W.M., Leschine, S.N. and Schloerb, F.P. (1980), Thermal history, chemical composition and relatinship of comets to the origin of life, *Nature*, **283**, 748–749.

Irvine, W.M., Schloerb, F.P., Crovisier, J., Fegley, B., Jr., and Mumma, M.J. (2000), Comets: a Link Between Interstellar and Nebular Chemistry, in *Protostars and Planets IV*, V. Mannings, A. Boss and S. Russell (eds.), Tucson: Univ. Arizona Press, pp. 1159–1200.

Jessberger E., Cristoforidis A., and Kissel J. (1988), Aspects of the major element composition of Halley's dust. *Nature*, **332**, 691–695.

Johnson, M.R., Montero, C.I., Conners, S.B., Shockley, K. R., Pysz, M.A., and Kelly, R.M. (2004) Functional genomic-based studies of the microbial ecology of hyperthermophilic micro-organisms. *Biochem. Soc. Trans.*, **32**, 188–192

Joss, P.C. (1974), Are stellar surface heavy-elements abundances systematically enhances? *Astrophys. Jour.*, **191**, 771–774.

Kamminga H. (1988), Historical perspective: the problem of the origin of life in the context of developments in biology. *Origins Life*, **18**, 1–11.

Kandler, O. (1992), Where next with the archaeabacteria? *Biochem. Soc. Symp.*, **58**, 195–207.

Kasting, J.F. (1990), Bolide impacts and the oxidation state of carbon in the Earth's earliest atmosphere. *Origins Life*, **20**, 199–231.

Kasting, J.F. (1993), Earth's earliest atmosphere. *Science*, **259**, 920–926.

Kasting, J. and Catling, D. (2003), Evolution of a Habitable Planet, *Ann. Rev. Astron. Astrophys.*, **41**, 429–463.

Kerr, R.A. (1985), Periodic extinctions and impacts challenged. *Science*, **227**, 1451–1453.

Khare, B.N., Sagan, C., Thompson, W.R., Arakawa, E.T., Suits, F., Callcott, T.A., Williams, M.W., Shrader, S., Ogina, H., Willingham, T.O., and Nagy, B. (1984), The Organic aerosols of Titan. *Adv. Space Res.*, **4**, (12) 59–68.

Kissel, J., and Krueger, F.R. (1987), The organic component in dust from comet Halley as measured by the PUMA mass spectrometer on board Vega 1. *Nature*, **326**, 755–760.

Knoll, A.H. and Barghoorn, E.S. (1977), Archean microfossils showing cell division from the Swaziland system of South Africa. *Science*, **198**, 396–398.

Kondo, Y. and Bruhweiler, F.C. (1985), IUE observations of Beta Pictoris: an IRAS Candidate for a proto-planetary system. *Astrophys. Jour. Lett.*, **391**, L1–L5.

Korth, A., Marconi, M.L., Mendis, D.A., Krueger, F.R., Richter, K.A., Lin, R.P., Mitchell, O.L., Andersen, K.A., Carlson, C.W., Réme, H., Savaud, J.A., and d'Uston, C. (1989), Probable detection of organic-dust-borne aromatic $CH_3H_3^+$ ions in the coma of comet Halley. *Nature*, **337**, 53–55.

Kresák, L. (1978), The Tunguska object: A fragment of comet Encke? *Bull. Astron. Inst. Czechosl.*, **29**, 129–134.

Krueger, F.R. and Kissel, J., (1989), Biogenesis by cometary origin: Thermodynamical aspects of self-organization. *Origins Life*, **19**, 87–93.

Kuan, Y., Charnley, S.B., Huang, H., Tseng, W., Kisiel, Z. (2003), Interstellar Glycine, *Astrophys. J.*, **593**, 848–867.

Lagrange, A.M., Ferlet, R., and Vidal-Majdar, A. (1987), The Beta Pictoris circumstellar disk IV. Redshifted UV lines. *Astron. Astrophys.*, **173**, 289–292.

Lagrange-Henri, A.M., Vidal-Majdar, A., and Ferlet, R. (1988), The Beta Pictoris circumstellar disk VI. Evidence for material falling on to the star. *Astron. Astrophys.*, **173**, 289–292.

Langevin, Y., Kissel, J., Berhaus, J.L., and Chassefiere, E. (1987), First statistical analysis of 5000 mass spectra of cometary grains obtained by PUMA (Vega 1) and PIA (Giotto) impacto ionization mass spectrometers in the compressed modes. *Astron. Astrophys.*, **187**, 761–766.

Lazcano, A. (1992a), Origins of life: The historical development of recent theories. In L. Margulis and L. Olendzenski (eds.), *Environmental Evolution: Effects of the Origin and Evolution of Life on Planet Earth* (MIT Press, Cambridge), pp. 57–59.

Lazcano, A. (1992b), *La Chispa de la Vida* (Pangea, México).

Lazcano, A. (1993), The significance of ancient paralogous genes in the study of the early stages of microbial evolution. In R. Guerrero and C. Pedrós-Aliós (eds.). *Proceedings of the 6th International Symposium of Microbial Ecology* (Soc. Catalana de Biología, Barcelona), pp. 559–562.

Lazcano, A. (1994a), The transition from non-living to living. In S. Bengston (ed.) *Early Life on Earth.* Nobel Symposium No. 84 (Columbia University Press, New York), pp 70–80.

Lazcano, A. (1994b), The RNA world, its predecessors and descendants. In S. Bengston (ed.), *Early Life on Earth.* Nobel Symposium No. 84. (Columbia University Press, New York), pp. 70–80.

Lazcano, A., Fox, G.E., and Oró, J. (1992), Life before DNA: the origin and evolution of Early Archean cells. In R.P. Mortlock (ed.) *The Evolution of Metabolic Function* (CRC Press, Boca Raton), pp. 237–295.

Lazcano-Araujo, A. and Oró, J. (1981), Cometary material and the origins of life on Earth. In C. Ponnamperuna (ed.) *Comets and the Origins of Life* (Reidel, Dordrecht), pp. 191–225.

Lederberg, J. (1992), Foreword to L. Margulis Symbiosis in *Cell Evolution: Microbial communities in the Archean and Proterozoic Eons* (Freeman, New York), pp. xv–xvi.

Lerner, N.R., Peterson, E., and Chang, S. (1991), Meteoritic amino acids from cometary/interstellar precursors. *Comets and the Origins and Evolution of Life.* Abstracts of a Meeting in Eau Claire, Wisconsin, Septmeber 30-October 2, 1991, p.19.

Levine, J.S., Augustsson, T.R., Boughner, R.E., Natajaran, M., and Sacks, L.J. (1980), Comets and the photochemistry of the paleoatmosphere. In C. Ponnamperuna (ed.) *Comets and the Origin of Life* (Reidel, Dordrecht), pp. 161–190.

Lewis, J.S. (1974), Volatile element influx on Venus from cometary impacts. *Earth Planet. Sci. Lett.*, **22**, 239–244.

Löb, W. (1913), Über das Verhalten des Formamids unter der Wirkung der stillen Entladagun. Ein Beilrag zur Frage der Stickstoff-Assimilation. *Berichte der Deutschen Chem. Gessellschaft*, **46**, 648–697.

MacMillan, W.D. (1929), The field of cosmogony. *Jour. Geol.*, **37**, 341–356.

Maher, K.A. and Stevenson, D.J. (1988), Impact frustration of the origin of life. *Nature*, **331**, 612–614.

Marcus, J.N. and Olsen, M.A. (1991), Biological implications of organic compounds in comets. In R.L. Newburn, M. Neugebauer, and J. Rahe (eds.), *Comets in the Post-Halley Era*, Vols. I-II (Dordrecht, Boston), pp. 439–462.

Matthews, C.N. and Ludicky, R. (1986), The dark nucleus of comet Halley: Hydrogen cyanide polymers. In B. Battrick, E.J. Rolfe, and R. Reinhard (eds.) *20th ESLAB Symposium on the Exploration of Halley's Comet* (ESA Report SP-250), pp. 273–277.

McKay, C.P., Boruki, W.R., Kujiro, D.R., and Church, F. (1989), Shock production of organics during cometary impacts. *Lunar Planet. Sci. Conf. XX*, 671–672.

McKinnon, W.B. (1989), Impacts giveth and impacts taketh away. *Nature*, **338**, 465–466.

Melosh, J. and Vickery, A. (1989), Impact erosion of the primordial Martian atmosphere. *Nature*, **338**, 487–489.

Mennella V, Colangeli L, Bussoletti E, Palumbo P and Rotundi A (1998), A New Approach to the Puzzle of the Ultraviolet Interstellar Extinction Bump. *Astrophys. J.*, **507**, L177–180.

Miller, S.L. (1957), The mechanism of synthesis of organic compounds under primitive Earth conditions. In J. Neyman (eds.), *The Heritage of Copernicus: Theories "Pleasing to the Mind"* (MIT Press, Cambridge), pp. 228–242.

Miller, S.L. (1991a), The relative importance of prebiotic synthesison Earth and input from comets and meteorites. In R.A. Wharton, D.T. Anderser, Sara E. Bzik, and J.D. Rummel (eds.). *Fourth Symposium on Chemical Evolution and the Origin and Evolution of Life* NASA Conference Publication No. 3129 (Washington DC), p. 105.

Miller, S.L. (1991b), Comets and meteorites were not a significant surce of organic compounds on the primitive Earth. *Comets and the Origins and Evolution of Life.* Abstracts of a Meeting in Eau Claire, Wisconsin, September 30-October 2, 1991, pp. 22–23.

Miller, S.L. and Bada, J.L. (1988), Submarine hot springs and the origin of life. *Nature*, **334**, 609-611.

Miller, S.L. and Lazcano, A. (2002) Formation of the building blocks of life. In J.W. Schopf (ed) *Life's Origin: The beginnings of biological evolution* (California University Press, Berkeley), pp.78–112

Miller, S.L. and Orgel, L.E. (1974), *The Origins of Life on Earth* (Prentice Hall, Englewood Cliffs, NJ).

Miller, S.L. and Urey, H.C. (1959), Organic compound synthesis on the primitive Earth. *Science*, **130**, 245–252.

Mitchell, D.L., Lin, R.P., Anderson, K.A., Carlson, C.W., Curtis, D.W., Korth, A., Réme, H., Sauvard, J.A., d'Uston, C., and Mendis, D.A. (1987), Evidence for chain molecules enriched in carbon, hydrogen and oxygen in comet Halley. *Science*, **237**, 626–628.

Moreels G., Clairemidi J., Hermine P., Brechignac P. and Rousselot P. (1994), Detection of a polycyclic aromatic molecule in comet P/Halley. *Astron. Astrophys.*, **282**, 643–656.

Morrison, D. (1997) The contemporary hazards of cometary impacts. In P.J. Thomas, C.F. Chyba, and C.P. McKay (eds), *Comets and the Origin and Evolution of Life.* (Springer-Verlag, New York), 243–258.

Moulton, F.R. and Chamberlin, T.C. (1900), Certain attempts to test the nebular hypothesis. *Science*, **11**, 311–312.

Mukhin, L.M., Gerasimov, M.V. and Safonova, E.N. (1989), Origin of precursors of organic molecules during evaporation of meteorites and rocks. *Adv. Space Res.*, **9**, 95–97.

Muller, R.A. (1985), Evidence for a solar companion star. In M.D. Papagiannis (ed), *The Search for Extraterrestrial Life: Recent Developments* (Reidel, Dordrecht), pp. 233–243.

Navarro-González R., Castillo-Rojas, S., and Negrón-Mendoza, A. (1991), Experimental and computational study of the radiation-induced decomposition of formaldehyde. Implications to cometary nuclei. *Origins Life*, **21**, 39–49.

Negrón-Mendoza, A., Chacón, E., Navarro-González, R., Draganic, Z.D., and Draganic, I.G. (1992), Radiation-induced synthesis in cometary simulated models. *Adv. Space Res.*, **12**, 63–66.

Oberbeck, V.R. and Aggarwal, H. (1992), Comet impacts and chemical evolution of the bombarded Earth. *Origins Life*, **21**, 317–338.

Oberbeck, V.R. and Fogelman, G. (1989a), Impacts and the origin of life. *Nature*, **339**, 434.

Oberbeck, V.R. and Fogelman, G. (1989b), Estimates of the maximum time require to originate life. *Origins Life*, **19**, 549–560.

Oberbeck, V.R., McKay, C.P., Scattergood, T.W., Carle, G.C., and Valentin, J.R. (1989), The role of cometary particle coalescence in chemical evolution. *Origins Life*, **19**, 35–55.

O'Dell, C.R., Wen, Z., and Hu, X. (1993), Discovery of new objects in the Orion Nebula on HST images: shocks, compact sources and protoplanetary disks. *Astrophys. Jour.*, **410**, 696–700.

Oparin, A.I. (1924), *Proiskhozhdenie Zhizni* (Moskovskii Rabochii, Moscow). Translated and published as an Appendix in J.D. Bernal (1967). *The Origin of Life* (Weidenfeld and Nicolson, London).

Oparin, A.I. (1938), *The Origin of Life* (MacMillan, New York).

Oró, J. (1960), Synthesis of adenine from ammonium cyanide. *Biochem. Biophys. Res. Comm.*, **2**, 407–412.

Oró, J. (1961), Comets and the formation of biochemical compounds on the primitive Earth. *Nature*, **190**, 389–390.

vOró, J. (1963), Synthesis of organic compounds by high-energy electrons. *Nature*, **197**, 971–974.

Oró, J. And Mills, T. (1989), chemical evolution of primitive solar system bodies. *Adv. Space Res.* **9**, 105–120.

Oró, J., Kimball, A., Fritz, R., and Master, F. (1959), Amino acid synthesis from formaldehyde and hydroxylamine. *Arch. Biochem. Biophys.*, **85**, 115–130.

Oró, J., Holzer, G., and Lazcano-Araujo, A. (1980), The contribution of cometary volatiles to the primitive Earth, *Life Science and Space Research XVIII*, pp. 67–82.

Oró, J., Miller, S.L. and Lazcano, A. (1990), The origin and early evolution of life on Earth. *Annu. Rev. Earth Planet Sci.*, **18**, 317–356.

Oró, J., Mills, T., and Lazcano, A. (1992a), The cometary contribution to prebiotic synthesis, *Adv. Space Res.*, **12**, 33–41.

Oró, J., Mills, T., and Lazcano, A. (1992b), Comets and the formation of biochemical compounds- a review. *Origins Life*, **21**, 267–277.

Oró, J., Mills, T., and Lazcano, A. (1995), Comets and life in the universe, *Adv. Space Res.*, **15**, 81–90.

Owen, T., Bar-Nun, A. and Kleinfeld, I. (1992), Possible cometary origin of heavy noble gases in the atmospheres of Venus, Earth and Mars. *Nature*, **358**, 43–46.

Pace, N.R. (1991), Origin of life -Facing up to the physical environment. *Cell*, **65**, 531–533.

Pollack, J.P. and Yung, Y.L. (1980), Origin and evolution of planetary atmospheres. *Ann. Rev. Earth Planet. Sci.*, **8**, 425–487.

Ponce de Leon, S. and Lazcano, A. (2003) Panspermia–true or false? *Lancet*, **362**, 406–407.

Prialnik D., Benkhoff J. and Podolak M. (2004), Modeling Comet Nuclei. In *Comets II* (M. Festou, H.U. Keller, and H. A. Weaver, eds.), Univ. of Arizona, Tucson, pp. 359–390.

Rampino, M.R. and Stothers, R.B. (1984), Terrestrial mass extinctions, cometary impacts and the Sun's motion perpendicular to the galactic plane. *Nature*, **308**, 709–712.

Raup, D.M. (1986), *The Nemesis Affair: A Story of the Death of the Dinosaurs and the Ways of Science* (W.W.Norton, New York).

Raup, D.M. (1988), Extinction in the geological past. In D.E. Osterbrock and P.H. Raven (eds.), *Origins and Extinctions* (Yale University Press, New Haven), pp. 109–119.

Raup, D.M. and Sepkoski, J. Jr. (1984), Periodicity of extinction in the geological past. *Proc. Natl. Acad. Sci. USA*, **81**, 801–805.

Rodgers, S.D. and Charnley, S.B. (2004), Physical Processes and Chemical Reactions in Cometary Comae. In *Comets II* (M. Festou, H.U. Keller, and H.A. Weaver, eds.), Univ. of Arizona, Tucson, pp. 505–522.

Rosing M.T. (1999), ^{13}C depleted carbon microparticles in >3700 Ma seafloor sedimentary rocks from West Greenland, *Science*, **283**, 674–676.

Sagan, C., Thompson, W.R. and Khare, B.N. (1992). A laboratory for prebiological organic chemistry. *Accounts of Chemical Research*, **25**, 286–292.

Schopf, W.J. ed (1983), *The Earth's Earliest Biosphere: its origin and evolution* (Princeton University Press, Princeton, NJ).

Schopf, W.J. (1994), The oldest known records of life: Early Archean stromatolites, microfossils and organic matter. In S. Bengston (ed.), *Early Life on Earth.* Nobel Symposium No. 84 (Columbia University Press, Princeton, NJ).

Schopf, W.J. and Packer, B.M. (1987), Early Archean (3.3 billion to 3.5 billion years-old) microfossils: New evidence of ancient microbes. *Science*, **237**, 70–73.

Schutte, W.A., Allamandola, L.J. and Sandford, S.A. (1992), Laboratory simulation of the photoprocessing and warm-up of cometary and pre-cometary ices: production and analysis of complex organic molecules. *Adv. Space Res.*, **12**, 47–51

Schwartz, R.D. and James, P.B. (1984), Periodic mass extinctions and the sun's oscillation about the galactic plane. *Nature*, **308**, 712–713.

Selsis, F. (2004), The prebiotic atmosphere of the Earth, In *Astrobiology: Future Perspectives*, eds.: Ehrenfreund, P. et al., Kluwer Academic Publisher, Dortdrecht.

Sill, G.T. and Wilkening, L.L. (1978), Ice clathrate as a possible source of the atmospheres of the terrestrial planets. *Icarus*, **33**, 712–713.

vSleep, N.H., Zanhle, K.J., Kasting, J.F. and Morowitz, H.J. (1989), Annihilation of ecosystems by large asteroid impacts on the early Earth. *Nature*, **342**, 139-142.

vSlettebak, A. (1975), Some interesting bright southern stars of early type. *Astrophys. Jour.*, **197**, 137–138.

Smith, B.A. and Terrile, R.J. (1984), A circumstellar disk around Beta Pictoris. *Science*, **226**, 1421–1424.

Stetter, K.O. (1994), The lesson of Archaebacteria. In S. Bengston (ed.), *Early Life on Earth.* Nobel Symposium No. 84 (Columbia University Press, New York), pp. 143–151.

Steel, D. (1997) Cometary impacts on the biosphere. In P.J. Thomas, C.F. Chyba, and C.P. McKay (eds), *Comets and the Origin and Evolution of Life* (Springer-Verlag, New York), pp. 209–242

Strazzulla, G. and Johnson, R.E. (1991), Irradiation effects on comets and cometary debris. In R.L. Newburn, M. Neugebauer, and J. Rahe (eds.), *Comets in the Post-Halley Era*, Vols. I-II (Dordrecht, Boston), 243–275.

Stribling, R. and Miller, S.L. (1987), Energy yields for hydrogen cyanide and formaldehyde synthesis: The HCN and amino acid concentrations in the primitive oceans. *Origins Life*, **17**, 261–273.

Strom, K., Strom, S.E., Edwards, S., Cabrit, S., and Skrutskie, M.F. (1989), Circumstellar material associated with stellar-type pre-main sequence stars: a possible constraint on the timescale for planet building. *Astron. J.*, **97**, 1451–1470.

Suess, H. and Urey, H.C. (1956), Abundances of the elements. *Rev. Mod. Phys.*, **28**, 53–62.

Theirstein, H.R. (1980), Cretaceous oceanic catastrophism. *Paleobiology*, **6**, 244–247.

Thomas, P.J. (ed) (1992), Comets and the Origin and Evolution of Life. *Origins Life*, **21**, Special Issue.

Thomas, P.J. and Brookshaw L. (1997) Numerical models of comet and asteroid impacts. In P.J. Thomas, C.F. Chyba, and C. P. McKay (eds), *Comets and the Origin and Evolution of Life* (Springer-Verlag, New York), pp. 131–146.

Urey, H.C. (1957), The origin of tektites. *Nature*, **179**, 556–557.

Urey, H.C. (1973), Cometary collisions and geological periods. *Nature*, **242**, 32–33.

Vidal-Majdar, A., Hobbs, L.M., Ferlet, R., Gry, C., and Albert, C.E. (1986), the circumstellar gas cloud around Beta Pictoris. II. *Astron. Astrophys.*, **167**, 325–332.

Von Helmholtz, H. (1871), The Origin of the Planetary System. In *Selected writings of Hermann von Helmholtz* (Weslayan University Press, 1971, p. 284) Quotation and reference are from J. Farley (1977). *The spontaneous generation controversy: From Descartes to Oparin* (John Hopkins University Press, Baltimore), p. 142.

Walker, J.C.G. (1986). Impact erosion of planetary atmospheres. *Icarus*, **68**, 87–89.

Westall, F. (2004), Early Life on Earth: the ancient fossil record, In *Astrobiology: Future Perspectives*, eds.: Ehrenfreund, P. et al., Kluwer Academic Publisher, Dortdrecht.

Wetherill, G.W. (1975), Late heavy bombardment of the moon and terrestrial planets. In *Proceedings of the 6th Lunar Science Conference* (Lunar and Planetary Institute, Houston), pp. 1539–1561.

Wetherill, G.W. (1990), Formation of the Earth. *Annu. Rev. Earth Planet. Sci.*, **18**, 205–256.

Whipple, F.L. (1976), A speculation about comets and the Earth. *Mem. Soc. Royale Sci. Liege*, **9**, 101–111.

Whitmire, D.P. and Jackson, A.A. (1984), Are periodic mass extinctions driven by a distant solar companion? *Nature*, **308**, 713–715.

Woese, C.R. (1987), Bacterial evolution. *Microbiol. Rev.* **51**, 221-271.

Wöhler, M.F. (1858), Über die Bestandteile des Meteorsteines von Kaba in Ungarn. *Sitzber. Akad. Wiss. Wein. Math-Naturwiss. Kl.*, **33**, 205–209.

Wöhler, M.F. and Hörnes, M. (1859), Die organische Substanz im Meteorsteine von Kaba. *Sitzber. Akad. Wiss. Wein. Math-Naturwiss. Kl.*, **34**, 7–8.

Wooden, D.H. (2002), Comet Grains: Their IR Emission and Their Relation to ISM Grains. *Earth, Moon, and Planets*, **89**, 247–287.

Zahnle, K. and Dones, L. (1992), Impact origin of Titan's atmosphere in *Proceedings of the Symposium on Titan*, Tolouse, France. (ESA SP-338), 14–25.

Zahnle, K. and Grinspoon, D. (1990), Comet dust as a source of amino acids at the Cretaceous/Tertiary boundary. *Nature*, **348**, 157–159.

Zahnle, K.J. and Sleep, N.H. (1997) Impacts and the early evolution of life. In P.J. Thomas, C.F. Chyba, and C.P. McKay (eds), *Comets and the Origin and Evolution of Life* (Springer-Verlag, New York), pp. 175–208.

Zhao, M. and Bada, J.L. (1989), Extraterrestrial amino acids in Cretaceous/Tertiary boundary sediments at Steuns Klint, Denmark. *Nature*, **339**, 463–465.

Zhao, M. and Bada, J.L. (1991), Limitations on impact delivery of organics to the Earth based on extraterrestrial amino acids in K/T boundary sediments. *Comets and the Origins and Evolution of Life.* Abstracts of a Meeting in Eau Claire, Wisconsin, September 30-October 2, 1991, 41.

2

The Origin of the Atmosphere and of the Oceans

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Summary. The atmosphere of the Earth, its oceans as well as most carbon contained in its carbonates and in organic matter, seems to have been brought by a large bombardment of comets that lasted almost one billion years before diminishing drastically to its present-day value.

2.1 Introduction

The origin of our atmosphere and oceans has never been properly elucidated. The reason is that there is no geological record for the first billion years of the Earth's evolution. "During that lost interval, all the volatiles of the Earth could have been derived and recycled many times while the evidence for the exact mechanism of supply was obliterated completely" (Turekian, 1972).

2.2 Hypothesis of the Volcanic Origin

The view that air and water were outgassed by volcanic activity has been the prevailing paradigm for about a century. This view was first proposed by the Swedish geologist G. Hogbom in 1894. It was substantiated more recently, in particular by Rubey's (1951–55) extensive work. The chemical composition of volcanic gases is highly variable; however, a crude average can be established from Anderson's (1975) comprehensive review. It yields some 60% water steam and 30% CO_2 while the residual 10% is made by a mixture of SO_2, H_2, CO, and N_2. The fact that volcanic gases do not contain any substantial amount of oxygen is not inconsistent with the composition of an early atmosphere, since it is known that oxygen is the by-product of the photosynthetic activity of vegetation and, earlier, of blue–green algae (Berkner and Marshall, 1965).

However, it has also become clear that a large fraction of the volcanic gases is not juvenile, but is constantly recycled by known geologic processes. Water comes mostly from the present oceans, CO_2 from the sedimentary carbonates,

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and sulfur from dissolved sulfates, that are transported by plate tectonics into subduction zones. The subduction zones appear where plates collide, which heats carbonates and water enough to produce new volcanic activity. The recycled fraction seems to be extremely large, but if there is a contribution of juvenile gases, they must have been stored inside the Earth for a long time. Are they the end of a phenomenon that has produced the bulk of the atmosphere and of the oceans very early, during that "lost interval" of the first billion years? There are no very good ways to know. One of the least ambiguous ways to study the problem is to rely on noble gases. They are chemically inert, hence their fractionation must be interpreted by physical processes only.

To do this, it is first necessary to distinguish between primordial noble gases (those dating back from the accretion of the Earth), and radiogenic noble gases (those steadily formed by the decay of radioactive elements, like ^{4}He from U or Th, or ^{40}Ar from ^{40}K, for instance). A less important but not negligible source is the spallation reaction coming from cosmic rays. Primordial ^{3}He, as well as radiogenic ^{4}He, ^{40}Ar, and ^{129}Xe, have been unambiguously detected in mantle-derived material (Eberhart, 1981) but no unambiguous answer on the degassing of the Earth has been obtained. It is interesting to note that submarine basalts indicate a uniform ^{3}He/^{4}He ratio of 1.4×10^{-5} (10 times smaller than the primordial ratio of 1.4×10^{-4} Reynolds et al., 1975); the uniformity of the ratio suggests a well mixed region in the upper mantle, in spite of the fact that the helium abundance is 50 times as large in the Atlantic as in the Pacific basalts. The presence of CO_2 and H_2O in the upper mantle is also indicated by stable isotope data (Eberhart, 1981).

The lack of conclusive answers on the early degassing of the Earth clearly comes from the large number of factors controlling the noble gas abundance patterns in deep-sea basalts (Dymond and Hogan, 1978): in particular, the exchange with atmospheric gases, the diffusion in the magma source during transit through the crust, the partition coefficients during partial melting and crystallization, bubble formation in erupting lava, hydrated phases that absorb large amounts of noble gases, etc. Attempts to deduce the outgassing history from noble gas isotopes are discussed in Alexander and Ozima (1978). The key questions left unanswered are summarized by Eberhardt (1981) as being:

- To what extent is the Earth degassed?
- Was the degassing uniform with time?
- Did an early catastrophic degassing occur?
- Is the degassing within the mantle uniform?

Standing in contrast, the elemental and isotopic patterns of the noble gases left in the atmosphere itself are much easier to understand, and their interpretation comes as a surprise: there is no trace left of a primary atmosphere.

2.2.1 The Missing Primary Atmosphere

During its accretion, as soon as the Earth was large enough to develop a sufficient gravity, it could have captured a sizeable atmosphere from the gases existing in the primeval solar nebula. These gases are the same as those now present in the Sun; therefore, the composition of this so-called "primary" atmosphere has been dubbed "solar." Signer and Suess (1963) have shown that the noble gases came from several reservoirs with different patterns in elemental, as well as in isotopic, abundances that have never been well mixed and can therefore be easily distinguished. The first reservoir of noble gases is clearly "solar" because it shows the undisturbed solar abundance ratios.

They dubbed the second reservoir "planetary" not because its primeval source had been identified, but only because the atmosphere of the terrestrial planets showed a more or less similar depletion pattern for their noble gases, like the contents of the carbonaceous chondrites. As Pepin (1989) mentions, the terminology was unfortunate since it led too many people to believe that the source of the "planetary" component could be identified with the carbonaceous chondrites.

In the "planetary" component, the pattern of progressively smaller depletion with increasing atomic mass for ^{20}Ne, ^{36}Ar, and ^{84}Kr suggests a mass-dependent fractionation of "solar" gases, whereas the very heavy ^{130}Xe remains about "solar" in the atmospheres of Venus, the Earth, and Mars. Standing in contrast, in carbonaceous chondrites, ^{130}Xe reaches 10 times the "solar" value, which suggests that chondrites are not the unique source of the "planetary" component.

However, the best proof that the primeval reservoir of the "planetary" component is neither the solar component properly fractionated nor the carbonaceous component only is found in the characteristic patterns of the isotopic ratios of the six isotopes of krypton of masses 78, 80, 82, 83, 84, and 86 as well as those of the seven isotopes of xenon with masses 124, 126, 128, 130, 132, 134, and 136. It is clear that here mechanisms capable of fractionating the isotopes have been at work, but the fractionation of xenon was not coupled to that of krypton (Pepin, 1989), and the possible mechanisms are not unambiguously understood (Pepin, 1991).

There is however one single inescapable conclusion. The "primary" atmosphere, with its solar composition, is completely at variance with the elemental and isotopic signatures of the noble gases in the present atmospheres of the terrestrial planets. Either this "primary" atmosphere was lost very early, or it was never captured to begin with.

Finally, since geophysics has never been able to explain in detail the origin of the "planetary" component in the noble gases of our atmosphere, the traditional explanation of the volcanic origin of the volatiles is not based on any empirical observations. The hypothesis is based only on a blind extrapolation of present mechanisms, back through the 1 billion year "lost interval" that hides the formation and very early history of the Earth. To understand what happened during that "lost interval," we must leave geophysics and look at the astronomical evidence about the origin of the Solar System

2.2.2 The Origin of the Solar System

Laplace (1796) is the first who tried to solve the problem of the origin of the Solar System by using observational facts. In the last pages of his "Exposition du Système du Monde," he lists first all the quasi-regularities of the Solar System, and then proposes that originally, a "fluid of immense extent enveloped the Sun as an atmosphere," whose primeval rotation enforced all those quasi-regularities. For a long time however, 19th-century astronomers believed that Laplace's model was wrong, because the Sun turned much too slowly to result from the central agglomeration of this "Solar Nebula" (dubbed this way by a false analogy with what we now call spiral galaxies).

The problem of the present angular momentum of the Sun disappeared, when the solar wind was discovered. Its spiral motion away from the Sun produces a magnetic brake that slows the solar rotation continuously. The apparent contradiction with a very fast primeval rotation had disappeared, and Laplace's hypothesis came back in favor some 50 years ago. However, it still was a speculative scenario difficult to analyze numerically. For instance, von Weiszäcker (1944) proposed to arrange the gas eddies in epicycles in order to explain the distances of the planets (Bode's law). Soon, his analysis was shown to be in quantitative disagreement with fluid mechanics, but it attracted the attention on a possible mechanism that had been neglected so far: viscous turbulence can dissipate energy and redistribute momentum in the primitive nebula.

To make a long story short, the basic theory of the *viscous* accretion disk has been given by Lynden-Bell and Pringle (1974). Numerical models have been developed, in particular by Cameron (1985), Lin and Papaloisou (1985), Wood and Morfill (1988), Morfill (1988), and Morfill and Wood (1989). There are still some difficulties with the model. For instance, the origin of the rather high viscosity needed to dissipate the angular momentum has not been properly clarified, although its most likely source is a strong convection driven by gas turbulence. Gas turbulence in the disk is itself maintained by the gravitational collapse of the interstellar cloud that feeds the disk. However, there are other possible mechanisms. A gravitational torque (Larson, 1984) could also dissipate angular momentum. Such a gravitational torque could be introduced by a spiral structure in the disk, or in general by mass distributions that are not axisymmetrical. If the gas is ionized enough, magnetic forces could also play an important role, as the action of the solar wind on the present Sun demonstrates. After all, the solar wind could still be the subsiding remnant of the mechanism involved in the shedding of the disk 5 billion years ago.

2.3 Existence of Accretion Disks

Observational evidence has established recently the ubiquity of large disks of dust around very young stars. The crucial observations came first from the Infrared Astronomical Satellite (IRAS). Observed in infrared (typically from 10 to 100 μm), a large number of very young stars were much brighter than expected from their visual magnitudes (Rowan-Robinson, 1985). This infrared excess was interpreted as coming from the radiation of a large circumstellar disk of cold dust, and most of these stars were shown to be very young T Tauri stars (Bertout, 1989). Some, like FU Orionis, were still probably accreting mass (Hartmann and Kenyon, 1985). Finally, optical pictures in the visual, obtained by hiding the central star in the field of the telescope, have detected and resolved dusty disks of sizes 500–1000 Astronomical Units (AU) among the nearest candidates, like in β Pictoris (Smith and Terrile, 1984).

The existence of numerous accretion disks has therefore been substantiated recently and has become the accepted explanation on the way Nature succeeds in making *single* stars: namely, by shedding the angular momentum in excess to the expanding margin of the disk during the buildup of the central mass. The first consequence of this explanation is that many single stars are likely to make a planetary system by the evolution of their accretion disk. Of course, the accretion disks are only visible around very young stars because at that time, and dust is fine enough to radiate a large amount of infrared in spite of its small total mass. As soon as it coalesces and accretes into larger objects (like planetesimals or eventually planets), their total cross section becomes much smaller and they become much more difficult to detect from afar.

Accretion disks have also become popular in a different context, namely, to explain the mechanism that produces the energy released in X-ray stars and quasars. The gravitational potential well that surrounds very dense compact objects is deep enough for a particle spiraling inward to transform a reasonable fraction of its *rest mass* to radiation. The deeper the gravitational well, the hotter the accretion disk, but this is not the type of interest here; we have mentioned them now not so much to avoid any confusion later, as to emphasize the generality of the accretion disk mechanism to extract energy and angular momentum from a central spinning mass.

For our concern, observational evidence revealing the ubiquity of large disks of dust around very young stars has given a sudden respectability to the theory that describes Laplace's "Solar Nebula" by a viscous accretion disk, even if the cause of the viscosity has not been properly elucidated.

2.4 Numerical Models for a Protosolar Accretion Disk

We will limit our discussion to the *viscous* accretion disks because their study has been developed more than that of other possible mechanisms. Following rather general assumptions that we will not review here, in particular on the viscosity behavior of the disk, there remains two parameters, the collapse time and the viscosity coefficient, that can be combined into one.

Larson (1984) has established the order of magnitude of the collapse time, by the following considerations. The center of the dense interstellar nodule collapses fast and its outer part falls down more slowly; in order to accrete one solar mass, the outskirts of the nodule will reach the accretion disk some 10^5 years later. The actual rate will vary because of density fluctuations, but it is useful to know that the *average* rate is about 10^{-5} solar masses per year. Cameron (1985) proposes accretion rates a few times larger to explain the high luminosities observed in very young (T Tauri) stars.

The viscosity coefficient is the second parameter. It sets the dissipation rate of the inner angular momentum, hence the lifetime of the disk evolution. By combining the uncertain rate of collapse and the uncertain coefficient of viscosity in one single variable, this variable can be adjusted to empirical data. Such an adjustment changes the temperature everywhere in the disk, but not its radial gradient. It is fortunate that the temperature gradient in the midplane of the disk, as a consequence of the virial theorem, reflects the shape of the gravitational potential well made by the protoSuns's mass.

Morfill (1988) can be used as an example of a rather evolved model. Its midplane temperature varies with $r^{-0.9}$ (r being the heliocentric distance) except at temperature plateaus due to the latent heat of condensation of the two major constituents, namely silicates within 0.4 AU, and water from 4 to 8 AU. Figure 2.1 shows Morfill's model. The two unknown parameters have been adjusted to the aggregation temperatures for the different terrestrial planets and two satellites of the giant planets, derived by Lewis (1974) from their empirical mean densities.

The success of the model adjustment (solid line) comes from the approximate temperature gradient in r^{-1} deduced by Lewis from the empirical condensation temperatures of the planets from a gas of solar composition. The two dotted lines represent the model for an accretion rate $\dot{M}$ larger (or smaller) by a factor of 10. A change in the viscosity coefficient would produce the same type of shift.

Lewis's (1972a, b) model assumed not only thermochemical equilibrium between gas and dust in the solar nebula, but also that planets accreted from dust captured only at the exact heliocentric distance of the planet. In spite of the gross oversimplification, the model predicted rather well the uncompressed densities of most of the planets. Lewis' model could not accurately predict the range of condensation temperatures for each planet, because it also depends on the location of the selected abiabat, hence on the model used for the solar nebula. However, its major virtue was to demonstrate that, at the time when dust sedimented from gas, the temperature gradient predicted by theory was empirically confirmed (Fig. 2.1).

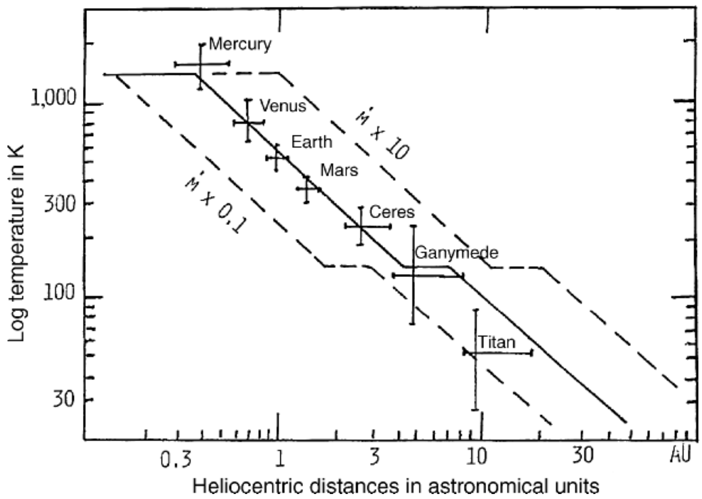

Fig. 2.1. midplane temperature of the accretion disk, as a function of the distance to the Sun, at the time of dust sedimentation. The solid line is the adjustment of the disk theoretical model (Morfill, 1988). For a given viscosity coefficient, the two dotted lines correspond to an accretion rate $\dot{M}$ 10 times smaller or 10 times later. The crosses are Lewis's (1974) aggregation temperatures of planets and satellites derived from their densities. The crosses are not error bars: they show the width of the zones from which planetesimals were presumably collected, and their corresponding temperature ranges. The two horizontal plateaus in the profile are produced by the condensation latent heat of the silicates (near 0.4 AU) and of water ice (from 4 AU to 7 AU). The success of the adjustment comes from the fact that the empirical gradient derived by Lewis from the planet's densities is also predicted by theory. The actual temperatures of condensation for the planets remain however somewhat uncertain because they depend on the pressure in the nebula, hence on the adiabat chosen by Lewis.

2.5 The Chondrites as Clues on Planetary Formation

Those primitive meteorites called chondrites provide empirical evidence on the way planetary bodies were formed. The chondrites come from primitive bodies because, with the exception of a few very volatile elements, most of their elements have remained accurately in the same abundance ratios as in the Sun. This establishes not only that they derived from the same primeval reservoir as the Sun's, but also that they have never been through any process of differentiation, such as those that have separated the cores from the mantles of the different planets.

The chondritic meteorites come from the asteroid belt, that is, roughly from 2 AU to 4 AU. This was established from accurate triangulation of three orbits of chondrite meteorites observed as meteors during their entry in the atmosphere and recovered on the ground later. The results were entirely confirmed by the orbits of about 30 bright meteors identified as chondritic but unrecovered later (Wetherill and Chapman, 1988). Chondrites are assumed to be the fragments of asteroidal collisions. Their parent bodies had a radius of the order of 100 km. This size is implied by their concordant radiogenic ages of 4 billion years or more, implying a rather fast cooling. This small size explains why they had no differentiation induced by gravitation, since their gravity was never larger than 10^{-2} g.

Chondrites are stony meteorites (made mostly of silicates) classified as carbonaceous, ordinary and enstatite chondrites according to their diminishing degree of oxidation. The enstatite chondrites are completely reduced, and the carbonaceous chondrites are completely (CI, CM) or almost completely (CO, CV) oxidized. The most oxidized carbonaceous chondrites are those that contain the most volatile elements and, in particular, very large amounts of organic compounds (there is typically 6% carbon in the CI type). The chondrite classes seem to sample different regions of the accretion disk across the asteroid belt. Although the evidence is indirect, the infrared spectra of asteroids seem to imply that the dark C asteroids have carbonaceous chondritic surfaces, whereas the light S asteroids look more like ordinary chondrites. See, however, the controversy about the identification of the S asteroids in Wetherill and Chapman (1988). Another important clue comes from the fact that the C asteroids begin to outnumber the S asteroids at distances beyond 2.6 AU (Morrison, 1977).

The silicate matrix of chondrites shows that it was made by a moderate compression of fine dust grains of *different* origins. In spite of their close contact, these often submicrometer-sized grains are chemically unequilibrated. For instance, oxidized grains touch reduced grains, some have been altered by liquid water and some have not, and some refractory grains are in close contact with volatile grains. The matrix also imprisons larger objects, such as millimeter-sized chondrules or CAI (calcium–aluminum inclusions). The chondrules show signs of transient (and often partial) melting (1,500–1,600 K). The CAI are refractory grains probably made at temperatures higher than 1,600 K.

This heterogeneous composition seems to imply a process entirely comparable to a *sedimentation*. In our rivers, when water turbulence subsides, sand sediments to the bottom, bringing together grains of quartz, feldspar, mica, calcite, or silicates of widely different origins. Since chondrites have never felt the gravity of a large planet, the sedimentation must have taken place in the solar accretion disk.

This is exactly what the models of the viscous accretion disks predict. During the gravitational collapse of the interstellar nodule into the disk, the gravitational energy of the infall kept a high rate of turbulence in the gas. This turbulence kept the dust in suspension perhaps for some 10^5 years. However, when the collapse rate subsided, before completely stopping, there was a time when the dust was not supported any more by turbulent eddies in the gas. In the quasi-quiescent disk, it fell down to the midplane: this is a sedimentation that is going to make thin equatorial rings of dust around the Sun, much wider than but otherwise entirely comparable to Saturn's rings.

2.6 From Dust to Planets

After sedimentation in the quiescent disk, the dust grains move in practically circular orbits (their different thermal histories come from the previous turbulence in the gas and from the different heights of their infall). A few years ago, it was thought by Goldreich and Ward (1973) that gravitational instablilties in the dust rings would suffice to make numberless 10 km planetesimals in a few years only. Now, Weidenschilling (1988) has given solid arguments, showing that some turbulence is still fostered in the dust ring by the small differential velocity existing between gas and dust: this low degree of turbulence is sufficient to prevent Goldreich and Ward's process. Weidenschilling concludes that planetesimals grew more slowly, by coagulation of grain aggregates that had numberless soft collisions due to their different settling rates and to the drag-induced decay of the orbits. His mechanism can form meter-sized bodies in a few thousand years; this is therefore the characteristic time needed to remove dust from its thermal equilibrium with gas in the midplane of the nebula. Further growth from meter- to kilometer-sized bodies takes again a few thousand years. The following growth of the planetesimals goes on indefinitely through accumulation by soft low-speed collisions from nearby quasi-circular orbits.

However, the nature of the process changes slowly as the planetesimals grow in size. The reason is that the gravitational influence of the growing bodies can be less and less neglected. The orbital perturbations due to close encounters are of the same order of magnitude as the escape velocity, which is itself proportional to the planetesimal size. A large body of work on this accumulation process has been summarized by Wetherill (1980). Without trying to repeat all his conclusions here, it is important to note for our purpose that the size distribution of the bodies widens considerably, so that larger and larger planetary embryos will appear in a time scale in the range of 10–100 million years. The largest of these embryos will eventually be hit by the smaller objects still present in their distance zones, until these zones are clear of solid matter. Most of the material accumulating to form the present Earth has therefore been collected from a zone extending radially from 0.8 to 1.3 AU, by radical diffusion of the orbits due to gravitational encounters. Numerical models have shown that such a radial diffusion occurs with approximately the same timescale as the accumulation of the terrestrial planets (Wetherill, 1980).

2.7 Temperature History of the Earth's Material

In order to find the temperature of the dust when it sedimented out of the nebular gas, we must find a cosmothermometer working at the right time and place. We know that igneous differentiation processes have erased any fossil trace of this temperature on the Earth and, for that matter, on all the planets. Chondrites are the only undifferentiated objects known in our neighborhood. Hence we have no choice and must use chondrites as cosmothermometers.

We mentioned earlier that chondrites come from the asteroid belt. From the reflection spectra of asteroids in the visible and in the infrared, there is consensus among astronomers that (dark) carbonaceous chondrites come from (dark) C asteroids, and (light) ordinary chondrites come from (light) S asteroids (Gaffey and McCord, 1979). But asteroids C outnumber asteroids S only beyond 2.6 AU (Morrison, 1977). It is true that the distribution of S asteroids extends beyond 2.6 AU, but their fraction falls off with a scale length of 0.5 AU (Zellner, 1979). The present distribution can be interpreted as resulting from the secular orbital diffusion through the original 2.6 AU limit, which was sharper 4.5 billion years ago.

To know the accretion temperature of chondrites, the best cosmothermometer is probably the partial loss of their volatile metals Pb, Bi, Tl, and In, which causes their fractionation. Using these latter elements, Larimer (1967) and Anders (1971) find, for a nebular pressure of 10^{-4} bars, a mean accretion temperature of 510 K for ordinary chondrites and of 450 K for the C3 type of carbonaceous chondrites (the other types of carbonaceous chondrites give slightly lower temperatures). If we take into account lower pressures used in recent models of the nebula, these values would become 480 and 430 K. Several other assessments are consistent with adopting a 450 K temperature to separate the two classes.

We can deduce that, at the epoch of dust sedimentation from the nebular gas, the temperature at 2.6 AU, in the central plane of the nebula, was 450 K. Since the temperature gradient predicted by theory for that epoch has been empirically confirmed, we conclude that the accretion temperatures of the planetesimals that were going to form the Earth were between 900 (at 1.3 AU) and 1,400 K (at 0.8 AU), during the 10 thousand years needed to grow from dust to meter- and kilometer-sized bodies; this removes them from thermochemical equilibrium with the nebular gas. Figure 2.2 summarizes the situation that we have just described.

2.8 Thermochemical Equilibrium in Solar Nebula

In the first place, we must consider whether the kinetics of the chemical reactions are sufficiently rapid for the dust to reach chemical equilibrium with the gas of the nebula. The chemical kinetics of a gas of solar composition has

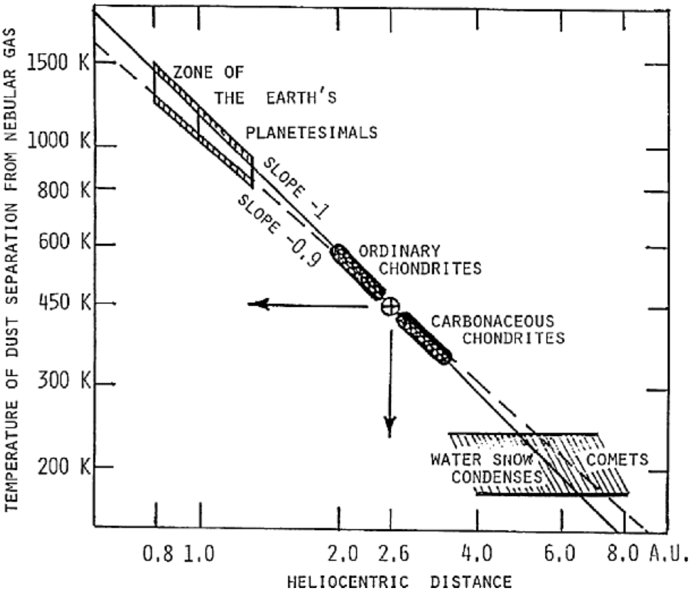

Fig. 2.2. The same diagram as in Fig. 2.1 is enlarged here in the vicinity of the Earth, with a view to improving our knowledge of the temperature in the Earth's zone, when dust sedimented from the nebular gas. Of course, all clues on this temperature have been erased by the igneous differentiation of our planet. The best cosmothermometer for this epoch lies in bodies that have never differentiated in the asteroid belt. It tells us that at the time of sedimentation, all ordinary chondrites were at a temperature higher than 450 K, and all carbonaceous chondrites at a temperature lower than that. Reflection spectra and colors of asteroids tell us that 2.6 AU represents the separation distance. Since the temperature gradient was in the vicinity of –1, possibly –0.9, but definitely larger (in absolute value) than –0.75, it is concluded that the temperature in the Earth's zone was such that the dust did not contain any volatiles. All water remains as steam in the nebular gas, carbon was in CO, and nitrogen in gaseous N_2. Hence the Earth accreted from an outgassed material, completely depleted of volatiles.

been very carefully and thoroughly discussed by Lewis et al. (1979) and Lewis and Prinn (1980).

The largest time constants that turn out to be significant are in the range of one century near 1,000 K. Since, after sedimentation to the midplane, the grains need 10^3–10^4 years to agglomerate into large objects (Weidenschilling, 1988), there is no doubt that thermochemical equilibrium will be reached in the Earth's zone before solids are completely separated from the gas phase. This means that all dust (which is originally in submicrometer-sized grains) has been completely dehydrated, degassed, and reduced (except a fraction of the silicate grains) before its incorporation into larger and larger planetesimals and their later integration into planetary bodies.

Lewis et al. (1979) have, in particular, considered the carbon problem, and they have rightly been puzzled by the retention of carbon in the terrestrial planets. Searching for a mechanism of carbon retention, they correctly deduce that the only way to imprison carbon in the solid phase is to put it in a solid solution inside reduced (metallic) iron grains. In spite of their efforts, they reach an amount two or three times smaller than the observed amount on the Earth (carbonates) or on Venus (CO_2); they do not address the question on how to extract the carbon from iron and bring it to the surface of the Earth or Venus.

However, in their efforts to reach an amount of carbon retention in the grains as large as possible, their choice of the adiabat in the solar nebula has put the Earth's zone near the peak of graphite activity (see Fig. 2.3). For any adiabat, graphite activity goes through a maximum in the vicinity of the line separating the domains of CH_4 and CO in Fig. 2.3. Bringing the Earth's zone here removes the 2.6 AU zone from the same location, whatever the model. Therefore, Lewis et al. (1979) quite reasonable efforts to bring enough carbon on the Earth have removed the possibility of explaining the observed separation of the C asteroids (carbonaceous chondrites) from the S asteroids (ordinary chondrites) at the distance of 2.6 AU.

Using Lewis et al. (1979) own data, if a proper adiabat (between C and CD on Figure 2.3) is used to get the 2.6 AU heliocentric distance close to the line separating CH_4 and CO on Fig. 2.3, the amount of carbon available in solid solution in the iron grains becomes in the Earth's zone *several hundred times smaller* than the observed amounts in the carbonates of the Earth, and the situation is even much worse for the CO_2 present on Venus.

Hence if we accept the accretion temperatures of chondrites as the best available cosmothermometer at the epoch of dust separation from gas, we have also to accept that the bulk of the observed carbon in the terrestrial planets has an exogenous origin.

The same conclusion can be reached for water, because at those temperatures no hydrated silicates exist, hence the total amount of water is in steam in the nebula; in the same fashion, all nitrogen is in gaseous N_2. The presence of the atmosphere and of the oceans on the Earth would therefore be quite mysterious, if the formation of the giant planets had not created the unavoidable mechanism that was going to put a veneer of volatile material on the terrestrial planets.

2.9 Discussion: Was the Earth Outgassed?

Is it possible to escape from the conclusion that the planetesimals that made the bulk of the Earth were completely outgassed and devoid of any volatiles. Let us consider the chain of arguments in detail.

(a) The cosmothermometer at 2.6 AU is valid. The heterogeneous microscopic composition of the chondrites, combined with their total lack of igneous

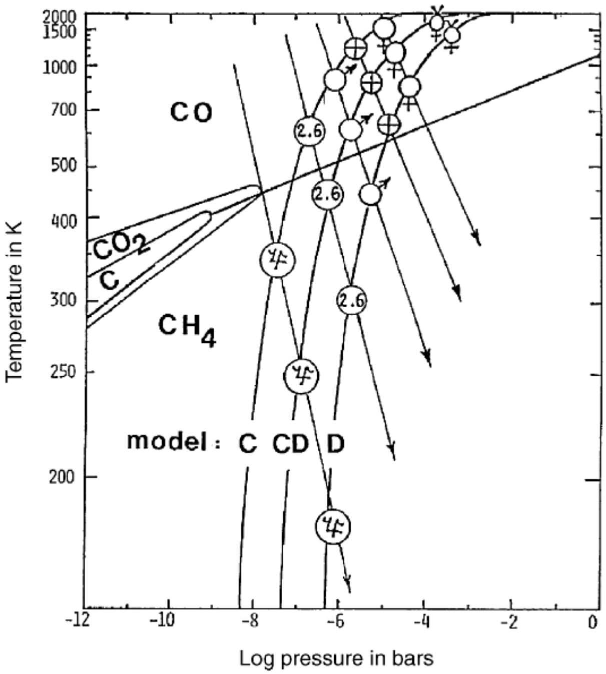

Fig. 2.3. This thermochemical equilibrium for carbon compounds, in a gas of solar composition, is used to understand the carbon chemistry in the solar nebula at the time of dust sedimentation. The quasi-vertical curves represent the adiabats of Cameron's (1985) models C and D, whereas curve CD is an interpolation of the two models C and D that brings all temperatures in agreement with those of Fig. 2.2. The different steady-state models C, CD, and D can be interpreted as a slow evolutionary sequence (shown by the arrows) corresponding to the time when the inflow of nebular gas onto the disk is slowly subsiding. This allows gas turbulence to diminish, eventually letting the dust separate from the gas and sediment to the midplane of the disk. Identification with Fig. 2.2 shows that this happens when adiabat CD is reached. Then, dust settles out and is removed from its chemical equilibrium with gas. At the Earth distance (circle with inside cross) this happens near 900 K; chemical kinetics are fast and dust grains are at thermochemical equilibrium with gas before their sedimentation. Beyond 2.6 AU, chemical kinetics prevails at temperatures lower than 450 K; there, metastable carbonaceous compounds separate from the nebular gas and are imprisoned in carbonaceous chondrites. The other lines on the diagram separate the zones; here CO, CH_4, CO_2, or C (graphite) are each the major constituent. If the conditions of adiabat CD are applicable as implied by Fig. 2.2, then all carbon was in gaseous CO in the Earth zone; carbon on the Earth must be exogenous and must have come later.

differentiation, leaves little doubt that the variable fractionation and loss of their volatile metals date back from their sedimentation as fine dust and is due to a temperature gradient. The temperature separating the two classes is confirmed by several independent comothermometers: the fractionation of the volatile metals (Pb, Bi, Tl, and In) (Larimer, 1967); oxidation state (olivine/pyroxene ratio) (Larimer, 1968); the presence of FeS and the absence of magnetite in carbonaceous chondrites confirms the temperature range (Anders, 1971); even if the Fischer-Tropsch Type (FTT) reactions are no more considered as unambiguous (Kerridge 1991), their possible presence in carbonaceous chondrites would bring only a further confirmation of the 450 K temperature separating the carbonaceous from the ordinary chondrites (Anders, 1971). Finally, there is not much doubt about the identification of the S (stony) asteroids with the ordinary chondrites and the C (carbonaceous) asteroids with the carbonaceous chondrites. If the present 2.6 AU distance had changed somewhat because of mass loss within the solar nebula, the 1 AU distance of the Earth would have shifted in the same proportion and the net result of our computation would be the same.

(b) The temperature gradient at sedimentation of dust is not much in doubt, because the theoretical prediction of Morfill's (1988) model is confirmed by the empirical gradient deduced by Lewis (1974); both are close to -1, which is also derived from a simple-minded argument based on the virial theorem. The virial theorem implies that, in the absence of any latent heat (due, for instance, to the condensation of silicates or of water) the temperature gradient is the same everywhere as that of the gravitation potential. This is close to –1 as soon as the mass is concentrated in the Sun.

The virial theorem can be used only if the angular acceleration of the disk is negligible. This is always the case when sedimentation takes place. Besides, the virial theorem tells only how much heat is available from the gravitational collapse; at steady state, the heat reradiated by the disk photosphere depends on its temperature, hence on the radial distance. This explains the corrected gradient of -0.9 introduced in Morfill's approximation.

Wood and Morfill (1988) also discuss simplified models of the three major stages of the accretion disk. Their stage 1 describes the period during which the disk mass is steadily increasing; it is irrelevant for our concern. Their stage 2 describes the epoch when the rate of inflow equals the mass rate fed to the Sun. During this steady state, the temperature gradient in the midplane of the disk is –1.5. Stage 3 is reached when the infall rate diminishes enough to stop the gas turbulence; the disk still feeds the Sun until its mass diminishes enough to make it transparent. At that time, the temperature gradient in the midplane has fallen down to –0.75. Since the sedimentation of dust is triggered by the disappearance of gas turbulence, the temperature gradient in the midplane falls down slowly from –1.5 to

–0.75. This is consistent with the empirical value close to −1 for the epoch of separation of dust from the gas. See also Lin and Papaloizou (1985). Cassen et al. (1985) have also compared the temperature distribution at different stages. They find that the *photospheric* temperature has a radial gradient of -0.75 regardless of the details of the viscous mechanism. However, when the disk is optically thick, its opacity implies that the midplane temperature remains closer to the results of the virial theorem, hence this remains consistent with the Morfill's (1988) temperature gradient of –0.9 *in the midplane.* We conclude that the consensus between theory data and empirical data is satisfactory.

(c) At sedimentation, the mean temperature of earthy dust is high enough to degass it. After sedimentation, earthy dust was on circular orbits located between 0.8 and 1.3 AU. Dust grains started to stick together, and their sizes grew slowly. After a few thousand years, they had become large enough to be called planetesimals, and the eccentricities of their orbits started to grow steadily, in step with their growing sizes (Wetherill, 1980). As seen on Fig. 2.2, their accretion temperatures were at least 800 K, even if the least steep gradient of –0.9 is used. The limiting gradient of –0.75 (which would yield 700 K for the coolest grains) is ruled out before the grains are imprisoned in meter-sized bodies; and even 700 K would outgas the grains.

Of course, we deal with a stochastic process; this means that, in the very final steps of accumulation, some of the major collisions with lunar-sized planetary embryos could come from objects whose initial heliocentric distance of accumulation were outside our definition of the Earth's zone (0.8–1.3 AU). An object that accumulated in a zone nearer to the Sun would be even more outgassed than the protoearth; but if a large embryo were coming from the inner asteroid belt (2.0–2.6 AU), it could bring ordinary chondritic material to Earth. Such a possibility was ruled out until recently, because it was believed that no object ever became larger than Ceres in the asteroid belt. However, Wetherill (1991) has shown by numerical Monte-Carlo experiments that it is conceivable that larger runaway embryos could have formed in the asteroid belt, then ejected later by Jupiter secular resonances. The self-clearing of the inner belt is assisted by collisions with terrestrial planets. However, the process induces higher eccentricities and inclinations than those observed for the terrestrial planets. Such a collision, which would not greatly change the orbit of the Earth, is a grazing collision, which seems more proper to explain the origin of the Moon (Cameron, 1988) without depositing volatile material deep into the Earth's mantle.

(d) The chemistry of the solar nebula is reasonably well understood, including its chemical kinetics (Prinn and Fegley, 1989). The fact that FTT reactions are likely beyond 2.6 AU, and that there is kinetic inhibition in the vapor-phase hydration of the silicates as well as in the chemical reduction for CO and N_2 does not change the conclusions that the chemical equilibrium was virtually reached in the Earth's zone (0.8–1.3 AU). The only possible exception is that of many minor metastable phases in the solid grains dating back from interstellar space, like submicrometer diamonds, fullerene balls, or large polyaromatic hydrocarbon molecules. The rest of all carbon was entirely in gaseous CO, except another very minor fraction in solid solution in reduced (metallic) iron grains. In the same way, all nitrogen was in gaseous N_2 and all water was in steam. No water, no nitrogen, and no organic carbon to speak of, were present in the protoearth.

2.10 Formation of the Giant Planets

To understand the origin of the volatile material present on the terrestrial planets and more specifically on the Earth, the formation of the giant planets must be discussed first. The study of their interiors (Hubbard, 1984) shows that the giant planets must have a large dense core; hence, they must have developed first a solid embryo before being able to accumulate a large atmosphere.

Three different arguments concur in suggesting that a solid embryo accreted early for Jupiter. In the first place, this embryo had to exist early enough to be the cause of the gross mass depletion of the asteroid belt and of the small mass of Mars (Wetherill, 1980). In the second place, the embryo had to be massive enough to capture the gaseous atmosphere of Jupiter *before* the dissipation of the nebular gas. The third argument comes form the empirical data on the interior of Jupiter; they imply that it has a dense solid core of about 30 Earth masses. Such a large core is more easily predicted by a fast runaway growth scenario (Safronov, 1991).

The first argument implies that Jupiter's embryo was already massive enough (10 Earth masses) early enough to stop the accumulation of asteroids into a single planet. In less than 10^7 years, it had to enlarge the eccentricities of the residual planetesimals of the Jupiter's zone, to make their orbits penetrate the zone of the asteroids and somewhat that of Mars. Their interactions with the asteroids scattered their orbits, enlarged their relative velocities, and transformed the accretion process in the belt into a fragmentation process, ejecting a large amount of that mass that was then in the 1.4–2.8 AU zone. If Jupiter's core had not been formed so early, the orderly accumulation of objects much larger than Ceres (1,000 km) could not have been stopped after a few times 10^7 years, and these lunar-to-Mars-sized bodies could not have all been destroyed later.

The second argument comes from the early dissipation of the nebular gas. Although this dissipation is not yet thoroughly understood, it has been linked by Horedt (1978) to the existence of the T Tauri wind. T Tauri stars are very young stars that are still in their contracting stage before reaching the main sequence in the Hertzprung–Russell diagram. Such a diagram drawn for 50 T

Tauri stars in the Taurus cloud shows the spread of their ages to be 10^7 years. Most of them are first surrounded by an accretion disk. The disk mass and its inflow rate seem to decrease steadily with their increasing age, but there is also an outflow (comparable to the solar wind but much larger). This is what is called the T Tauri wind. The T Tauri wind seems to halt the inflow. The mass outflow is very large first (10^{-6} $\mathrm{M}_\odot$/year) but it falls down quickly to 10^{-8} or 10^{-9} $\mathrm{M}_\odot$/year. The accretion disk disappears and the wind stops just before the stars reach the main sequence. The observed luminosity of 3 $L_\odot$ for a T Tauri star of one solar mass, assumed to come from the gravitational energy of its contraction, confirms a lifetime of 3×10^7 years. Hence it seems that, to capture enough nebular gas, Jupiter's embryo must be massive enough in no more than 10^7 years. Mizuno (1980) has established that, to produce this gas collapse, the embryo must reach about 10 Earth masses. This result is universal, in the sense that it does not depend on the location in the solar nebula. This explains why there was no gravitational collapse of the nebular gas on the terrestrial planets.

We are left with the problem of explaining how a solid planetary embryo can reach a mass of 10 terrestrial masses in 10 million years, whereas the classical mechanism of accretion requires 1 hundred million years for the Earth in a gas free medium, and probably 40 million years in a gaseous medium (Wetherill, 1980). Such a timescale for the accumulation of the terrestrial planets is also confirmed by Safronov (1991) from other considerations.

However, two possible scenarios for the accumulation of the growing protoplanets are not mutually exclusive. They are

(a) an orderly growth, without separation of the largest body from the general mass distribution of the smaller bodies; and
(b) a faster runaway growth of the largest body, which grows much beyond the general mass distribution of the smaller bodies.

Safronov (1991) suggests that a runaway growth took place in the zone of Jupiter, but that there was an orderly growth in the asteroid belt as well as in the terrestrial planet zone. The two processes start in the same fashion by mechanism (a). However, at about the time Jupiter's embryo is close to the Earth's mass, mechanism (b) starts until it reaches 30 Earth masses. Safronov claims that a core of 30 Earth masses is needed instead of 10 Earth masses. This is linked to the need for the final accumulation of five or six runaway embryos before their final accretion into a single body. The reason is the narrow width of the feeding zones, but this is irrelevant to our discussion. The essential point is that the runaway growth mechanism produces a 30 earth-mass embryo, hence the gaseous collapse into a full-size Jupiter in 10 million years. The observational data that support the existence of a large core in Jupiter (Hubbard, 1984) (see Table 2.1) can therefore be interpreted as a third argument for a 10 million-year runaway growth.

Why have the giant planets been able to accumulate solid cores much larger than one Earth mass? This may be connected to the fact that, as the radial

Table 2.1. Giant planet embryo mass.

Planet	Total mass[a]	Embryo's mass[a]
Jupiter	317 $M_\oplus$	29 $M_\oplus$
Saturn	95 $M_\oplus$	19 $M_\oplus$
Uranus	14.6 $M_\oplus$	13 $M_\oplus$
Neptune	17.3 $M_\oplus$	15.4 $M_\oplus$

[a] $M_\oplus$ represents the mass of the Earth.

temperature of the accretion disk diminishes with the heliocentric distance, the nature of the solid grains changes. Dust was formed in the zone of the terrestrial planets, from anhydrous silicates and reduced iron grains. When we move to the future asteroid belt, the volatile metal abundances grow in the grains, until they progressively become chondritic near 2.6 AU. Beyond that distance, the diminishing temperature allows silicates to keep more and more organic matter as well as hydration water. This explains why bodies become darker beyond 2.6 AU (Fig. 2.2). Up to about 5 AU we call the material present in these bodies "carbonaceous chondrites."

It is a matter of semantics to decide where comets begin. We choose to call "comets" those planetesimals that contain water, not only as hydration water in a mineral, but also as free water ice. It is remarkable that water ice condenses near 5.2 AU in the nebula with the temperature gradient adopted on Fig. 2.2. It is probably not a coincidence that it is the place where Jupiter's solid embryo was formed. Using elemental abundances (Anders and Grevesse, 1989), it is easy to verify that the total solid fraction available at 5.2 AU (dust plus CHON ice) is 4.6 times as massive as the dust (silicates plus reduced iron) available in the Earth zone. Finally, the dust grains loaded by frost condense any extra water vapor that reaches them. The diffusive redistribution of water vapor in the solar nebula (Stevenson and Lunine, 1988) makes it a runaway phenomenon.

The previous discussion has made it clear that the solid cores of the giant planets have accreted from comets and comets only; the extra mass of solid ices available in comets is the major reason why the solid cores were so large. The fate of the numerous planetesimals (i.e., comets) that did not accrete on the giant planets must now be discussed in detail.

2.11 Orbital Diffusion of Comets

Safronov (1972) has shown how the total mass of the perturbed comets is linked to the total mass of the giant planets' embryos. When these embryos became large enough, they were able to eject comets out of the solar system, as well as to store a small fraction of them in a sphere of some 50,000 AU radius. Stellar perturbations removed most of the perihelia of the latter comets from the zones of the planets; hence, their orbits became secularly stable and formed the primitive Oort cloud whose source was what I will call the Safronov comets.

Beyond Neptune and up to several hundred AU, the planetesimals left over by the accretion disk did not form very large objects, and are now called the Kuiper belt comets. In the Kuiper belt, resonances with the giant planets also work but with a much longer time scale than in the asteroid belt; they have been removing comets from the Kuiper belt, by ejecting them out of the solar system, by throwing them into the Oort cloud, or by sending them into short-period orbits. These comets ejected from the Kuiper belt will be called the Kuiper comets. Because of the longer time scales involved, they do not play an active role in the origin of the planets, although they are the source of the present short-period comets. Besides, as repeated perturbations from stars, from galactic tides, and from giant molecular clouds have considerably depleted the original Oort cloud, most of its present comets are now Kuiper comets.

In the zones of the giant planets, the scattering of the comets grows in step with the sizes of the giant planets. Since this gravitational scattering is a random process, a fraction of the perturbed comets (including those that are ejected out of the solar system) is sent first through the zone of the terrestrial planets. Using Safronov's (1972) method, I have computed the total mass of those comets that pass through a sphere of 1 AU centered on the Sun. I have multiplied this mass by the mean collision probability with the Earth for all comets. In my early estimates (Delsemme 1991a, b and 1992), I had not changed the masses selected for the giant planets' embryos by Safronov (1972). They were only 9 terrestrial masses for Jupiter's embryo, 12 for Saturn, 14 for Uranus, and 17 for Neptune (in 1991, I had also neglected the small contribution from Uranus and Neptune). Since then, I found it easier to compute it than to convince people that it is negligible in the present approximation.

Recently, I recomputed new masses for the embryos of the giant planets, based on Hubbard's (1984) empirical data on the density distribution in their interiors, and assuming that the embryos have the same composition as the one I found for comet Halley (Delsemme, 1991 a) namely 23% rocks, 41% water, and 36% CHON. The masses I found for the embryos are given in Table 2.1.

The new mass for Jupiter's embryo seems to confirm Safronov's (1991) recent arguments that, since a runaway accretion is implied to make Jupiter's embryo with a time scale of at most 10 million years, then the feeding zone remains several times narrower than the planet's zone even up to an embryo larger than 20 masses (this is due to the lower relative velocities of the bodies). This implies that there will be first a transition to several independent embryos and that the gaseous collapse will not start before 30 Earth masses, a value close to that of Table 2.1 deduced from Hubbard's (1984) data.

In Delsemme (1993) I have revised my former assessments by using the new masses given in Table 2.1 for the embryos's masses. The new results are higher than those published earlier. They are submitted in Table 2.2. The missing mass in the present asteroid belt is assumed to be 10 Earth masses. To translate the masses into a uniform layer covering the Earth, the density of silicates was assumed to be 3.0 and that of carbonaceous compounds was assumed to be 2.0. The distribution of silicates, water, organics, and gases is based on the comet Halley's data previously mentioned. The contribution of the asteroid belt is based on a chondritic average with more weight on ordinary chondrites. Finally, the amplification factor due to resonances, far encounter effects, and the focusing due to terrestrial gravity turns out to be a global factor of 3.5.

Because of the numerous uncertainties associated with such a model, the results must, of course, be understood as orders of magnitude only. However, it is encouraging to see that there is a general consensus on the amount of matter brought down to the Earth by this bombardment. Matsui and Abe (1986) find that comets brought down to Earth *four times* as much water as the mass of the oceans. Fernandez and Ip (1981, 1983) had revised Safronov's evaluations upward. Ip and Fernandez (1988) now find that *10 times* the present mass of our oceans has been brought down to Earth by comets. From the visible craters on the Moon, Chyba (1991) finds that the total mass of the oceans corresponds to a bombardment of only 10% of the lunar craters.

The model of Table 2.2 brings six times the amount of water than what remains now in the oceans and in the atmosphere. Note: This corrects a numerical error in the results calculated in Delsemme (1997). For a further explanation, see Delsemme (2000). This not only is explainable, but probably required to justify the considerable losses of volatiles due to the numerous impacts predicted in the last stages; I mean not only the cometary impacts, but also those of larger planetesimals that have accreted in the zones of the giant planets before being ejected by them, as well as lunar-to-Mars-sized bodies predicted by theory, mostly from the Earth zone (Wetherill, 1980), but even possibly some from the asteroid zone (Wetherill, 1991). At least one of these objects could be responsible for the grazing collision that would have created the Moon (Cameron, 1985). Since all these events are stochastic, it is, of course, impossible to introduce them in a precise chronology.

2.12 Chronology

A possible chronology model is described in Table 2.3. It summarizes the different assessments coming from the previous speculations. These order-of-magnitude estimates ignore the considerable difficulties that are still present everywhere.

The chronology model of Table 2.3 assumes that the sedimentation of solid particles to the midplane of the disk occurred almost simultaneously

Table 2.2. Thickness of uniform layer covering the earth.

Origin of terrestrial bombardment	Chondritic silicates	Water	Carbon compounds	Atmosphere
Chondrites from asteroids	2.0 km	0.20 km	0.10 km	—
Comets from Jupiter's zone	3.0 km	11.0 km	4.0 km	600 bars
Comets from Saturn's zone	1.0 km	3.0 km	1.0 km	140 bars
Comets from Uranus' zone	0.15 km	0.5 km	0.15 km	23 bars
Comets from Neptune's zone	0.06 km	0.2 km	0.06 km	10 bars
Totals	6 km	15 km	5 km	770 bars

Table 2.3. Time scales for the early solar system.

Chronology for the beginning of the planetary system	
Sedimentation of solids to the midplane	Age zero
10 km planetesimals on circular orbits	10^4 years
10^2–10^3 km planetesimals	10^5 years
Planetary embryos (Moon to Mars size)	1 M years
Runaway growth of Jupiter embryo	1 M years
Runaway growth of Saturn embryo	2 M years
Dissipation of nebular gas	5 M years
Runaway growth of Uranus embryo	7 M years
Runaway growth of Neptune embryo	14 M years
Earth accumulation: 85–90% finished	42 M years
Formation of the Moon (grazing impact)	50 M years
Time scales for orbital diffusion of comets	
Comets from zone of Jupiter	50 M years
Comets from zone of Saturn	120 M years
Comets from zone of Uranus	300 M years
Comets from zone of Neptune	600 M years
Cometary bombardment of Earth 99% finished	1000 M years

everywhere, so the small planetesimals also appeared simultaneously. We assumed that a bifurcation appeared after the first million years: there was a fast runaway growth in the region of the giant planets, whereas there was a much slower orderly growth for the terrestrial planets. The two regimes of growth can coexist (Wetherill, 1989) although the details that can trigger one or the other have not been completely quantified (for instance, it could be the difference in the sticking factors of snows and silicates). The model explains the absence of a planet in the asteroid zone and the small size of Mars by the early appearance of Jupiter. It also assumes that, if Saturn has captured gravitationally a smaller amount of gas than Jupiter, from the solar nebula, that is because the dissipation of the nebula had already begun. Finally, the nebular gas had completely disappeared when Uranus and Neptune's embryos reached their final sizes, explaining the minimal amount of hydrogen and helium in their atmospheres.

The missing primary atmosphere of the Earth, testified by the patterns in the abundances of the noble gas isotopes in our present atmosphere, is explained by the slow orderly growth of the protoearth that reached its final size after the dissipation of the nebular gas. The present atmospheres of the terrestrial planets and the oceans of the Earth are explained by the late accreting veneer brought by the orbital diffusion of the large number of comets that were deflected by the building up of the giant planets' solid cores. Comets were the building blocks of these cores. All of those that missed a direct hit on the giant planets' embryos were ejected faraway by the strong gravitational attraction of the large embryos. Most of them were lost from the solar system, but some of them were stored in the Oort cloud, and some of them hit the terrestrial planets when their ejection orbits crossed the inner solar system.

The time scales for the orbital diffusion of comets have been normalized in such a way that they grow in proportion to the revolution periods in the zone where the diffusion comes from (Everhart, 1977). Of course, the diffusions begin at different times, namely, the time when the accretion of the relevant embryo has become large enough; this means about at the end of the runaway growth of the embryo. The times scales are exponential time scales; they express when the Earth bombardment had diminished by a factor $1/e$.

2.13 Chronology Discussion

The chronology model leads to an accretion rate of comets on the Earth that is steadily diminishing with time. This rate is displayed on Fig. 2.4 for the first two and a half billion years after "age zero" (the epoch of dust sedimentation from the nebular gas). The contribution of the asteroid belt and of Jupiter's comets comes early; it is half finished during the first 200 million years. Since the different zones decay at different rates, the total accretion rate represented by the dotted line subsides drastically after 600 million years. The contribution of the zone of Jupiter prevails for the first 400 million years,

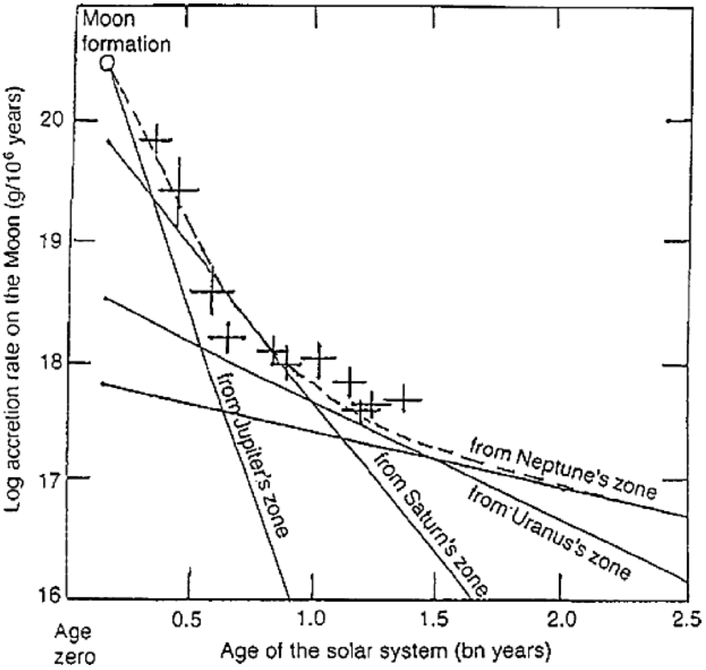

Fig. 2.4. Accretion rate of comets on the Earth, in grams per million years, as a function of time since dust sedimentation in the midplane of the accretion disk 4.56 billion years ago. The contributions of the zones of the giant planets start at different times and decay at different rates. The mass of each contribution is deduced from Table 2.2 and the exponential time scales are from Table 2.3. The exponential time scales for orbital diffusion have been normalized by using Everhart's (1977) results of random walk numerical experiments for the orbital diffusion of comets by the giant planets, and the exponential lifetimes of decay were chosen in proportion to the orbital periods of the giant planets. Each of the contributions of the different planet zones is a straight (solid) line on this logarithmic diagram. The sum of all contributions is the dashed line with an exponential rate varying with time, to be compared with the cratering rate on the Moon (Carr et al., 1984), whose data have been normalized to our units. The agreement is surprisingly good, not only for the mass rates, but also for the subsiding rate with time (reproduced, with permission, from Delsemme (2000)).

then Saturn takes over up to 1 billion years, then Uranus up to 1.4 billion years, and finally Neptune. Neptune's contribution contains the 2:1 resonance with Neptune in the Kuiper Belt; after 4.6 billion years (beyond the limit of Fig. 2.4) it still contributes 5×10^{18} g/Myr, or 50 comet collisions per million years, coming from the short-period comets that we still observe nowadays. This is a fair estimate for such a simplistic model. The difference between the times needed by the (short) runaway growth of Jupiter and the (longer) orderly growth of the Earth is the decisive factor that marshals the fraction of volatiles imprisoned in the Earth mantle. If our chronology model is correct, when the chondritic and cometary bombardment induced by Jupiter started, the Earth embryo had probably reached some 90% of the present mass of the Earth, and numerous collisions with 10^{22}–10^{23} g bodies were still to come.

We presume that the accumulation of the Earth was essentially finished in 40–50 million years, assuming that it was somewhat enhanced at the beginning by the presence of nebular gas. It is not implausible either that it ended by a small period of runaway growth due to a large value of the gravitational focusing factor for the largest two or three bodies involved. However, if the nebular gas had dissipated much earlier and if there was no runaway growth, the standard orderly growth would yield 100 million years for the accumulation of the Earth, in which case one half of the chondritic contribution of the asteroid belt and one fourth of the comets coming from Jupiter's zone would be buried deep into the Earth's mantle. This represents a total of somewhat less than 10^{24} g of volatile material buried in the mantle, as opposed to a veneer of 6×10^{25} g brought after the accumulation of the Earth is essentially finished. Of course, this 1% of the total mass of exogenous bodies brought early onto the Earth does not seem very significant, until it is realized that its volatile material may explain a nonnegligible amount that would be recycled again and again in the mantle.

The chronology model of Table 2.3 implies the more likely view of a 40 million year accumulation for the Earth. In this case, the contribution to the lower mantle is minimal, and the early contribution to the upper mantle becomes undistinguishable from the late major contribution of the next 600 million years. This comes from the "gardening" of the crust and upper mantle by large impacts and because of the subsequent convection of the upper mantle.

2.14 Observational Confirmations

2.14.1 Cratering Record

Observational data on impact craters now exist for all terrestrial planets, the Moon, and the satellite systems of Mars, Jupiter, Saturn, and Uranus. See a review by Weissman (1989). The similarity of the cratering density distribution versus size on the Moon, Mars, and Mercury (Carr et al., 1984) suggests that the massive bombardment concerned the whole inner solar system and was simultaneous on all three bodies. Wetherill (1975) has also clearly shown that the mass of the impactors was much too large to be only the subsiding tail of the remnant bodies in the terrestrial planets' zones.

The only accurate chronology has been obtained from lunar data. The lunar rocks brought back from the Apollo and Luna missions have been dated by those radioactive isotope techniques that establish the solidification age of the relevant rock. The younger solidification ages were systematically found where the number of craters per square kilometer was smaller. Assuming that the missing craters had been erased from the record by the latest tectonic events that had melted the rocks, it was possible to establish an absolute chronology of the residual crater density. Carr et al. (1984) data have been normalized to the units of Fig. 2.4 and are represented by circles on the diagram. To do this, we assumed that dust sedimentation from gas (our "age zero") occurred 4.56 billion years ago. The comparison is encouraging, in particular, because it seems to explain the subsiding rate observed in the lunar craters, by the combination of the different time scales derived from the orbital diffusion of comets by the different giant planets' zones and of the different masses coming from each zone. The mass rates are equally well predicted.

My model uses different exponential time rates of diffusion, chosen in proportion to the orbital periods in the asteroid belt and of the four giant planets. These lifetimes are normalized by using the results of Everhart (1977) random walk numerical experiments for the orbital diffusion of comets by the giant planets. I have also compared with Kazimirchak-Polonskaya (1972), which confirms the order of magnitude of my estimate.

Chyba (1987) has used the visible craters of the Moon to assess the mass flux of the impacts on the Earth for the same period. He finds that the total mass of our oceans could be explained by a bombardment of comets corresponding to 10% of the lunar craters. His assessment is in complete agreement with the present model if the bulk of the lunar craters comes mostly from comets.

2.14.2 Geochemistry

As judged from comet Halley, elemental abundances in comets are almost chondritic. C, N, and O are even closer to solar than to chondritic abundances, as can be seen in Fig. 2.5 (Delsemme, 1991a). In particular, the siderophile elements are in solar (or chondritic) proportions in the cometary silicates, and their contribution to the outer layers of the Earth (crust and upper mantle) is of the order of 2×10^{25} g (see Table 2.2). This is quite enough to solve the apparent paradox of the "siderophile excess," which is a puzzle that has not been easy to explain in geochemistry.

The term *siderophile* dates back to V.M. Goldschmidt, who suggested in 1922 a geochemical classification of the elements, on the basis of their tendency to concentrate in one of the three principal solid phases that appear in a cooling magma. The elements that follow metallic iron are called siderophiles, as opposed to those that follow sulfur (chalcophile) and those that follow silicates (lithophile). Because of the formation of an iron core at the center of the Earth, liquid iron should have scavenged the siderophile elements like Ni, Co, Ir, Au, Os, and Pd. However, they are still found in chondritic proportions in some samples of the crust and the mantle (Morgan et al., 1981).

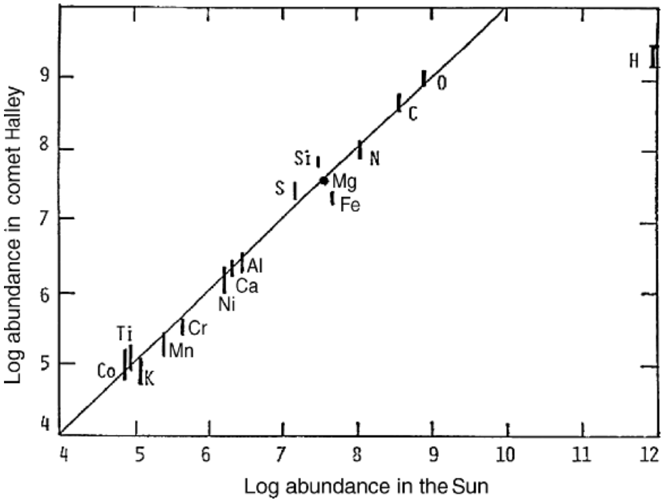

Fig. 2.5. The abundance of known element in comet Halley is compared with the same elements in the Sun. Except hydrogen (and presumably the noble gases) all elements seem to be in solar proportions in comet Halley. A curious exception is the Fe/Si ratio which is only 25% of that in the Sun. The silicon seems to be overabundant by a factor of 2, and the iron underabundant by the same factor, in comet Halley. This diagram is shown to establish that most siderophile elements are in solar proportions in comet Halley and, assumedly in all comets, explaining the surprising "siderophile excess" of the Earth's crust, as well as their depletion in the upper mantle.

Murthy (1991) suggests a possible explanation, on the basis of a purely geophysical model, for this "excess" of siderophiles. In his explanation, the "excess" of volatiles remains unexplained. The "excess" volatiles are those elements that are found in the biosphere and cannot be derived by weathering of igneous rocks (Rubey, 1955). The exogenous origin of both the "excess volatiles" and the "excess siderophiles" on the terrestrial planets is a natural explanation that does not require any "ad hoc" hypothesis, because it derives, of necessity, from the formation mechanism of the planets by planetesimals, and of the growth of the giant planets. This growth has deflected chondritic and cometary bodies whose bombardment of the Earth brought the needed amounts of "excess" volatiles and of "excess" siderophiles.

Chyba (1991) has also shown that the mass flux of the impacts corresponding to the visible craters on the Moon, when properly extrapolated by the gravitation focusing action of the Earth, explains the right order of magnitude for the "excess" siderophiles.

2.14.3 Geochemical Model

Chemical models for the interior of the Earth are still essentially indeterminate. We know the existence of a dense core containing about 31% of the Earth's mass, only because the global density of the Earth and its moment of inertia concur with seismologic data to reveal its density and size. The results are consistent with a core of metallic iron whose density is slightly diminished by a minor fraction of lighter element(s). The bulk of the Earth is the lower mantle, which is probably its least understood part. For instance, its iron content is not certain, and its redox state has been disputed. Is the ratio Fe_2O_3/FeO high or very low? Is it partially equilibrated with the Fe core? Is the mantle homogenized by mixing throughout its 2,900-km depth? Are mantle plumes (responsible for volcanic activity at dozens of hot spots around the world, including Iceland and Hawaii) coming only from the upper mantle, 670 km thick, or do they come from much deeper?

Our accretion model predicts a 99% fraction of outgassed and partially reduced grains in planetesimals, equilibrated with the nebular gas in the temperature range of 800 K (at 1.3 AU) to 1,300 K (at 0.8 AU). The last 1% is a veneer of cometary material that contributes to the much larger fraction of volatiles and oxidized material present in the outer mantle and the crust of the Earth. The model predicts a small enrichment of refractory elements and a large depletion of volatile elements that should already become apparent in the upper mantle.

The chemical composition of the upper mantle is known incompletely, and mostly through mantle-derived rocks brought to the surface by volcanic eruptions. Wänke et al. (1984) have compared the abundances of metals in such samples with their abundances in chondrites. They conclude that the refractory elements are indeed slightly *enriched* (by a factor of 1.30 ± 0.15), whereas the moderately volatile elements are *depleted* (factors of 0.1 to 0.2) and the very volatile elements are *strongly depleted* (factors from 10^{-2} to 10^{-4}). The highly siderophile elements are also *strongly depleted*, but the reason of this depletion is assumedly different, since they have been scavenged by the formation of the iron core.

Ringwood (1977) and Wänke (1981) have also proposed a two-component model for the formation of the terrestrial planets. Ringwood used 90% ordinary chondrites and 10% carbonaceous chondrites. Wänke used 15% of C1 carbonaceous chondrite for his component B; his residual 85% does not correspond to any class of chondrite: it is highly reduced and free of all elements with a volatility at least equal to that of Na. The two models, in particular that of Wänke, seem to go in the right direction, but the two components are arbitrary and the mixture is adjusted empirically. None of the models try to justify the amount of the two components by a numerical argument based on the history of the solar system.

Standing in contrast, the model described in this chapter is based on a quantitative mechanism that is an inescapable consequence of (a) the dust sedimentation in the accretion disk for the Earth zone and (b) the existence of the giant planets.

2.14.4 Noble Gases

In the section "The Missing Primary Atmosphere," I mentioned that the isotopic pattern shown by the abundances of krypton and xenon on Earth remains a mystery. The source for the so-called "planetary" component of the noble gases is not chondritic at least for Kr and Xe. Without looking at the isotopic patterns, the relative abundance of ^{130}Xe reaches 10 times the "solar" value in carbonaceous chondrites, whereas ^{130}Xe remains about "solar" in the atmospheres of Venus, the Earth, and Mars.

In our present model, volatiles are brought about by comets. Could comets solve the mystery of the anomalous abundances of xenon and of the surprising fractionation of the krypton and xenon isotopes? Low-temperature trapping of gases on ices is a possible source for rare-gas enrichment. An extreme form of gas trapping is the possible existence of gas clathrates. The existence of clathrates of gas was proposed a long time ago (Delsemme and Swings, 1952) to explain some peculiarities in the vaporization rates of comets. Gas adsorption in snows was studied in the laboratory (Delsemme and Wenger, 1970) and clathrates mentioned as adsorption limits (Delsemme and Miller, 1970). The enrichment factors of Kr/Ar and Xe/Ar obtained by trapping the gases on ice was studied at temperatures varying from 30 to 75 K by Bar-Nun et al. (1988) and by Bar-Nun and Kleinfeld (1989) corresponding to the very low temperatures of comet formation in the outskirts of the solar accretion disk. Since large enrichment factors are found, stochastic processes involving only one or two collisions with large comets may explain variations in planetary atmospheres. In particular, Owen et al. (1991) think that a plausible reservoir for the "planetary" component with the anomalous abundances of noble gases and anomalous ratios on Venus is the first clear indication of the presence of a cometary component in a planetary atmosphere.

Of course, the abundances of no noble gases have ever been measured in comets, and since there might be large variations from one comet to another, only a rather large sampling could yield a final solution to the problem. In the meantime, it is encouraging that studies in the laboratory point to a possible solution to the puzzling "planetary" abundances of the noble gases.

2.14.5 Deuterium

Standing in contrast to noble gases, the deuterium–hydrogen ratio has been measured in comets Halley, Hyakutake, and Hale-Bopp. Each has a HDO/H_2O enrichment in the same range, about twice as large as its enrichment in Earth's seawater. Some authors (e.g., Meier et al., 1998) have therefore argued that comets cannot be the only source of seawater on Earth.

This conclusion is premature, as I have explained (Delsemme, 1999). The lower deuterium enrichment of seawater compared to these comets can be explained by the large amount of comets arriving at the Earth from Jupiter's zone (see Table 2.2), where a different process drastically diminished their average deuterium enrichment. In contrast, most of the comets we see now come either from the Oort cloud (long-period comets) or from the Kuiper belt (short-period comets); in both cases the deep cold of space has kept the deuterium enrichment of the icy mantles of their interstellar grains in their pristine condition. Some comets originating in Jupiter's zone were also ejected to the Oort cloud, but the large gravitation of Jupiter threw most of them beyond the Oort cloud into interstellar space. Only about 4% of the comets now arriving from the Oort cloud should have accreted in Jupiter's zone, but they should have a deuterium enrichment of about 6, or 3/4 that of seawater (Delsemme, 1999). During the early intense bombardment of the Earth by comets, most of the seawater was brought by comets from Jupiter's zone, so that the deuterium enrichment of seawater is quantitatively consistent with its origin from a cometary bombardment (Delsemme, 1999, 2000).

2.15 Nature of the Early Atmosphere

The possibility of building a consistent model of the volatile fraction escaping from the cometary nucleus has been reached for the first time with comet Halley (Delsemme, 1987, 1991a). It was also shown that the apparent diversity of different comets is not inconsistent with the bulk homogeneity in the cosmic material that has accreted into comets. In particular, the abundance ratios of the light elements in all the bright comets that have been observed recently (Delsemme, 1987) seem to be the same. This bulk homogeneity is not inconsistent with the large diversity in the microscopic composition of dust grains discovered in comet Halley (Jessberger et al., 1988), which suggests that individual interstellar grains coming from different stellar environments have been preserved in comets (Delsemme, 1991c).

The model of the volatile fraction of comet Halley, given in Table 2.4, is not final and must be used in a heuristic way only, but it is not in disagreement with an early atmosphere that would have been altered, processed, and recycled many times to provide the bulk of oceanic water, the nitrogen still present in the atmosphere, the carbon of the carbonates and of the biosphere, and the residual gases recycled by present-day volcanoes.

Table 2.4 is in quantitive agreement with the mean element ratios of comet Halley and of several other recent bright comets, and in semiquantitive agreement with spectroscopic moleculer data; however the error bars are large. I have used $C_4H_4N_2$ as a symbol for heterocyclies with N, like pyrimidine, which is almost as volatile as water (boiling point 123°C at atmospheric pressure). Several heterocyclics including pyrimidine have been identified in the CHON grains of comet Halley by Krueger and Kissel (1987). At the present time, we

Table 2.4. The volatile fraction of comet halley.

78.5% H_2O	2.6% N_2	1.4% C_2H_2	0.1% H_2S
4.5% HCO.OH	1.0% HCN	0.5% CH_4	0.05% CS_2
4.0% H_2CO	0.8% NH_3	0.2% C_3H_2	0.05% S_2
3.5% CO_2	0.8% N_2H_4		
1.5% CO	0.4% $C_4H_4N_2$		
92.0% with O	5.6% with N	2.2% hydrocarbons	0.2% with S

must wait for better data coming from other comets, before discussing the possible evolution of the early atmosphere, which is clearly out of the scope of this chapter.

2.16 Prebiotic Organic Syntheses

The origin of the atmosphere and of the oceans that has just been described has direct connections with the origins of life on Earth. In particular, the carbonaceous chondrites that were brought onto the Earth (Table 2.2) from the asteroid belt, mostly during the first 200 million years (Fig. 2.4), contained numerous amino acids. As an example, 74 different amino acids were extracted from the Murchison meteorite, a CM carbonaceous chondrite that fell in 1969 near Murchison, Australia (Cronin et al., 1988). Among these amino acids, eight of the protein amino acids (glycine, alanine, valine, leucine, isoleucine, proline, aspartic acid, and glutamic acid) have been identified along with 11 less common amino acids used by life. The total concentration of amino acids in the Murchison meteorite is about 60 parts per million (ppm). Assuming from the statistics (Sears and Dodd, 1988) that 3% of the meteorites are carbonaceous chondrites, this is still 6×10^{19} g (6×10^7 million tons!) of amino acids that would have reached the Earth. Assuming that everything would be destroyed by heat during the first 130 million years, 6×10^5 million tons would still reach the atmosphere later, and 6×10^3 million tons after the first 260 million years.

The Murchison meteorite also contains a complex mixture of aliphatic and aromatic hydrocarbons, of carboxylic acids and of nitrogen heterocycles. The latter are of particular interest because of the use of purines and pyrimidines as coding elements of the biological DNA and RNA. One pyrimidine (uracil) and four purines (xanthine, hypoxanthine, guanine, and adenine) used in biological DNA and RNA have been found at the ppm level in the Murchison meteorite (Cronin et al., 1988).

Comets have also brought to the Earth a much larger amount of organic compounds than the carbonaceous chondrites, and on the average much later. Their flux to the Earth has drastically subsided, but in a way it is not yet finished (Fig. 2.4). Their chemistry is still very poorly known, and the information available comes almost entirely from comet Halley. Its dust particles revealed a large amount of fine grains coated with mostly unsaturated organic material (Krueger and Kissel, 1987). The presence of purines and pyrimidines were inferred from the mass spectra, but amino acids were not detected; if present, they were at least a factor of 30 less abundant than the purines and pyrimidines.

The argument that the heat of the impacts with the Earth is going to destroy all this organic material, is brought to rest when one realizes that a large fraction of it is brought to the Earth by cometary dust. This dust, visible in the beautiful dust trails of comets, is braked by the upper atmosphere and gently brought to the ground. Prebiotic organic compounds came from space, and were brought again and again for aeons until they found the right “little pond” to get life started.

2.17 Summary

We have first established that the volcanic origin of our atmosphere and our oceans is an assumption that has never been demonstrated by any empirical data. It was based only on a blind extrapolation of the present recycling of volcanic gases back to a period that cannot be explored by geophysical means.

The only way to handle the problem is to consider the formation of the Earth in the more general paradigm of the origin of the solar system and the formation of the planets. This paradigm has received considerable support from recent observational evidence. It explains that Nature has found a way to make single stars by getting rid of the excess angular momentum through an accretion disk. Most of the mass falls first onto the accretion disk, before being fed into the central star. When the mass stops falling from afar, the turbulence stops in the disk and its dust sediments to the midplane of the disk, making big flat rings of solid particles that are the possible source of a planetary system. In the case of the Sun, these particles were mainly silicate and metallic iron dust for the terrestrial planets.

This sedimentation is convincingly documented by meteorites that came from the asteroid belt: the undifferentiated chondrites. Chondrites tell us that the gas dust separation occurred at a temperature close to 450 K at a distance of 2.6 AU from the Sun. Theory and observations concur to a value for the temperature gradient in the nebula, which implies that the dust particles that were going to agglomerate to form the Earth, were removed from the nebular gas in a range of temperatures going from 800 to 1,200 K (Fig. 2.6).

These temperatures imply that the silicate and metallic iron particles were outgassed before their agglomeration into larger objects. So water was in nebular steam, carbon in gaseous CO, and nitrogen in gaseous N_2. The first 99% of the protoearth were therefore completely devoid of volatiles. Isotopic abundances of the noble gases on the Earth confirm that there is no trace

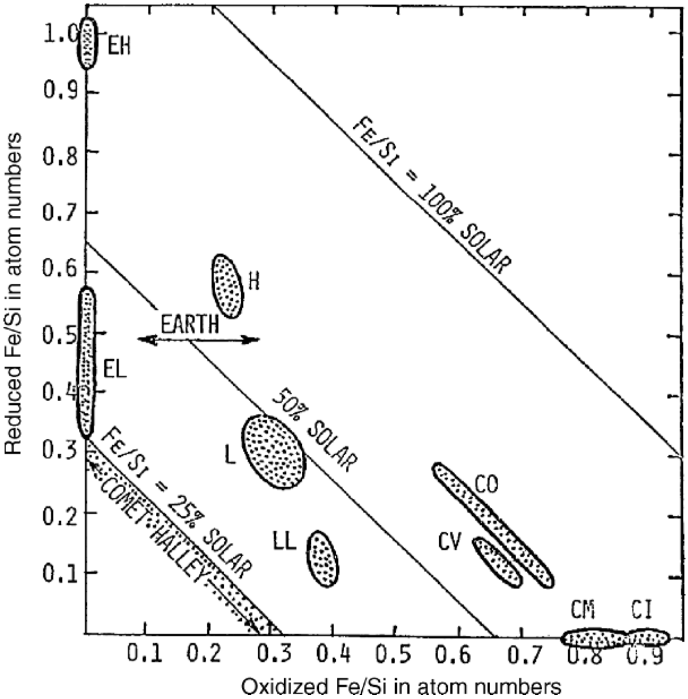

Fig. 2.6. This plot of the reduced Fe/Si ratio versus the oxidized Fe/Si ratio for chondritic meteorites is usually referred to as a Urey–Craig diagram. The position of the comet Halley grains is indicated, as well as the place that would represent the Earth if it were homogenized. The arrows indicate the limits of our ignorance as far as a reduced phase of iron in the mantle is concerned. One understands that the outgassed and partially reduced fraction, collected near 1,000 K, would correspond rather well to the enstatite chondrites of group H. An admixture of a small volatile fraction coming from comets would easily bring the mixture onto the Earth's position. Such a model should not be overinterpreted, because we do not know the zone of origin of the H chondrites.

left of an early atmosphere. Volatile metals are depleted as shown by upper mantle samples.

The giant planets formed at a location where the temperature was much lower; hence, their early building blocks were not stony, but icy, with a large fraction of volatile materials: the comets. The mass of the giant planets became large enough to deflect comets to the inner solar system; the final 1% of the Earth mass was a veneer of volatile material brought about by a late cometary bombardment due to the growth of the giant planets. In this veneer, gases were depleted by a factor of 2,000, and water by a factor of 100, by the numerous collisions with larger and larger objects predicted for the final stages of accretion. Some of the collisions with lunar- or Mars-sized bodies, as the one that has been proposed for the formation of the Moon, are likely to have completely vaporized and lost all the volatiles to space, which implies that the buildup of the atmosphere and the oceans started anew from the last of these collisions, whose epoch is difficult to specify since it was a stochastic event.

A small fraction of the volatile veneer, at most of the order of 0.1%, has been brought onto the Earth before the major accretion was complete, hence was buried in the mantle. The residual 0.9% has been brought mostly during the first half billion years of the Earth's existence, as testified by the ages of the lunar craters that were the relics of the same bombardment. In a general way, this bombardment has considerably rarefied but is not entirely finished, since comets must eventually hit the Earth from time to time. In particular, short-period comets still come from the Kuiper belt by the same orbital diffusion process that started some four and a half billion years ago, and long-period comets derive from those "new" comets coming from the Oort cloud, where they were also stored by an orbital diffusion that started in the same way.

2.17.1 Verified Predictions of the Model

1. The cratering record for the Moon, Mars, and Mercury confirms an early massive bombardment larger than the possible "tail" of the early bodies from the terrestrial planets' zones. The lunar record predicts a similar bombardment of the Earth, of the right order of magnitude, and covering mostly the first half billion years.
2. The diffusion rate of the cometary orbits predicts the subsiding mass rate of the flux reaching the Earth, by the combination of four exponential time constants produced by the four giant planets. The fact that time constants in proportion to the periods of the four giant planets explain satisfactorily the decline in time of the observed cratering flux on the Moon is particularly striking.
3. The 1% *volatile* fraction coming from comets explains the presence in the right proportions of the many siderophile metals still present in the Earth's crust. They were not scavenged by the formation of the iron core of the Earth, because they were brought later as a veneer when the Earth was cooler. It also explains the origin of the oceans' water and of the atmosphere. The large excesses of water and gases brought by comets were needed to compensate for the large volatile depletions coming from the bombardment of large bodies during the last stages of the accretion. The "siderophile excess" and the "volatile excess" still considered as a puzzle by geologists are explained.
4. The fact that refractory elements are slightly enriched in samples of the upper mantle, whereas the volatile elements are depleted, and the very volatile elements are strongly depleted, is explained by the accretion temperature of the planetesimals in the zone of the Earth, implying that the bulk of the Earth is not chondritic in the usual sense, but was formed by reduced iron grains with silicate grains depleted in most volatile elements.

5. The “planetary” component of the noble gases on the Earth seem to be derived from anomalous enrichment factors by low-temperature trapping in the cometary snows.
6. The 10-fold enhancement of the deuterium-to-hydrogen ratio was quenched at 200 K by the condensation of water snow from the nebular gas, which was eventually stored in comets before being brought into our oceans.

2.17.2 Unverified Predictions of the Model

The prediction that the lower mantle is completely outgassed cannot be verified yet. This is still a vigorously debated controversy in geophysics, whether the mantle plumes responsible for volcanic activity, in particular in the middle of the oceans like in Hawaii, come only from the upper mantle or throughout the 2,900 km depth of the whole mantle. The present model takes sides and claims that no lower mantle source is likely; however, it is quite clear that the “gardening” of the Earth during the late phase of impacts, followed by vigorous convection in the upper mantle, may have buried volatiles down to 600 km or more, that could become the source of hot plumes.

The mean chemical composition of comets is still poorly known. For this reason, the composition of the early atmosphere and its evolution is still difficult to predict, in particular, because of its temperature history during the first half billion years which corresponds to the final phases of accretion for the volatiles.

2.18 Conclusion

The idea that the primary organic syntheses started in space is not new. Without even going back to van Hise (1904) or Chamberlin and Chamberlin (1908), the possibility of an organic cosmochemistry was presumed by Oro (1961) and Bernal (1968). Whipple (1979), Chang (1979), and Delsemme (1979) concurred (in the same meeting) that comets may have provided most of the volatiles present nowadays on the Earth. Later, Delsemme (1981) took one step further, showing that the new paradigm on the origin of the solar system implies that the Earth first accreted from outgassed planetesimals then received a veneer of comet material as the result of the growth of the giant planets. This chapter has quantified this idea and shown that it connects a series of apparently unrelated problems, like the age record of the lunar craters, the reason why siderophile elements of the Earth’s crust were not scavenged by the formation of the Earth’s iron core, the reason why the “siderophile excess” and the “volatile excess” are linked, the source of the “planetary” component of the noble gas abundances on the Earth, the origin of the deuterium in the oceanic water, as well as the depletion of the volatile and siderophile metals in the upper mantle. To understand better our early atmosphere, we must now study comets.

References

Alexander, E.C., Ozima, M. (eds.) (1978), Terrestrial Rare Gases, *Adv. Earth Planet. Sci.*, **3** (Japan Sci. Soc. Press, Tokyo), 229 pages.

Anders, E. (1971), Meteorites and the early solar system. *Ann. Rev. Astronom. Astrophys.*, **9**, 1–34.

Anders, E., Grevesse, N. (1989), Abundances of the elements: meteoritic and solar. *Geochim. Cosmochim. Acta*, **53**, 197–214.

Anderson, A.T. (1975), Some basaltic and andesitic gases. *Rev. Geophys. Space Phys.*, **13**, 37–55.

Bar-Nun, A. Kleinfeld, I., Kochavi, E. (1988), Trapping of gas mixtures by amorphous water ice. *Phys. Rev B*, **38**, 7749–7754.

Bar-Nun, A., Kleinfeld, I. (1989), On the temperature and gas composition in the region of comet formation. *Icarus*, **80**, 243–253.

Berkner, L.V Marshall, L.C. (1965), On the origin and rise of oxygen concentration in the earth's atmosphere. *J. Atmos. Sci.*, **22**, 225–261.

Bernal, J.D. (1968), *Origins of Prebiotic Systems.* S.W. Fox (ed.) (Academic Press, New York), pp. 65–68.

Bertout, C. (1989), *Annu. Rev. Astronom. Astrophys.*, **27**, 351–395.

Cameron, A.G.W (1985), Formation and evolution of the primitive solar nebula. In D.C. Black and M.S. Matthews (eds.), *Protostars & Planets II* (University of Arizona Press, Tucson), pp. 1073–1099.

Cameron, A.G.W. (1988), Origin of the solar system. *Annu. Rev. Astron. Astrophys.*, **26**, 441–472.

Carr, M.H., Saunders, R.W, Strom, R.G., Wilhelms, D.E. (1984), *Geology of the Terrestrial Planets* (NASA SP-469, Washington DC).

Chamberlin, T.C. and Chamberlin, R.T. (1908), Early terrestrial conditions that may have favored organic synthesis. *Science*, **28**, 897–910.

Cassen, P., Shu, F.H., Tereby, S. (1985). In D.C. Black and M.S. Matthews (eds.), *Protostars and Planets II* (Univ. of Arizona Press, Tucson), pp. 448–483.

Chang, S. (1979), Comets: Cosmic connections with carbonaceous meteorites, interstellar molecules and the origin of life. In M. Neugebauer, D.K. Yeomans, J.C. Brandt and R.W Hobbs (eds.), *Space Missions to Comets* (NASA SP-2089, Washington, DC), pp. 59-III.

Chyba, C.F. (1987), The cometary contribution to the oceans of primitive Earth. *Nature*, **330**,632–635.

Cronin, J.R., Pizzarello, S., Cruikshank, D.P. (1988), Organic matter in carbonaceous chon- drites, planetary satellites, asteroids and comets. In J.F. Kerridge & M.S. Matthews (eds.), *Meteorites and the Early Solar System* (Univ Arizona, Tucson), pp. 819–857.

Delsemme, A.H. (1979), Scientific returns from a program of space missions to comets,. In Neugebauer et al. (eds.) *Space Missions to Comets*, (NASA SP-2089, Washington DC), pp. 139–178.

Delsemme, A.H. (1981a), Nature and origin of organic molecues in comets. In C. Ponnamperuma (ed.), *Comets and the Origin of Life* (D. Reidel Publishing Company, Dordrecht, Holland), pp. 33–42.

Delsemme, A.H. (1981b), In C. Ponnamperuma (ed.), *Comets and the Origin of Life* (D. Reidel Publishing Company, Dordrecht, Holland), pp. 141–159.

Delsemme, A.H. (1987). In *Diversity and Similarity of Comets*(European Space Agency, ESA-SP-278, Paris), pp. 19–30.

Delsemme, A.H. (1991a), Nature and history of the organic compounds in comets: An astrophysical view. In R.L. Newburn, M. Neugebauer, and J. Rahe (eds.), *Comets in the Post-Halley Era*, Vols. I-II (Dordrecht, Boston), pp. 377–427.

Delsemme, A.H. (1991 b), Origin of the biosphere of the Earth. In J. Heidmann & M.J. Klein (eds.), *Lecture Notes in Physics 390: Bioastronomy* (Springer-Verlag, New York), pp. 117–123.

Delsemme, A.H. (199Ic), International Halley Watch. In Z. Sekanina (ed.), *The Comet Halley Archives* Summary Volume (NASA-JPL, Pasadena), pp. 317–330.

Delsemme, A.H. (1992), Cometary origin of carbon, nitrogen and water on the Earth. *Origins Life Evol. Biosphere*, **21**, 279–298.

Delsemme, A.H. (1995), Cometary origin of the biosphere: A progress report. *Adv. Space Res.*, **15**, 49–57.

Delsemme, A.H. (1997), The origin of the atmosphere and of the oceans. In P.J. Thomas, C.F. Chyba and C.P. McKay (eds.), *Comets and the Origin and Evolution of Life* (Springer-Verlag, New York), pp. 29–67.

Delsemme, A.H. (1999), The deuterium enrichment observed in recent comets is consistent with the cometary origin of seawater, *Planet. Space Sci.*, **47**, 125–131.

Delsemme, A.H. (2000), 1999 Kuiper Prize: Cometary Origin of the Atmosphere, *Icarus*, **146**, 313–325.

Delsemme, A.H. and Miller, D.C. (1970), Physico-chemical phenomena in comets -II: Gas adsorption in the snows of the nucleus. *Planet. Space Sci*, **18**, 717–730.

Delsemme, A.H. and Wenger, A. (1970), Physico-chemical phenomena in comets -I: Experimental study of snows in a cometary environment. *Planet Space Sci.*, **18**, 709–716.

Delsemme, A.H. and Swings, P. (1952), Gas hydrates in cometary nuclei and interstellar grains. *Ann. Astrophys.*, **15**, 1–6.

Dreibus, G. and H. Wanke (1989), Supply and loss of volatile constituents during the accretion of terrestrial planets. In S.K. Atreya, J.B. Pollack, and M.S. Matthews (eds.), *Origin and Evolution of Planetary and Satellite Atmospheres* (Univ. Arizona Press, Tucson), pp. 268–288.

Dymond, J. and Hogan, L. (1978), Factors controlling the noble gas abundance patterns of deep-sea basalts. *Earth planet. Sci. Lett.*, **38**,117–128.

Eberhart, P. (1981). In *Basaltic Volcanism Study Project* (Pergamon, New York), pp 1025–1031.

vEberhart, P., Dolder, U. and Schulte, W., Krankowsky, D., Lammerzahl, P., Hoffmann, J.H., Hodges, R.R., Bertheller, J.J, and Illiano, J.M. (1987), The D/H ratio in water from Comet P/HaIley, *Astron. and Astrophys.*, **187**, 435–437.

Everhart, E. (1977), The evolution of comet orbits as perturbed by Uranus and Neptune. In A.H. Delsemme (ed.), *Comets, Asteroids, Meteorites* (Univ. Toledo), pp 99–104.

Fernandez, J.A. and Ip, W.H. (1981), Dynamical evolution of a cometary swarm in the outer planetary region. *Icarus*, **47**, 470–479.

Fernandez, J.A. and Ip, W.H. (1983), On the time-evolution of the cometary influx in the region of the terrestrial planets. *Icarus*, **54**, 377–387.

Gaffey, M.J. and Mc Cord, T.B. (1979), Mineralogical and petrological characteristics of asteroid surface materials. In T. Gehrels (ed.), *Asteroids* (Univ. Arizona), pp. 688–723.

Geiss, J. and Reeves, H. (1981), Deuterium in the solar system. *Astron. Astrophys.*, **93**, 189–199.

Goldreich, P. and Ward, W.R. (1973), The formation of planetesimals, *Astrophys. J.*, **183**, 1051–1061.

Grinspoon, D.H. and Lewis, J.S. (1987), Deuterium fractionation in the pre solar nebula: kinetic limitations on surface catalysis. *Icarus*, **72**, 430–436.

Hartmann, L.W, Kenyon, S.J. (1990), Optical veiling disk accretion, and the evolution of T Tauri Stars. *Astrophys. J.*, **349**, 190–196.

Horedt, G.P. (1978), Blow-off of the protoplanetary cloud by a T Tauri like solar wind. *Astron. Astrophys.*, **64**, 173–178.

Hubbard, W.B. (1984), *Planetary Interiors* (Van Nostrand-Reinhold, New York).

Ip, W.H. and Fernandez, J.A. (1988), Exchange of condensed matter among the outer and terrestrial protoplanets and the effect on surface impact and atmospheric accretion. *Icarus*, **74**, 47–61.

Jessberger, E.K., Christoforidis, A and Kissel, J. (1988), Aspects of the major element composition of Halley's dust. *Nature*, **332**, 691–695.

Kazimirchak-Polonskaya, E.I. (1972), The major planets as powerful transformers of cometary orbits. In G.A Chebotarev, E.I. Kazimirchak-Polonskaya, B.G. Marsden (eds.), *The Motions, Evolution of Orbits and Origins of Comets* (D. Reidel Publishing Co., Dordrecht, Holland), pp. 373–397.

Kerridge, J.F. (1991) (personal communication). See also Anders, E. and Kerridge, J.F. (1988), Future directions in meteorite research. In J.F. Kerridge and M.S. Matthews (eds.), *Meteorites and the Early Solar System* (Univ. of Arizona, Tucson), pp. 1155–1186.

Krueger, F.R. and Kissel, J. (1987), The chemical composition of the dust of Comet P/Halley as measured by "PUMA" on board VEGA-1. *Naturwiss.*, **74**, 312–316.

Laplace, P.S. (1796), *Exposition du Système du Monde* (Vve Courcier, Paris), pp. 431 in the 4th edition of 1813.

Larimer, J.W. (1967), Chemical fractionations in meteorites -I: Condensation of the elements. *Geochim. Cosmochim. Acta*, **31**, 1215–1238.

Larimer, J.W. (1968), An experimental investigation of oldhamite, CaS; and the petrologic significance of oldhamite in meteorites. *Geochim. Cosmochim. Acta*, **32**, 965–982.

Larimer, J.W. (1968), Experimental studies on the system Fe-MgO-SiO_2-O_2 and their bearing on the petrology of chondritic meteorites, Geochim. Cosmochim. Acta, **32**, 1187–1207.

Larson, R.B. (1984), Gravitational torques and star formation. *Mon. Not. Royal Astron. Soc.*, **206**, 197–207.

Lewis, J.S. (1972 a), Low temperature condensation from the solar nebula. *Icarus*, **16**, 241–252.

Lewis, J.S. (1972 b), Metal/silicate fractionation in the solar system. *Earth Planet. Sci. Lett.*, **15**, 286–290.

Lewis, J.S. (1974), The temperature gradient in the solar nebula. *Science*, **186**, 440–443.

Lewis, J.S., Barshay, S.S. and Noyes, B. (1979), Primordial retention of carbon by the terrestrial planets. *Icarus*, **37**, 190–206.

Lewis, J.S. and Prinn, R.G. (1980), Kinetic inhibition of CO and N_2 reduction in the solar nebula. *Astrophys. J.*, **238**, 357–364.

Lin, D.N.C. and Papaloizou, J. (1985), On the dynamical origin of the solar system. In D.C. Black and M.S. Matthews (eds.), *Protostars and Planets II* (Univ. of Arizona, Tucson), pp. 981–1072, in particular Fig 7.

Lynden-Bell, D. and Pringle, J.E. (1974), The evolution of viscous discs and the origin of l the nebular variables. *Mon. Not. Royal Astron. Soc.*, **168**, 603–637.

Matsui, T. and Abe, Y. (1986), Impact induced atmospheres and oceans on Earth and Venus. *Nature*, **322**, 526–528.

Meier, R., Owen, T.C., Matthews, H.E., Jewitt, D.C., Bockelée-Morvan, D., Biver, N., Crovisiet, J., Gautier, D. (1998). A determination of the HDO/H_2O ratio in Comet C/1995 O1 (Hale-Bopp). *Science*, **279**, 842–844.

Mizuno, H. (1980), Formation of the giant planets. *Progr. Theoret. Phys.*, **64**, 544–557.

Morfill, G.E. (1988), Protoplanetary accretion disks with coagulation and evaporation. *Icarus*, **75**, 371–379.

Morfill, G.E. and Wood, J.A. (1989), Protoplanetary accretion disc models: the effects of several meteoritic, astronomical, and physical constraints. *Icarus*, **82**, 225–243.

Morgan, J.W., Wandless, G.A., Petrie, R.K., and Irving, A.J. (1981), Composition of the earth's upper mantle. I- siderophile trace elements in ultramafic nodules. *Tectonophys.*, **75**, 47–67.

Morrison, D. (1977). In A.H. Delsemme (ed.), *Comets, Asteroids, Meteorites* (Univ. of Toledo, Ohio), pp. 177–184.

Oró, J. (1961), Comets and the formation of biochemical compounds on the primitive earth. *Nature*, **190**, 389–390.

Owen, T., Bar-Nun, A., and Kleinfeld, I. (1991). In Newburn et al. (eds.), *Comets in the post-Halley Era, vol. I* (Kluwer Publ., Netherlands), pp. 429–437.

Pepin, R.O. (1989), Atmospheric compositions: key similarities and differences. In Atreya et al. (eds.), *Origin and Evolution of Planetary and Satellite Atmospheres* (Univ. of Arizona, Tucson), pp. 291–305.

Pepin, R.O. (1991), On the origin and early evolution of terrestrial planet atmospheres and meteoritic volatiles. *Icarus*, **92**, 2–79.

Prinn, R.G. and Fegley, B. (1989). In Atreya et al. (eds.), *Origin and Evolution of Planetary and Satellite Atmospheres* (Univ. of Arizona, Tucson), pp. 78–137.

Rama Murthy, V. (1991), Early differentiation of the Earth and the problem of mantle siderophile elements: a new approach. *Science*, **253**, 303–306.

Reynolds, J.H., Frick, U., Neil, J.M., and Phinney, D.L. (1975), Rare-gas-rich separates from carbonaceous chondrites. *Geochim. Cosmoshim. Acta*, **42**, 1775–1797.

Ringwood, A.E. (1977), *Composition and Origin of the Earth*, (School of Physics, Pub. 1299, Australian National Univ., Canberra).

Rowan-Robinson, M. (1985), Infrared observations of interstellar clouds. *Physica Scripta*, **T11**, 68–70.

Rubey, W.W. (1951), Geologic history of sea water: an attempt to state the problem. *Bull. Geol. Soc. Am.*, **62**, 1111–1147.

Rubey, W.W. (1955). In Poldervaart (ed.), *Crust of the Earth*, (Geol. Soc. of America, New York), pp. 630–650.

Safronov, V.S. (1972). In G.A Chebotarev, E.I. Kazimirchak-Polonskaya, B.G. Marsden (eds.), *The Motions, Evolution of Orbits and Origins of Comets* (D. Reidel Publishing Co., Dordrecht, Holland), pp. 329–334.

Safronov, V.S. (1991), Kuiper Prize Lecture: Some problems in the formation of the planets. *Icarus*, **94**, 260–271.

Sears, D.W.G. and Dodd, R.T. (1988), Overview and classification of meteorites. In J.F. Kerridge and M.S.Matthews, (eds.), *Meteorites and the Early Solar System* (Univ. of Arizona, Tucson), pp. 3–31.

Signer, P. and Suess, H.E. (1963). In Geiss and Goldberg (eds.), *Earth Science and Meteoritics* (North Holland, Amsterdam), pp. 241–278.

Smith, B.A. and Terrile, R.J. (1984), A circumstellar disk around β Pictoris. *Science*, **226**, 1421–1424.

Stevenson, D.J. and Lunine, J.I. (1988), Rapid formation of Jupiter by diffusive redistribution of water vapor in the solar nebula. *Icarus*, **75**, 146–155.

Turekian, K.K. (1972). In *Chemistry of the Earth* (Holt, Rinehart & Winston, New York), pp. 102.

Van Hise, N. (1904). In *A Treatise on Metamorphism* (United States Geological Survey, Mon. 40), pp. 970, 973, & 974.

Vidal-Madjar, A. (1983). In Audouze et al. (eds.), *Diffuse Matter in Galaxies* (ASI Series C No 110, Reidel Dordrecht), pp. 57–94.

Von Weiszäcker (1944) quoted by Kuiper in A. Hyneck (ed.), *Astrophysics: a topical symposium* (Univ. of Chicago Press, Chicago).

Wänke, H. (1981), Constitution of terrestrial planets, *Phil. Trans. Roy. Soc. London, Ser.A*, **303**, 287–302.

Wänke, H., Dreibus, G., and Jagouts, E. (1984). In Kroner et al. (eds.), *Archaean Geochemistry* (Springer Verlag, Berlin), pp. 1–24.

Weidenschilling, S.J. (1988), Formation processes and time scales for meteorite parent bodies. In J.F. Kerridge and M.S. Matthews (eds.), *Meteorites and the Early Solar System* (Univ. of Arizona, Tucson), pp. 348–371.

Weissman, P. (1989). In Atreyaet al. (eds.), *Origin and Evolution Planetary and Satellite Atmospheres* (Univ. of Arizona, Tucson), pp. 230–267.

Wetherill, G.W. (1975), Late heavy bombardment of the moon and terrestrial planets. In *Proceedings of the 6th Lunar Science Conference* (Lunar and Planetary Institute, Houston), 1539–1561.

Wetherill, G.W. (1980), Formation of the terrestrial planets. *Annu. Rev. Astron. Astrophys.*, **18**, 77–113.

Wetherill, G.W. (1989). In Binzel et al. (eds.), *Asteroids II* (Univ. Arizona, Tucson), pp. 666–670.

Wetherill, G.W. (1990), Comparison of analytical and physical modeling of planetesimal accumulation. *Icarus*, **88**, 336–354.

Wetherill, G.W. (1991), Occurrence of Earth-like bodies in planetary systems. *Science*, **253**, 535–538.

Wetherill, G.W. and Champman, C.R. (1988), Asteroids and meteorites. In J.F. Kerridge and M.S. Matthews (eds.), *Meteorites and the Early Solar System* (Univ. Arizona, Tucson), pp. 35–67.

Wetherill, G.W and Cox, L.P. (1985), The range of validity of the two-body approximation in models of terrestrial planet accumulation. *Icarus*, **63**, 290–303.

Wetherill, G.W. and Stewart, G.R. (1989), Accumulation of a swarm of small planetesimals. *Icarus*, **77**, 330–357.

Whipple, F.L. (1979), Scientific need for a cometary mission. In Neugebauer et al. (eds.), *Space Missions to Comets* (NASA SP-2089, Washington DC), pp. 1–32.

Wood, J.A., Morfill, G.E. (1988), A review of solar nebula models. ln J.F. Kerridge and M.S. Matthews (eds), *Meteorites and the Early Solar System* (Univ. of Arizona, Tucson), pp. 329–347.

Zellner, B. (1979). In *Asteroids*, T. Gehrels (ed.), University of Arizona Press, Tucson, pp. 783–806.

3

Cometary Micrometeorites in Planetology, Exobiology, and Early Climatology

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Summary. Large unmelted Antarctic micrometeorites with sizes ≥100 μm that survive upon atmospheric entry started to be exploited in planetology and exobiology in the early 1990s. This chapter mostly focuses on micrometeorites that are destroyed upon atmospheric entry, through either volatilization or melting. Their "ashes" behave as powerful "tracers" that help decrypting some mysteries of our distant past, such as the formation of the Earth's atmosphere and the early history of the Earth's mantle. Moreover, they probably opened new reaction channels in the prebiotic chemistry of life, and they were involved in the post-lunar greenhouse effect that allowed the birth of life on the Earth. These large micrometeorites would be dominantly cometary dust grains that were released in the inner solar system, and which kept an astonishing invariant and simple composition over the last ∼4.4 Gyr.

3.1 Introduction

Large Antarctic micrometeorites (AMMs) with sizes ≥100 μm were recovered for the first time in December 1987. Over the next decade we intensely studied these micrometeorites that survive unmelted upon their frictional heating during atmospheric entry. The large micrometeorites are of particular importance to the field of exobiology as they were assimilated into "chondritic" chemical reactors that contributed to the synthesis of prebiotic molecules during their interactions with gases and waters (Maurette, 1998).

However, in 1999 it was realized that micrometeorites that are destroyed upon atmospheric entry (through either volatilization and/or melting) could also contribute to planetology and exobiology. In particular, it was inferred that the Moon has necessarily been formed near the end of the formation time interval of the Earth, $\Delta(Earth)$. This was the only way to account for the micrometeoric purity of the atmosphere (see below) with a model based on the accretion of "juvenile" micrometeorites by the early Earth (Maurette et al., 2000a). In August 2001, Canup and Asphaug (2001) did show that this deduction, which was the first prediction of this model coined ***EMMA***

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(Early MicroMeteorite Accretion), was justified. Since then, we pursued a kind of hectic cosmic detective investigation searching for the role of juvenile micrometeorites in the mysteries of our origins.

In the next section we briefly outline the unique relationship between AMMs and the volatile-rich primitive hydrous–carbonaceous chondrites (HCCs). We next develop the idea that the formation of the Moon by a giant Mars-sized Moon forming impactor played a decisive role in the formation of the post-lunar atmosphere, while blowing off the complex pre-lunar atmosphere of the early Earth, thus leaving a vacant "niche" for the formation of a pure micrometeoritic atmosphere. This atmosphere was delivered during a kind of giant storm of juvenile micrometeorites, with composition similar to that of contemporary AMMs, and which lasted for about 100 Myr after the formation of the Moon.

In particular, from the wt% contents of the constituent volatile species of micrometeorites (i.e., Ne, N_2, H_2O, and C), we inferred their total "post-lunar" amounts in the atmosphere. They fit the contemporary values within a factor 2–3, even though these volatiles have not the same origins and show huge differences in concentrations in AMMs by factors of *up ∼10 millions!* We next predicted rightly the micrometeoritic content of a highly siderophile and highly refractory element, iridium, in rocks from the Earth's upper mantle. After this additional testing, ***EMMA*** was used with increased confidence to assess the role of juvenile micrometeorites in planetology, exobiology, and early climatology. Some of these contributions require the identification of the parent bodies of micrometeorites (i.e., either asteroids or comets), and we devote a full section to this problem.

3.2 Dark Micrometeorites in Blue Ices: Relationships with Hydrous–Carbonaceous Chondrites

During the Antarctic summer field seasons of 1987, 1990, and 1994, a team set off for the "blue ice" fields of Cap-Prudhomme in Antarctica, to recover the glacial sand trapped in the ice. This sand turned to be amazingly rich in large *unmelted* micrometeorites (Maurette et al., 1991). In the best 50–100-µm size fraction, a daily collect recovered from 10 to 15 m^3 of melted ice, typically yields approximately 2000 unmelted micrometeorites, approximately 500 cosmic spherules (i.e., melted micrometeorites), and approximately 10,000 terrestrial particles – mostly morainic debris. In this sand, about 20% of the particles are unmelted micrometeorites (Fig. 3.1).

About 2,000 Antarctic micrometeorites (AMMs) have already been analyzed by a consortium mostly including M. Christophe, E. Delousle, J. Duprat, C. Engrand, M. Gounelle, C. Hammer, G. Kurat, G. Matrajt, M. Maurette, and C. Olinger (see Maurette et al., 1991; Kurat et al., 1994; Engrand and Maurette, 1998; Maurette et al., 2000; Matrajt et al., 2001; Maurette et al.,

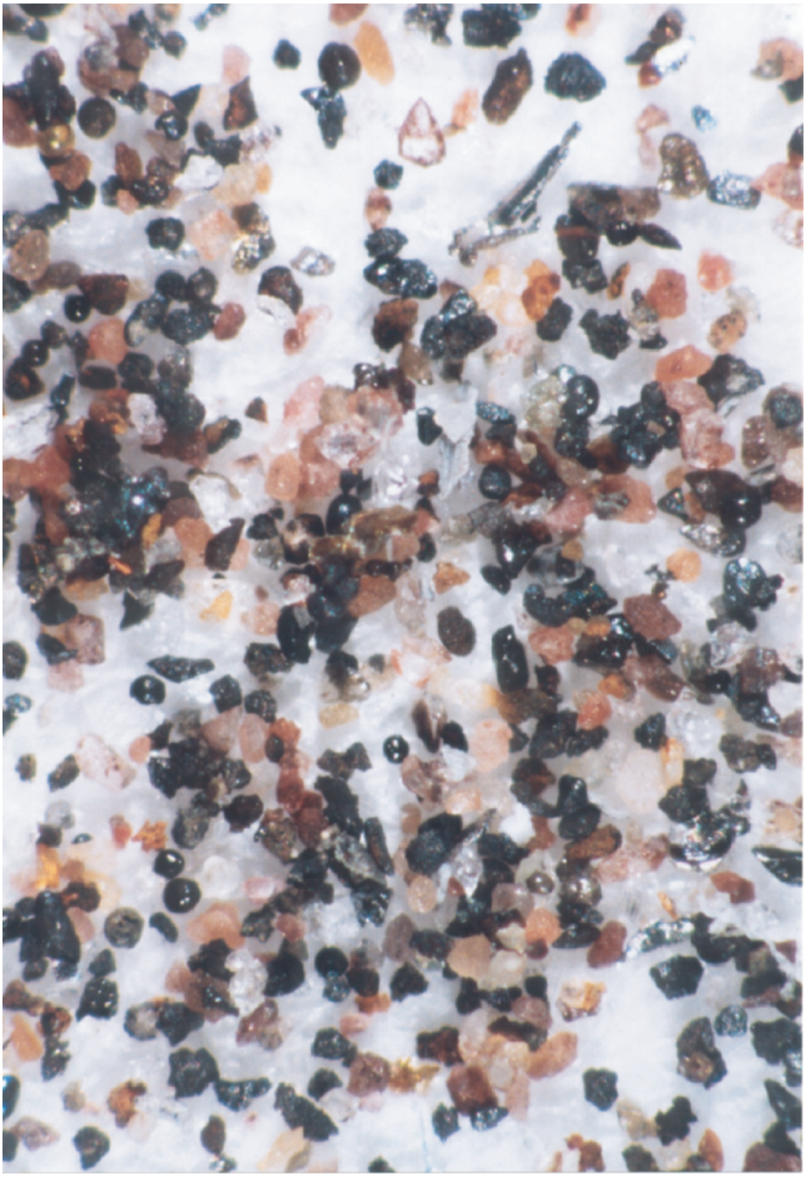

Fig. 3.1. Glacial sand recovered from the blue ice fields of Cap–Prudhomme, at approximately 2 km from the margin of the Antarctica ice sheet. Steam generators, adjusted to deliver hot water at approximately 70°C, were used to make pockets of melt ice water at a few degree centigrades. Each daily collect was recovered from a total volume of water of about 10–15 m^3, which was pumped and filtered on stainless steel sieves with openings ranging from about 25 µm up to 400 µm. This picture represents the best 50–100-µm size fraction of this sand, where one grain out of five is an unmelted micrometeorite. Unmelted and melted micrometeorites appear as "dark-irregular-charcoal" looking grains and glassy cosmic spherules, respectively.

2001; Duprat et al., 2003). Their mineralogical, chemical, and isotopic compositions first show that about 99% of them are related only to the group of the HCCs. These relatively rare meteorites (about 2.5% of the meteorite falls) include the three subgroups of the CI1, CM2, and CR2 type chondrites, containing about 100, 50, and 25% of hydrous minerals, respectively.

In the complex classification of meteorites, which already involved about 80 distinct groups in 1980 (Dodd, 1980) – 50% of them correspond to minor groups of iron meteorites – HCCs are considered as the most primitive meteorites, i.e., their constituent grains have never been exposed to temperatures higher than approximately 600 K since their formation in the early solar nebula. These "wet" carbonaceous objects are the most volatile-rich material delivered to the Earth. They can release neon, nitrogen, water, CO_2, SO_2, etc., during their volatilization and/or melting upon atmospheric entry, but also during the subduction of the oceanic crust on which they end up being deposited.

More surprisingly, about 95% of the AMMs are only related to the CM subgroup of HCCs, thought to originate from a single family of carbonaceous asteroids. The first hints about this "deceptively" simple micrometeorite classification led to disappointment. Indeed, the major initial objective of the "blue ice" team was to discover new solar system objects, not represented as yet in the complex classification of meteorites, and the hope to find new objects among AMMs was quickly vanishing.

However, this disappointment turned to excitement when the following deductions were made: (i) this simple classification implies that AMMs are not a mixture of microscopic fragments originating from the $\geq$80 distinct parent bodies of meteorites. Therefore, they likely originate from other types of parent bodies; (ii) the chemical and isotopic compositions of their volatile species are well mimicking those of the Earth's atmosphere; (iii) the proportion of large micrometeorites with sizes $\geq$100 µm which survive unmelted upon atmospheric entry is about 25%. This value, which is two times higher than previous estimates, was deduced for a new set of *unweathered-highly-friable* AMMs collected by Duprat and Engrand in central Antarctica (Duprat et al., 2003). Today, with this revised value, micrometeorites deliver to the Earth's surface a mass of unmelted *hydrous–carbonaceous* material at least ~20,000 times larger than that expected for the HCCs . If this enhancement factor was not decreased by a factor $\geq$1,000 in the distant past, the micrometeorite flux was the major extraterrestrial source of volatiles and organics on the early Earth's surface, after the giant impact by a Mars-sized body, which blew off the complex pre-lunar atmosphere of the young Earth (see first rubric in Sect. 3.10).

3.3 Formation of the Earth's Atmosphere: Previous Scenarios

Accordingly to the definition of Ozima and Podosek (2002), the Earth's atmosphere refers to all volatiles in surface reservoirs, including air, water, and sedimentary rocks such as carbonates in which early CO_2 is trapped. Over the last ∼50 years, the formation of the atmosphere was successively attributed to (i) volcanic outgassing (Rubey, 1955) which did recycle a mixture of volatiles inherited from the variety of materials that fed the growth of the young Earth during successive stage of accretion, starting with the ≤ 1 Myr "sticking" period of dust grains in the early solar nebula and ending up with the ∼100 Myr accretion period of tens to hundreds of planetary embryos with sizes up to that of Mars (for a short summary of previous works, see Abee et al., 2002); (ii) the direct capture of gases from the solar nebula (Urey, 1952); and (iii) the explosive impact of comets (Owens, 1998; Delsemme, 1997) and/or that of a giant "wet" asteroid – cf. Morbidelli et al. (2000) for a review of previous works.

3.3.1 Volcanism, Nebular Gases, and Comets

The two first processes are generally disregarded to day (cf. Owens (1998) and Delsemme (1997)). In particular, Hawaiian volcanoes eject gases generated by the most primitive deep-seated magma originating from the undegassed part of the Earth's mantle. Their H_2O/N_2 and CO_2/N_2 ratios (Table 3.1, column 6) do not fit the corresponding ratios measured for the atmosphere (column 4). About the capture of nebular gases, the Ne/N_2 ratio predicted for the solar nebula is about 10^5 times higher than the atmospheric value.

A few scientists still invoke the impact of cometary ices with the Earth because they were impregnated with nebular gases during their formation (cf. for a review of previous works). A preferential adsorption of the heavy noble gases could possibly account for their odd mass fractionation in the atmosphere, illustrated in particular by the stumbling problem of the "missing" xenon (cf. Ozima and Podosek, 2002).

However, the general consensus is that the direct hits of comets on the young Earth delivered less than ∼10% of the oceans mass. This was deduced from the average D/H ratio of the constituent water of three comets (all originating from the Oort cloud), which is about two times higher than the standard terrestrial value, SMOW, measured for an average of the terrestrial oceans.

But as stressed by Delsemme (1999), these ratios have been measured for three comets from the Oort cloud only, which were likely formed in the outer solar system, thus possibly preserving a memory of the high D/H ratio of the interstellar medium. It cannot be excluded that comets that impacted the early Earth–Moon system were formed much nearer to the Sun, in the Jupiter–Saturn zone, where the D/H ratio of their constituent water might have been reprocessed to a smaller value. More recently, Podolak et al. (2002) argue that the D/H ratio measured in the coma of comets is larger than that of the parent water ice. In this case the constituent ices of comets could have delivered, at least partially, the water in the Earth's ocean.

This minor role of comets is also compatible with other data, such as the average H_2O/N_2 and $(CO_2 + CO)/N_2$ ratios of their transient atmosphere (Table 3.1, column 7), produced during the sublimation of their "dirty" ices in the inner solar system, which do not fit the composition of the Earth's atmosphere (column 4).

3.3.2 A Wrong Neon in the Giant Asteroid?

After this screening, the only surviving model is the impact of a giant wet asteroid (***GwetA***). Its composition is adjusted as to yield the right amount of ocean water (1.4×10^{24} g) but also the "minimum" asteroid size, as to avoid a marked heating during its formation, due to radioactive decay and accretional heat. This last condition is important as a modest formation temperature in excess of ~600 K effective over ~1 Myr would already trigger an important loss of the constituent volatiles of the ***GwetA*** before its impact with the Earth.

The *most favorable* assumption is to assume that its bulk composition is just similar to that of an *undegassed* "chunk" of the most water-rich meteorites (~20 wt% of water), the CI type chondrites (CIs). They belong to the relatively rare group of the HCCs (see Sect. 2). A "minimum" size of approximately 1,500 km is deduced from this remarkably high-water content, corresponding to a body made of approximately 100% of clays! This body is already sufficiently massive as to probably suffer a noticeable degassing during its formation. But the assessment of its exact state of dehydration cannot be made because such hydrous "giants" do not exist any more.

The Misleading "Bulk" Solar Neon of HCCs

The bulk average contents of neon and nitrogen in CIs, of about 3×10^{-7} cc STP/g and 2500 ppm, respectively (Masson, 1971), already show that a CI-type ***GwetA*** would deliver an atmosphere with a Ne/N_2 ratio about 100 times smaller than the value measured in the Earth's atmosphere. But the real misfit between predictions and the corresponding observations is even worst. It started to be decrypted recently, relying on studies of the reprocessing of material in extraterrestrial regoliths (Maurette, 2002). The key observations leading to this tricky misfit is that HCCs are all *regolith breccias*, like most rocks found on the lunar surface. They are compacted chunks of the loose layer of debris, coined as regolith, which tops the surface of both the Moon and large asteroids.

Langevin retraced the depth trajectories of many test particles in the lunar regoliths with a Monte Carlo computer code nicknamed "SOLMIX" (Duraud et al., 1975; Langevin, 1978; Langevin and Maurette, 1976). This model takes into consideration the "gardening " of the particles in the regolith, because of their repeated excavations (by impact craters), deposition on the surface through ejecta blankets emitted from craters (crater "rays"), and burial by a "sedimentation" process fed by the deposition of successive crater rays, until the time of the next excavation. The coupling of these depth trajectories with adequate depth-dependant production rates of SW–Ne, SEP–Ne, cosmogenic ^{21}Ne and ^{10}Be, etc., allowed predicting their concentrations. The good fits between predictions and observations for lunar samples validated this model, which was subsequently extrapolated to the regolith of $\geq$10 km size asteroids (Dran et al., 1979; Durand et al., 1979; Langevin, 1981).

The predictions for asteroids are well compatible with recent observations of Nakamura et al. (1999), based on laser microprobe studies of the distribution of neon isotopes in approximately 100-µm size zones of thin sections of two of the most gas-rich HCCs – Nogoya and Murchison, which belong to the most abundant CM subgroup of HCCs. Their petrographic and mineralogical characteristics were first carefully investigated. As expected from SOLMIX, about 10% of the grains have been exposed on the top surface of the regolith to solar neon carried by both solar wind (SW) and solar energetic particles (SEPs), which have short penetrations in solids ($\leq$100 µm). These "gas-rich" grains are loaded with solar neon up to the high *average* contents of about $\sim(1\text{–}3)\times10^{-5}$ cc STP/g, observed in both micrometeorites and "mature" lunar soil samples – such values are compatible with an integrated residence time at depth "0" on the surface of their parent regolith of approximately 5,000 years. Consequently, the bulk solar neon content of HCCs will be about 10 times smaller than the micrometeorite value. But what about neon in the dominant fraction of the gas-poor grains?

The Gas-Poor Grains of HCCs

The family of "gas-poor" grains represents about 90% of the HCC mass. In the case of the CMs, most of them belong to cm-sized "clasts" of a material defined as "PARs" (Primary Accretion Rocks), in which they were shielded from the implantation of SW and SEPs neon. Consequently, they do not contain solar neon, even though their parent clasts might have been exposed to solar neon on the top surface of the regolith. Instead, they show a very different residual neon component coined as "planetary," and characterized by both a smaller concentration and a much smaller (~8). *This component, which has not been "contaminated" by solar neon, should be similar to that trapped in rocks below the regolith, well shielded from SW and SEPs ions, and which represents ~99.99% of the mass of a ~1500-km-sized **GwetA**.*

The average content of primordial neon in the "PARs" is about 5×10^{-8} cc STP/g (see "pits" 59 and 60 in figure 6 reported by Nakamura et al. (1999)). This content can be reasonably extrapolated to the CIs – and thus to the

GwetA – because it was measured in the PARs, which were likely the building blocks of the parent bodies of the CIs (Eiler and Kitchen, 2003). Furthermore, the content of nitrogen (∼2500 ppm) in the CIs (Mason, 1971), which is carried by the carbonaceous component, does not result from a regolith contamination. Consequently, if the early atmosphere was delivered by a CI-type ***GwetA***, its Ne/N_2 ratio should be approximately 1,000 times smaller than the atmospheric value!

The Wrong Neon Isotopic Composition of a CI Type GwetA

There is an additional wrong prediction, which deals with the nature of neon in the early atmosphere. There is a general consensus that this neon was "solar," being characterized by a high $^{20}Ne/^{22}Ne$ ratio bracketed between 13.8 and 11.2. Subsequently, a mass-dependent process of isotopic fractionation did trigger a preferential loss of the *lightest* ^{20}Ne isotope, which decreased this initial solar ratio to the atmospheric ratio of 9.8 (see Sect. 4.2). But the ***GwetA*** model would generate an early atmosphere, showing a very different "planetary" neon, with a $^{20}Ne/^{22}Ne$ ratio ∼8. To be compatible with the atmospheric ratio, this would require a preferential loss of the *heaviest* ^{22}Ne isotope through a mysterious unnatural process, still to be discovered!

These two wrong predictions were trickily camouflaged in the complexity of regolith reprocessing. In brief, the bulk solar neon of HCCs reflects a negligible and misleading surface contamination of the ***GwetA***, and not its bulk "primordial" composition. In contrast, studies reported in the next section indicate that the constituent neon of micrometeorites now simultaneously yields this solar composition and the right Ne/N_2 atmospheric ratio. This unexpected fit already suggests that the formation of the early Earth's atmosphere did occur with the only remaining alternative of a *giant-long-duration-storm* of early micrometeorites, astonishingly similar to large contemporary Antarctic micrometeorites.

3.4 The Micrometeoritic "Purity" of the Earth's Atmosphere

The chemical composition of the atmosphere can be defined from the Ne/N_2, H_2O/N_2 and CO_2/N_2 ratios reported in Table 3.1 (column 5), which are deduced from the ratios of the total amounts of these four volatiles measured in the atmosphere (column 2). The same volatiles are released by micrometeorites similar to AMMs mostly upon frictional heating as to generate a micrometeoritic model atmosphere. Its composition is inferred from the wt% contents of ^{20}Ne, N_2, H_2O and total carbon measured in about 500 AMMs from the ∼100–200-μm size fraction (column 3). They are bracketed between a lower and upper value discussed below, and which give the "average" content used to define the chemical composition of the micrometeoric atmosphere.

3.4.1 Concentrations of Volatiles in Antarctic Micrometeorites

Neon

Noble gas analyses indicate that the neon trapped in unmelted AMMs has a solar isotopic composition and an average concentration of approximately 1.5×10^{-5} cc STP/g (Olinger et al., 1990; Maurette et al., 1991; Nakamura and Takaoka, 2000; Osawa et al., 2000; Osawa and Nagao, 2002). This put micrometeorites on a par with lunar dust grains. They both represent the most gas rich extraterrestrial material known as yet, with the exception of the minor fraction (∼10%) of the constituent gas-rich grains of the "gas-rich" meteorites, which show similar high solar neon contents.

The comparison of the ^{20}Ne/^{22}Ne ratios measured in micrometeorites (∼11.8), the solar wind (13.8), and solar energetic particles (11.2) shows that micrometeoritic neon is composed of about 25% SW–Ne and 75% SEP–Ne neon carried by solar energetic particles (see next section). However, the flux of SW–Ne is about 10^5 times higher than that of SEP-Ne at 1 AU. So, where is the lost SW–Ne? Most colleagues believe that the neon content of micrometeorites has been drastically altered upon atmospheric entry. Indeed, solar wind neon is implanted at a much shallower depths than SEP-Ne. Therefore, it should have been preferentially lost through a "random walk" to the surface. However, as this lost neon was just released and trapped in the atmosphere, its mass should have been similar to that of nitrogen and not approximately 10^5 times smaller.

We argued elsewhere (Maurette, 2005) that contrarily to this widely spread conventional view, the characteristics of neon in unmelted micrometeorites were mostly fashioned during their flight times to the Earth of about 200,000 years, when they were exposed to a destructive high fluence of SW–He of about 2.5×10^{19} He cm^{-2}. This SW–He induced a repeated blistering of their surface that did flake off to space. The resulting erosion did cut through the deeper accumulation zone of SEP–Ne. A very small residual "saturation" concentration of SW–Ne was thus injected in this zone where it lost its identity (i.e., its high ^{20}Ne/^{22}Ne ratio). Therefore, the characteristics of solar neon stored in micrometeorites, which survived unmelted upon atmospheric entry at the first place, would reflect their preatmospheric values.

Nitrogen

The measurements performed until 2000 indicated a low concentration of this element, which was near the limit of sensitivity (about 0.1%) of our technique of electron energy loss spectroscopy in a high voltage electron microscope. With this limit, only a few AMMs gave a weak signal above background around 400 eV, which was too small to be quantified. Thus the upper limit of the nitrogen content of AMMs is approximately 0.1%. Recently, Matrajt et al. (2001) measured the C and N contents of both AMMs and two HCCs

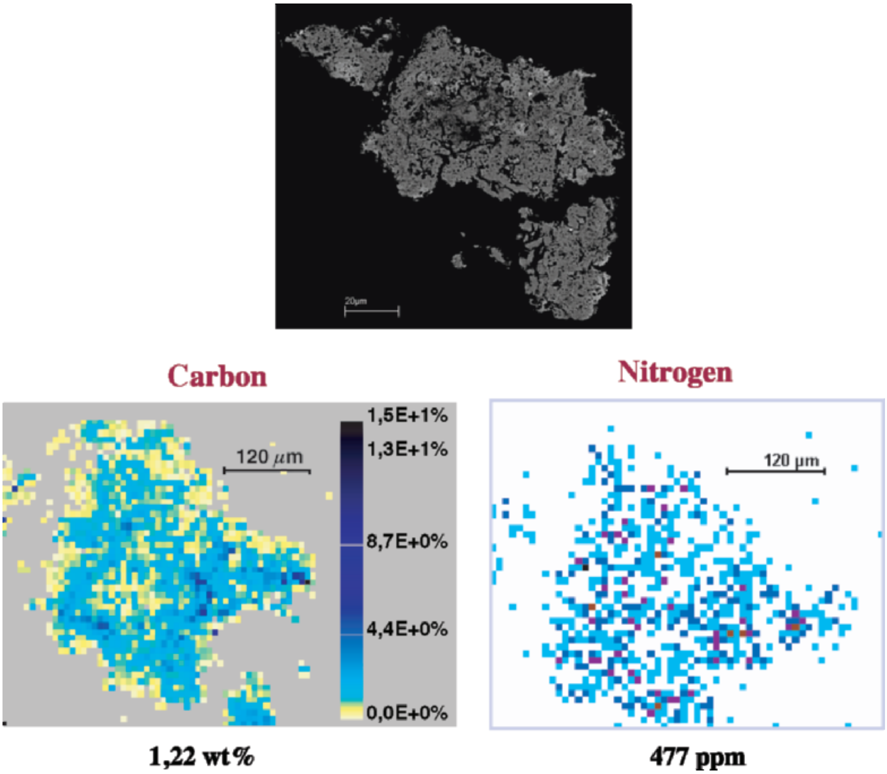

Fig. 3.2. A beam of deuterons was used in a nuclear microprobe to get the micromappings of the carbon and nitrogen concentrations in a fine-grained Antarctic micrometeorite collected at Cap-Prudhomme (top), throughout the $^{12}C(d,p_0)^{13}C$ and $^{14}N(d,p_0)^{15}N$ reactions. The C and N concentrations are clearly correlated. They yield average values of the N/C ratio ranging from about 20 to 40. This indicates that the dominant C-rich component of micrometeorites is related to "kerogen." (Courtesy of J.P. Gallien and G. Matrajt).

relying on a nuclear microprobe with a much improved lower limit of detection (Fig. 3.2). The minimum nitrogen content of micrometeorites was thus found to be approximately 0.03%.

Water

For water in micrometeorites, in our two first papers (Maurette et al., 2000a,b), we quoted a content of ~4%, which was directly inferred with an ion microprobe. We thus ended up with a real deficit of water by a factor of 4 while injecting this value in the accretion formula (see Sect. 5.1). This content could be a lower limit because this water is carried by hydrous silicates, which are partially dehydrated upon atmospheric entry. In fact, its value could be reliably inferred only after identifying the type and the relative abundance of these minerals, and understanding their thermal degradation upon atmospheric entry. In CM-type chondrites, the total abundance of major hydrous silicates (mostly serpentine and saponite) is about 20% and this yields a water content of approximately 7.7%. The same dominant minerals were also found in AMMs. However, saponite starts dehydrating at only 100°C, and the loss of water upon atmospheric entry is unavoidable. Fortunately, the dehydrated hydrous minerals can still be identified from the relic chemical composition of their dry residues. It can thus be deduced that the total abundance of hydrous silicates is similar to the value observed in the CMs ($\sim$20%). But now saponite, which contains more water than serpentine, is the dominant hydrous silicates in AMMs. Consequently, the bulk water content of micrometeorites *before atmospheric* is slightly larger ($\sim$10%) than that of CMs, i.e., about 2.5 times higher than our earlier estimate! The carbonaceous component of micrometeorites (mostly kerogen) would yield a negligible contribution of water upon pyrolysis.

CO_2

To evaluate the "potential" content of CO_2 that can be released by micrometeorites upon atmospheric entry, the total amounts of carbon stored in both the carbonates and carbonaceous components of AMMs have to be estimated. One can deduce that about 0.5% of the total carbon of AMMs is trapped as carbonates (Maurette et al., 1992). The average *organic* carbon content of AMMs, of about 2.5%, was measured with the ion microprobe of *Centre de Recherches Pétrographiques et Géochimiques* (Engrand and Maurette, 1998). These carbon contents allow computing the "equivalent" concentration of CO_2 that will be released upon atmospheric entry, and then subsequently transformed into carbonates, which will settle down to the ocean floors. During atmospheric entry carbonates decrepitate, whereas organics generate CO_2 upon pyrolysis. The lower limit reported in Table 3.1 corresponds to the decrepitation of carbonates and the upper limit is obtained adding the amount of CO_2 resulting from the full oxidation of the organic carbon.

3.4.2 The Micrometeoritic "Purity" of the Earth's Atmosphere

Chemical Composition

These concentrations of micrometeoritic volatiles, A(%), have been reported in Table 3.1 (column 3), *in wt%*. The ratios directly give the Ne/N_2, CO_2/N_2, and H_2O/N_2, ratios (columns 5) expected for a small "puff" of gases of approximately 1 mg that would be released upon atmospheric entry by the aliquot of about 500 contemporary micrometeorites used to make the measurements of the A(%) values. The composition of this "micrometeoritic atmosphere" turns to be strikingly similar (i.e., *within a factor* $\sim$*2)* to that of the massive

Table 3.1. Volatiles in various "atmospheres".

Volatile (A)	Mass (g) (atmosphere)	A (%) (AMMs)	Chemical composition (relative to N_2) A/N_2	Earth	AMMs	Hawaii[a]	Comet[a]
Ne	6.5×10^{16}	$(1 - 3) \times 10^{-6}$	Ne/N_2	1.6×10^{-5}	3×10^{-5}	?	?
N_2	4×10^{21}	$(0.3 - 1) \times 10^{-1}$	N_2/N_2	1	1	1	1
H_2O	1.4×10^{24}	10	H_2O/N_2	350	153	10	30
CO_2	0.33×10^{24}	1.8 – 11	CO_2/N_2	85	100	4	2 – 6

[a] The data necessary to evaluate the ratios quoted for the "atmospheres" produced by Hawaiian volcanoes and the sublimation of cometary ices have been found in Hartmann (1999), Delsemme (1997), and Boice and Huebner (1999), respectively.

($\sim 2 \times 10^{24}$ g) Earth's atmosphere (column 5), which is given by the ratio of the total amounts of the corresponding volatiles, listed in column 2.

Isotopic Composition of Neon

Neon is considered as one of the best tracer to decrypt the history of the Earth's atmosphere. It is not sequestered during chemical reactions, and, with the exception of a minor fraction of ^{21}Ne, it is not produced during the decay of radioactive elements, contrarily to helium and some isotopes of the heavier noble gases. Its isotopic composition in unmelted AMMs turns to be "solar." It is bracketed between the ^{20}Ne/^{22}Ne ratios observed in the solar wind (SW) and solar energetic particles (SEPs), which are about 13.8 and 11.2, respectively (Wieler, 1998). *The average micrometeoric ratio of ~11.85*, which can be deduced from the accurate measurements reported by Nakamura and Takaoka (2000) constitutes a unique signature of micrometeoritic neon that reflects a specific distribution of their flight times to the Earth (see the previous section).

We remind that it is generally assumed that neon in the early atmosphere has initially a solar composition (Ozima and Podosek, 2002). Subsequently, the high solar ^{20}Ne/^{22}Ne ratio was lowered by a preferential loss of ^{20}Ne triggered by mass-dependent fractionation processes such as hydrodynamical escape (Ozima and Zahnle, 1993). Most models assume that this neon was not delivered by micrometeorites. It was initially incorporated during the formation of the building material of the Earth in the solar nebula, before the formation of the planets, and then subsequently degassed into the atmosphere.

We support another alternative, where this pre-lunar neon was blown off during the Moon forming impact, thus leaving a new niche for the accumulation of a pure component of solar micrometeoritic neon in the atmosphere.

Isotopic Composition of Water

The isotopic composition of the constituent water of individual HCCs and AMMs can be plotted as the distribution of their D/H ratios. In Fig. 3.3, we first reported the distributions measured for CI and CM chondrites (top and middle histograms, respectively), which were deduced from data recently reported by Eiler and Kitchen (2003). The bottom histogram refers to the distribution obtained from the ion microprobe analysis of 52 AMMs (Engrand and Maurette, 1998; Engrand et al., 1999). Other ratios include values measured for an average of the terrestrial oceans ("SMOW" value), Antarctic melt ice water, and three comets originating from the Oort cloud.

These histograms can be compared to that relevant to much smaller micrometeorites (coined as IDPs), collected in the stratosphere by NASA, and showing much higher D/H ratios (see Fig. 6 in Engrand et al. (1999)). It clearly shows that from all extraterrestrial material investigated yet, including cometary water, AMMs give the best fit to the SMOW value. It could be argued that they were contaminated by terrestrial water. But micrometeorites were recovered from Antarctic melt ice water, which shows the lowest D/H ratio measured on the Earth, about 1.5 times smaller than SMOW. Furthermore, experiments discussed in Engrand et al. (1999) indicate that isotopic exchange between AMMs and terrestrial water is very unlikely to have happened.

The astonishing similarity between the chemical and isotopic compositions of the terrestrial atmosphere and the mixture of gases to be released during atmospheric entry from a small aliquot of AMMs of a few milligrams strongly suggests that the suspect responsible for the formation of the atmosphere was the accretion of a gigantic "storm" of juvenile micrometeorites. Their composition was similar to that of AMMs, and thus invariant with time. This important feature allows predicting the total amounts of micrometeoritic volatiles injected in the early atmosphere with a simple "accretion" formula.

3.5 Formation of the Post-Lunar Earth's Atmosphere

3.5.1 An Accretion Formula Born with the Moon

The Moon was formed by a giant Mars-sized impact with the Earth, which occurred near the end of the formation time interval of the Earth, *Δ(Earth)*, as shown by Canup and Asphaug (2001). This impact blew off the pre-lunar atmosphere (cf. Sect. 10, first rubric). It thus left a vacant "niche" for the

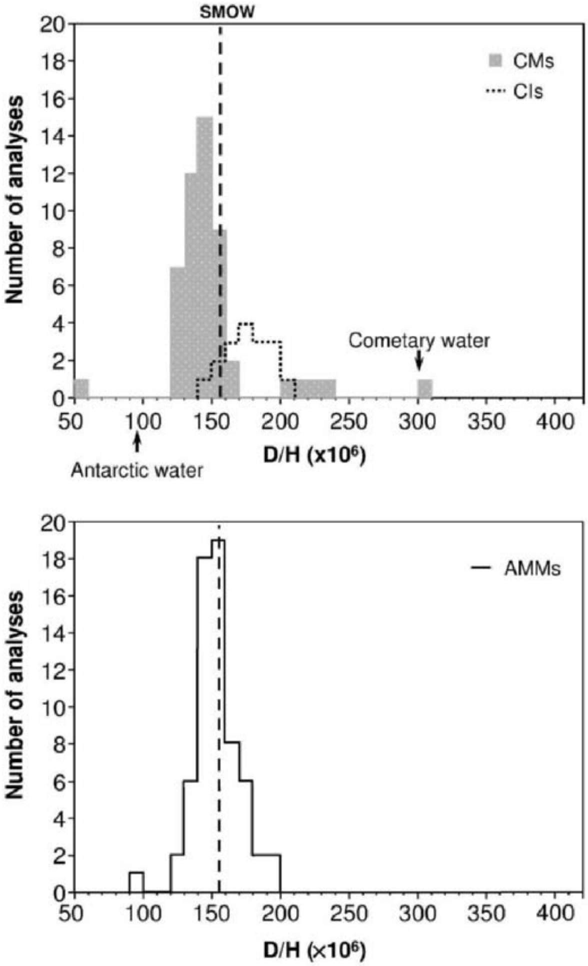

Fig. 3.3. Isotopic composition of various types of waters, including the constituent water of the CI and CM hydrous–carbonaceous chondrites (upper histogram), and the constituent water of Antarctic micrometeorites (lower histogram). From left to right, the arrows refer to (i) Antarctic melt ice water showing the lowest terrestrial D/H ratio; (ii) an average of the terrestrial oceans that defines the "SMOW" value; and (iii) an average of the D/H ratios measured in three nonperiodic comets (Courtesy C. Engrand).

accumulation of a new *"post-lunar"* atmosphere. The invariance of the composition of the micrometeorites with time (Sect. 4.2) allows assuming that the wt% content $A(\%)$ of a given volatile, A, in early micrometeorites, back to 4.4 Gyr ago, is just given by the corresponding value measured in Antarctic micrometeorites.

If a method is found to estimate the integrated mass flux of micrometeorites, Φ_0, deposited on the Earth since the formation of the Moon, the total amount, M_A, of A deposited by micrometeorites in the post-lunar atmosphere is given by a "simple" accretion formula: $M_\mathrm{A} \sim A(\%) \times 10^{-2} \times \Phi_0$. The next section briefly outlines two fully independent methods that unexpectedly yielded a similar value of Φ_0.

Integrated Mass Flux of "Post-Lunar" Micrometeorites: The Neon and Nitrogen Estimates

During atmospheric entry, micrometeorites which either get fully volatilized and/or transformed into "dry" melted cosmic spherules during frictional heating with air molecules directly inject volatiles in the atmosphere. About 75% of the incoming flux of micrometeorites with sizes ≥100 µm is thus "destroyed." Large unmelted micrometeorites that survive atmospheric entry essentially settle down on the oceanic crust, and they are degassed at shallow depths during the subduction of their host crust. As a first approximation, the full incoming flux of hydrous–carbonaceous micrometeorites delivers volatiles in the atmosphere.

The invariance of the composition of the micrometeorite flux with time allows two independent "direct" estimates of Φ_0 from the total amounts of the neon and nitrogen in the atmosphere (Table 3.1, column 2) and the content of these elements in AMMs, which differ by a factor of approximately 100,000. For each element, these contents are bracketed between a lower limit and an upper limit (Table 3.1 column 3), which yield two "average" values of Φ_0 of about 3.2×10^{24} g and 6.1×10^{24} g, from neon and nitrogen, respectively.

Each one of these values can already be considered as fully independent because the constituent neon and nitrogen of micrometeorites have not the same origin. They allow estimating the total amounts of the three other volatiles, which already fit the observed amounts within a factor 2–3. This straightforward method presents the unique advantage that it is fully independent of any speculation about the early history of the micrometeorite flux. But it is not satisfactory because neon and nitrogen are key elements to reconstitute the history of planetary atmospheres. We thus derived a third fully independent method to estimate Φ_0 and the total amounts of micrometeoritic neon and nitrogen in the atmosphere.

The Integrated Micrometeorite Flux: The Lunar Cratering Estimates

We used the smooth, roughly exponential decay, of lunar cratering rates, $K(t)$, relatively to the present-day value (Fig. 3.4), given by Hartmann (1999). This curve gives a monitoring of the dominant population of crater forming bodies with sizes ≥500 m existing in the interplanetary medium at any given time.

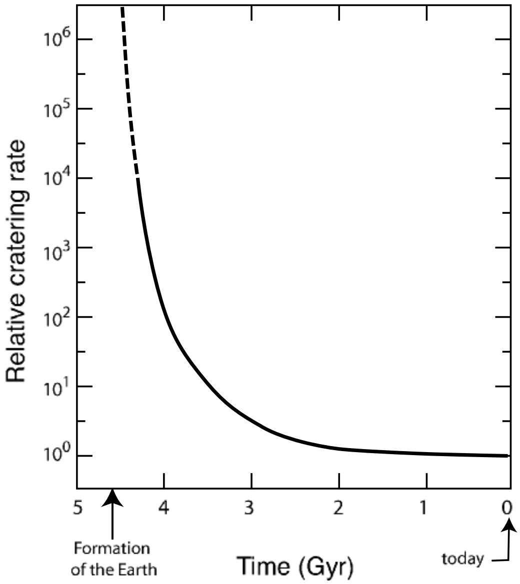

Fig. 3.4. Variation with time of relative lunar cratering rates, $K(t)$. This curve represents the conjuncture of the *late heavy bombardment*, proposed by Hartmann. Such rates refer to the number of impact craters with size $\geq$4 km, per unit time and unit area, relatively to the present-day value. Beyond 3.9 Gyr ago, they cannot be measured and have to be conjectured with models (Courtesy W.K. Hartmann).

The basic assumption of ***EMMA*** is that these bodies were also the dominant parent bodies of early micrometeorites. Therefore, if the flux of lunar impactors was multiplied by $K(t)$, the micrometeorite flux, $\sim\phi_0 \times K(t)$, was increased by the same factor, relative to the present-day annual flux before atmospheric entry, ϕ_0. In brief, $K(t)$ would directly scale to the variation with time of the amplification factor of the micrometeorite flux, relative to the present-day value.

The approximate exponential variation of $K(t)$ allows the integration of $\phi_0 \times K(t)$. Gounelle (2000) noted that the integrant is always larger than 1 during the ***LHBomb***. He showed that the integration from an upper limit, t_1, just reduces to a simple multiplication of three terms:

$$\phi(t_1) \sim K(t_1) \times \tau \times \phi_0 \tag{3.1}$$

where $K(t_1) \sim 2 \times 10^6$ is the value directly read on Fig. 3.4 at $t_1 \sim 4.45$ Gyr; $\tau = 70$ Myr is a reasonable average value of the "mean life" of the population of impactors that rules the slope of the $K(t)$; ϕ_0 is the present-day micrometeorite flux measured at the Earth's orbit, of about 40,000 tons per year for the whole Earth (Love and Brownlee, 1993).

For the Earth, this formula gives an integrated micrometeoric flux since the formation of the Moon, $\Phi_0 \sim 5.6 \times 10^{24}$g. This value is astonishingly similar to the average value ($\sim 4.7 \times 10^{24}$ g) directly inferred from the neon and nitrogen contents of micrometeorites. This striking fit is still hard to believe!

3.5.2 Total Amounts of Micrometeoritic Volatiles in the Post-Lunar Atmosphere

The accretion formula shows that 90% and 99% of the total mass of micrometeorites were delivered during the first 100 and 200 Myr, respectively, of the post-lunar period of the ***LHBomb***. Table 3.2 reveals an unexpected good fit (i.e., within a factor of 2) between the observations (column 2) and the corresponding predictions (column 3) of these total amounts, with the possible exception of H_2O which might be depleted by a factor ∼2–3 (Maurette et al., 2001).

Table 3.2. Total amounts of volatile species in the Earth's atmosphere.

Volatiles	Observed values	EMMA (M_A)[a]
Ne	6×10^{16} g	$(5.5 - 17) \times 10^{16}$ g
N_2	4×10^{21} g	$(1.7 - 5.6) \times 10^{21}$ g
H_2O	1.4×10^{24} g	0.6×10^{24} g
CO_2 (as carbonates)	0.75×10^{24} g	$(0.5 - 1.7) \times 10^{24}$ g

[a] $M_A \sim A(\%) \times 10^{-2} \times 5.6 \times 10^{24}$ g

This is astonishing considering (i) the very long extrapolation back in times, beyond 3.9 Gyr ago, in a kind of blind zone where lunar cratering rates could not be measured (due to the saturation of the lunar surface with impact craters); (ii) the enormous mass difference between the Earth's atmosphere ($\sim 2 \times 10^{24}$ g) and the tiny puff of micrometeoritic gases of ∼1 mg that would be released upon atmospheric entry from ∼500 AMMs, used to measure $A(\%)$; (iii) the huge differences in the contents of neon, nitrogen, and water in AMMs, with neon *being ∼100,000 and ∼10 millions times less abundant* than nitrogen and water, respectively; (iv) the very different origins of these four volatiles. Solar neon was implanted into micrometeorites by both solar wind ions and solar energetic particles during their flight time to the Earth. But nitrogen and water were mostly locked in the carbonaceous component and the hydrous silicates of micrometeorites, respectively, which were formed in different zones of the inner solar nebula.

Such huge differences suggest that even in the case of water the misfit by a factor 2–3 between predictions and observations might not be sufficient to conclude that there is an excess of SMOW water in the present-day oceans. In planetology and astrophysics, when going so far back in time, a misfit between predictions and observations within a factor 2–3 can hardly be considered as significant. Further work is required to establish the reality of this depletion.

All these unexpected fits between predictions and observations support the scenario EMMA (Early Micrometeorites Accretion), where approximately 90% of the atmosphere was formed over a time interval of ~100 Myr, during the steepest part of $K(t)$***, just after the Moon forming impact. This "cleaning" impact did prepare a new "niche" for a*** post-lunar ***atmosphere, which was mostly delivered by a long duration "storm" of early micrometeorites with a composition astonishingly similar to that of AMMs, and probably originating from comets (see Sect. 9).***

3.6 Micrometeoritic Siderophile Elements in Planetology

The work summarized in this section is primarily intended to further test the validity of ***EMMA***, switching from the volatiles in the Earth's atmosphere to a highly siderophile and highly refractory element found in AMMs, iridium. We tracked its fate in the very different environment of the Earth's mantle. But it also illustrates how the search for early micrometeoritic "ashes" in planetary material yields new hints about the early evolution of this material.

3.6.1 Micrometeoritic Iridium in the Earth's Mantle

Accordingly to a conventional view about the fate of iridium on the early Earth (cf. Rushmer et al., 2000), iridium was initially stored in both the planetesimals that did form the proto-Earth and the planetary embryos (i.e., protoplanets) that subsequently merged to it. Each impact by bodies ranging from ~10-km size planetesimals, comets, and asteroids to Mars-sized planetary embryos would lead to the production of pockets of "liquid" silicates in which "droplets" of liquid iron nucleate.

Metal sinking to the core can take place remarkably quickly (i.e., in a matter of weeks) from this initial "emulsion" of liquid iron in melted silicates after a segregation of the droplets into large metal "diapirs" that pierce the mantle. In particular, the last giant planetary embryo that did form the Moon at time t_1 probably induced the last "terminal" scavenging of any residual iridium. In this case, iridium now found in the mantle had to be delivered after the formation of the Moon by a late veneer of *small* extraterrestrial bodies, which could be fully decelerated before their impact on the Earth, as to avoid the formation of pockets of melted silicates that would initiate the scavenging of their iridium throughout the mantle. This is compatible with the deduction that micrometeorites dominated the delivery of extraterrestrial material to the Earth since the formation of the Moon.

After the Moon forming impact, both the Earth and the Moon were melted down to depths of ~1000 km, thus looking like gigantic magma oceans. If the Earth crust was formed very soon after this impact (see below), micrometeoritic iridium started to accumulate on the crust since t_1. It was then delivered to the mantle through the subduction of the oceanic crust. From the conjunction of the integrated micrometeorite flux since the formation of the Moon, $\Phi(t_1) \sim 5.6 \times 10^{24}$ g, and the iridium content of fine-grained AMMs of ~620 ppb (Kurat et al., 1994), the total mass of micrometeorite iridium deposited on the oceanic crust can be estimated to be about 3.5×10^{18} g. It can be assumed that the efficiency of transfer of this highly refractory and siderophile element to the Earth's interior during subduction was about unity.

If micrometeoritic iridium was homogeneously distributed in the whole mantle, with a total mass of ~0.7 time the Earth's mass, its average content would be approximately 0.9 ppb. If this transfer was restricted to the upper mantle, this content increases up to about 3.2 ppb, i.e., a value surprisingly close to that quoted by Morgan (1986) for the "primitive" upper mantle ($\sim 3.4 \pm 0.3$ ppb), which was deduced from the measurements of the Ir contents of a variety of rocks from the upper mantle, such as *spinel lherzolites*. This further validates the conjuncture of the ***LHBomb***, with a totally different element in a very different environment.

This right prediction yields a few hints about the early history of the mantle: (i) the continental crust was formed around the time of formation of the lunar crust (4.46 Gyr: see Carlson and Lugmair, 1988) and that (~4.4 Gyr) of the oldest detrital zircons found by Wilde et al. (2001), as to collect the right amount of micrometeoritic iridium; (ii) the convection of material in the mantle responsible for the thorough mixing of the post-lunar iridium was essentially limited to the upper mantle (Richter, 1979) and this runs against a mantlewide convection flow (Van der Hilst et at., 1997); (iii) the earlier iridium content of the building material of the Earth was very efficiently scavenged during the formation of the metallic core of the Earth; and (iv) this scavenging has to be effective until the date of formation of the Moon, because the large amount of **pre-lunar** micrometeoritic iridium would have largely offset the amount found in the upper mantle. Another alternative is that the giant Moon forming impact did produce its own terminal scavenging of siderophiles into the core.

3.6.2 A Difficult Extrapolation to the Moon and Mars

The validity of ***EMMA*** was tested on the Earth, while predicting the characteristics of four key volatiles in the atmosphere and iridium and sulfur in the mantle (see Sect. 7.1). One thus builds up some confidence to use this model in an orderly fashion to make predictions about the still mysterious early history of the Moon and Mars, which are the second best known bodies of the solar system. We first moved with iridium to the Moon, as to hopefully get new clues about a confusing problem that nobody clearly apprehends since 1970. It deals with the so-called "Meteoritic" contamination of the lunar crust in siderophile elements such as iridium, which was previously attributed to the crater forming impactors and not to micrometeorites. We next moved to Mars to try to check whether ***EMMA*** can account for the high sulfur and nickel contents of Martian soils measured at the Gusev crater and Meridiani Planum (a far distant site at the antipodal position of the Gusev crater) with the Alpha Particles X-Ray Spectrometer (APXS) carried by the rovers Spirit and Opportunity in 2004.

Before 1999, this obscure contamination looked at first glance of limited interest. Consequently, it was neglected in earlier works. We discovered recently that the true reason of this neglect was that the description of this contamination on the Moon and Mars requires surmounting an astonishing diversity of very difficult problems in planetology, in which we become bogged down. But it was too late to quit.

Unexpectedly, we possibly found new hints about the history of the Martian atmosphere. This work should also contribute to the understanding of the first ~500 Myr of the inner solar system history, when the Sun was surrounded by a debris disk. This is one of the most obscure parts of our history, even though such disks represent a major phenomenon observed around about 45% of the stars (Greaves, 2005). The reader, who is interested to be bogged down on the Moon and Mars with us, might consider also reading Maurette et al. (2004a) and Maurette (2005).

3.7 Micrometeoritic Sulfur and Ferrihydrite in Exobiology

A more detailed summary of previous works supporting the role of unmelted micrometeorites (about 25% of the incoming flux of micrometeorites) in prebiotic chemistry is given elsewhere (Maurette, 1998). Krueger and Kissel (1987) quoted thermodynamic computations suggesting that cometary dust grains of the Halley type, when added to a preexisting "soup" of organics, could trigger the formation of nucleic acids. Anders (1989) relied on the characteristics of the tiny micrometeorites collected in the stratosphere (10–20 μm), which amount to about 1% of the micrometeorite mass flux, to argue that micrometeorites played a major role in the delivery of organics to the Earth. As first quoted by Ponchelet (1989), we proposed that hydrous–carbonaceous micrometeorites might have been functioning as microscopic chemical "reactors" on the early Earth during their interactions with gases and waters (Maurette, 1990; Maurette et al., 1991). Subsequently, Chyba and Sagan (1992) ceased supporting the role of the direct impact of comets in the delivery of such organics and started to also quote that of micrometeorites.

All these previous contributions did focus on the role of micrometeorites that survive unmelted upon atmospheric entry. However, our work on the formation of the early Earth's atmosphere (Sect. 4 and 5) suggested that even micrometeorites, which are destroyed upon atmospheric entry, could have contributed in various ways to prebiotic chemistry (Maurette et al., 2001; Maurette et al., 2003a; Maurette et al., 2004b). We discuss below some of these recent contributions.

3.7.1 Micrometeoritic Sulfur and the "Worlds" of Iron Sulfides and Thioesters

About 80% of the AMMs collected near the margin of the Antarctic ice sheets did show anomalous low sulfur contents ($\sim$0.1%) with regard to the value of $\sim$3% measured in CM1 chondrites. So, sulfur could have been preferentially lost during either atmospheric entry (as SO_2) or "cryogenic weathering" near the sea shore, involving the preferential leaching of sulfides in the fine-grained matrix of AMMs. The fact that their solar neon is not markedly lost favors this last possibility, because it is mostly retained in much more inert anhydrous silicates.

Duprat and Engrand (2003) recently recovered friable micrometeorites from snow samples deposited over the last few years in central Antarctica. These particles are essentially unweathered (Fig. 3.5), and their average sulfur content is approximately 5% (Fig. 3.6), a value even larger than that of the CMs ($\sim$3%). We make the simple maximizing assumption that all the sulfur that was released upon volatilization and/or melting into cosmic spherules gets initially oxidized in the early atmosphere (like organic carbon). This yields an enormous initial input rate of SO_2, about 0.5×10^{16} g/year, that lasted about 100 Myr. This SO_2 input was comparable to that of water and CO_2. For a comparison, the amount of sulfur required to maintain the present day stratospheric sulfate aerosol layer on the Earth during quiet time period of volcanic activity is $\sim 10^{11}$ g/yr (Murphy, 2001).

What could be the contributions of this post-lunar SO_2 input in prebiotic chemistry? It was probably quickly transformed into stratospheric sulfate aerosols – i.e., mostly H_2SO_4 molecules with approximately 30% of water – that finally got deposited in early waters. A plausible reaction pathway to eliminate such an excess of sulfates was suggested by André Brack (Maurette et al., 2004b). Hydrothermal sources mostly formed at shallow depths in early water did probably functioned as "reactors" converting sulfates dissolved in water into both huge deposits of iron sulfides and exhalations of H_2S (Fouquet

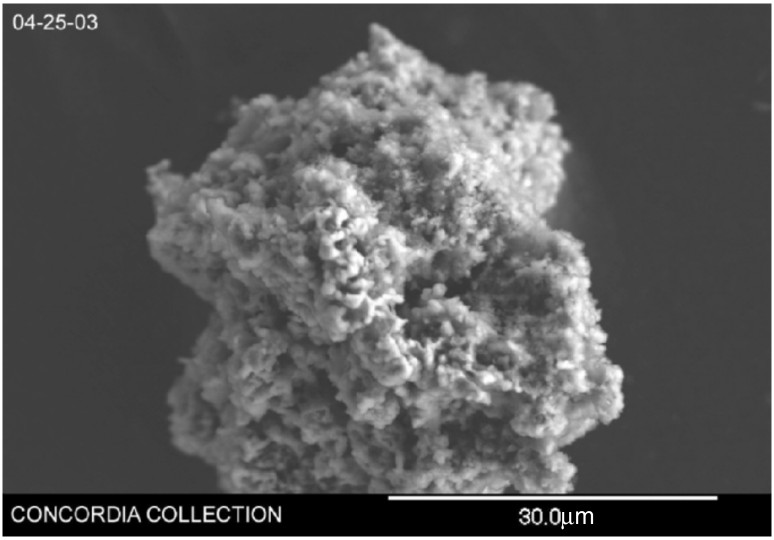

Fig. 3.5. Scanning electron microscope observation of one of the smallest unmelted Antarctica micrometeorite recovered from fresh snow, at a depth of ∼0.5 m, at Dome C. This new type of *highly-friable-fine-grained* micrometeorites is very rich in sulfur and nickel. This particle was partly masked to have a scale bar of 30 µm that corresponds to the size of a fairly large typical IDP collected in the stratosphere by NASA. Their discovery led to an increase to about 25% of the estimated proportion of the incoming flux of large (≥100 µm) micrometeorites that survive unmelted upon atmospheric entry. This high proportion cannot be predicted with previous models of atmospheric entry (Courtesy J. Duprat).

et al., 1996). Surprisingly, micrometeoritic iron sulfides volatilized upon atmospheric entry would have been converted back into terrestrial iron sulfides, thus making the early oceans more suitable for swimming!

This amount of reprocessed sulfides is just enormous. The upper limit of their mass (about 7×10^{23} g) is equivalent to a global ∼300-m-thick layer around the Earth. Thus, micrometeoritic sulfur could have intervened in prebiotic chemistry in at least two different ways (Maurette et al., 2004). Sulfides are requested in the so-called iron sulfide "world" chemistry promoted by Wächstershäuser (1988). Moreover, FeS and H_2S can reduce CO_2 to organic sulfides (thiols), as demonstrated in laboratory simulation of hydrothermal synthetic reactions (Heinen and Lauwers, 1996). Methyl- and ethyl-thiol were the principal thiols formed along with smaller amounts of others containing up to five carbon atoms. Thiols can lead to thioesters, which probably activated important organic prebiotic chemical reactions in the world of thiols proposed by de Duve (1998).

One can wonder about the final fate of this sulfur. In fact, it likely ended up being trapped in the upper mantle of the Earth like iridium. Indeed, by

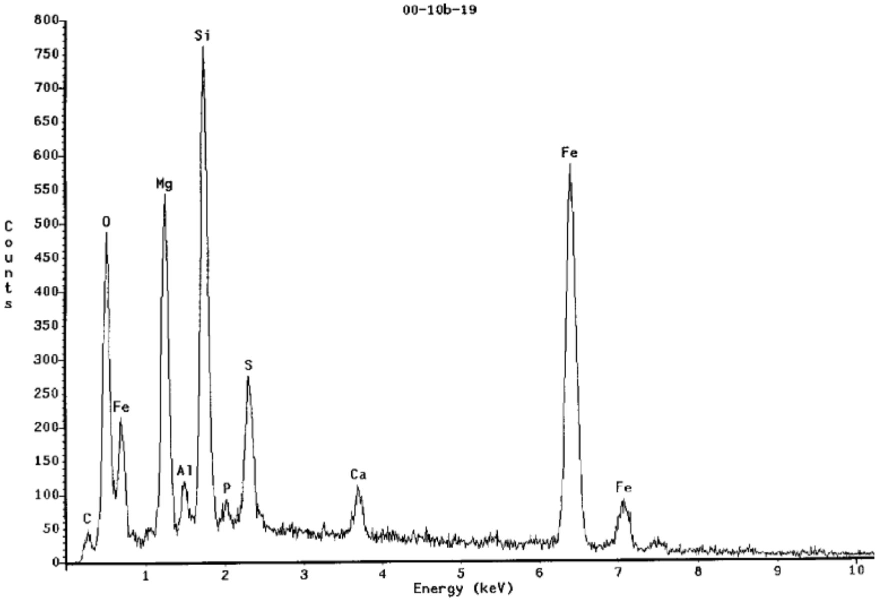

Fig. 3.6. Energy dispersive X-ray spectrum of the bulk composition of one of the new highly friable Antarctic micrometeorites. The sulfur peak corresponds to a high sulfur content (~5%) mostly carried by iron sulfides. The weaker phosphorus peak corresponds to a concentration of approximately 0.5%. This element is stored in ferrihydrite, one of the two only known forms of magnetic iron hydroxide, which is probably quite abundant on the Martian surface (Courtesy C. Engrand).

diluting the total amount of micrometeoritic sulfur delivered to the Earth during the first 100 Myr of the post-lunar ***LHBomb*** in the upper mantle, one predicts that its content would be about 300 ppm. This value well fits the range of values (150–300 ppm) measured for the primitive upper mantle (Lorand, 1990), but also the highly siderophile character of S on the early Earth.

3.7.2 Ferrihydrite in Unmelted and Melted Micrometeorites

About 20% of the fine-grained unmelted micrometeorites collected at Cap-Prudhomme – their constituent sulfides have been leached out – still show a bulk residual amount of sulfur of about 0.2%. It was shown that this residual sulfur is hosted at high concentration levels of ~10% in a minor constituent phase of micrometeorites made of a variety of "dirty" hydrous iron oxide (ferrihydrite), which also contains comparable amounts of carbon and phosphorus (Maurette et al., 2001; Maurette, 1998; Maurette et al., 2003a). We even found a micrometeorite only made of this dirty variety of ferrihydrite.

Unexpectedly, ferrihydrite was also observed on the external surface of about 10% of the completely melted micrometeorites, e.g., cosmic spherules.

There, it protrudes as either a tiny "nugget" or a disgorged spread of material (Fig. 3.7). It is very likely that they result from a very fast process of density segregation in the tiny droplet of silicate melt resulting from the "pulse" heating of micrometeorites upon atmospheric entry. These microscopic concentrations of ferrihydrite were centrifuged to the external surface of the spherules during their fast rotation. They were probably ejected most of the time from the "melt," thus feeding micrometeoritic "smoke" with the ferrihydrite ashes of the "dead" micrometeorites.

Gero Kurat and Mike Zolensky cautioned that ferrihydrite (that they call "rust") could have been formed by cryogenic weathering of a primary nugget of FeNi metal. However, the external magnetite rim of the nugget reported in Fig. 3.7 (top) has not been destroyed, whereas the volume change expected during the transformation of a FeNi nugget into a hydrous iron oxide should have flaked off the rim. When large *flower-efflorescences* of ferrihydrite are observed on top of a primary ferrihydrite nugget coated with a magnetite rim, these nuggets were probably behaving as seed nuclei for the growth of much larger volumes of ferrihydrite during cryogenic weathering!

Several evidences indicate that ferrihydrite could have formed microscopic centers of prebiotic chemistry in waters, while being either a component of unmelted micrometeorites or after ejection from their parent-melted micrometeorites. Graciela Matrajt synthesized two varieties of ferrihydrite to investigate the characteristics of this mineral as an adsorbent of amino acids and catalyst of their polymerization in small bits of proteins (oligopeptides). This ferrihydrite, composed of "ordinary" ∼10-μm-sized crystals, already behaved as one of the best adsorbent of amino acids and catalyst of their polymerization into oligopeptides (Maurette, 1998; Matrajt et al., 2001; Matrajt et al., 2002; Matrajt et al., 2003; Maurete et al., 2003a). As this mineral is also used as an efficient drug to remove excess phosphates from the blood, it could have extracted at least phosphates from early seas, and probably other dissolved salts such as sulfates.

It can be predicted that the micrometeoritic variety of ferrihydrite was probably much more reactive than the single crystals of the synthetic variety (see also Sect. 10). It concentrates in a small volume all major biogenic elements (C, H, O, N, P, S), as well as Fe, an important oligoelement. When ferrihydrite is imbedded into the fine-grained matrix of an unmelted micrometeorite, such bioelements are in contact on a nanoscale with both: (i) minerals that have well-established catalytic properties (e.g., saponites and iron sulfides); (ii) organics, which can be detected above detection threshold in a 100-μm-size grain, such as the most abundant amino acid (AIB) found in HCCs (Brinton et al., 1998); (iii) a rich mixture of PAHs-moieties (including reactive vinyl-PAHs) desorbed from the major carbonaceous component of micrometeorites, kerogen (Clemett et al., 1998); (iv) molecules bearing the carbonyl group; and (v) a mixture of complex organics still to be identified, which yield a rather similar and typical smooth raise in fluorescence observed

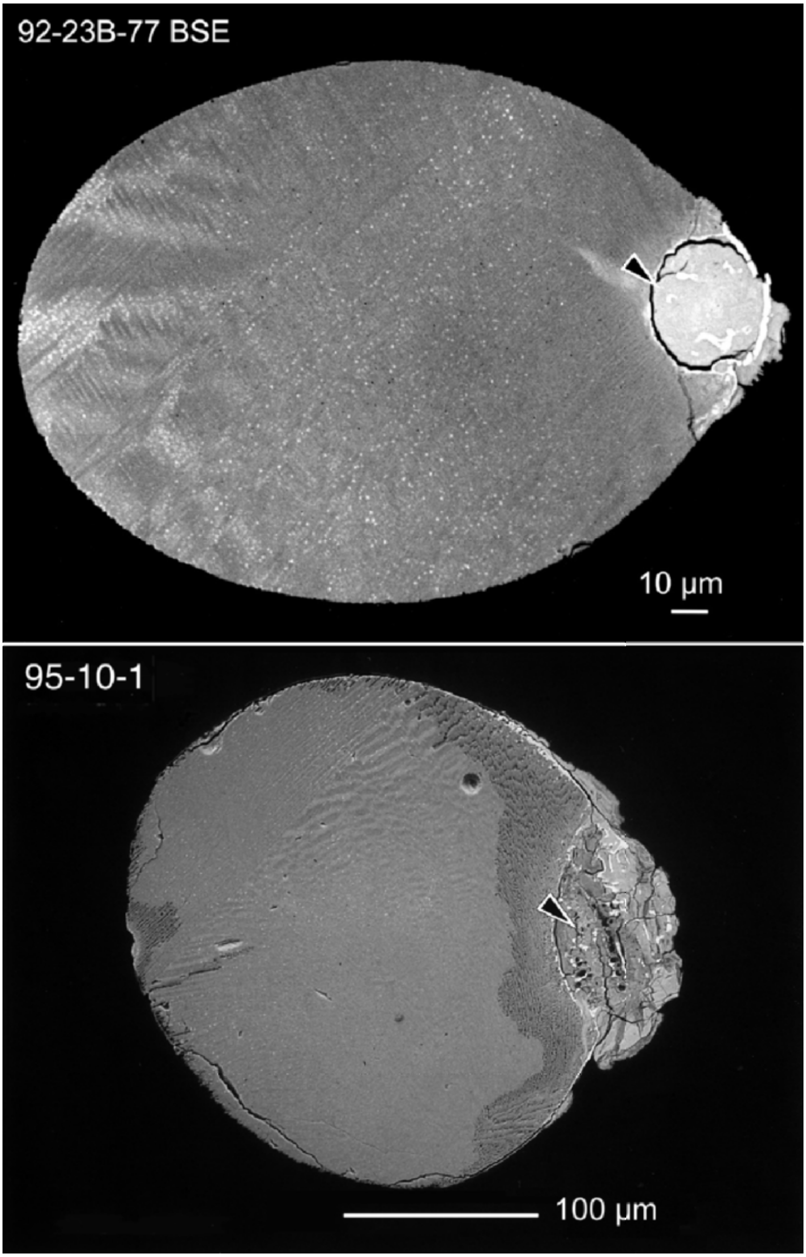

Fig. 3.7. SEM micrographs of polished sections of two cosmic spherules showing either a nugget (top) or a "disgorged" spread (bottom) of ferrihydrite on their external surfaces (Courtesy C. Engrand).

on Raman spectra of both micrometeorites and all HCCs, between ~1000 and ~1300 cm (Matrajt, 2002).

3.8 A Post-Lunar Micrometeoritic Greenhouse Effect?

A remarkable balance between the absorption and scattering of solar radiation by the early Earth produced the gentle greenhouse effect that allowed the birth of life. But when was it triggered? In the last 20 years, all models have attributed a key role to the paradox of the “faint” early Sun, where the lower luminosity of the Sun (by up to a factor of 30%) would have frozen the early oceans. But, this cooling was counterbalanced by the effects of greenhouse gases, such as CO_2 and H_2O (Owens et al., 1979) thought to mostly originate from the degassing of the building material of the Earth (Kasting, 1993). In these models the contribution of SO_2 was not considered and the simplifying assumption of a “dry” stratosphere was made.

The accretion of micrometeorites releases gases and very fine “smoke” particles right into the thermosphere between 150 and 80 km, above all cloud systems. It triggered a kind of long duration giant soft volcanism “falling from the sky,” which did spread its products homogeneously over the whole Earth’s surface for about 100 Myr after the formation of the Moon. It can be expected that both the dust, the sulfuric acid aerosols, and the greenhouse gases produced by this cosmic volcanism unavoidably participated to both the cooling and the heating of the Earth.

In Sect. 7.1, we quoted an enormous input rate of SO_2 of about 0.6×10^{16} g/year, comparable to that of water and CO_2–SO_2 is known to be a stronger greenhouse gas than CO_2, being on a par with H_2O. These high input rates of the three major greenhouse gases lasted for about 100 Myr, and the input rate of fine-grained micrometeoritic smoke particles was about seven times higher than that of SO_2.

A surprising prediction can be made while comparing the yearly micrometeoritic input rates of sulfuric acid aerosols and fine dust in the upper thermosphere to the corresponding total stratospheric burdens of aerosols and dust estimated for the two most important volcanic eruptions identified since the late quaternary, which are the eruption of Rosaz, in British Columbia (about 14.7 My ago), and the last Toba eruption in Sumatra (about 74,000 years ago). The eruption of Rosaz lasted about 10 years (Thordarson and Self, 1996). The Toba eruption lasted two weeks. It is the largest known explosive volcanic event, which injected material up to heights of 27–37 km, thus loading the stratosphere with a dense cloud of H_2SO_4 aerosols and dust.

Rampino and collaborators (1988, 1992, 2000) deduced that the Toba stratospheric dust did produce *total darkness for weeks to months.* But this was a short event because dust is quickly scavenged. On the other hand, the lifetime of the Toba sulfuric acid stratospheric aerosols was approximately 6 years (this was directly inferred from acidity depth profiles in

Greenland ice cores). Moreover, they backscatter solar radiation efficiently, and a stratospheric aerosol burden of approximately 5×10^{15} g would attenuate sunlight by a factor of approximately 10^5! As these burdens did range from about $(1\text{–}5)\times 10^{15}$ g to $(6\text{–}12)\times 10^{15}$ g for the Toba and Rosaz supereruptions, respectively, they did produce marked climatic effects.

The resulting climatic effects are expected to be strongly dependent on the duration of the "volcanism" (cf. Bailey et al., 1994). A short eruption such as Toba should not produce long-term effects. For a shower of cometary debris initiated by the fragmentation a giant comet (size $\geq$100 km), and lasting about 10^4 years, worldwide glaciations are expected.

However, Rampino and collaborators (1992, 2000) argued that the extra "kick" in cooling produced by the stratospheric Toba cloud caused the climate to plunge into glaciation during a time of slow warm–cold transition. Analysis of DNA samples indicates that all humans derive from a common African ancestor who appeared about 150,000 years ago, but acquired the unique characteristic of modern man (i.e., "imagination"), about 50,000 years ago, when he showed the capability to make for the first time rock carvings. Therefore, some paleontologists (cf. Ambrose, 2005) also believe that the mega-eruption of Toba, which occurred approximately 74,000 years ago, triggered abrupt climatic changes that would have produced a worldwide glaciation that made Europe and China uninhabitable for early men. In Africa, these conditions just triggered a much drier climate. This led to a catastrophic decimation of early humanoids responsible for human population bottlenecks. In Africa, only a few thousands of the best fitted of our ancestors would have adapted as to learn to survive with "imagination." What about the climatic effects of the post-lunar micrometeorite volcanism?

The micrometeoric cloud of aerosol and dust was constantly fed by fresh greenhouse gases and smoke particles over a much longer period of 100 Myr. It was capping any other cloud layers of the atmosphere. As it was homogenously distributed "instantaneously" to the whole Earth, one has not to worry anymore about some tricks to inject volcanic products in the stratosphere as to ensure their worldwide dispersion requested for a global climatic effect. Therefore, something quite drastic should have happened during this post-lunar micrometeoritic volcanism. Let us just focus on the sulfuric acid aerosols burden delivered by micrometeoprites in the thermosphere, of about 8×10^{15} g per year. The studies of the Rosaz and Toba supereruptions suggest that the sun was looking like… the full moon… during the first $\sim$100 Myr of the post-lunar period!

How did the Earth manage to rightly counterbalance the cooling effect of this second period of faint early Sun? It probably involved a complex feedback among dust, aerosols, and greenhouse gases that were constantly outpouring from the thermosphere, but also the functioning of a giant IR heater effective in the whole thermosphere! Indeed, there was a new heat source to warm up the thermosphere from the inside. It was never discussed before. This is the frictional heating of air molecules against the leading edge of micrometeorites.

A simple estimate reported elsewhere gives an energy input rate about 250 times higher than the present-day solar EUV insolation ($\sim$1 erg cm^{-2} s^{-1}), for the average speed of micrometeorites inferred from radar meteors ($\sim$14 km s^{-1}) (see Maurette (2005), his Sect.17.2.) This qualitative outline of a plausible micrometeoritic post-lunar greenhouse effect conflicts with all classical views of this problem. Quantitative predictions have now to be worked out by professionals.

3.9 Controversies About the Parent Bodies of Micrometeorites

To apply the accretion formula to the Earth–Moon system, it is not necessary to identify the parent bodies of micrometeorites. However, the extrapolation of this formula to the other terrestrial planets, such as Mars, and to debris disks around other stars, requires in particular the knowledge of the variation of the micrometeorite flux with the heliocentric distance, which depends on the nature of their parent bodies (i.e., comets or asteroids). We report on a few arguments that have not been sufficiently well advertised yet. They run against the conventional view that most micrometeorites originate from the collisions and/or erosion of asteroids. Therefore, the only remaining alternative is that they mostly originate from comets.

Conventional Views: A Small Abundance of Cometary Dust Grains in the Present-Day Micrometeorite Flux

The Infrared Astronomical Satellite (IRAS) observed dust bands (IRAS-band) associated with families of main belt asteroids as well as dust trails delineating the orbits of comets, in the zodiacal cloud – this cloud, in which micrometeorites are temporarily stored, fed the flux of the dominant "sporadic" micrometeorite accreted by the Earth. This shows that the micrometeoric complex includes dust particles originating from both interasteroidal collisions (occurring between $\sim$2 and $\sim$5 AU) and the sublimation of the dirty ices of comets, mostly observed at heliocentric distance smaller than $\sim$2.5 AU.

There is already some discordance about the measurements of the relative abundance of cometary dust particles in the micrometeorite flux, *Comet (%)*, made with Earth-orbiting spacecrafts. Micrometeorite impact measurements from Earth's orbit would show that the cometary contribution is higher than 75% of the total dust influx rate for the whole Earth (Zook, 2001). This is compatible with the view that in the large size range typical of AMMs, the abundance of asteroidal particles sharply decreases with size. Indeed, large particles are more affected by their lifetime against mutual collisions, τ_{col}, during which they fragment into smaller dust particles, than by their longer lifetime, τ_{pr}, against the radiative drag due to sunlight, known as the Poynting–Robertson effect, which induces their spiraling to the Sun (Burns et al., 1979). Moreover, they are also more frequently temporarily trapped in orbital resonances (Liou and Zook, 1997).

But, a numerical modeling of the IRAS-bands concludes that *Comet (%)* is smaller than 25% before atmospheric entry (Dermott et al., 2001). Moreover, atmospheric entry would sharply decrease *Comet (%)* because the higher speeds of cometary dust particles would enhance their destructive frictional heating upon atmospheric entry. All types of simulations of atmospheric entry as yet reported (including "pulse" heating with furnaces and numerical and/or close form mathematical calculations) would indicate that in the large size range ($\geq$100 µm) of AMMs, *Comet (%)* would be reduced to a few percent (see Brownlee (2001) for a review of some of these works).

These "corrected" proportions are not reliable. This was shown by Bonny (1990), who developed the most elaborated computer simulation never surpassed, yet. The only trustable prediction that can be directly confronted to a straightforward measurement is the proportion of unmelted to melted (i.e., cosmic spherules) particles in the collections of micrometeorites recovered on the Earth's surface. He concluded that none of the simulations (i.e., including his own) can account for the high proportion of 25% that was already measured in November 1984 for $\geq$100-µm-size micrometeorites recovered from the melt zone of the Greenland ice sheet. In fact, predictions of this proportion grew steadily from about 1% in 1985 (Brownlee, 1985) to less than 10%. But the misfit got even worst about 1 year ago, when Duprat and Engrand measured a proportion of about 1 in their new Concordia collect (Duprat et al., 2003). Consequently, micrometeorites are much better preserved upon atmospheric entry than previously thought, and reliable predictions of the final value of *Comet (%)* after atmospheric entry cannot be made.

The Very Short ^{21}Ne and ^{10}Be Exposure Ages of Antarctic Micrometeorites in the Interplanetary Medium

^{21}Ne and ^{10}Be are "cosmogenic" nuclides produced during the nuclear interactions of energetic protons with the constituent atoms of micrometeorites. These irradiations can occur either during the flight time of micrometeorites to the Earth and/or during their complex reprocessing in the regolith of their parent asteroids.

Micrometeoritic neon has a unique isotopic signature relatively to that found in CM type chondrites and lunar mare soils. It can be observed on the three isotope plots reported in Fig. 3.8, where the ^{21}Ne/^{22}Ne ratio of approximately 0.034 reflects a very small excess of cosmogenic ^{21}Ne relatively to the primordial ratio of approximately 0.029 observed in the Earth's atmosphere. This excess of ^{21}Ne is much larger in HCCs (see opened and closed diamonds) that are compacted chunks of asteroidal regolith but also in soils collected in the 5-m-thick regolith of lunar mare (cf. a similar plot reported in figure 1 of the paper of Wieler, 1998).

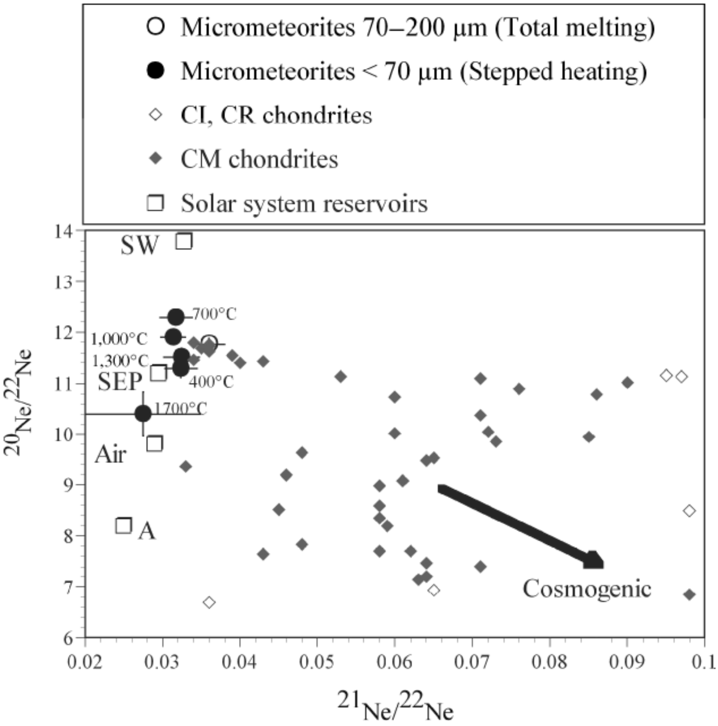

Fig. 3.8. Neon isotopic composition of the Dome–Fuji micrometeorites (circles) and hydrous carbonaceous chondrites (open and closed diamonds). These ratios were determined for aliquots of about 200 micrometeorites recovered from two size fractions of the glacial sand collected at Dome Fuji (≤70-μm and 70–200 μm). The 70–200-μm particles were analyzed by total melting at 1,700°C, while the ≤70-μm particles were characterized by the powerful technique of stepped pyrolysis at 400, 700, 1,000, 1,300, and 1,700°C. The interpretation of the bulk measurements for HCCs is less straight forward than for lunar soils and micrometeorities (see below). First, it is difficult to make a meaningful comparison between data obtained by various groups because the mass of the analyzed sample ranges from that of a fragment of a micrometeorite (∼1 μg) to ∼100 mg of "bulk" material. Moreover, the analytical techniques used to extract neon can be as different as a single laser impact, total melting, stepped heating, stepped oxidation, stepped *in vacuo* etching (i.e., stepwise dissolution of grains in concentrated nitric acid between about 0.5–100 h) (Courtesy T. Nakamura).

These large excesses represent a typical effect of the reprocessing of material within a regolith. During this reprocessing, the grains follow complex depth trajectories, where they can be exposed to protons from both the SEPs and the galactic cosmic rays (GCRs), when they reside at depths of ≤1 mm and of a few meters, respectively (cf. Sect. 3.2). But the excess of ^{21}Ne observed in Fig. 3.8 for bulk samples of HCCs is dominated by their cosmogenic component, which was produced during their flight time to the Earth, i.e., their conventional cosmic ray exposure ages (GCR-ages). This component blurs the much larger excesses acquired by about 10% of the meteoritic grains (coined as solar gas-rich) during their individual precompaction regolith history. Fortunately, they can still be found running this gas-rich component with a laser microprobe on a scale of approximately 100 µm (see Hohenberg et al. (1990) and Nakamura et al. (1999)). They well plot along the lunar correlation line up to the highest ^{21}Ne/^{22}Ne rations of $\sim$0.6 (see Wieler (1998), his figure 1. They thus constitute a reliable signature of a regolith history, which is not observed in AMMs. Therefore, AMMs should originate from parent bodies *"denuded"* of a regolith.

This would exclude an asteroidal origin, because remote sensing studies show that all observable stony asteroids are capped with regoliths (Hasgawa and Abe, 2001). The only plausible alternative is that their parent bodies are periodic comets, probably originating from the Edgeworth–Kuiper belt, and which lost their very heavily irradiated top "crust" after a few returns to the inner solar system as first suggested by Osawa et al. (2000). This small content of ^{21}Ne in AMMs is also compatible with the *wide* distribution of their *low* exposure ages in the galactic cosmic rays, deduced from another cosmogenic isotope, ^{10}Be. This distribution was observed by Raisbeck and Yiou (1989) in melted and unmelted micrometeorites from both Greenland and Antarctica. They already did use it about 25 years ago to argue that large micrometeorites have a cometary origin!

Not Enough Mass in the Asteroidal Belt During the Post-Lunar Period?

This discussion depends on whether or not the orbit of Jupiter (and consequently that of asteroids) was stabilized at the time of formation of the Moon, t_1.

In the first case, the lifetimes of asteroids against gravitational perturbations (mainly from Jupiter) were very long in the post-lunar period, except for the minor fraction of those that were kicked on chaotic orbits, from which they will be ejected from the belt in a few thousands years. Their lifetimes, which are then ruled by collisional cascades, are about 2 and 10 Gyr for 10 and 100 km asteroids, respectively. Furthermore, even though asteroids "die" they are regenerated by the largest bodies that will fragment and/or the re-accretion of the debris into "rubble piles." Consequently, the general consensus among planetary dynamicists is that the asteroidal belt has quickly reached a kind of stationary state (after the formation of Jupiter in less than $\sim$10 Myr). One can assume that after the formation of the Moon, the number of asteroids was not much higher than today.

The present-day mass of the asteroidal belt, M_{ast}, is equivalent to about 4% of the lunar mass and 90% of this mass is already locked in the largest asteroids with sizes $\geq$100 km. Therefore, the mass available in smaller asteroids that collide more frequently only represents *about 5% of the mass of micrometeorites accreted by the Earth during the first 100 Myr of the post-lunar area.* Gomes et al. (2005) predict that the orbit of Jupiter was stabilized only around 3.8 Gyr ago, and that prior to this date the early asteroidal belt was ∼10 times more massive than today. This value is still too small to feed the micrometeorite flux accreted by the Earth–Moon system even by considering the most favorable but unrealistic assumption that all asteroids were crushed into fine-grained dust particles that did not reaccrete into rubble piles. Indeed, the Earth–Moon system, as viewed from ∼3 AU, looks like a tiny star, which can intercept only a minute fraction of the asteroidal dust released in the inner solar system.

The High Friability of the New Concordia Micrometeorites Runs Against a Regolith History

Figure 3.5 illustrates the very delicate structure of one of the highly friable S-rich micrometeorites with sizes of 100 μm, recovered from the new Concordia Antarctic collection, and which represent about 50% of the unmelted micrometeorites. Some of them are so much friable that they just crush into fragments when they are delicately touched with a needle. Such particles could not have survived through the harsh reprocessing of particles in a parent asteroidal type regolith that involves multiple depositions and ejections generated upon impacts (Sect. 3.2). Again, we are stuck with the only alternative that these friable particles are cometary dust grains ejected *very* softly from cometary nuclei.

3.10 From Prospects to Unsolved Problems

The isotopic and chemical compositions of four key volatile species in Antarctic micrometeorites and the terrestrial atmosphere are unexpectedly similar and ***EMMA*** rightly predicts, with a *single* "accretion" formula, their total amounts in the present-day atmosphere, even though they differ by factors of up to approximately 10 millions. This same formula also accounts for the content of iridium and sulfur in the upper mantle of the Earth. These unexpected fits support its validity.

It was used with some confidence to tackle and/or set new problems as different as the functioning of the Earth's upper mantle, the prebiotic chemistry of life, and the post-lunar greenhouse effect, which was the only one important for the birth of terrestrial life. But like any new model, ***EMMA*** faces criticisms. Unexpectedly, the discussion of their relevance gives new hints about using unmelted micrometeorites and various "ashes" of volatilized micrometeorites to decrypt early planetary processes.

Micrometeorites as "Tracers" of Early Planetary Processes

The micrometeoric "purity" of the Earth's atmosphere, as well as the right micrometeoritic iridium content of the Earth's mantle, fixes unexpected constraints on several key events in the early history of the Earth–Moon system, including their timing relatively to *Δ(Earth).* We just outline below a preliminary listing of these constraints still to be further exploited. They include the following. (i) The timing of the Mars-sized Moon forming impact, which had to happen near the end of *Δ(Earth)*, in accordance with the recent predictions of Canup and Asphaug (2001). Otherwise, the micrometeoritic atmosphere would have been heavily contaminated by volatiles delivered by big bodies still to be accreted by the growing Earth during the post-lunar period. In brief the Moon forming impactor was the last giant body in the history of the Earth accretion. (ii) The physics of this impact, which had to blown off a large fraction of the complex pre-lunar atmosphere of the early Earth. Among theoreticians the situation is quite confusing. Cameron (1992) and Ahrens (1993) first argued that the mechanical effect of this impact did blown off the atmosphere. But this view was challenged by our Japanese colleagues (Abe et al., 2002; Genda and Abe, 2003), who estimated that only 20% of the Earth's atmosphere was blow off. Subsequently, Ahrens et al. (2003) noted *ground motion alone is not sufficient to propel the full atmosphere. However, this process is one of the many propelling processes, which can significantly accelerate atmosphere to escape the Earth's gravity field.* Then, Genda and Abee (2005) found that *the presence of an ocean significantly enhances the loss of atmosphere during a giant impact.* Both groups might now consider the new experimental constraint that the Moon forming impact did completely remove the pre-lunar atmosphere and allowed the birth of a pure post-lunar micrometeoritic atmosphere. (iii) The degassing of the Earth's mantle, which had to be quenched before the end of *Δ(Earth).* This deduction was first suggested by Sarda et al. (1985) from measurements of the isotopic composition of argon in both the upper mantle and the atmosphere. It allows minimizing another major contamination of the post-lunar micrometeoric atmosphere by the complex residual mixture of volatiles initially trapped in the building materials of the Earth (unless they were already quite "dry") during their formation in the early solar nebula. (iv) The recycling of the atmosphere through plate tectonics and volcanism. Such a recycling, which is still quoted today, is known to produce alterations of the initial gas mixture by processes such as the generation of an overwhelming amount of pyrolysates from alteration of organic matter and "serpentinisation" by aqueous alteration. Table 3.1 shows that the chemical composition of the atmosphere is astonishingly similar to the predicted "micrometeoric" atmosphere, within a factor of 2. But both values markedly differ from those reported for Hawaiian volcanoes, ejecting gases extracted from the most primitive deep seated magma (see Table 3.1, column 7). Therefore, the recycling of the initial inventory of volatile species injected by juvenile micrometeorites in the atmosphere was quite modest. (v) The formation time interval of the Earth of approximately 100 Myr, which would fit the values deduced from both the I-Xe chronometer (Pepin and Phinney, 1975) and theoretical estimates of dynamicists (Wetherill, 1993), but not the shorter value recently inferred from the Hf-W chronometer (Schoenberg et al., 2002).

Search for "Leonids" from the Cold

All the arguments presented in favor of a cometary origin of micrometeorites in Sect. 9 will probably be rejected by the tenants of their asteroidal origin. Moreover, it is not certain that a comparison between approximately 10-µm cometary dust grains returned by the Stardust mission and AMMs (about a thousand times more massive) will help show that AMMs originate from comets or not. Indeed, the orbits of these two families of small and "giant" particles were certainly perturbed quite differently in the early solar system, and they might have different origins even though they ended up being trapped in the same chunk of cometary ices.

Therefore, since January 2000, Duprat prepares a crucial testing of our claim, facing the hard challenge of recovering a few tons of snow from specific *annual* snow layers deposited in both Greenland and Antarctica at the time of intense historical meteor showers of the *Leonids* (Duprat et al., 2001). These showers, such as those of 1833 and 1966, are produced when the Earth intersects the dusty orbit of comet Temple-Tuttle. Hopefully, these annual snow samples should have captured ∼100-µm-size "*Leonids*" *with a well-certified cometary origin.* If AMMs are indeed cometary dust particles, they should be strikingly similar to the "*Leonids*" with two exceptions. Similarities include their mineralogical, chemical, and isotopic compositions. The two exceptions are both related to their much shorter flight times in the interplanetary medium of a few centuries at most (Jenniskens, 2001). Therefore, they should show a pure component of solar wind neon with no measurable contamination of SEP neon (Cuillierier et al., 2002), and their carbonaceous component would have been much less degraded into a kerogen by SEPs ionization effects (Maurette et al., 2003). These two exceptions should greatly help identify such *Leonids*, in the expected case where they turn to be similar to the dominant background of micrometeorites from the sporadic flux.

From "Nanotubes" to Debris Disks

Micrometeoric ferrihydrite was certainly much more reactive than the single crystals of the synthetic variety used in the simulation experiments (cf. Sect. 7.2). One cause of this much enhanced chemical reactivity would be related to the filamentary texture of micrometeoritic ferrihydrite probably made of an entanglement of "nanotubes," which fill up the interstices and voids between the grains (Fig. 3.9). They were probably implicated in a still-unexplored

Fig. 3.9. Transmission electron microscope micrograph of an ultra-microtomed section of a Cap-Prudhomme Antarctic micrometeorite. The fibrous material filling the voids between crystals is very likely made of "nanotubes" of ferrihydrite. The associated electron diffraction pattern clearly shows that they are made of ferrihydrite (Courtesy G. Matrajt).

area of prebiotic chemistry involving interactions of organics with the astonishing world of "nanomaterials." In particular, the huge specific area of the nanotubes should have at least drastically amplified their characteristic of adsorbent of organics and salts.

The conjuncture of Hartmann, which predicts a huge amplification ($\times 10^6$) of the impactor flux at the time of formation of the Moon, looks validated within a factor 2–3. Indeed, it rightly predicts the total amounts of volatiles in the atmosphere, and the right content of iridium and sulfur in the upper Earth's mantle. This is quite astonishing because Hartmann constantly warns that lunar cratering rates beyond 3.9 Gyr ago are known only within a factor of 10, and Tolstikhin and Marty (1998) quote even a factor 100! By assuming that micrometeorites are delivered by periodic comets from the Edgeworth–Kuiper belt Morbidelli concluded that "most models seem to produce a maximum flux of comets, which is smaller by several orders of magnitude to the value conjectured with the Hartman's curve during the first 100 Myr that followed the formation of the Moon. Is it possible that this apparent contradiction suggests that the configuration of the young solar system was very different of both the present day configuration and from all we can conceive"? In brief, we still do not understand the huge amplification of the impactors flux in earlier times (cf. Maurette and Morbidelli, 2001).

During its evolution to the main sequence along a T-Tauri phase, a young Sun-like star is surrounded by a disk-shaped parent nebula that lasts for about 1–20 Myr. Since 2001, astronomers investigating the thermal emission of dust around stars with IR telescopes got progressively convinced that a high proportion of stars (about 45%) are "debris disk" stars (DD stars), where dust would have been continuously regenerated by the collisions of planetesimals after the clearing of the early stellar nebula (Greases, 2005). It was first thought that such disks could hardly survive beyond a few 100 Myr. But it has been recently found that they can persist for much of the lifetime of the stars. Therefore, a Sun like star with a short-lived DD might represent a minor fraction of the stars (∼15%).

Greaves (2005) even suggested that *the debris phase might be analogous to Earth's early period with a high-impact rate called the heavy bombardment*. Moreover, after the formation of the Moon, it is likely that the rocky planetesimals formed in the inner solar system were essentially locked in planetary embryos, which merged as to fabricate the terrestrial planets and the possibly rocky cores of the giant planets, i.e., a total mass of material of about 50 Earth mass. Therefore, the residual planetesimals still present during the post-lunar period in the large volume of the solar DD (such disks have radius ranging from about 50 to 500 AU) were essentially comets that accreted in the outer solar system, and that we still observe today.

In this case, the basic assumption of ***EMMA*** (i.e., the flux of micrometeorite scales as the declining flux of lunar impactors) just becomes an ordinary ineluctable outcome of the early Sun being a DD-star with a relatively normal lifetime of a few 100 Myr, with regard to the wide range of values observed today, i.e., 10–20 Myr for the so-called transition objects to 100–10,000 Myr for main sequence stars (see Greaves, her Table 1). Indeed, if one increases the number of comets, one also increases the fraction of both small comets with perihelion smaller than 2.5 AU that release interplanetary dust during the sublimation of their dirty ices, and giant comets that fragment into multiple bodies. This concept of debris disk might help tackling the stumbling problem of the high lunar cratering rates conjectured by Hartman (1999).

A promising approach related to this concept has just been proposed by Gomes et al. (2005) – see also Levinson et al. (2001). The key process is a powerful mean motion resonance (resonance crossing) between the orbits of Neptune and Jupiter, which did destabilize in particular the EdK-belt about 3.8 Gyr ago, thus firing a huge spike of comets to the inner solar system. It thus ejected 97% of the comets from the belt. A back of the envelope estimate suggests that if an additional early spike was occurring before this late spike, it could have both delivered the right mass of cometary micrometeorites to the Earth and formed the lunar megaregolith, which extends up to depths of ∼20 km.

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References

Abe Y., Genda H., Nishikawa K. (2002) A mixed pro-atmosphere during the runaway accretion. *Geochim. Cosmochim. Acta*, **66**, number 15A, A5.

Ahrens T.J. (1993) Impact erosion of terrestrial planetary atmosphere. *Ann. Rev. Earth Planet. Sci.*, **21**, 525–555.

Ambrose S.H. (2005) Population bottleneck. In, Robinson R. (Ed.) *Genetics*, (MacMillan Reference Books).

Anders E. (1989) Pre-biotic organic matter from comets and asteroids. *Nature*, **342**, 255–256.

Bailey M.E., Clube S.V.M., Hahn G., Napier W.M., Valsecchi, G.B. (1994) Hasards due to giant comets: climate and short-term catastrophism. In, Gehrels T. (Ed) *Hazards due to comets and asteroids* (Univeristy Arizona Press), pp. 479–536.

Boice D. and Huebner W. (1999) Physics and chemistry of comets. In, Weisman P. R., McFadden L., Johnson T.V. (Eds.) *Encycolpedia of the solar system* (Academic Press, New York), pp. 519–536.

Bonny Ph. (1990) Entrée atmosphérique de micrométéorites pierreuses chargées en matiére organique. *ONERA, Rapport TP*, **110**, pp. 1–110.

Burns J.A., Lamy P., Soter S. (1979) Radiation forces on small particles in the solar system. *Icarus*, **40**, 1–48.

Bardintzeff J.M. (1991) *Vocanologie* (Dunod, Paris), pp. 1–284.

Brinton K., Engrand C., Glavin D.P., Bada J.F., Maurette M. (1998) A search for extraterrestrial Amino acids in carbonaceous Antarctic micrometeorites. *Origin Life Biosphere*, **28**, 413–424.

Brownlee D.E. (2001) The origin and properties of dust impacting the Earth In, Peucker-Ehrenbrink and Schmitz B. (Eds) *Accretion of extraterrestrial matter throughout Earth's history* (Kluger Academic / Plenum Publishers, N.Y.), pp.1–12.

Cameron A.G.W. (1992) The giant impact revisited. *Lunar Planet Sci.*, **XXIII**, 199–200.

Canup R. and Asphaug E. (2001) Origin of the Moon in a giant impact near the end of the Earth's formation. *Nature*, **412**, 708–712.

Carlson R.W. and Lugmaier G.W. (1988) The age of ferroan anorthosite 60025: Oldest crust on a young Moon. *Earth Planet. Sci. Lett.*, **90**, 119–130.

Chyba C.F. and Sagan C. (1992). Endogenous production, exogenous delivery and impact-shock synthesis of organic molecules: an inventory for the origin of life. *Nature*, **355**, 125–132.

Chyba C.F. and Sagan C. (1997) Comets as a source of prebiotic molecules for the early Earth. In, Thomas P.J., Chyba C.F., McKays, C.P. (Eds.) *Comets and the origin and evolution of life* (Springer Verlag, New York), pp. 147–174.

Clemett S.J., Chillier X.D., Gillette S., Zare R.N., Maurette M., Engrand C., Kurat M. (1998) Observation of indigenous polycyclic aromatic hydrocarbons in "giant" carbonaceous Antarctic micrometeorites. *Ibid*, 425–448.

Cuillierier R., Duprat J., Maurette M., Hammer C. (2002) The crucial role of neon to identify cometary micrometeorites from historical and future *Leonids* showers trapped in Antarctic and Greenland snows. *Lunar Planet. Sci.*, **XXXIII**, A1519 (CD-ROM).

De Duve C. (1998) Clues from present-day biology: the thioester world. In A.Brack (ed.), *The molecular origin of Life* (Cambridge University Press), pp. 147–186.

Delsemme A. (1997) The origin of the atmosphere and oceans. In, Thomas P.J., Chyba C.F., McKays C.P.(Eds) *Comets and the origin of life* (Springer Verlag, New York), pp. 29–68.

Delsemme A. (1999) The deuterium enrichment observed in recent comets is consistent with the cometary origin of seawater. *Planet. Space Sci.*, **47**, 125–131.

Dermott S.F., Crogan K., Durda D.D, Jayaraman S., Kekoe T.J., Kortenkamp S.J, Wyatt M.C. (2001) Orbital evolution of Interplanetary dust. In E. Grün, B.A.S. Gustafson, S.F. Dermott, H. Fechtig (Eds.), *Interplanetary Dust*, (Springer-Verlag, Berlin), pp. 569–640.

Dodd R.T. (1981) *Meteorites: A petrological-chemical synthesis* (Cambridge University Press).

Dran J.C., Duraud J.P., Langevin Y., Maurette M. (1979) The predicted irradiation record of asteroidal regoliths and the origin of gas-rich meteorites. *Lunar Planet. Sci.*, **X**, 309–311.

Duprat J., Hammer C., Maurette M., Engrand C., Matrajt G., Gounelle M., Kurat G. (2001) Search for past and future "frozen" Leonid showers in Antarctica and Greenland. *Lunar Planet. Sci.*, **XXXII**, A1773 (CD-ROM).

Duprat J., Engrand C., Maurette M., Gounelle M., Hammer C., Kurat G. (2003) The Concordia-Collection : pristine contemporary micrometeorites from central Antarctica surface snow. *Lunar Planet. Sci.*, **XXXIV**, A1727 (CD-ROM).

Duraud J.P., Langevin Y., Maurette M., Comstock G., Burlingame A.L. (1975) The simulated depth history of dust grains in the lunar regolith. *Geochim. Cosmochim. Acta Suppl.*, **6**, 3471–3482.

Duraud J.P., Langevin Y., Maurette M. (1979) An analytical model for the regolith evolution of small bodies in the solar system. *Lunar Planet. Sci*, **X**, 323-325.

Eiler J.M. and Kitchen N. (2004). Hydrogen isotope evidence for the origin and evolution of the carbonaceous chondrites. *Geochim. Cosmochim. Acta*, **68**, 1395–1411.

Engrand C. and Maurette M. (1998) Carbonaceous micrometeorites from Antarctica. *Meteoritics Planet. Sci.*, **33**, 565–580.

Engrand C., Deloule F, Robert F., Maurette M., Kurat G. (1999) Extraterrestrial water in micrometeorites and cosmic spherules from Antarctica: an ion microprobe study. *Meteoritics Planet. Sci*, **34**, 773–787.

Fouquet Y, Knott R., Cambon P., Fallick A., Rickard D., Desbruyeres D. (1996) Formation of large sulfide minerals deposits along fast spreading ridges. *Earth Planet. Sci.*, **44**, 147–162.

Genda H., and Abe Y. (2003) Survival of a proto-atmosphere through the stage of giant impacts. *Lunar Planet. Sci*, **XXXIV**, 1623–1624.

Genda H., Abe Y. (2005) Enhanced atmospheric loss on protoplanets at the giant impact phase in the presence of oceans. *Nature*, **433**, 842–844.

Gomes R., Levinson H.F., Tsiganis K., Morbidelli A. (2005) Origin of the cataclysmic late heavy bombardment of the terrestrial planets. *Nature* **435**, 466-469.

Gounelle M. (2000) Matière extraterrestre sur Terre: des océans aux protoétoiles. PhD thesis, University Paris 7, pp. 1–163.

Greaves J.S. (2005) Disks around stars and the growth of planetary systems. *Science*, **307**, 68–71.

Hartman W. K. (1999) Moons and Planets, 4th Edition (Wadsworth, Belmont), pp. 1–428.

Hasgawa S. and Abe M. (2001) An estimate of surface regolith condition from IRAS observed asteroids using the free beam parameter thermal model. In, Eds, Mizutani H. and Kato M. (ISAS, Kanakawa, Japan) Proc. 34th ISAS *Lunar Planet. Sci.*,91–94.

Heinen W. and Lauwers A.M. (1996) Sulfur compounds resulting from the interaction of iron sulfide and carbon dioxide in an anaerobic aqueous environment. *Origins of Life Evol. Biosphere*, **26**, 131–150 (1996).

Hohenberg C.M., Nichols R.H., Olinger C.T., Goswami J.N. (1990) Cosmogenic neon from individual grains of CM meteorites: Extremely long pre-compaction exposure histories or an enhanced early particle flux. *Geochim. Cosmochim Acta*, **60**, 3311-3340.

Hunten D.M., Turco R.P., Toon O.B. (1980) Smoke and dust particles from meteoritic origin in the mesosphere and stratosphere. *J. Atmos. Sci.*, **37**, 1342–1357.

Jenniskens P. (2001) Discoveries from observations and modeling of the 1998/99 *Leonids*. In, E. Grün, B.A.S. Gustafson, S.F. Dermott, H. Fechtig (Eds.) *Interplanetary Dust* (Springer, New York), pp. 233–252.

Kasting J.F. (1993) Earth's early atmosphere. *Science*, **259**, 920–926.

Krueger F.R. and Kissel J. (1987) The organic component in dust from comet Halley as measured with the PUMMA mass spectrometer on board of Vega 1. *Nature*, **326**, 755–760.

Kurat G., Koeberl C., Presper Th., Brandstatter F., Maurette M. (1994) Petrology and geochemistry of Antarctic micrometeorites (1994). *Geochim. Cosmochim. Acta*, **58**, 3879–3904.

Langevin Y. and Maurette M (1976) A Monte-Carlo simulation of galactic cosmic rays effects in the lunar regolith. *Geochim. Cosmochim. Acta, Supp.*, **7**, 75–85.

Langevin Y. (1978) Etude de l'évolution de la surface des petits corps du système solaire. PhD Thesis, University Paris XI, pp. 1–298.

Langevin (1981) Evolution of an asteroidal regolith: granulometry, mixing and maturity. *Proc. Conf. on lunar breccias and meteoritical analogs* (Lunar Planetary Institute, Houston), pp. 87–93.

Langevin Y. and Maurette M. (2004) CM2-type micrometeoritic lunar "winds" during the late heavy bombardment. *Lunar Planet. Sci.*, A1610, CD-ROM.

Leipunskii O.I., Konstantinov J.E., Federov G.A., Skotnikova O.G. (1970) Mean residence time of radioactive aerosols in the upper layers of the atmosphere based on fall-out of high-altitude tracers. *J.Geophys.Res.*, **75**, 3569–3574;

Levinson H.F., Dones L., Chapman C.R., Stern S.A., Ducna M.J., Zahnle K. (2001) Could the lunar "late heavy bombardment" have been triggered by the formation of Uranus and Neptune? *Icarus*, **151**, 286–306.

Liou J. and Zook H.A. (1997) Evolution of interplanetary dust particles in mean motion resonances with planets. *Icarus*, **128**, 354–367.

Lorand J.P. (1990) Are spinel Iherzolite xenoliths rerepsentative of the abundance of sulfur in the upper mantle? *Geochim. Cosmochim. Acta*, **54**, 1487–1493.

Love S.G. and Brownlee D.E. (1993) A direct measurement of the terrestrial mass accretion rate of cosmic dust. *Science*, **262**, 550–553.

Mason B. (1971) *Handbook of elemental abundances in meteorites* (Gordon and Breach Science Publishers), pp.1–555.

Matrajt G., Gallien J.P., Maurette M. (2001a) Nuclear microprobe analysis of carbon and nitrogen in Murchison and Antarctic micrometeorites. *Meteoritics Planet. Sci.*, **36**, A127.

Matrajt G., Maurette M., Blanot D. (2001b) Ferrihydrite in micrometeorites: a potential adsorbent of aminoacids and catalyst of oligopeptide formation. *Lunar Planet.Sci.*, **XXXII**, A1037 (CD-ROM).

Matrajt G. (2002) La contribution des micrométéorites à l'origine de la vie sur Terre (Ph.D thesis, Université Paris VI), pp.1–166.

Matrajt G., Blanot D., Perreau M., Lebreton J.M. (2003) Adsorption measurements of aminoacids on synthetic ferrihydrite. In, Celnikier L.M. and Trân Thanh Vân J. (Eds) *Frontiers of life. Proc. XIIth Rencontres de Blois, July 2000* (Thê Gioi Publishers, Hanoï), pp. 7–22.

Maurette M., Beccard B., Bonny Ph., Brack A., Christophe M., Veyssieres P. (1990) C-rich micrometeorites on the early Earth and icy planetary bodies. In, Heidmann J. and Klein M.J. (Eds) *Proc. 24 th ESLAB Symp. On the formation of stars and planets, and the evolution of the solar system.* ESA, SP-315, 167–172.

Maurette M., Bonny Ph., Brack A., Jouret C., Pourchet M., Siry P. (1991a) C-rich micrometeorites and prebiotic synthesis. In J. Heidmann and M.J. Klein (Eds) *Bioastronomy. Lecture Notes in Physics 390* (Springer-Verlag, New-York), pp. 124–132.

Maurette M., Olinger C.T., Christophe M., Kurat G., Pourchet M., Brandstätter F., Bourot-Denise M. (1991b) A collection of diverse micrometeorites recovered from 100 tonnes of Antarctic blue ice. *Nature*, **351**, 44–46.

Maurette M., Kurat G., Presper Th., Brandstatter F., Perreau M. (1992) Possible causes of depletion and enrichment of minor elements in Antarctic micrometeorites. *Lunar Planet. Sci.*, **28**, 861–862.

Maurette M. (1998) Micrometeorites on the early Earth. In A.Brack (ed.), *The molecular origin of Life*, (Cambridge University Press), pp. 147–186.

Maurette M., Duprat J., Engrand C., Kurat G., Gounelle M., Matrajt G., Toppani A. (2000a) Accretion of neon, organics, CO_2, nitrogen and water from large interplanetary dust particles on the early Earth. *Planet. Space Sci.*, **48**, 1117–1137.

Maurette M., Matrajt G., Gounelle M., Engrand C., Duprat J. (2001a) La matière extraterrestre primitive et les mystères de nos origines. In Gargaud et al. (Eds), *"L'environnement de la Terre primitive"* (Presses Universitaires de Bordeaux), 99–127.

Maurette M. and Morbidelli A. (2001b) Confirmation of high lunar cratering rates: new clues about the early configuration of planets, small bodies and nearby stars in the early solar system. *Lunar Plane. Sci.*, **XXXII**, A1565, CD-ROM.

Maurette M. (2002) L'origine cosmique de l'air et des océans. *Pour la Science*, **298**, 36–43.

Maurette M., Matrajt G., Gounelle M., Duprat J., Engrand C. (2003a) "Juvenile" KBOs dust and prebiotic chemistry. In, Celnikier L.M. and Trân Thanh Vân J. (Eds) *Frontiers of life. Proc. XIIth Rencontres de Blois*, July 2000 (Thê Gioi Publishers, Hanoï), 7–22.

Maurette M., Balanzat E., Duprat J. (2003b) Cosmic irradiations of carbonaceous material in space and prebiotic chemistry. *Lunar Planet. Sci.*, **XXXIV**, A1743 (CD-ROM).

Maurette M., Duprat J., Engrand C., Kurat G. (2004a) From the Earth to Mars with micrometeorite volatiles. *Advance Space Res.*, submitted.

Maurette M, Brack A., Duprat J., Engrand C., Kurat G. (2004b) High input rates of micrometeoritic sulfur, "smoke" particles and oligoelements on the early Earth. *Lunar Planet. Sci.*, **XXXV**, A1625, CD–ROM.

Maurette M. (2005) *Micrometeorites and the mysteries of our origins* (Springer).

Morbidelli A., Chambers J., Lunine J.I., Petit J.M., Robert F., Valsecchi G.B., Cyr K.E. (2000) Source regions and timescales for the delivery of water to Earth. *Meteoritics Planet. Sci.*, **35**, 1309–1320.

Morgan J.W. (1986) Ultramafic Xenoliths: clues to Earth's late accretionary history. *J.Geophys.Res.*, **91**, 12375–12387.

Murphy D.M. (2001). Extraterrestrial material and stratospheric aerosols. In, Peucker-Ehrenbrink and Schmitz B. (Eds) *Accretion of extraterrestrial matter throughout Earth's history* (Kluger Academic / Plenum Publishers, N.Y.), pp.129–142.

Nakamura T., Nagao K., Metzler K., Takaoka N. (1999) Heterogeneous distribution of solar and cosmogenic noble gases in CM chondrites and implications for the formation of CM parent bodies. *Geochim. Cosmochim. Acta*, **63**, 257–273.

Nakamura T. and Takaoka N. (2000) Solar wind derived light noble gases in micrometeorites collected at the Dome Fuji Station: Characterisation by stepped combustion. *Antarct. Meteorite Res.*, **13**, 311–321.

Olinger C.T., Maurette M., Walker R.M., Hohenberg C. (1990) Neon measurements of individual Greenland sediment particles: proof of an extraterrestrial origin. *Earth Plan. Scien. Lett.*, **100**, 77–93.

Osawa T., Nagao K., Nakamura T., Takaoka N. (2000) Noble gas measurement in individual micrometeorites using laser gas-extraction system. *Antarct. Meteorite Res.*, **13**, 322–341.

Osawa T. and Nagao K. (2002) Noble gas composition of Antarctic micrometeorites collected at the Dome Fuji station in 1996 and 1997. *Meteoritics and Planet Sci.*, **37**, 911–936.

Ozima M. and Podosek F. (2002) *Noble Gas Geochemistry.* (Cambridge University Press), 1–286.

Ozima M. and Zahnle K. (1993) Mantle degassing and atmospheric evolution: Noble gas view. *Geochemical Journal*, **27**, 185–200.

Owen T., Cess R.D., Ramanathan V. (1979) Enhanced CO_2 greenhouse to compensate for reduced solar luminosity on the early Earth. *Nature*, **277**, 640–642.

Owens T. (1998) The origin of the atmosphere. In A.Brack (Ed.) *The molecular origin of life* (Cambridge University Press), pp. 13–34.

Pepin R.O. and Phinney D. (1975) The formation interval of the Earth. *Lunar Sci. Conf.*, **VII**, 682–683.

Podolak M., Mekler Y., Prialnik D. (2002) Is the D/H ratio in the comet coma equal to the D/H ratio in the comet nucleus? *Icarus*, **160**, 208–211.

Ponchelet H. (1989) Astrophysique. Tous Fils du Ciel. *Le Point*, **860**, 121–122.

Raisbeck G.M. and Yiou F. (1989) Cosmic rays exposure ages of cosmic spherules. *Meteoritics*, **24**, 318A.

Rampino H.R., Self S., Tothers R.B. (1988) Volcanic winters. *Ann. Rev. Earth Planet. Sci.*, **16**, 73–99.

Rampino M.R. and Self S. (1992) Volcanic winter and accelerated glaciations following the Toba super-eruption. *Nature*, **359**, 50–53.

Rampino M.R. and Ambrose S.H. (2000) Volcanic winter in the garden of Eden: the Toba super-eruptions and the late pleistocene human population crash, In, Volcanic hazards and disasters in human antiquity, Special paper. *Geological Society of America*, **345**, 71-82.

Richter F.M. (1979) Focal mechanism and seismic energy release of deep and intermediate earthquakes in the Tonga-Kermadec region and their bearing on the depth extent of mantle flow. *J. Geophys. Res.*, **84**, 6783–6795.

Rubey W.W. (1955) In Polderwaart (Ed.) *Crust of the Earth* (Geol. Soc. of America, New-York), pp. 630–650.

Rushmer T., Minarik W.G., Taylor G.J. (2000) Physical processes of core formation. In, Eds Canup R. and Righter K., *Origin of the Earth and the Moon* (University of Arizona Press), 227–243.

Sarda Ph., Staudacher Th., Allègre C.J. (1985) ^{40}Ar/^{36}Ar in MORB glasses: constraints on atmosphere and mantle evolution. *Earth Planet. Sci.*, **72**, 357–375.

Schoenberg R., Kamber B.S., Collerson K.D., Eugster O. (2002) New W-isotope evidence for rapid terrestrial accretion and very early core formation. *Geochim. Cosmochim. Acta*, **66**, 3150–3160.

Shu F.H., Shang H., Gounelle M., Glassgold A., Lee T. (2000) The origin of chondrules and refractory inclusions in chondritic meteorites. *Astrophys. J.*, **548**, 1029–1050.

Thordarson T. and Self S. (1996) Sulfur, chlorine, and florine degassing and atmospheric loading by the Rosaz eruption, Columbia River basalt group, Washington, USA. *J. Volcanol. Geotherm. Res.*, **74**. 49–79.

Thordarson T., Oskarsson N., Husebosch T. (1996) Sulfur, chlorine and fluorine degassing and atmospheric loading by the 1783–1784 AD Laki eruption in Iceland. *Bull. Volc.*, **58**, 205–225.

Tolstikhin I.N. and Marty B. (1998) The evolution of the terrestrial volatiles: a view from helium, neon, argon and nitrogen isotope modeling. *Chem. Geol.*, **147**, 27–52.

Urey H.C. (1952) On the early chemical history of the Earth and the origin of life. *Proc. Natl. Acad. Sci.*, **38**, 351–363.

Van der Hilst R.D., Widiyantoro S., Engdahl E.R. (1997) Evidence for deep mantle circulation from global tomography. *Nature*, **386**, 578–584.

Wächtershäuser G. (1998) Origin of life in an iron-sulfur world. In A.Brack (ed.), *The molecular origin of Life*, (Cambridge University Press), pp. 206–218.

Wieler R. (1998) The solar noble gas record of lunar samples and meteorites. *Space Sci. Rev.*, **85**, 303–314.

Wilde S.A., Valley J.W., Peck W.H., Graham C.M. (2001) Evidence from detrital zircons for the existence of continental crust and oceans on the Earth 4.4 Gyr ago. *Nature*, **409**, 175–178.

Wooden D.H., Harker D.E., Woodward C.E., Butner H.M., Koike C., Witteborn F.C., McMurty C.W. (1999) Silicate mineralogy of the dust in the inner coma of comet C/1995 01 (Hale-Bopp) pre- and post-perihelion. *Astrophysical Journal*, **517**, 1034–1058.

Zook (2001) Spacecraft Measurements of the cosmic dust. In, Peucker-Ehrenbrink. and Schmitz B. (Eds) *Accretion of extraterrestrial matter throughout Earth's history* (Kluger Academic / Plenum Publishers, N.Y.), pp.75–90.

4

Macromolecules: From Star-Forming Regions to Comets to the Origins of Life

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Summary. Molecules of increasing complexity are being found in comets. Comets played an important role in delivering water and other volatiles to the terrestrial planets in the early history after their formation. They also may have supplied essential prebiotic organics to the early Earth. Macromolecules with potential links to biological molecules have been identified in the gas phase in hot cores of massive star-forming regions. They are now also found in hot cores of star-forming clouds of low mass stars similar in size to the Sun. A close relationship between the list of cometary molecules and interstellar molecules suggests that macromolecules existed also in the solar nebula. These results strengthen the perception that molecules of biological interest may be found in comets. To pursue this argument successfully, we must link the relationship of ices in the interstellar medium with ices in comets and establish more firmly the production of complex molecules by laboratory simulations of interstellar conditions involving these ices. We discuss observational links between the interstellar sources of macromolecules and their reservoirs in comets via the solar nebula.

4.1 Introduction

Amino acids are essential molecular components of all living organisms on the Earth. However, the early Earth was a barren planet not equipped for spontaneous generation of life. The influx of water, organic, and possibly prebiotic molecular compounds by comets may have changed these initially very harsh and austere conditions. This form of initiation for the origins of life still is keenly debated, even though several amino acids have been identified in meteorites. Small-body (asteroid and comet) migration in the solar system led to collisions with the inner planets. The probability of a collision with Earth of a comet crossing Jupiter's orbit was calculated to be $1 - 3 \times 10^{-6}$ (Levison et al., 2001), 4×10^{-6} (Morbidelli et al., 2000), and 4.5×10^{-6} (Marov, 2004). We will review the progress that has been made since our earlier summary and review (Huebner and Boice, 1996) and expand the hypothesis that comets significantly contributed to the origins of life on the Earth.

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Huebner and Boice (1996) listed 17 neutral molecules and radicals (excluding metal atoms) in the gas phase that had been identified in comets and drew parallels to about 85 identified neutral interstellar molecules and radicals. The list of neutral species identified in comet comae has grown to 32 (Huebner, 2002) while the corresponding list of interstellar neutral species has grown to more than 100 (Lovas and Snyder, 2003). More than 22 cometary neutral species have been detected, with the majority found in comets Hyakutake (C/1996 B2) and Hale-Bopp (C/1995 O1) (see, e.g., Crovisier et al., 2004b). Most of the newly identified species are complex, with 10 atoms per molecule for ethylene glycol ($HOCH_2CH_2OH$) in comets (Crovisier et al., 2004a) and 13 for cyanodecapentyne ($HC_{11}N$) in the interstellar medium. With few exceptions, all species found in comets have also been found in interstellar space. A few exceptions (N_2, S_2, and C_2H_6) are molecules that have no dipole moment and thus are difficult to identify in the radio range of the spectrum. Radio astronomy is still the predominant tool for finding interstellar molecules.

Comparing a list of cometary molecules with a list of interstellar molecules is a necessary starting point for establishing the relationship. The next step is to relate relative abundances. However, here one has to be very careful. The interstellar radiation field, which influences dissociation and ionization and therefore chemical reactions involving radicals, molecules, and ions, is very different from the solar radiation field. A more meaningful comparison of cometary molecules with interstellar molecules would result if we also considered relative abundances of molecules and included interstellar ices. However, as we have pointed out (Huebner and Benkhoff, 1999), the relative abundances of the ices in a comet nucleus are not easily related to the relative abundances observed in the coma. Abundance data of interstellar ices is now becoming available (Ehrenfreund and Charnley, 2000). In making the comparisons of interstellar (and in particular dark cloud) molecules with solar system molecules, we must also remember that the Sun is a G2 star for which the relative abundance of elements O to C is about 2. Thus, comparisons between comet compositions and dark interstellar clouds are meaningful only for clouds with $O/C \approx 2$. Finally, the list of interstellar molecules is based primarily on observations of high-mass protostars. High-mass protostars evolve in a manner different from that of low-mass protostars, such as the Sun. However, until recently, low-mass protostars were too faint for detailed molecular observations with available instrumentation. The advent of 8-m class telescopes changes this now, making meaningful observations of weak near-IR features of ice components possible for the first time.

We will summarize recent observations of interstellar ices and related laboratory work in which exposure of these ices to interstellar conditions is simulated and explored.

4.2 Interstellar Ices

Observing the circumstellar disk around the edge-on class I object CRBR 2422.8–3423 in Ophiuchus with a resolution of about 10,000 in the 3–5-μm band, Thi et al. (2002) found direct evidence for sublimation of carbon monoxide (CO) gas. They found strong absorption of solid CO with a lower limit on the column density of $2.2 \times 10^{18}\text{cm}^{-2}$. The ratio of gas to solid CO was about 1 along the line of sight. The CO in the gas phase most likely originated close to the star. In contrast, the solid CO absorption originated mostly in the cold, shielded outer parts of the flaring disk. This interpretation is consistent with the predominance of apolar solid CO in the spectrum and the nondetection of solid OCN^-, which is an indicator of thermal or ultraviolet (UV) processing of ice-covered dust particles.

The solid CO column density is the highest observed so far, including high-mass protostars and background field stars. Based on the weakness of solid CO absorption toward nearby sources and the absence of gaseous C^{18}O $(J = 2 \rightarrow 1)$ emission at 30 arcsec further south, the absorption by foreground cloud material may account for only a small fraction of the total solid CO. Gas-phase ro-vibrational CO absorption lines are also detected with a mean temperature of 50 ± 10 K.

Medium resolution ($\lambda/\Delta\lambda$ = 5,000–10,000) ISAAC spectra in the 3–5 μm band were found at the Very Large Telescope (VLT) in 39 young stellar objects (YSOs) in nearby low-mass star forming clouds showing the 4.67-μm stretching vibration mode of solid CO by Pontoppidan et al. (2003a). The exceptionally large sample, the high signal-to-noise ratio, and the high spectral resolution, made it possible to identify similarities in the ice in various sources. They found excellent fits to all the spectra by using a phenomenological decomposition of the CO stretching vibration profile at 4.67 μm into three components centered on 2143.7, 2139.9, and 2136.5 cm^{-1} with fixed widths of 3.0, 3.5, and 10.6 cm^{-1}, respectively. All observed interstellar CO profiles could therefore be uniquely described by a model depending on only three linear fit parameters, indicating that a maximum of three specific molecular environments of solid CO existed under astrophysical conditions. A simple physical model of the CO ice was presented showing that the 2139.9 cm^{-1} component is indistinguishable from pure CO ice. They concluded that in the majority of the observed lines of sight, 60–90 % of the CO was in a nearly pure form. In the same model the 2143.7 cm^{-1} component could possibly be explained by the longitudinal optical component of the vibrational transition in pure crystalline CO ice, which appears when the background source is linearly polarized. Therefore, the model predicts the polarization fraction at 4.67 μm, which can be confirmed through imaging polarimetry. The 2152 cm^{-1} feature characteristic of CO on or in an unprocessed water matrix is not detected toward any source and stringent upper limits were given. When this is taken into account, the 2136.5 cm^{-1} component is not consistent with the available water-rich laboratory mixtures and they suggested that the carrier is not yet fully understood. A shallow absorption band centered between 2,165 and 2,180 cm^{-1} was detected toward 30 sources. For low-mass stars, this band is correlated with the CO component at 2136.5 cm^{-1}, suggesting the presence of a carrier different from XCN at 2175 cm^{-1}. Furthermore, the absorption band from solid ^{13}CO at 2092 cm^{-1} is detected toward IRS 51 in the ρ-Ophiuchi cloud complex and an isotopic ratio of $^{12}\mathrm{CO}/^{13}\mathrm{CO} = 68 \pm 10$ is derived. It was shown that all the observed solid ^{12}CO profiles, along with the solid ^{13}CO profile, were consistent with grains that have an irregularly shaped CO ice mantle that can be simulated with a continuous distribution of ellipsoids, but is inconsistent with the commonly used models of spherical grains in the Rayleigh limit.

Taban et al. (2003) analyzed the near-infrared spectrum of the high-mass, embedded YSO W 33A obtained with the VLT. They positively identified the 2.27-µm band of methanol (CH_3OH). Its derived abundance was very similar to values derived earlier from the methanol bands at 3.54 and 3.91 µm. A search for the 2.21-µm NH_3 band in W 33A was negative giving an upper limit of less than 5 % with respect to H_2O ice when compared with relevant laboratory spectra. Pontoppidan et al. (2003b) carried out a large spectroscopic survey of about 40 protostars. They detected the solid CH_3OH absorption band at 3.53 µm toward three low-mass ($M<1$ solar mass) YSOs located in the Serpens and Chameleon molecular cloud complexes. The abundances of solid CH_3OH compared to H_2O ice for the three sources are in the range 15–25 %, which is comparable to the abundances for the most methanol-rich massive sources known. The presence of abundant CH_3OH in the circumstellar environment of some low-mass young stars is important for the formation scenarios of methanol and more complex organic species near young solar-type stars.

Pontoppidan et al. (2004) presented 3–5-µm VLT-ISAAC spectroscopy, showing the presence of CO and CH_3OH ices in edge-on disks of young embedded stars. Examples include the well-known disks of L1489 IRS in Taurus and CRBR 2422.8–3423 in Ophiuchus. The latter has the highest column density of solid CO known toward a YSO. Several additional low-mass sources in the Serpens and Chameleon molecular clouds exhibit abundant solid CH_3OH although it is not clear whether the ice is associated with a disk or with the envelope. These are the first detections of solid CH_3OH in the disks and circumstellar environments of embedded young low-mass stars providing evidence that complex molecular species previously observed only in the solid state toward high-mass star forming regions are also present near solar-type young stars.

Spoon et al. (2003), using ISAAC at the VLT to obtain spectra around 4.65 µm, detected "XCN" and CO ice in the nuclear region of the nearby dusty starburst/AGN galaxy NGC 4945. The profile of the solid CO band reveals the importance of thermal processing of the ice while the prominence of the XCN band attests to the importance of energetic processing of the ice by far UV (FUV) radiation and energetic particles. In analogy to the processing of ices by embedded protostars in our Galaxy, they attribute the processing of the ices in the center of NGC 4945 to ongoing massive star formation. Their spectrum in the 3–5-μm band also shows strong HI Pf_β and H_2 0-0 S(9) line emission and gas phase CO absorption lines. The HI, H_2, PAH, gas phase CO, and the ices appear to be embedded in a spinning molecular disk that is undergoing vigorous star formation. Recently, strong OCN^- absorption has been detected in the spectrum of the Galactic center star GC: IRS 19. The most likely environment for the OCN^- absorption is the strongly UV-exposed GC molecular ring. The presence of processed ice in the center of NGC 4945 and our Galactic center leads them to believe that processed ice may be a common characteristic of dense molecular material in star forming galactic nuclei.

Boogert and Ehrenfreund (2004) compiled and updated a list of detected interstellar ice absorption features as a function of wavelength, λ, on a Web site: www.astro.caltech.edu/∼acab/icefeatures.html. This list (Table 4.1) summarizes the current identifications of the observed features, which are not necessarily the same as the originally proposed identifications. Tentative identifications are indicated by (?). Most of the absorption features are attributed to the vibrational modes of the ices. The references are those of the original discovery papers of the absorption features in the spectra of protostars and background stars in interstellar molecular clouds. This list does not include molecules seen only in solar system objects, in the gas phase, in refractory dust features (e.g., silicates), or in absorption features seen only in the diffuse medium (unless the origin is disputed to be either refractory or volatile).

In Table 4.2, abundances of interstellar ices are compared to abundances of cometary ices. This table is a work in progress.

4.3 Laboratory Simulations

Meierhenrich et al. (2001) and Muñoz Caro et al. (2002) produced amino acids by simulating interstellar conditions in the laboratory, using hard UV irradiation of a mixture of H_2O, CO, CO_2, CH_3OH, and NH_3 ices at a temperature $T \approx 12$ K. Upon warming the ice residue to room temperature, they identified 16 different amino acids, using gas chromatography-mass spectrometry (GC-MS). Some of these amino acids have also been identified in carbonaceous chondrites. In addition, they found pyrroles and furans in the residues. The products were confirmed by ^{13}C-labelling of the ice. Chiral amino acids showed enantiomeric separation.

Muñoz Caro and Schutte (2003) performed a detailed quantitative infrared analysis of complex organic refractory material produced by photo- and thermal processing of interstellar ice analogs. They investigated the effects of the most relevant free parameters, such as ice composition, UV dose, photon energy, and temperature. They presented evidence for the presence of carboxylic

Table 4.1. Detected Interstellar Ice Absorption Features. (From Web page of Boogert, 2004).

λ (µm)	Identification	Object	Reference
2.27	CH_3OH	W33A	Taban et al. (2003)
2.70	CO_2	S140:IRS1	Keane et al. (2001a)
2.78	CO_2	S140:IRS1	Keane et al. (2001a)
2.96	NH_3, H_2O	BN	Knacke et al. (1982)
3.07	H_2O	BN	Gillett and Forrest (1973)
3.2-3.7	NH_3, H_2O	BN, +	Merrill et al. (1976)
3.25	PAH(?), NH_4+(?)	Mon R2:IRS3	Sellgren et al. (1994)
3.47	–CH, NH_4+(?)	W33A, +	Allamandola et al. (1992)
3.54	CH_3OH	W33A	Grim et al. (1991)
3.85	CH_3OH	W33A	Geballe, et al. (1985)
3.94	CH_3OH	W33A	Geballe, et al. (1985)
4.1	CH_3OH	W33A	Teixeira et al. (1999)
4.27	CO_2	GL 2136, +	de Graauw et al. (1996)
4.38	$^{13}CO_2$	GL 2136	de Graauw et al. (1996)
4.5	H_2O	Elias 29	Boogert et al. (2000)
4.62	XCN (=OCN^-?)	W33A	Lacy et al. (1984)
4.67	CO	W33A	Soifer et al. (1979)
4.78	^{13}CO	NGC 7538:IRS9	Boogert et al. (2002)
4.92	OCS	W33A	Geballe, et al. (1985)
5.83 broad	HCOOH	NGC 7538:IRS9	Schutte et al. (1996)
5.83 narrow	H_2CO	W33A, +	Keane et al. (2001b)
6.0	H_2O, +	W51:IRS2	Puetter et al. (1979)
6.25	PAH(?)	NGC 7538:IRS9	Schutte et al. (1996)

Table 4.1. continued. (From webpage of Boogert, 2004).

λ(µm)	Identification	Object	Reference
6.85	CH_3OH, NH_4+(?), & others	W51:IRS2	Puetter et al. (1979)
7.25	$HCOOH^+$(?)	W33A	Schutte et al. (1997)
7.41	HCOO-(?), CH_3HCO(?)	W33A	Schutte et al. (1997)
7.60	SO_2(?)	W33A	Boogert et al. (1997)
7.67	CH_4	NGC 7538: IRS9	Lacy et al. (1991)
8.9	CH_3OH	GL 2136	Skinner et al. (1992)
9.01	NH_3	NGC 7538: IRS9	Lacy et al. (1998)
9.7	CH_3OH	GL 2136	Skinner et al. (1992)
13.6	H_2O	AFGL 961	Cox (1989)
15.2	CO_2	GL 2136, +	de Graauw et al. (1996)
44.	H_2O	RAFGL 7009S	Dartois et al. (1998)

acid salts and the formation of hexamethylenetetramine [HMT, $(CH_2)_6N_4$] after warming to room temperature. The analysis of the products by GC-MS led to the detection of nitrogen-heterocyclic species, sulfur-bearing molecules, and amines. Figure 4.1 shows the gas chromatogram obtained from a mixture of photolyzed ices in the ratios H_2O:CH_3OH:NH_3:CO:CO_2=2:1:1:1. Figure 4.2 shows the determination of alinine enantiomers in the same sample. In another experiment, using a mixture of H_2O:CO:NH_3:H_2S = 2:1:1:0.04, sulfur-polymerization was found to be efficient while other detected species, like pentathian (S_5CH_2), show chemical interaction between the C and the S elements. Some of these species are of prebiotic interest and may exist in comets.

Muñoz Caro et al. (2004) simulated experimentally the physical conditions present in dense interstellar clouds by means of a high vacuum experimental setup at a low temperature of $T \approx 12$ K. The accretion and photoprocessing of ices on grain surfaces was simulated by depositing an ice layer with composition analogous to interstellar ices on a substrate window, while irradiating it with UV light. Upon slowly warming a sample to room temperature, a residue was obtained that contained the most refractory products of photo- and thermal processing. Fourier transform-infrared (FT-IR) spectroscopy and GC-MS were carried out on the refractory organic material that had formed under

Table 4.2. Comparison of Interstellar Ices to Cometary Ices (Modified from Allamandola et al., 1999).

Molecule	Interstellar abundance	Cometary abundance
H_2O	100	100
CO (polar)	1–10	
CO (nonpolar)	10–40	6
CH_3OH	<4–20	1.7
CO_2	1–10	5
XCN	1–10	
NH_3	5–10	0.9
H_2	1	
CH_4	1	0.7
HCO	1	
H_2CO	1–4	1.8
N_2	10–40	1
O_2	10–40	
OCS	few	0.2

a wide variety of initial conditions such as ice composition, UV spectrum, UV dose, and sample temperature. The refractory products obtained in these experiments were identified, and the corresponding efficiencies of formation were recorded. They found the first evidence for carboxylic acid salts as part of the refractory products. The features in the IR spectrum of the refractory material were attributed to hexamethylenetetramine [HMT, $(CH_2)_6N_4$], ammonium salts of carboxylic acids [$(R\text{-}COO^-)(NH_4^+)$], amides [$H_2NC(=O)$-R], esters [R-C(=O)-O-R′] and species related to polyoxymethylene [POM, $(\text{-}CH_2O\text{-})_n$]. Also a number of molecules based on HMT were identified: methyl-HMT ($C_6H_{11}N_4$-CH_3), hydroxy-HMT ($C_6H_{11}N_4$-OH), methanyl-HMT ($C_6H_{11}N_4$-CH_2OH), amin-aldehyd-HMT ($C_6H_{11}N_4$-NH-CHO), and methanyl-

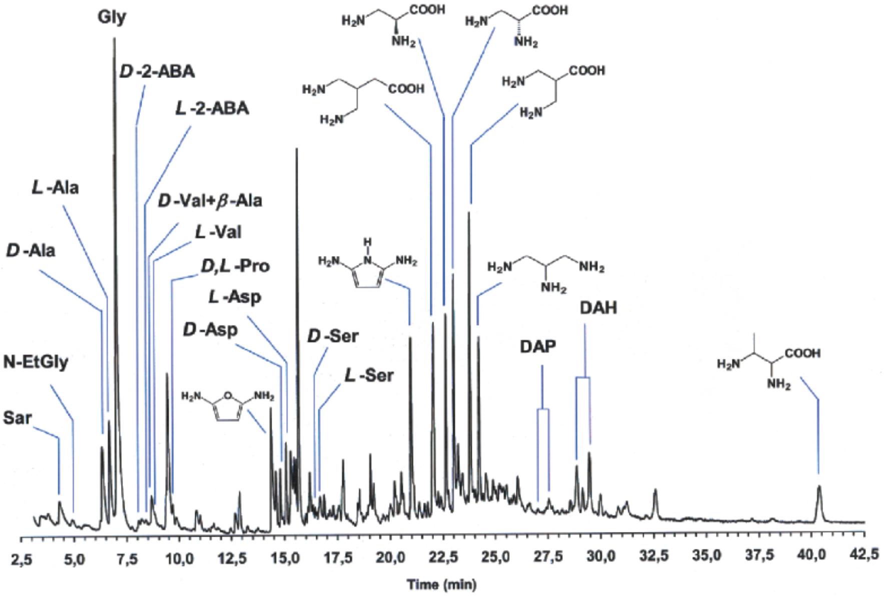

Fig. 4.1. Gas chromatogram showing the sulfur- and nitrogen-species generated under simulated interstellar or circumstellar conditions, corresponding to a photolyzed ice mixture of H_2O:CH_3OH:NH_3:CO:CO_2 = 2:1:1:1 after warm-up to room temperature. (Courtesy Muñoz Caro et al., 2002).

aldehyd-HMT ($C_6H_{11}N_4$-CHOH-CHO). These were the heaviest identified components of the residue. They also presented evidence for the formation of HMT at room temperature, and the important role of H_2O ice as a catalyst for the formation of complex organic molecules.

Also the behavior of CO on an acidic ice, HCOOH, and of CO ices on a number of astrophysical grain analogs, including hydrogenated amorphous carbon (HAC), has been investigated. CO can be easily trapped in any hydrogen-bonding ice system, but the final desorption temperature of the CO depends intrinsically on the interplay between the crystallization and desorption behavior of the trapping matrix. High spectral resolution of the CO-ice band has been deconvolved into at least two and sometimes three components, consistent with new solid state features observed by Pontoppidan et al. (2003a) at 2175 cm^{-1}.

Van Broekhuizen et al. (2004) explored laboratory simulations for the formation of OCN^- in interstellar ices. This ion, which can be probed through its vibrational stretching mode at 4.62 μm, has been observed toward a large number of mostly high-mass protostars. Several pathways were investigated involving either UV photolysis or thermal processing of relevant ice mixtures. Photolysis of CO with NH_3 is too inefficient to account for the observed high abundances, but photolysis of CH_3OH with NH_3 showed an unexpectedly high

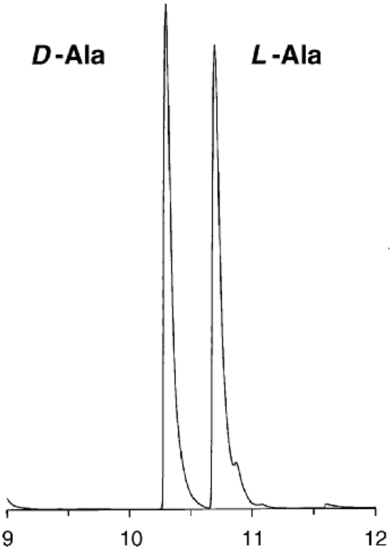

Fig. 4.2. Alanine enantiomers in the sample of Fig. 4.1. (Courtesy Muñoz Caro et al., 2002).

OCN^- production rate. Thermal processing of mixtures involving HNCO can also meet the observational constraints.

4.4 Observations from Massive Star-Forming Regions

What were the initial mass, structure, motions, and temperature of the solar nebula and the time scales over which planets formed? What processes were responsible for the patterns of chemical fractionation observed in the primitive meteorites and the volatile abundances in the planets? Studies of star formation regions attempt to address these questions. Typically, observational star formation programs consist of either studies of regions that form high mass stars (>10 solar masses), or studies of regions that form low mass stars (<10 solar masses). Features that identify high mass star formation regions include ultracompact (UC) HII regions and H_2O masers (Watt and Mundy, 1999). In order to drive the high luminosity, observed radio continuum, and recombination lines of the UC HII region or the pumping for the H_2O maser emission, these regions are believed to lie very close to high mass (O and B) stars in formation. Much progress has been made toward understanding formation of young stellar objects (YSOs) by focusing on low mass star formation regions (see, e.g., Mundy et al., 2000). In contrast, the newest approach is directed toward hot molecular cores (HMCs) in high mass regions. There are good reasons for this emphasis. First, a more complex chemistry has been detected in high mass regions than in low mass regions. Large, highly saturated (i.e., the structure contains three or more H atoms with no carbon–carbon multiple bonds) molecules have been detected mainly in high mass regions. Examples are vinyl cyanide (CH_2CHCN), ethyl cyanide (CH_3CH_2CN), methyl formate ($HCOOCH_3$), methanol (CH_3OH), dimethyl ether [$(CH_3)_2O$], acetone [$(CH_3)_2CO$], glycolaldehyde (CH_2OHCHO), and acetic acid (CH_3COOH). In contrast, the most complex molecule detected in typical low mass regions is methanol (Blake 2003). (We note that methanol could be regarded as a fully saturated CO molecule.) The high temperatures in HMCs permit a warm gas phase chemistry to take place that ordinarily would not occur in cold dark clouds (see, e.g., Ehrenfreund and Charnley, 2000). The rich, active chemistry of HMCs is concentrated in a geometry that enhances detections of molecular rotation spectra by telescopes that have high spatial resolution, such as interferometric arrays. As new, high-resolution telescopes with greater sensitivity come on line, it is likely that a similar chemistry will be detected in low mass sources. A second reason is that as telescope sensitivity and spatial resolution have improved, it has been found that the typical high mass source is resolved into multiple sources of lower mass. For example, as an exercise in the history of radio astronomy, one can trace three decades back in the literature and find articles where the Orion star formation region was considered to be adequately resolved at approximately 6 arcmin resolution, in contrast to today's observations where 1 arcsec resolution often is inadequate for many star-formation studies. This suggests that many low mass stars, such as our Sun, may be formed in high mass regions. In support of this view, we know that (a) there is no evidence that the initial mass function (IMF) varies among giant molecular clouds (GMCs) in the Galaxy; (b) most of the mass in molecular clouds is in the most massive GMCs; and (c) essentially all large GMCs have massive star formation. Therefore, it is certain that the vast majority of low mass stars form in the same giant nurseries as high mass stars. Since high mass star formation is accompanied by significant outflows, it is likely that the dust chemistry (via dust grains formed in HMCs) becomes mixed through a typical GMC.

HMCs are dense ($n > 10^6$ cm^{-3}), hot ($T > 150$ K), and regarded as among the most visible markers of the earliest phase of star formation (see reviews by Churchwell, 1990; Kurtz et al., 2000). We have argued that the chemistry of HMCs in high mass sources should be studied to determine its relevance to the chemistry of the solar nebula, but clearly there are many gaps in our knowledge about the evolutionary progression from a primitive hot molecular core to a primordial solar nebula. For example, we do not have enough detailed data about HMC sizes, masses, structures, kinematics, and temperatures to firmly connect them to the solar nebula. However, much of this information can be obtained through high spatial resolution studies of large, highly saturated molecules in HMCs. Large, saturated molecules cannot be formed efficiently from the mechanisms of cool gas ion–molecule chemistry, yet they have extraordinarily high column densities in hot molecular core regions. Some are likely produced by grain surface chemistry and are known to be highly abundant in icy grain dust mantles. The rich chemistry of large complex molecules is thought to be driven by the evaporation of such grain mantles by nearby HMCs. Coincidentally, many of the large saturated molecular species observed in HMCs are also of biological interest, which makes the potential connection to the solar nebula and comets even more interesting.

If the astrochemistry of HMCs is the precursor to the chemistry of the primordial solar nebula, it is therefore relevant to the patterns of chemical fractionation observed in the primitive meteorites and to the volatile abundances in the planets. When dense interstellar clouds collapse to form stellar systems, comet nuclei, asteroids, and meteoroids are also formed contemporaneously. Such formation processes can be categorized by their characteristic temperatures; the extremely hot processes of stellar and planetary formation would tend to destroy interstellar cloud molecules. Molecules are less likely to be destroyed in cooler processes such as comet formation; such objects have been classified as conglomerations of dirty ices. Even so, the cold interstellar cloud material is heated in these cooler formation routes, and the basic raw material can thereby be changed. For example, while no amino acid monomers have been found in meteorites, amino acid derivatives abound in these objects and their parent bodies may well be cometary. Thus, the connection between the molecules in HMCs and molecules found in meteorites, that were previously formed under heated conditions, depends on the chemical history of the raw material being processed. Laboratory investigation of meteorite chemical makeup is an important observational constraint regarding the chemistry of HMCs and, of course, the converse is true. Only through both studies will a consistent, coherent picture emerge regarding the basic chemistries involved in the evolution from HMCs to comets and meteoroids.

4.4.1 Current Research on Macromolecules in HMCs and Comets

The emission regions associated with macromolecules in HMCs are compact and hot, so they can be studied by utilizing three important properties of radio interferometric arrays: high angular resolution over a large field of view; very high pointing precision for the high angular resolution synthesized beam, and spatial filtering. Autocorrelation spectra from single-element telescopes are useful for observing extended low-temperature clouds of molecular gas that form via cool gas-phase ion–molecule reactions. In contrast, array spatial filtering suppresses the extended emission from less complex molecules formed by ion–molecule chemistry and resolves individual cores, thereby greatly lessening the spectral line confusion encountered with single element telescopes. To date, there has been much success in using arrays to study the dense regions of hot molecular gas associated with these UC HII regions and H_2O masers. We give a brief summary of the work on the high-mass HMC regions and discuss some possibilities for extending this work to HMCs associated with low-mass regions.

4.4.2 Sgr B2(N-LMH)

Over the last few years, interferometric array work has revealed a hot core of unusually high column density embedded within the more extended molecular cloud in Sgr B2(N). The emission spectra from large, highly saturated molecules peak toward this HMC (see, e.g., Vogel et al., 1987; Miao et al., 1995; Miao and Snyder, 1997). This HMC is called the Large Molecule Heimat source, or Sgr B2(N-LMH), due to its extraordinarily high column densities of large, highly saturated molecules, including many of prebiotic interest (Snyder et al., 1994). Of the more than 120 gas-phase interstellar molecules that have been found (e.g., van Dishoeck and Blake, 1998; Lovas and Snyder, 2003), about half were initially detected in the region around or near Sgr B2(N-LMH). We can present several arguments that Sgr B2(N-LMH) is a very important hot molecular core for the study of the initial chemistry, mass, structure, motions, and temperature in the presolar nebula. First, Sgr B2(N-LMH) is the most chemically interesting interstellar source that has been studied to date because it tends to have stronger emission signals and larger detected molecules than any other interstellar source. When solar systems form, this active chemistry ultimately may be related to the nebular chemical processes responsible for the patterns of chemical fractionation observed in the primitive meteorites and the volatile abundances in the planets. Second, as will be discussed, recent spectroscopic observations with the BIMA Array and the Very Large Array (VLA) have produced new values for the mass, structure, and kinematics of this source. These interferometric measurements were made with synthesized beams that ranged from 1 arcsec to 14 arcsec in width. Given the distance to Sgr B2 of 7.1 kpc (Reid, 1993), an angular resolution of 1 arcsec corresponds to a physical scale of about 7500 AU, or on the order of 1/10 the size of the Oort comet cloud that surrounds our Solar System. Our Sgr B2(N-LMH) measurements are therefore sampling astrochemical composition, mass, structure, and kinematics on scales of the order of the size of the Oort cloud. The gas temperature of this source is $T_{\mathrm{rot}} > 170$ (13) K (Pei et al., 2000). Therefore, its prolific chemistry is thought to be the result of the evaporated products of a grain surface chemistry driven by heating from embedded young stars or protostars.

To appreciate the magnitude of the active chemistry in Sgr B2(N-LMH), a consistent set of beam-averaged column densities measured with the BIMA Array at similar angular resolution has been determined (Snyder et al., 2002) for several large dust-generated molecular species in Sgr B2(N-LMH): $2.9(3) \times 10^{16}$ cm^{-2} for acetone [$(CH_3)_2O$]; $0.6(1) \times 10^{16}$ cm^{-2} for acetic acid (CH_3COOH); $1.1(3) \times 10^{16}$ cm^{-2} for formic acid ($HCOOH$); $4.6(1) \times 10^{16}$ cm^{-2} for ethyl cyanide (CH_3CH_2CN); and $11.2(10) \times 10^{16}$ cm^{-2} for methyl formate ($HCOOCH_3$). The synthesized beams were very similar for these remarkably high column densities: 11×4 arcsec^2 for acetic acid, 12×5 arcsec^2 for acetone, and 14×4 arcsec^2 for formic acid, ethyl cyanide, and methyl formate. The first interesting point is that the column densities for ethyl cyanide and the other molecules are several orders of magnitude greater than earlier values from single-element telescope observations (see, e.g., Turner, 1991). This happens because the array observations generally have smaller beam dilution and, because array synthesized beams can be precisely positioned within the large field of view, column densities can be obtained exactly at the position of the LMH. A second point is the relatively high column density of acetic acid. Acetic acid is of possible prebiotic importance because its structure is separated only by an NH_2 radical from glycine, the simplest amino acid. Its column density is comparable to that of the much simpler formic acid, but it is about 20 times less than the column density of its isomer, methyl formate. This suggests that large molecules in the presolar nebula are not formed from randomly assembled constituent atoms on interstellar grains unless either their molecular abundances are modified by subsequent chemical reactions, or such large molecules are the products of structurally driven processes that may not particularly favor prebiotic molecules. Taken at face value, the column density comparisons could be regarded as defining an important set of boundary conditions for the precursor chemistry of the primordial solar nebula. However, there are important caveats. One caution is that even though the column density estimates are high, they may be underestimated because of the standard assumption of low optical depth, or because of a gas temperature that may be higher for the hot core of Sgr B2(N-LMH) than the 170–200 K that is typically used. In addition, some extended flux is often resolved out by interferometric measurements. The final caution is that beam-averaged column densities are dependent on the coupling between the source and the telescope beam because they are determined from spatially unresolved array measurements. As an example, when the $10_{1,10}$–$9_{1,9}$ transition of ethyl cyanide at $\lambda = 3$ mm was measured toward Sgr B2 (N-LMH) by Liu and Snyder (1999) with the BIMA Array using a synthesized beam of 1.2×0.5 arcsec^2, the estimated mean column density was found to be about five times higher than that found by Liu et al. (2001) for ethyl cyanide using a 14×4 arcsec^2 synthesized beam. The ethyl cyanide measurements were extended to $\lambda = 7$ mm with the VLA when the $5_{1,5}$–$4_{1,4}$ transition of ethyl cyanide was observed with the D array of the VLA toward Sgr B2 (N-LMH) by Hollis et al. (2003). The naturally weighted synthesized beam was 1.5×1.4 arcsec^2, so that beam dilution was minimal. Two emission sources of ethyl cyanide appeared. The bulk of the ethyl cyanide emission resides in the LMH hot core source itself that is in proximity to the ultracompact HII regions K2 and K3. However, approximately 5 arcsec north of the LMH, there is a secondary ethyl cyanide emission source that was also detected by Liu and Snyder (1999). It is coincident with the quasi-thermal methanol (CH_3OH) emission core “h” (Mehringer and Menten, 1997) and thus can be labelled Sgr B2(N-h). Extended ethyl cyanide absorption can be seen east of Sgr B2(N-LMH), and is apparently absorbing against the continuum emission; this continuum has been previously shown to be optically thin free–free emission (Mehringer and Menten, 1997).

The molecular emission associated with Sgr B2(N-LMH) has an LSR velocity centered near 64 $\mathrm{km\,s^{-1}}$. This is the dominant LSR emission velocity observed at $\lambda = 3$ mm with the BIMA Array for vinyl cyanide, ethyl cyanide, methyl formate, methanol, acetone, formic acid, and acetic acid. By treating Sgr B2(N-LMH) as a rotating molecular disk, Hollis et al. (2003) calculated that its mass is about 2600 solar masses for a disk diameter of 3 arcsec and a circular velocity of 15 $\mathrm{km\ s^{-1}}$. This is close to the mass estimated by Vogel et al. (1987). The emission source Sgr B2(N-h), about 5 arcsec north of Sgr B2(N-LMH), has lower mass but a very interesting chemistry. Hollis et al. (2003) found that the peak LSR velocity associated with Sgr B2(N-h) is centered near 72 $\mathrm{km\ s^{-1}}$. This LSR velocity was also seen in the $\lambda = 3$ mm ethyl cyanide data of Liu and Snyder (1999), but with a lower signal-to-noise ratio. The significance of this velocity is that 72 $\mathrm{km\ s^{-1}}$ is the characteristic LSR velocity of three large molecules first detected with the NRAO 12-m telescope: glycolaldehyde, the simplest sugar (Hollis et al. 2000); ethylene glycol (Hollis et al. 2002); and vinyl alcohol (Turner and Apponi, 2001). Thus, these three macromolecules appear to be associated with the Sgr B2(N-h) core. The cores of both sources are smaller than the Oort cloud. While acetic acid and methyl formate are concentrated in Sgr B2(N-LMH), their isomer glycolaldehyde appears to be more diffusely spread through Sgr B2(N) (Hollis et al., 2001). This example demonstrates the importance of using higher spatial resolution if we want to understand the complex chemistry of HMCs and its ultimate connection to the chemistry of the solar nebula.

4.4.3 Other Sources

Interferometric searches have been conducted for new sources of large molecules that are outside the galactic center region because it is important to learn how well the astrochemistry found in the hot molecular cores Sgr B2(N-LMH) and Sgr B2(N-h) really represents the astrochemistry of HMCs in the disk of the Galaxy. A major goal is to determine the relative column densities of the most prominent and highly saturated species as a function of galactocentric distances. If successful, this work should set critical standards that future dust chemistry models will have to meet. On the other hand, if the rich dust chemistry that generates highly saturated macromolecules of prebiotic interest is confined to HMCs in the Sgr B2 region, it will be regarded as a curious phenomenon that has little overall impact on studies of the Galaxy. Recent searches have focused on acetic acid because, among the large highly saturated interstellar molecules, its relation to glycine makes it prebiotically the most interesting. In addition, if the relative abundances toward Sgr B2(N-LMH) are representative, a source that contains detectable amounts of acetic acid should also contain greater amounts of formic acid, acetone, ethyl cyanide, and methyl formate, all indicators of a rich dust chemistry.

To date, 13 galactic hot molecular cores other than Sgr B2(N-LMH) have been surveyed for interstellar acetic acid with the BIMA Array (Remijan et al., 2002; 2003). Some of the selected sources, such as W51e2G, W3(H_2O), Orion KL, and G34.3 + 0.2 already had detections of large species such as methyl formate and dimethyl ether. Other sources looked promising because they have a considerable amount of dust continuum emission, which should be correlated with the dust chemistry that generates large highly saturated molecules. As a result of these surveys, two other unresolved HMC sources of acetic acid have been found: W51e2 and G34.3+0.2. Acetic acid in W51e2 has a column density comparable to that in Sgr B2(N-LMH). The relative abundance ratio of acetic acid to its isomer methyl formate also is comparable in both sources. Acetic acid in G34.3+0.2 has a column density range of $(0.77-1.64)\times 10^{15}$ cm^{-2} and a relative (acetic acid)/(methyl formate) abundance ratio of about 3.3×10^{-2}, which is comparable to the abundance ratio found toward Sgr B2(N-LMH) and W51e2 (3–6 $\times 10^{-2}$) by Remijan et al. (2002). Other sources were surveyed by Remijan et al. (2003), but they yielded no detections of acetic acid. The high-mass star forming regions that gave negative results were W3(H_2O), W3(OH), Orion hot core, Orion compact ridge, M17-SW, and W49 A. The negative result low-mass star forming regions were L1448C, NGC 1333 IRAS4, NGC 2024 FIR5, IRAS 16293–2422, and Serpens SMM1.

Even though the available acetic acid survey sample is still too small to draw statistically meaningful conclusions, the current data suggest that a detectable amount of acetic acid is present in regions that follow certain constraints (Remijan et al., 2002; 2003). First, the three main acetic acid sources are within 7 kpc of the Galactic center, but more extensive observations will be necessary to determine whether galactocentric distances really are a factor in the chemical abundance of acetic acid. On the other hand, it is apparent that mass has an influence on whether acetic acid is detectable toward star forming regions. This is important because the only acetic acid detections that have been made are in star-forming regions with total masses more than 200 solar masses. As these sources are observed with next-generation arrays that have higher spatial resolution and greater sensitivity than current arrays, the total masses should not change; however, the sources may be resolved into multiple sources, obviously each smaller than the original. Remijan et al. (2003) compared the acetic acid column density to those of other macromolecular species. In a typical acetic acid source, the column density of acetic acid appears to be about 15–100 times below the abundance of methyl formate, about 2–10 times below the abundance of formic acid, and about 2–10 times below the abundance of ethyl cyanide. In those sources where acetic acid was not detected, such as W3(H_2O) and W3(OH), these detection limits were not reached. Toward the Orion hot core and the compact ridge, these detection limits were reached, but acetic acid was not detected. However, the W3 sources and Orion KL may differ from the other sources. For example, the survey observations reveal no detection of acetic acid in any HMC that shows a chemical differentiation of the O-bearing and N-bearing species, such as Orion KL, where Blake et al. (1987) characterized the hot core and compact ridge as N-rich and O-rich molecular sources, respectively. The observations of Remijan et al. (2003) clearly show this chemical differentiation toward both Orion KL and W3(OH). While the spectra toward W3(H_2O) show several strong transitions of ethyl cyanide, no transitions are seen toward W3(OH). Therefore, it is possible that the formation of acetic acid may depend strongly on a mix of nitrogen and oxygen chemistry. Regions that do not have significant O and N chemistry occurring cospatially may not produce acetic acid in detectable quantities. However, these results are very preliminary.

As noted earlier, evidence that the solar nebula and its prebiotic chemistry pass through the HMC phase has been problematical because of the dearth of observational evidence for the existence of a hot core phase in low-mass star formation regions. Until recently, HMCs were found only in regions of massive star formation, even though many young stellar regions have physical conditions that are suggestive of HMCs (see, e.g., Jørgenson et al., 2002). Some low-mass young stellar regions even have grain mantle chemistry products such as formaldehyde and methanol (see, e.g., Blake et al., 1995; Bachiller and Pérez Gutiérrez, 1997). However, new observations that appear to support the argument have been reported by Cazaux et al. (2003). They used the IRAM 30-m telescope to indirectly document the existence of an HMC in the low-mass young stellar object IRAS 16293-2422. The highly saturated macromolecules that they detected may include acetic acid, but at a column density below the BIMA Array upper limit found by Remijan et al. (2003). Cazaux et al. (2003) suggest that HMCs found in low-mass regions are somewhat colder ($\sim$100 K) and much smaller ($<$20 AU) than HMCs found in high-mass regions. Since there are some differences in physical conditions, the chemistry may also exhibit differences. It should be possible to directly observe these differences with the next generation of interferometric arrays.

4.4.4 Comets

Bockelée-Morvan et al. (2000) conducted an extensive three telescope study of comet C/1995 O1 (Hale-Bopp) with the Caltech Submillimeter Observatory, the Iram 30 m, and the Plateau-de-Bure interferometer, all in autocorrelation mode. They observed 16 molecular species, including six new – SO, SO_2, HC_3N, NH_2CHO, HCOOH, and $HCOOCH_3$. For purposes of this discussion, we will focus on three of the molecules observed by Bockelée-Morvan et al. (2000) likely to be made either abundantly or exclusively by grain chemistry: H_2CO (formaldehyde), CH_3OH (methanol), and $HCOOCH_3$ (methyl formate or MeF). Formaldehyde and methanol are grain mantle chemistry products found in low-mass young stellar regions. The detection of MeF (stack of eight transitions in Comet Hale-Bopp) provides the first clear chemical link between the chemistry of comets and that of biomolecules observed in high-mass hot molecular cores. Bockelée-Morvan et al. (2000) calculated a molecular abundance relative to H_2O of 0.08 % for MeF and a gas production rate $Q(\mathrm{MeF}) = 2.8 \times 10^{28}\ \mathrm{s}^{-1}$. The BIMA Array limits were more than three times higher, so the array did not detect MeF. From the surveys of acetic acid in the HMCs of Sgr B2(N-LMH), W51, and G 34.3+0.2 (Remijan, 2003), it is found that NT(AcA) ranges from 15 to 100 times less than NT(MeF). Thus, if the same chemical formation mechanisms apply to the molecules found in Comet Hale–Bopp (and they may not), to find acetic acid would require reaching Q(AcA) = (3–20)$\times 10^{26}$ s^{-1}. The BIMA Array limit was 5×10^{28} s^{-1}, or 100 times greater than the best possible case for detecting acetic acid.

4.5 Summary and Prognosis

The identification of interstellar ices discussed in Sect. 2 and the laboratory simulations discussed in Sect. 3 suggest that the spontaneous generation of amino acids in the interstellar medium is possible and supports the suggestion that prebiotic molecules may have been delivered to the early Earth by comet dust, meteoroids, or interplanetary dust particles. The laboratory equipment such as a GC-MS cannot be carried into the interstellar medium, but it can be taken to comet nuclei in space missions.

The Cometary Sampling and Composition (COSAC) Experiment on board of European Space Agency's Rosetta mission to Comet 67P/Churyumov-Gerasimenko (launched February, 2004) is designed for *in situ* identification of organic molecules in comets by a combined pyrolysis gas chromatographic and mass spectrometric techniques. The instrument's capillary columns are coated with chiral stationary phases and designed for separations of noncomplex enantiomers to allow the determination of enantiomeric ratios of chiral organic compounds in the comet. This would provide data if molecular parity violation in biomolecules occurs in comets. To get gas chromatographic access to organic compounds on the comet, where macromolecules and complex organic polymers of low volatility are expected to make up the main organic ingredients, two injection techniques will be applied. The pyrolysis technique will be performed by heating samples of cometary matter stepwise to defined temperatures in specific ovens. It will result in thermochemolysis reactions of polymers. A chemical derivatization technique, in which the reagent dimethylformamide dimethylacetal assists pyrolysis derivatization reactions, will produce methyl esters of polar monomers.

There are also many unidentified spectral lines collected in comet observations. Using the list of identified interstellar molecules as an aid may lead to the identification of many new comet species including prebiotic molecules. For example Brown et al. (1996), using high-resolution spectra obtained with the Hamilton echelle spectrograph at Lick Observatory, constructed a catalogue of emission lines, observed in Comets Swift-Tuttle and Brorsen-Metcalf. The spectra cover the range between 380 and 990 nm with a medium spectral resolution $\lambda/\Delta\lambda = 42,000$. Of the 2997 observed emission lines they identify 2437. They find cometary lines due to H, O, C_2, CN, NH_2, C_3, H_2O+, CH, and CH^+. They also list 559 unidentified lines from the two spectra. Zhang et al. (2001) generated a catalogue of emission lines in spectra of comet

C/1995 O1 (Hale-Bopp). A list of unidentified spectral lines found in Comet 122P/de Vico is given for the wavelength range 383.0 to 1019.2 nm at a resolution $\lambda/\Delta\lambda = 60,000$ in the Planetary Data System's Small Bodies Node *http://pdssbn.astro.umd/edu* (Cochran and Cochran, 2001). 12,358 lines were identified, but 4,095 lines remain unidentified.

The COSAC experiment on the Rosetta comet mission may be one of the most important investigations for the origins of life. It may confirm, as conjectured by Bonner (1991, 1992), that "at evolution's opposite extreme," to quote Robert Frost, life started not only from specks of circumstellar and interstellar matter, but that starlight, polarized by the interstellar medium, initiated the basic structure of homochirality of biological molecules.

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References

Allamandola, L.J., Sandford, S.A., Tielens, A.G.G.M., Herbst, T.M. (1992). Infrared spectroscopy of dense clouds in the C-H stretch region – methanol and 'diamonds'. *Astrophys. J.*, **399**, 134–146.

Allamandola, L.J., Bernstein, M.P., Sandford, S.A., Walker, R.L. (1999). Evolution of interstellar ices. *Space Sci. Rev.*, **90**, 219–232.

Bachiller, R., Pérez Gutiérrez, M. (1997). Shock chemistry in the young bipolar outflow L1157. *Astrophys. J.*, **487**, L93–L96.

Blake, G.A., Sutton, E.C., Masson, C.R., Phillips, T.G. (1987). Molecular abundances in OMC-1- The chemical composition of interstellar molecular clouds and the influence of massive star formation. *Astrophys. J.*, **315**, 621–645.

Blake, G.A., Sandell, G., van Dishoeck, E.F., Groesbeck, T.D., Mundy, L.G., Aspin, C. (1995). A molecular line study of NGC 1333/IRAS. *Astrophys. J.*, **441**, 689–701.

Blake, G.A. (2003). Private communication.

Bonner, W.A. (1971) The origin and amplification of biomolecular chirality. *Origins Life Evol. Biosphere*, **21**, 59–111.

Bonner, W.A. (1972) Terrestrial and extraterrestrial sources of molecular homochirality. *Origins Life Evol. Biosphere*, **21**, 407–420.

Bockelée-Morvan, D., Lis, D.C., Wink, J.E., Despois, D., Crovisier, J., Bachiller, R., Benford, D.J., Biver, N., Colom, P., Davies, J.K., Gérard, E., Germain, B., Houde, M., Mehringer, D., Moreno, R., Paubert, G., Phillips, T.G., Rauer, H. (2000). New molecules found in comet C/1995 O1 (Hale-Bopp). Investigating the link between cometary and interstellar material. *Astron. Astrophys.*, **353**, 1101–1114.

Boogert, A.C.A., Schutte, W.A., Helmich, F.P., Tielens, A.G.G.M., Wooden, D.H. (1997). Infrared observations and laboratory simulations of interstellar CH_4 and SO_2. *Astron. Astrophys.*, **317**, 929–941.

Boogert, A.C.A., Tielens, A.G.G.M., Ceccarelli, C., Boonman, A.M.S., van Dishoeck, E.F., Keane, J.V., Whittet, D. C.B., de Graauw, T. (2000). Infrared observations of hot gas and cold ice toward the low mass protostar Elias 29. *Astron. Astrophys.*, **360**, 683–698.

Boogert, A.C.A., Blake, G.A., Tielens, A.G.G.M. (2002). High-resolution 4.7 micron Keck/NIRSPEC spectra of protostars. II. Detection of the ^{13}CO isotope in icy grain mantles. *Astrophys. J.*, **577**, 271–280.

Boogert, A.C. A, Ehrenfreund, P. (2004). Interstellar Ices. In *Astrophysics of Dust.* A.N. Witt, G.C. Clayton, and B.T. Draine, (eds.) ASP Conference Series, **309**, p. 547–572.

Brown, M.E., Bouchez, A.H., Spinrad, H., Johns-Krull, C. M. (1996). A high-resolution catalogue of cometary emission lines. *Astron. J.*, **112**, 1197–1202.

Cazaux, S., Tielens, A.G.G.M., Ceccarelli, C., Castets, A., Wakelam, V., Caux, E., Parise, B., Teyssier, D. (2003). The hot core around the low mass protostar IRAS16293-2422: Scoundrels rule! *Astrophys. J.*, **593**, L51–L55.

Crovisier, J., Bockelée-Morvan, D., Biver, N., Colom, P., Despois, D., Lis, D.C. (2004a). Ethylene glycol in comet C/1995 O1 (Hale-Bopp). *Astron. Astrophys.*, **418**, L35–L38.

Crovisier, J., Bockelée-Morvan, D., Colom, P., Biver, N., Despois, D., Lis, D.C. (2004b). The composition of ices in comet C/1995 O1 (Hale-Bopp) from radio spectroscopy. Further results and upper limits on undetected species. *Astron. Astrophys.*, **418**, 1141–1157.

Churchwell, E. (1990). Ultracompact HII regions – The impact of newly formed stars on their Environment. *Astron. Astrophys. Rev*, **2**, 79–123.

Cochran, A.L., Cochran, W.D. (2001). Spectral ATLAS of Comet 122P/de Vico. A tapestry of linelists and spectra. *BAAS*, **33**, 1076.

Cox, P. (1989). The line of sight towards AFGL 961 – Detection of the libration band of water ice at 13.6 microns. *Astron. Astrophys.*, **225**, L1–L4.

Dartois, E., Cox, P., Roelfsema, P.R., Jones, A.P., Tielens, A.G.G.M., d'Hendecourt, L., Jourdain de Muizon, M., Schmitt, B., Lim, T., Swinyard, B., Heras, A.M. (1998). Detection of the "44 μm" band of water ice in absorption in combined ISO SWS-LWS spectra. *Astron. Astrophys.*, **338**, L21–L24.

De Graauw, T., Whittet, D.C.B., Gerakines, P.A., Bauer, O.H., Beintema, D.A., Boogert, A.C.A., Boxhoorn, D.R., Chiar, J.E., Ehrenfreund, P., Feuchtgruber, H., Helmich, F.P., Heras, A.M., Huygen, R., Kester, D.J.M., Kunze, D., Lahuis, F., Leech, K.J., Lutz, D., Morris, P.W., Prusti, T., Roelfsema, P.R., Salama, A., Schaeidt, S.G., Schutte, W.A., Spoon, H.W.W., Tielens, A.G.G.M., Valentijn, E.A., Vandenbusshe, B., van Dishoeck, E.F., Wesselius, P.R., Wieprecht, E., Wright, C.M. (1996). SWS observations of solid CO_2 in molecular clouds. *Astron. Astrophys.*, **315**, L345–L348.

Ehrenfreund, P., Charnley, S.B. (2000). Organic molecules in the interstellar medium, comets, and meteorites: A voyage from dark clouds to the early Earth. *Ann. Rev. Astron. Astrophys.*, **38**, 427–483.

Geballe, T.R., Baas, F., Greenberg, J.M., Schutte, W. (1985). New infrared absorption features due to solid phase molecules containing sulfur in W 33 A. *Astron. Astrophys.*, **146**, L6–L8.

Gillett, F.C., Forrest, W.J. (1973). Spectra of the Becklin-Neugebauer point source and the Kleinmann-Low nebula from 2.8 to 13.5 microns. *Astrophys. J.*, **179**, 483–491.

Grim, R.J.A., Baas, F., Greenberg, J.M., Geballe, T.R., Schutte, W. (1991). Detection of solid methanol toward W33A. *Astron. Astrophys.*, **243**, 473–477.

Hollis, J.M., Lovas, F.J., Jewell, P.R. (2000) Interstellar glycolaldehyde: the first sugar. *Astrophys. J.*, **540**, L107-L101.

Hollis, J.M., Vogel, S.N., Snyder, L.E., Jewell, P.R., Lovas, F.J. (2001). The spatial scale of glycolaldehyde in the galactic center. *Astrophys. J.*, **554**, L81–L85.

Hollis, J.M., Lovas, F.J., Jewell, P.R., Coudert, L.H. (2002). Interstellar antifreeze: ethylene glycol. *Astrophys. J.*, **571**, L59–L62.

Hollis, J.M., Pedelty, J.A., Boboltz, D.A., Liu, S.-Y., Snyder, L.E., Palmer, P., Lovas, F.J., Jewell, P.R. (2003). Kinematics of the Sgr B2(N-LMH) molecular core. *Astrophys. J.*, **596**, L235–L238.

Huebner, W.F. (2002). Composition of Comets: Observations and Models. *Earth, Moon, Planets*, **89**, 179–195.

Huebner, W.F., Benkhoff, J. (1999). On the Relationship of Chemical Abundances in the Nucleus to those in the Coma. *Earth, Moon, Planets*, **77**, 217–222.

Huebner, W.F., Boice, D.C. (1996). Polymers and other Macromolecules in Comets. In *Comets and the Origins and Evolution of Life.* P.J. Thomas, C.F. Chiba, and C.P. McKay (eds.) Springer-Verlag, New York, p. 111–129.

Jørgenson, J.K., Schöier, F.L., van Dishoeck, E.F. (2002). Physical structure and CO abundance of low-mass protostellar envelopes. *Astron. Astrophys.*, **389**, 908–930.

Keane, J.V., Boogert, A.C.A., Tielens, A.G.G.M., Ehrenfreund, P., Schutte, W.A. (2001a). Bands of solid CO_2 in the 2–3 μm spectrum of S 140:IRS1. *Astron. Astrophys.*, **375**, L43–L46.

Keane, J.V., Tielens, A.G.G.M., Boogert, A.C.A., Schutte, W.A., Whittet, D.C.B. (2001b). Ice absorption features in the 5–8 μm region toward embedded protostars. *Astron. Astrophys.*, **376**, 254–270.

Knacke, R.F., McCorkle, S., Puetter, R.C., Erickson, E. F., Kraetschmer, W. (1982). Observation of interstellar ammonia ice. *Astrophys. J.*, **260**, 141–146.

Kurtz, S., Cesaroni, R., Churchwell, E., Hofner, P., Walmsley, C.M. (2000). Hot molecular cores and the earliest phases of star formation. In *Protostars and Planets IV.* V. Mannings, A.P. Boss, and S.S. Russell, (eds.) University of Arizona Press, Tucson p. 299–326.

Lacy, J.H., Baas, F., Allamandola, L.J., van de Bult, C.E.P., Persson, S.E., McGregor, P.J., Londsdale, C.J., Geballe, T.R. (1984). 4.6 micron absorption features due to solid phase CO and cyano group molecules toward compact infrared sources. *Astrophys. J.*, **276**, 533–543.

Lacy, J.H., Carr, J.S., Evans II, N.J., Baas, F., Actermann, J.M., Arens, J.F. (1991). Discovery of interstellar methane – Observations of gaseous and solid CH_4 absorption toward young stars in molecular clouds. *Astrophys. J.*, **376**, 556–560.

Lacy, J.H., Faraji, H., Sandford, S.A., Allamandola, L.J. (1998). Unraveling the 10 micron "silicate" feature of protostars: The detection of frozen interstellar ammonia. *Astrophys. J.*, **501**, L105–L109.

Levison, H.F., Dones, L., Chapman, C.R., Stern, S.A., Duncan, M.J., Zahnle, K. (2001). Could the Lunar "late heavy bombardment" have been triggered by the formation of Uranus and Neptune? *Icarus*, **151**, 286–306.

Liu, S.-Y., Snyder, L.E. (1999). Subarcsecond resolution observations of Sagittarius B2 at 85 GHz. *Astrophys. J.*, **523**, 683–689.

Liu, S.-Y., Mehringer, D.M., Snyder, L.E. (2001) Observations of formic acid in hot molecular cores. *Astrophys. J.*, **552**, 654–663.

Lovas, F.J., Snyder, L.E. (2003). Listing by empirical formula, name, and isotopic forms of the interstellar, circumstellar, and cometary species observed. *CRC Handbook of Chemistry and Physics, 82nd Edition*, David R. Lide, (ed.) CRC Press, New York, **14**, p. 6–8.

Marov, Ya. M. (2004). Migration processes and volatiles inventory to the inner planets. *LPSC*, **XXXV**, 24.

Mehringer, D.M., Menten, K.M. (1997). 44 GHz methanol masers and quasi-thermal emission in Sagittarius B2. *Astrophys. J.*, **474**, 346–361.

Meierhenrich, U.J., Thiemann, W.H.-P., Muñoz Caro, G. M., Schutte, W.A., Greenberg, J.M. (2001). Simulated cometary matter as a test for enantiomer separating chromatography for use on Comet 46P/Wirtanen. *Adv. Space Res.*, **27**, 329–334.

Merrill, K.M., Russell, R.W., Soifer, B.T. (1976). Infrared observations of ices and silicates in molecular clouds. *Astrophys. J.*, **207**, 763–769.

Miao, Y., Snyder, L.E. (1997). Full synthesis observations of CH_3CH_2CN in Sagittarius B2: Further evidence for grain chemistry. *Astrophys. J.*, **480**, L67–L70.

Miao, Y., Mehringer, D.M., Kuan, Y.-J., Snyder, L.E. (1995). Complex molecules in Sagittarius B2(N): The importance of grain chemistry. *Astrophys. J.*, **445**, L59–L62.

Morbidelli, A., Chambers, J., Lunine, J.I., Petit, J.M., Robert, F., Valsecchi, G.B., Cyr, K.E. (2000). Source regions and time scales for the delivery of water to earth. *Meteorit. Planet. Sci.*, **35**, 1309–1320.

Mundy, L.G., Looney, L.W., Welch, W.J. (2000). The structure and evolution of envelopes and disks in young stellar systems. In *Protostars and Planets IV.* V. Mannings, A.P. Boss, and S.S. Russell (eds.) University of Arizona Press, Tucson p. 355–376.

Muñoz Caro, G.M., Schutte, W.A. (2004). UV-photoprocessing of interstellar ice analogs: Detection of hexamethylenetetramine-based species. *Astron. Astrophys.*, **413**, 209–216.

Muñoz Caro, G.M., Meierhenrich, U.J., Schutte, W.A., Barbier, B., Arcones Segovia, A., Rosenbauer, H., Thiemann, W. H.-P., Brack, A., Greenberg, J.M. (2002). Amino acids from ultraviolet irradiation of interstellar ice analogues. *Nature*, **416**, 403–406.

Muñoz Caro, G.M., Meierhenrich, U.J., Schutte, W.A., Thiemann, W.H.-P., and Greenberg, J.M. (2004). UV-photoprocessing of interstellar ice analogs: Detection of hexamethylenetetramine-based species. *Astron. Astrophys.*, **413**, 209–216.

Pei, C.C., Liu, S.-Y., Snyder, L.E. (2000). Identification of new methanol lines toward Sagittarius B2. *Astrophys. J.*, **530**, 800–805.

Pontoppidan, K.M., Fraser, H.J., Dartois, E., Thi, W.-F., van Dishoeck, E.F., Boogert, A.C.A., d'Hendecourt, L., Tielens, A.G.G.M., Bisschop, S.E. (2003a). A 3–5 μm VLT spectroscopic survey of embedded young low mass stars I. Structure of the CO ice. *Astron. Astrophys.*, **408**, 981–1007.

Pontoppidan, K.M., Dartois, E., van Dishoeck, E.F., Thi, W.-F., d'Hendecourt, L. (2003b). Detection of abundant solid methanol toward young low mass stars. *Astron. Astrophys.*, **404**, L17–L20 .

Pontoppidan, K.M., Dartois,, E., Thi, W.-F., van Dishoeck, E.F. (2004). Processed and unprocessed ices in disks of low-mass YSOs. In *Formation of Cometary Materials, Highlights of Astronomy, IAU Joint Discussion 14.*

Puetter, R.C., Russell, R.W., Soifer, B.T., Willner, S. (1979). Spectrophotometry of compact H II regions from 4 to 8 microns. *Astrophys. J.*, **228**, 118–122.

Reid, M.J. (1993). The distance to the center of the Galaxy. Adv. Res. *Astron. Astrophys.*, **31**, 345–372.

Remijan, A., Snyder, L.E., Liu, S.-Y., Mehringer, D., Kuan, Y.-J. (2002). Acetic acid in the hot cores of Sgr B2(N) and W51. *Astrophys. J.*, **576**, 264–273.

Remijan, A.J., Snyder, L.E., Fridel, D.N., Liu, S.Y., Shah, R. (2003). A survey of acetic acid toward hot molecular cores. *Astrophys. J.*, **590**, 314–332.

Schutte, W.A., Tielens, A.G.G.M., Whittet, D.C.B., Boogert, A., Ehrenfreund, P., de Graauw, T., Prusti, T., van Dishoeck, E.F., Wesselius, P. (1996). The 6.0 and 6.8 μm absorption features in the spectrum of NGC 7538: IRS9. *Astron. Astrophys.*, **315**, L333–L336.

Schutte, W.A., Greenberg, J.M., van Dishoeck, E.F., Tielens, A.G.G.M., Boogert, A.C.A., Whittet, D.C.B. (1997). ISO-SWS observations of weak bands of trace components of ices towards the young stellar object W 33A. *Astrophys. Space Sci.*, **255**, 61–66.

Sellgren, K., Smith, R.G., Brooke, T.Y. (1994). The 3.2–3.6 micron spectra of Monoceros R2/IRS-3 and Elias 16. *Astrophys. J.*, **433**, 179–186.

Skinner, C.J., Tielens, A.G.G.M., Barlow, M.J., Justtanont, K. (1992). Methanol ice in the protostar GL 2136. *Astrophys. J.*, **399**, L79–L82.

Snyder, L.E., Kuan, Y.-J., Miao, Y. (1994). Where is the heavy molecule Heimat in Sgr B2? In *The Structure and Content of Molecular Clouds, 25 Years of Molecular Radioastronomy.* T.L. Wilson and K.J. Johnston (eds.). Springer-Verlag, p. 187–198.

Snyder, L.E., Lovas, F.J., Mehringer, D.M., Miao, N.Y., Kuan, Y.-J., Hollis, J.M., Jewell, P.R. (2002). Confirmation of interstellar acetone. *Astrophys. J.*, **578**, 245–255.

Soifer, B.T., Puetter, R.C., Russell, R.W., Willner, S. P., Harvey, P.M., Gillett, F.C.(1979). The 4–8 micron spectrum of the infrared source W33 A. *Astrophys. J.*, **232**, L53–L57 .

Spoon, H.W.W., Moorwood, A.F.M., Pontoppidan, K.M., Cami, J., Kregel, M., Lutz, D., Tielens, A.G.G.M. (2003). Detection of strongly processed ice in the central starburst of NGC 4945. *Astron. Astrophys.*, **402**, 499–507.

Taban, I.M., Schutte, W.A., Pontoppidan, K.M., van Dishoeck, E.F. (2003). Stringent upper limits to the solid NH_3 abundance towards W 33A from near-IR spectroscopy with the Very Large Telescope. *Astron. Astrophys.*, **399**, 169–175.

Teixeira, T.C., Devlin, J.P., Buch, V., Emerson, J.P. (1999). Discovery of solid HDO in grain mantles. *Astron. Astrophys.*, **347**, L19–L22.

Thi, W.-F., Pontoppidan, K.M., van Dishoeck, E.F., Dartois, E., d'Hendecourt, L. (2002). Detection of abundant solid CO in the disk around CRBR 2422.8–3423. *Astron. Astrophys.*, **394**, L27–L30.

Turner, B.E. (1991). A molecular line survey of Sagittarius B2 and Orion-KL from 70 to 115 GHz. II – Analysis of the data. *Astrophys. J. Suppl.*, **76**, 617–686.

Turner, B.E., Apponi, A.J. (2001). Microwave detection of interstellar vinyl alcohol, CH_2CHOH. *Astrophys. J.*, **561**, L207–L210.

Van Broekhuizen, F.A., Keane, J.V., Schutte, W.A. (2004). A quantitative analysis of OCN^- formation in interstellar ice analogs. *Astron. Astrophys.*, **415**, 425–436.

Van Dishoeck, E.F. Blake, G.A. (1998). Chemical evolution of star-forming regions. *Adv. Res. Astron. Astrophys.*, **36**, 317–368.

Vogel, S.N., Genzel, R., Palmer, P. (1987). The dispersal of dense protostellar material – NH_3 hot cores and outflows in Sagittarius B2. *Astrophys. J.*, **316**, 243–257.

Watt, S., Mundy, L.G. (1999). Molecular environments of young massive stars: G34.26+0.15, G11.94-0.62, G33.92+0.11, and IRAS 18511+0146. *Astrophys. J. Suppl.*, **125**, 143–160.

Zhang, H.W., Zhao, G., Hu, J.Y. (2001). A catalogue of emission lines in spectra of Comet C/1995 O1 (Hale-Bopp). *Astron. Astrophys.*, **367**, 1049–1055.

5

Impact Delivery of Prebiotic Organic Matter to Planetary Surfaces

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Summary. Organic compounds, liquid water, and a source of energy are necessary requirements for life as we know it. Few places in the solar system appear to satisfy these requirements. Besides Earth, Mars and Europa may have provided at some point during their history the most promising environments for the origin of life. Here we address the role of impacts as a mechanism for the delivery of organic compounds to Earth, Mars, Europa, and the Moon through high-resolution hydrocode simulations. The results suggest that on the Earth some amino acids (such as aspartic acid and glutamic acid) could survive large cometary impacts at the percent level, enough to equal or exceed concentrations due to Miller–Urey synthesis in a CO_2-rich atmosphere. In particular, a grazing impact could have delivered to early Earth amounts of certain amino acids comparable to the background steady-state production. Substantial survival of some amino acids occurs in cometary impacts for Mars as well. Analogous to the situation on Earth, asteroid impacts on Mars do not seem to result in significant survival, even if lower impact velocities increase the survival of amino acids. In cometary impacts, however, the increased amino acid survival in part counteracts the effect of the lower Martian escape velocity (5 km/s for Mars versus 11.2 km/s for the Earth) that causes some projectile material to escape Mars gravity and be lost to space. Projectile escape becomes dominant in grazing impacts, which are thus not a significant source of organics on Mars. Projectile escape is dominant on Europa (escape velocity of 2 km/s); as a result, cometary impacts provide a negligible contribution to Europa's prebiotic organic inventory. However, as models of the circum-Jovian nebula suggest that Europa might have formed largely bereft of some biogenic elements, cometary impacts could be the primary source of some of Europa's biogenic elements. Finally, although subject to an impact history similar to that of the Earth and Mars, impact delivery on the Moon is limited by the lower gravity field, just as with Europa. This drastically limits the amount of organic molecules that can be successfully delivered intact to the lunar surface.

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5.1 Introduction

Life originated on Earth more than 3.5 billion years (Gyr) ago. Traditional models held that it came from a "primordial soup," an ancient pond or ocean in which organic material somehow combined to form a primitive living cell. This theory has provided the basis for the more general concept of the origin of life as we know it requiring the presence of liquid water, a supply of prebiotic organic compounds, and a source of energy. Any planetary object that at some stage of its evolution hosted near-surface liquid water and a supply of complex organic compounds may have been in the position of harboring life. Besides Earth, few places in the solar system appear to satisfy these requirements, with Mars and Europa being the most promising possibilities. But where does the initial organic material come from? Both endogenic and exogenic mechanisms could be important sources of organic matter (Chyba and Sagan, 1992). Among the most popular endogenic mechanisms suggested are the standard electrical discharge Miller–Urey synthesis in the atmosphere (Miller, 1953) or synthesis in hydrothermal systems (e.g., Shock and Schulte, 1998). Exogenic mechanisms proposed include impacts of large objects, comets, and asteroids (Chamberlin and Chamberlin, 1908), as well as soft-landing of micron-sized Interstellar Dust Particles (IDPs; Anders, 1989).

New recent experimental and theoretical studies have renewed interest in the role of impacts of large objects in providing complex organic molecules to planetary bodies of the solar system. Our knowledge of the potential effects of shock loading on the modification of organic material is still sparse. However, laboratory experiments have shown that high stresses and elevated temperatures typical of shock waves may cause organic matter to decompose, to racemize, or to recombine into secondary products (e.g., Peterson et al., 1997; Blank et al., 2001). Theoretical experiments have modeled the effect of planetary scale impacts on amino acid degradation as due to thermal degradation from impact shock heating (Blank and Miller, 1998; Pierazzo and Chyba, 1999a; 2002; 2003).

5.2 Sources of Organic Material

Amino acids are the building blocks of the proteins and enzymes that are essential for life as we know it today, as well as of peptides that could have been fundamental ingredients of the first protocells (e.g., Pohorille, 2002). Many of the protein-building amino acids have been synthesized abiotically in laboratory experiments of the early Earth's atmosphere from simple precursors (Miller, 1953; Schlesinger and Miller, 1983; Stribling and Miller, 1987). The earliest experiments started from the assumption of a reducing primitive atmosphere dominated by CH_4 (often including also significant amounts of NH_3, H_2O, and sometimes H_2), and amino acid production occurred via the standard electrical discharge Miller–Urey synthesis (Miller, 1953; 1998).

However, it is now thought that the early Earth's atmosphere was a weakly reducing mixture of CO_2, N_2, and H_2O, probably with a number ratio of H_2 to CO_2 less, and possibly much less, than unity (Walker, 1986; Kasting, 1993; Kasting and Brown, 1998). In this case, the production of amino acids appears to be very limited (Schlesinger and Miller, 1983), making it difficult to justify an exclusive endogenic source of amino acids on the Earth. The early atmosphere on Mars had probably a composition similar to that on Earth, and thus a similar Miller-Urey type production of complex organic molecules. Other solar system bodies of interest for the origin of life, such as Europa, may have never had an atmosphere.

Hydrothermal systems in the deep ocean have also been proposed as possible environments for the synthesis of prebiotic organic molecules on the Earth (e.g., Holm and Andersson, 1995; 1998; Shock and Schulte, 1998). Laboratory experiments that test this hypothesis suggest formation of amino acids in vent environments, in some cases with even higher yields than that reported for electric discharges (e.g., Hennet et al., 1992; Yanagawa and Kobayashi, 1992). It has been suggested that the high temperatures would preclude the survival of the newly formed organic molecules, but laboratory work to simulate a typical deep-sea hydrothermal system circulation suggests that significant amounts of complex organic molecules can build up (Imai et al., 1999). As Europa may harbor an extensive ocean underneath its icy crust, it is plausible that deep-sea hydrothermal systems similar to the Earth may develop, providing an endogenic source of organics (e.g., McCollom, 1999). Other endogenous sources of organics are also possible on Europa (Chyba and Phillips, 2001). Hydrothermal systems have also been hypothesized for Mars, where organic synthesis may have somewhat greater potential than in Earth case (Shock and Schulte, 1998).

Amino acids are abundant in some extraterrestrial material. Certain carbonaceous chondrites, the most volatile-rich meteorites, contain up to 5% by weight of organic matter, covering over 70 different amino acids, including eight protein-building amino acids (Cronin, 1976; Cronin and Pizzarello, 1983; Shock and Schulte, 1990; Cronin et al., 1988; Cronin; 1998). Comets show substantial organic material (Krueger and Kissel, 1987; Delsemme, 1988; Chyba et al., 1990), although there is no direct spectral identification of amino acids. Evidence for the amino acid glycine in the interstellar medium (ISM) remains ambiguous (Snyder, 1997), but if amino acids do exist in the ISM, comets may inherit them directly during accretion. Since it is improbable that we may uniquely identify many complex organic compounds from cometary spectra (because of the heavy overlapping of their spectral signatures with simpler molecules; Bernstein, personal communication), only an *in situ* analysis or sample return mission may provide this type of information. Recently, amino acids have been identified in simulated cometary material (Bernstein et al., 2002; Muñoz Caro et al., 2002), a promising indication of the possible presence of these complex organic molecules inside comets. When analysis of Comet Wild-2 samples, returned to Earth in January 2006, becomes available, we

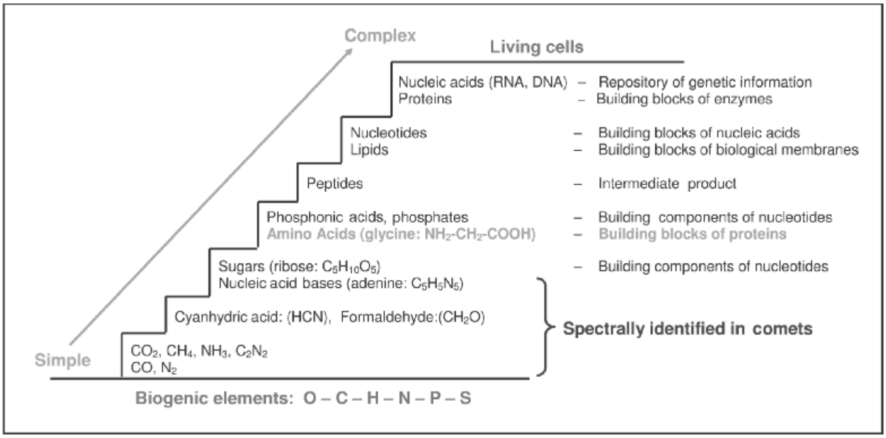

Fig. 5.1. Organic molecules: From biogenic elements to living cells.

may find out for sure. Even if amino acids are not present, however, many of the aspects of this analysis would carry over to other organic molecules of prebiotic interest (see Fig. 5.1) that are certainly present in comets (for Arrhenius parameters for other organics, including some based on shock-tube experiments, see Chyba et al., 1990).

Biomolecules like amino acids are thermally fragile; that is, they tend to be destroyed into constituent gases (CO_2, H_2O, NH_3, CO) and a variety of volatile organic compounds (amines, nitriles, hydrocarbons, etc.) when subject to temperatures above about 700–800 K (e.g., Basiuk and Navarro-Gonzales, 1998). In the solid phase, the thermal behavior of typical amino acids is influenced by their structures. Overall, thermal degradation of amino acids follows an Arrhenius-like decay law:

$$dM = -MAe^{[-E_a+P(t)V]/RT(t)}dt \tag{5.1}$$

where E_a (cal/mol) and A (1/s) are the activation energy and preexponential constant, respectively, for the organic molecule; R=1.987 cal/mol is the gas constant; $P(t)$ and $T(t)$ are the time-dependent pressure (in Pa) and temperature (in K); V is the activation volume of the molecule (in m^3/mol); and M is the mass of the organic material (in kg). New experimental values in the solid phase for E_a and A for the biological protein amino acids (Rodante, 1992) differ substantially from previously available kinetic parameters for thermal degradation in solution (Vallentyne, 1964). Neither case provides the best simulation of impact shock heating. The ideal kinetic parameters for these simulations would derive from shock-tube or impact gun experiments, but such data for amino acids are not currently available. We believe that Rodante's kinetic parameters in the solid phase are more appropriate for impact simulations (as amino acids are contained inside solid projectiles) than those from solution (where hydrolysis will occur, especially during slow heating experiments; e.g., Bada, 1991).

The suggestion that a substantial fraction of the Earth's prebiotic inventory of organic matter may have been delivered by incoming comets and asteroids was first proposed in 1908 by Thomas and Rollin Chamberlin, (Chamberlin and Chamberlin, 1908). This theory acquired greater importance when spacecraft missions to comet Halley revealed it to be nearly 25% organic by mass (consistent with its elemental cosmic abundances; e.g., Krueger and Kissel, 1987; Delsemme, 1988; Chyba et al., 1990). However, a conservative numerical investigation by Chyba et al. (1990) indicated that with the exception of some thermally hardy compounds, such as polycyclic aromatic hydrocarbons (PAHs), the high temperatures involved in large comet and asteroid impacts would probably destroy most organic molecules (this does not preclude the possibility of substantial postimpact organic synthesis in an expanding impact plume: e.g., Oró, 1961; Barak and Bar-Nun, 1975; Oberbeck and Aggarwal, 1992; Chyba and Sagan, 1992; McKay and Borucki, 1997). This conclusion seems to be reinforced by recent laboratory studies (Basiuk and Navarro-Gonzales, 1998; Basiuk et al., 1999), suggesting that simple amino acids (and some nucleic acids) cannot survive rapid heating to temperatures substantially higher than about 1,000 K. It should be pointed out, however, that these experiments also showed survival of amino acids at the 1–10% level when subject to temperatures of about 700–800 K, for periods of time exceeding 10 min. It appears, then, that on the Earth the most promising source of exogenous organics would have been interplanetary dust particles (IDPs), which appear to be roughly 10% organic by mass, and which decelerate gently in the atmosphere and can thus deliver their organics intact (Anders, 1989; Chyba and Sagan, 1992). This idea has recently been challenged by an investigation that simulated the heating experienced by IDPs during atmospheric entry (Glavin and Bada, 2001). After subjecting grains (<100 μm in size) of the carbonaceous chondrite Murchison to heating to about 820 K under reduced pressures, Glavin and Bada (2001) found that only glycine was able to survive heating by sublimating while other amino acids appeared to be completely destroyed.

Organic survival in large impacts has received new life from a combination of theoretical and experimental studies. Early incentive was provided by the identification of what appear to be extraterrestrial amino acids, α-aminoisobutyric acid, and racemic isovaline, at the Ir-rich Cretaceous/Tertiary (K/T) boundary layer at Sussex and Raton Basin sites (Bunch, personal communication), and not only above and below the boundary, as it was found, early on, at the Stevns Klint (Denmark) K/T boundary layer (Zhao and Bada, 1989). Since then, laboratory experiments have shown that significant fractions of amino acids can survive large shocks (e.g., Tingle et al., 1992; Peterson et al., 1997; Blank et al., 2001). Finally, theoretical studies suggest that significant amounts of some amino acids can be delivered to the Earth's surface via a large comet impact (Blank and Miller, 1998; Pierazzo and Chyba, 1999a).

5.3 Hydrocode Simulations

We carried out numerical simulations of impact cratering events on various planetary surfaces, using both two-dimensional (2D) and three-dimensional (3D) hydrocodes. Earlier studies were carried out using the 2D Eulerian hydrocode CSQ , developed at Sandia National Laboratories; (Thompson, 1979; 1985). By assuming axial symmery, CSQ is used to model vertical impacts. However, it is well known that the most probable impact angle is 45° (Gilbert, 1893; Shoemaker, 1962). Modeling the impact process in its full complexity, including the nonnormal impact angle of the incoming impactor, requires thus a fully 3D hydrocode, which is highly computation intensive. Because of this, the use of 3D hydrocodes has been sporadic; only recently have computer hardware advances allowed a more general use of 3D codes. We carried out oblique impact simulations for Mars and the Moon, using the 3D Eulerian hydrocode SOVA, developed at the Institute for Dynamics of Geospheres (Shuvalov, 1999). The code has been benchmarked in 3D simulations against the well-known hydrocode CTH (the latest hydrocode from Sandia National Laboratories; McGlaun et al., 1990). The results show similar shock melting and vaporization patterns in CTH and SOVA simulations (Pierazzo et al., 2001), with a better efficiency (faster runs for the same spatial resolution) for SOVA.

An important drawback with 2D simulations is that they tend to overestimate shock temperatures (and underestimate shock pressures) by at least a factor of 2, with possible excursions of up to an order of magnitude when compared to equivalent 3D simulations (Thomas and Brookshaw, 1997; Pierazzo and Melosh, 2000). This translates into a higher internal energy of the impact plume, resulting in a higher plume temperature and a larger fraction of the projectile material reaching escape velocity in 2D simulations. Therefore, results from 2D simulations (e.g., Chyba et al., 1990) can be considered conservative, in that they overall underestimate the amount of organic material surviving the impact and successfully delivered to the planetary surface.

The angle of impact affects shock intensity. Shock heating declines with increasing angle to the vertical (Chyba et al., 1990; Thomas and Brookshaw, 1997; Pierazzo and Melosh, 2000). Thus, simple 2D simulations underestimate the survivability of organic molecules compared to oblique impacts. In some cases, however, it is possible to correct ad hoc results of 2D simulations in a simplified approach that takes into account the effect of impact angle (Pierazzo and Chyba, 1999a; 2002).

In our simulations, hundreds of Lagrangian tracer particles were regularly distributed in half of the projectile (taking advantage of axial, for 2D, or bilateral, for 3D, symmetry). The tracers allow us to record the trajectories and thermodynamic histories of the projectile during the impact. Resolution plays an important role in the thermodynamic evolution of the impact event (Pierazzo et al., 1997); we kept the resolution of the 2D Eulerian mesh to 50 cells (2%) per projectile radius in all the simulations, substantially higher than that used in earlier simulations (e.g., Chyba et al., 1990; Thomas and

Brookshaw, 1997). The 3D simulations are much more computer intensive; therefore, our highest resolution in 3D runs is 20 cells per projectile radius. The thermodynamic state of the tracers was recorded every 0.005–0.01 seconds of simulation time.

The hydrocodes make use of the semianalytical equation of state ANEOS, a FORTRAN code designed for use with a number of hydrocodes (Thompson and Lauson, 1972). Utilizing valid physical approximations in different regimes, ANEOS uses the Helmholtz free energy to construct thermodynamically consistent pressures, temperatures, and densities. A major advantage of ANEOS over other analytical equations of state (e.g., the Tillotson EOS; see Melosh, 1989) is that it offers a limited treatment of phase changes. Asteroid impacts were modeled using granite (Pierazzo et al., 1997) and dunite (Benz et al., 1989) projectiles. Comets are "dirty iceballs," a combination of ice and silicate grains, but for simplicity in our modeling the comets are treated as pure water ice (Turtle and Pierazzo, 2001). Initial impact conditions varied depending on the planetary body of interest (Table 5.1). We used the granite ANEOS equation of state (Pierazzo et al., 1997) to model rocky targets, and the ice equation of state to model icy targets (Europa). In the oceanic impact

Table 5.1. Comparison of origin of life conditions on Earth, Mars, Europa, and the Moon, and summary of the properties important for the impact delivery hypothesis.

	Earth	Mars	Moon	Europa
In situ organic production	Yes	Probable	Difficult	Difficult
Surface liquid water	Stable over geologic time	Stable for limited time	No (Dry formation?)	No (Subsurface ocean?)
Surface gravity (m/s^2)	9.78	3.72	1.6	1.33
Escape velocity (km/s)	11.2	5	2.4	2
Likely impactor population	>90% asteroids	>90% asteroids	>90% asteroids	>90% J-F comets
Median impact velocity (km/s)[a]				
Asteroids	∼15–17	∼7.7	∼12	
Comets	∼23	∼15	∼20	∼26

[a] Median impact velocities are from Chyba (1991) for Earth and Moon, from Olsson-Steel (1987) for comets on Mars, and from Zahnle et al. (1998) for Europa.

simulations, a 3-km-deep ocean (using the equation of state for water) overlaid a granite crust. The simulations extended long enough for the projectile material to be released from the shock state and for the pressure and temperature to reach a plateau. Impact-related temperature histories (from tracer particles) were extracted from the hydrocode simulations. A good resolution of the shock wave generated by the impact is guaranteed by the high temporal resolution of the recorded histories.

The application of Eq. (5.1) to all the tracers' temperature histories provides a map of survival of amino acids in the projectile (assuming that amino acids are present). An example is shown in Fig. 5.2 for a comet impact on the Earth's ocean. The fraction of amino acids surviving the impact event is then obtained by integrating the survival fraction obtained through Eq. (5.1) over the volume of the projectile (see Tables 5.2, 5.4, and 5.5 for various planetary bodies). Amino acid survival depends strongly on the peak shock temperature and the postshock temperature experienced by the projectile. The peak shock temperature decreases away from the impact point, resulting in lower survival near the incident face of the projectile, where the shock temperatures are highest, as shown in Fig. 5.2. To maintain a conservative approach to the problem, we neglect the pressure contribution, $P(t)V$, in the exponent of Eq. (5.1). As discussed in Blank et al. (2001), the high pressures associated with shocks should retard the kinetics of reactions that involve the breaking of bonds, and therefore pyrolysis, associated with the very high shock temperatures. This occurs essentially because the activation volumes for bond breaking are positive (Asano and Le Noble, 1978). When introducing the pressure contribution in Eq. (5.1), we find that the estimated amino acid survival increases by up to an order of magnitude.

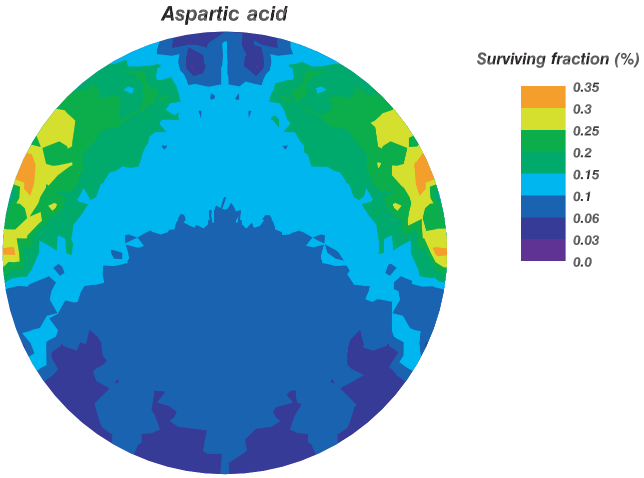

Fig. 5.2. Survival map for aspartic acid within a comet 2 km in diameter impacting the Earth's surface at 20 km/s. From Pierazzo and Chyba (1999a).

5.4 Earth: Significant Delivery

To assess the survival of amino acids in large impacts on the Earth, we carried out high-resolution 2D hydrocode simulations of asteroid and comet impacts with CSQ (Pierazzo and Chyba, 1999a). We model spherical asteroid and comet projectiles 2 to 10 km in diameter impacting both a continental crust and a 3-km-deep ocean. An impact velocity of 15 km/s, the median asteroid impact velocity with Earth, was used for asteroid impacts (Chyba, 1991). For comet simulations we used impact velocities of 15, 20, and 25 km/s. The latter is just above the median short-period comet impact velocity with Earth (Chyba, 1991). One hundred Lagrangian tracer particles were regularly distributed in half of the projectile to record the trajectories and thermodynamic histories of the projectile during the impact. The simulations show that organic survival is affected by various factors, such as projectile type and composition, size, impact velocity, and impact angle.

Projectile composition affects thermodynamic evolution, and therefore organic survival. Cometary material is easily shock vaporized, thus entering the expansion plume early in the impact event, whereas asteroidal material is mostly melted and remains at significantly higher temperatures for a longer time. As a result, in cometary material temperatures decrease to values well below 1,000 K relatively early, while asteroidal material experiences much higher temperatures (up to and above 2,000 K) for longer time (more than 4 s), resulting in virtually no amino acid survival.

To quantify the effect of impactor size on organic survival, we carried out comet impact simulations, using projectiles 2, 6, and 10 km in diameter at impact speeds of 20 km/s (Pierazzo and Chyba, 1999a). The shock experienced by the projectile does not differ much in the three cases. However, in a larger projectile the shock wave must travel farther to reach the rear of the projectile, where it is then reflected back as a rarefaction wave that unloads the material from the shocked state. At constant impact speed, the shock waves takes three to five times longer for the 6- and 10-km projectiles to reach the projectile's rear end than for the 2-km impactor. During this time the material is subject to extremely high temperatures, which are detrimental to amino acid survival (material near the rear of the projectile will experience a shorter shock pulse than material close to the impact point).

Impact velocity also affects organic survival: The higher the impact speed, the stronger the resulting shock, and relative pressures and temperatures experienced by the projectile. This, in turn, decreases the survival of organic matter. Figure 5.2 shows the surviving fraction of aspartic acid in a comet impacting at 20 km/s.

To investigate the effect of angle of impact, we took advantage of the scaling studies of Pierazzo and Melosh (2000). Through a series of high-resolution 3D hydrocode simulations, Pierazzo and Melosh (2000) concluded that projectile shock temperature scales with the sine of the angle of impact (θ) to the 3/2 power, while the postshock temperature scales with the sine to the

0.8 power. A simple scaling of the projectile's temperature histories of the 2D simulations by $(\sin\theta)^{0.8}$ provides a conservative correction for impact angle (i.e., it overestimates the peak shock temperature for oblique impacts thus decreasing the probability of amino acid survival). Figure 5.3 shows the survival of selected amino acids for a 2-km-diameter comet impact at 20 km/s as function of θ. At 45°, the most probable angle of impact (Gilbert, 1893; Shoemaker, 1962), survival has increased over that for vertical impacts by a factor of 3 for aspartic acid, and by a factor of 5 for glutamic acid.

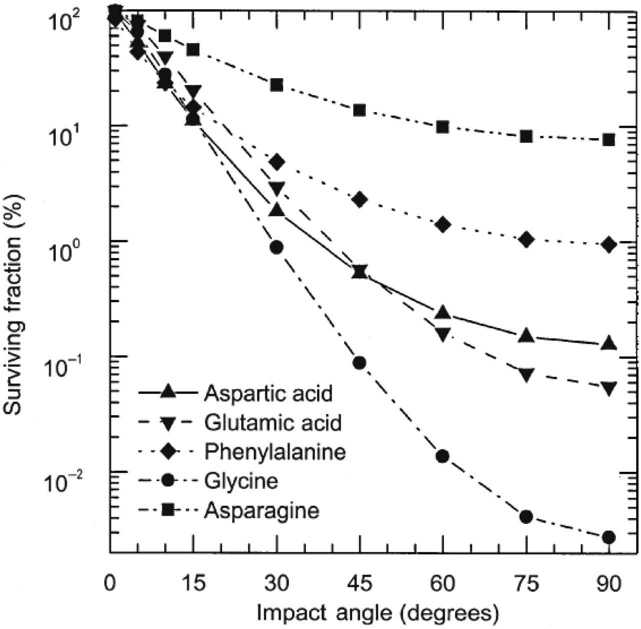

Fig. 5.3. Survival fraction for selected amino acids as a function of the angle of impact from the horizontal, using an ad hoc angle correction (see text). From Pierazzo and Chyba (1999a).

Among other factors that can influence the survival of organics in impacts are projectile inhomogeneities. Porosity is an important factor in generating inhomogeneities inside the impactor. For a porous material, extra work must be done to close the pores. Therefore, during an impact, more energy is partitioned to a porous projectile, causing higher peak and postshock temperatures. The simulation of a comet with 0.6 g/cm^3 bulk density impacting at 25 km/s showed an increase of 50–75% in the average temperature of the projectile during the impact relative to the fully dense case. This, in turn, results in a decrease in survival of amino acids, which ranges between about 15% for asparagine and 40–50% for aspartic and glutamic acid.

Table 5.2. Fraction (relative to the initial amount in the projectile) of amino acids surviving impact in 2D hydrocode simulations of cometary impacts on the Earth. D = comet diameter; v_{imp}= impact velocity.

D (km)	v_{imp} (km/s)	Glycine (%)	Aspartic acid (%)	Glutamic acid (%)
2	15	0.14	0.29	0.91
2	20	0.003	0.13	0.05
2	25	2×10^{-5}	0.02	0.002
6	20	0	0	3×10^{-5}
10	20	0	0	10^{-8}

Table 5.2 shows the survival of few amino acids in comet impacts on the Earth. The conclusion that certain amino acids would survive even large cometary impacts is itself a remarkable result. To determine the quantitative importance of the potential cometary source, we compare resulting concentrations within the global ocean for certain amino acids resulting from Miller–Urey synthesis and cometary input. These concentrations are given by

$$d[C]/dt = S/V - k[C] \tag{5.2}$$

where $[C]$ is the concentration (mol/l), S is the source term (mol/yr), V is the ocean volume (1.4×10^{21}l), and k is the destruction rate (1/yr) for the amino acids. In the limit of large t, integration of Eq. (5.2) gives a steady-state value: $[C]_{\text{inf}} = S/(Vk)$. A variety of sinks can be considered (see discussion in Pierazzo and Chyba, 1999a). Following Stribling and Miller (1987), we use the circulation of the entire ocean through submarine vents at 300°C with a timescale of 10^7 years (Edmond et al., 1982) as the dominant sink for amino acids. Taking half the ocean to circulate through 300°C vents in 5 Myr gives $k = 1.4 \times 10^{-8}$/yr.

In Pierazzo and Chyba (1999a), we used Schlesinger and Miller (1983) abundances of various amino acids for a $[H_2]/[CO_2] = 0.1$ model atmosphere (it may be a value that greatly overestimates endogenous amino acid production, which falls off rapidly as $[\mathrm{H_2}]/[\mathrm{CO_2}]$ drops below ~1; values for $[\mathrm{H_2}]/[\mathrm{CO_2}]$ of ~0.01 on early Earth have been suggested; see, e.g., Kasting, 1993), as a source term for endogenous production of various amino acids on early Earth). Relative to glycine (=100), the abundance of alanine, aspartic acid, and glutamic acid are 7.0, 0.22, and 0.06, respectively. Integrating equation (5.2) yields values for [C] for aspartic acid, glutamic acid, and glycine

Table 5.3. Estimated oceanic amino acid concentrations from various sources (10^{-12} mol/l) 4 Gyr ago.

Source	Glycine	Aspartic acid	Glutamic acid
Electrical discharge $[H_2]/[CO_2] = 0.1$ atm.	2000	5	1
Steady-state cometary input	400	10	70
Low-angle 5-km-radius comet impact	30	0.7	4

shown in Table 5.3 (these are amino acids produced in detectable quantities in CO_2 atmospheres that may be present in comets, by analogy with the Murchison meteorite, and have a nonnegligible survival in cometary impacts).

To determine the source term for cometary delivery to early Earth, we take initial concentrations in the Murchison meteorite for glycine, aspartic acid, and glutamic acid to be 37.8 (3 ppm by mass), 1.5, and 3.9 nmol/g, respectively (Cronin, 1976; see discussion in Pierazzo and Chyba, 1999a). These numbers are much lower than those listed in typical compilations of Murchison amino acid abundances (Cronin and Pizzarello, 1983; Shock and Schulte, 1990), because we make the conservative assumption that amino acid precursors in comets do not contribute to amino acids in the Earth's oceans. We multiply the Murchison amino acid concentrations by 10 to scale crudely for the fact that the overall organic fraction of comets is 10 times that found in carbonaceous chondrites (Chyba et al., 1990).

Following Chyba and Sagan (1992), we then determined the mass flux (based on the lunar record) of objects with masses between m_{min} and m_{max} impacting Earth 4 Gyr ago; m_{min} is equivalent to an asteroid 0.5 km in diameter (large enough to pass through the atmosphere unaffected; Chyba et al., 1993); m_{max} is given by an asteroid 6 km in diameter (above which our simulations show amino acid survival to be minimal). Finally, we make the assumption that only 10% of the mass flux is due to short-period comets. This assumption is consistent with previous modeling (Chyba et al., 1990) and current estimates (e.g., Kring and Cohen, 2002). The total cometary mass accreted by the Earth is thus 5×10^{11} g/year, conservatively assuming that about half of the mass from impacting comets would be lost from the atmosphere (Melosh and Vickery, 1989; Chyba, 1991). Integrated over 10^9 years, this rate would give 5×10^{20} g of cometary water delivered to the Earth, well below the upper limit of 10^{23} g now seemingly permitted by three observed cometary D/H ratios (Bockelée-Morvan et al., 1998). To determine the fraction of cometary amino acids that would survive impact, we integrated over comet radii (bins centered around the sizes simulated, therefore: 1–4 km, 4–8 km, 8–12 km), impact velocities (15, 20, and 25 km/s), and impact angles. Averages over impact angle were performed using the previously described temperature scaling with impact angle, weighted by impact angle probability (Gilbert, 1893; Shoemaker, 1962; see Pierazzo and Chyba, 1999a). Statistics for Earth impact velocities for short-period comets are poor, but suggest that 30% of impacts occur with velocities between 15 and 20 km/s and 30% of impacts occur at velocities between 20 and 25 km/s (Chyba, 1991). The surviving fraction of amino acids in each velocity bin was calculated by averaging survival for the velocity extrema of the bin, while impacts at velocities >25 km/s are taken to give zero contribution.

The estimated cometary contributions to oceanic concentrations, [C], are shown in Table 5.3, which compares the steady-state cometary input with Miller–Urey production rates. Concentrations are very low in both cases; to be credible for the origin of life, both cases must therefore appeal to concentration mechanisms in evaporating ponds or other special environments. Our results are based on the simple assumption that all surviving cometary amino acids are mixed into 1.4×10^{21} L of ocean water, giving a resulting amino acid molarity in the global ocean; therefore, regional or local instantaneous concentrations could be considerably higher. It is interesting in this context that Monnard et al. (2002) show that salt concentrations in Earth's oceans strongly interfere with some important prebiotic syntheses; they suggest that the origin of life on the Earth was therefore more likely to have occurred in freshwater environments than in the oceans.

Table 5.3 also displays results for the unlikely, but probably nevertheless realized, case of a single 5-km-radius comet striking the surface of the ocean at 20 km/s with an inclination of 5° to the horizontal (about 0.5% of all incident comets should have struck Earth at or below this inclination). This simulation of a special case is in the spirit of Clark's suggestion (Clark, 1988) that rare fortuitously low-angle cometary collisions may have been important for the origin of life. For this particular case, our simulations indeed show substantial amino acid survival, often in the tens-of-percent range; a single object may thereby itself deliver an abundance of certain amino acids comparable to that due to background production or delivery. Thus there may have been occasional periods of duration approximately 10^7 years with oceanic concentrations of certain amino acids above that of the steady-state cometary value.

These results suggest the possibility that the apparently extraterrestrial amino acid AIB found at K/T boundary sites could indeed have been directly delivered by the K/T impactor. The concentrations detected (Zhao and Bada, 1989) could be provided by a 10-km-diameter comet provided that much of the AIB present within the object survived impact. (This assumes cometary amino acid levels at least 10 times that of Murchison. Intriguingly, sample A91 suggests that some micrometeorites have AIB concentrations 100 times higher than Murchison; Brinton et al., 1998.) In the absence of thermal degradation parameters in the solid state (Rodante, 1992) for AIB, this problem cannot yet be addressed quantitatively. However, the results described here suggest that this scenario should be considered possible.

Additional endogenous sources for amino acids may also have existed. For an early atmosphere with CO_2 about 100 times the present atmospheric level, and a methane flux equal to the modern abiotic hydrothermal flux (Chang, 1993), the HCN rainout rate via the production of N from solar Lyman alpha photolysis of N_2 in the middle atmosphere could have been 1×10^{-2} nmol/cm^2/yr, or about twice that produced by electrical discharge in a $[H_2]/[CO_2]=0.1$ atmosphere (Zahnle, 1986; Chang, 1993). Substantially higher HCN production would have occurred for correspondingly higher CH_4 fluxes (Zahnle, 1986). It is clear that there are substantial uncertainties in estimates for both exogenous and endogenous sources of organics, as well as the dominant sinks. All of the likely mechanisms described here lead to extremely low global concentrations of amino acids, emphasizing the need for substantial concentration mechanisms or for altogether different approaches to the problem of prebiotic chemical synthesis.

5.5 Mars: Balancing Factors

Mars is the most Earth-like of the other planets of the solar system with respect to possible environments for life, showing widespread evidence of both heat sources and water. The prospect that early Mars conditions may have been suitable for the origin of life is one of the main reasons for biological interest in Mars (e.g., McKay, 1997). Present knowledge on past Martian atmospheric and surface conditions support two possibilities: (1) a warm, wet early-Mars with a thick CO_2-based atmosphere and a long-lasting greenhouse climate (e.g., Pollack, 1979; Pollack et al., 1987); (2) a cold, dry Mars, characterized by an almost endless winter broken by either volcanic or impact events causing subsurface water to melt (and evaporate) and run to the surface, for temporary periods of temperate climate (e.g., Segura et al., 2002). Both possibilities are conductive to liquid water being stable on the martian surface for some part of its history (although liquid water is not stable at the martian surface today). The organic material could have been endogenic in origin via a Miller–Urey synthesis in the atmosphere (although production would be reduced in a thin atmosphere), or in hydrothermal systems. However, overall endogenic production of organics on Mars may not have been as successful as on the Earth, especially in the case of a cold, dry Mars. Extraterrestrial delivery, thus, might have been very important for Mars.

An early study using 2D hydrocode simulations to investigate impact delivery on Mars (Pierazzo and Chyba, 1999b) indicated results similar to those for the Earth, that is a substantial survival for some amino acids in comet impacts on Mars with little or no survival in asteroidal impacts, even though the mean asteroidal impact velocity (9.3 km/s) is lower than that on the Earth (Pierazzo and Chyba, 1999b). However, Mars has a much lower escape velocity than the Earth, which increases the probability of projectile escaping after the impact. The 2D impact simulations showed that in vertical impacts significant escape of cometary material occurs even at the lowest impact velocity modeled, 12.5 km/s (Pierazzo and Chyba, 1999b). As found by Pierazzo and Melosh (2000), this effect should become even more important in oblique impacts, where a larger fraction of the initial impact energy is partitioned to the projectile.

To assess the importance of projectile escape with angle of impact, we have carried out 3D impact simulations with SOVA spanning different angles of impact, while keeping other input parameters constant (Pierazzo and Chyba, 2003). We model spherical comets 2 km in diameter impacting Mars' surface at 15.5 km/s (see Fig. 5.6). This corresponds to the median impact velocity for short-period comets on Mars according to the data from Olsson-Steel (1987). A very thin CO_2 atmosphere was included in the simulations to model the present-day Martian atmosphere (although a thicker atmosphere could have been present early in Martian history, favoring retention of ejected material).

Around 1,000 Lagrangian tracers were regularly distributed inside the (model half-) projectile to follow its thermodynamic history during the impact. The Arrhenius equation (5.1) is integrated over time and over the projectile volume using the temperature histories from the projectile tracers. The fraction of amino acids successfully delivered to Mars in the impact event is then determined by integrating over the volume of the projectile that does not reach escape velocity.

The angle of impact affects significantly the postimpact dynamical evolution of the projectile. Table 5.4 and Figs. 5.4 and 5.5 summarize the results from this study compared to the earlier 2D simulation for the same cometary impact (D_{pr}=2 km; v_{imp}=15.5 km/s) and normal incidence angle. In Table 5.4 the fraction of surviving amino acids contained in the fraction of the projectile that reaches escape velocity (and is considered lost) is shown in parentheses. Contrary to the earlier 2D numerical simulations, which showed a loss of 1/3 of the projectile, we find a much lower escape of projectile material in the 3D vertical impact simulation with SOVA. This discrepancy is a consequence of the switch from 2D to 3D numerical simulations (as discussed in the Hydrocode Simulations section). The lower impact temperature in the 3D simulation of a vertical impact (90°) results in a larger survival fraction for amino acids relative to the earlier 2D (CSQ) counterpart (Pierazzo and Chyba, 1999b). The 3D simulations also show that projectile escape increases rapidly with decreasing impact angle. For the most probable impact angle, 45°, almost half of the cometary material reaches Mars escape velocity, and well over 2/3 of the projectile escapes for impact angles below 30°.

Overall, Fig. 5.5 shows that the delivered fraction of surviving amino acid is significant for impact angles as low as 30° (which includes 75% of all cometary impacts on Mars). This is due to a balance between the increased loss of projectile material with decreasing impact angle and a weakening of the overall shock effects (e.g., Pierazzo and Melosh, 2000), which, in turn, increases the

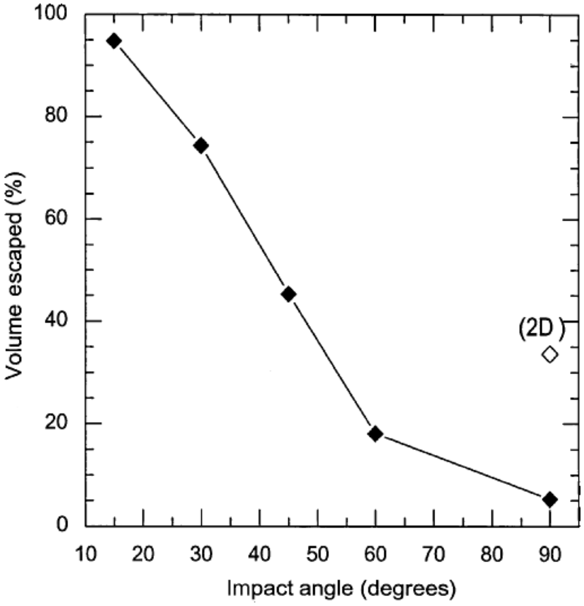

Fig. 5.4. Projectile volume reaching escape velocity for a comet 2 km in diameter impacting Mars surface at 15.5 km/s at various impact angles. For comparison, the open diamond shows an earlier estimate from a 2D simulation (with CSQ).

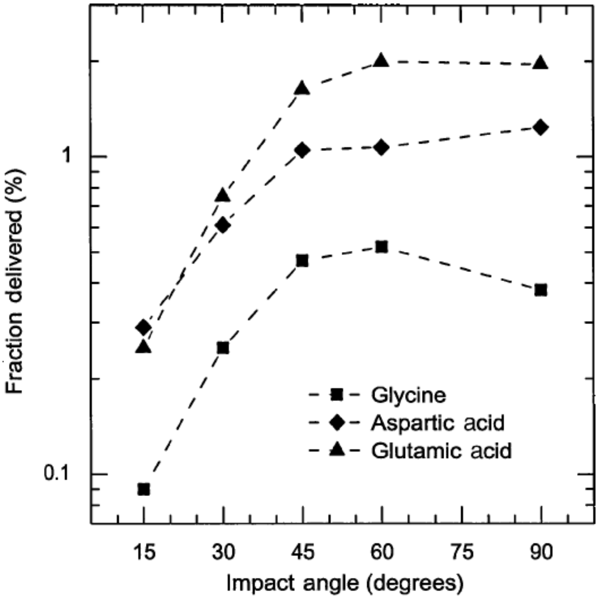

Fig. 5.5. Survival for selected amino acids in impacts of a comet 2 km in diameter at 15.5 km/s as function of impact angle.

Table 5.4. Fraction of projectile that escapes from the target world (V_{esc}) and fraction (relative to the initial amount in the projectile) of amino acids surviving impact in 3D hydrocode simulations of comet (D=2 km) impacts on Mars and on the Moon, as a function of impact velocity (v_{imp}) and impact angle. Results from an equivalent 2D simulation are also shown for comparison. In parentheses are surviving amino acids in the fraction of projectile that reached escape velocity.

Angle	v_{imp} (km/s)	V_{esc} (%)	Glycine (%)	Aspartic acid (%)	Glutamic acid (%)
Mars					
2D	15.5	33.6	0.11 (0.1)	0.5 (0.77)	0.65 (0.63)
90°	15.5	5.27	0.33 (0.09)	1.13 (0.19)	1.74 (0.35)
60°	15.5	18.5	0.52 (0.4)	1.1 (1.05)	2.0 (1.1)
45°	15.5	45.3	0.5 (2.1)	1.05 (5.0)	1.65 (5.3)
45°	12	35.2	1.9 (3.4)	1.4 (3.5)	4.8 (7.1)
45°	22	55.3	0.04 (0.5)	0.8 (3.9)	0.3 (2.1)
30°	15.5	69.4	0.3 (8.1)	0.9 (7.0)	1.0 (15.6)
15°	15.5	96.3	0.09 (38.9)	0.29 (6.7)	0.25 (49.3)
Moon					
45°	20	69.9	0.02 (1.0)	0.42 (4.1)	0.16 (3.4)

overall amino acid survival (as discussed in Pierazzo and Chyba, 1999a). Below 30°, however, the fraction of surviving organics retained decreases rapidly. Grazing impacts, thus, are not a favorable condition for the delivery of a large amount of organics to Mars. According to our adopted escape criterion, in a 15° impact over 95% of the projectile quickly reaches escape velocity (Table 5.4), thus very little of the surviving organic material can be considered successfully delivered. On the other hand, in the case of lower impact angles (e.g., Fig. 5.6a), most of the projectile ends up moving downrange in the lower and denser part of the martian atmosphere, as shown in Fig. 5.6b. It is thus possible that some component of the projectile will be slowed down by the martian atmosphere before escape, and end up being retained on Mars. An accurate investigation of very low impact angles requires a more sophisticated and time-consuming modeling the hydrodynamic of two phases, which includes the interaction (momentum and heat exchange) of solid and molten particles with the postimpact gas flow (similar to the work presented in Stöffler et al., 2002).

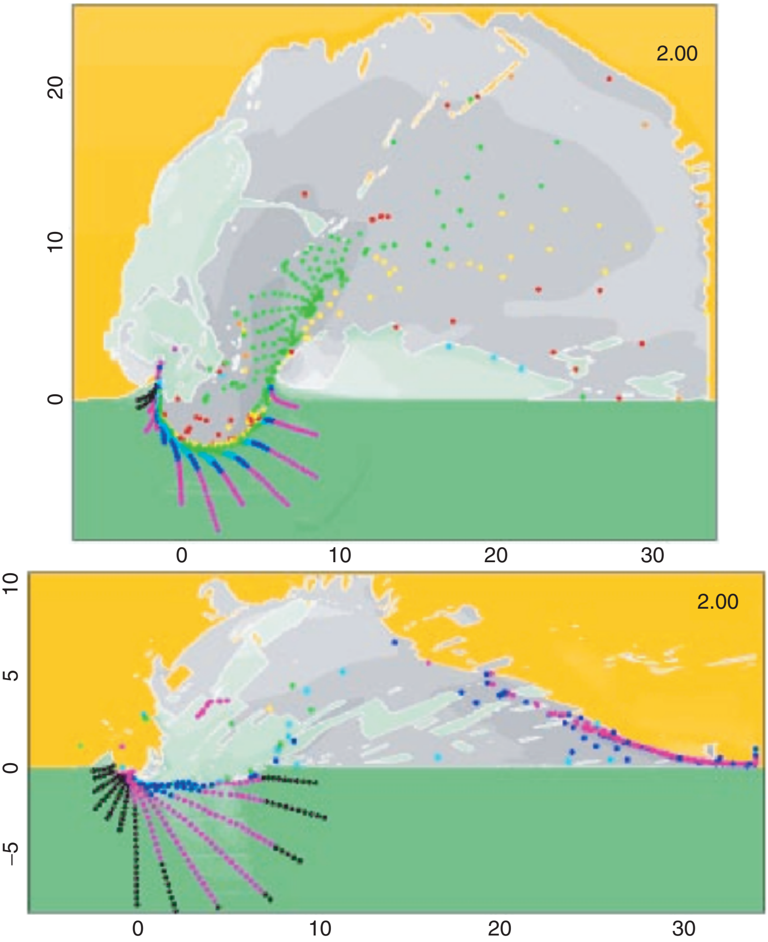

Fig. 5.6. Outputs from 3D simulations (with SOVA) 2 s after impact for a comet 2 km in diameter impacting at 15.5 km/s at (a) 45° and (b) 15° from the surface. Different colors represent different materials: green = granite; yellow = atmosphere; gray = projectile. All colors are graded according to density variation. Tracers are represented as dots, colored according to peak shock pressure: red = 150–250 GPa; yellow = 100–150 GPa; green = 50–100 GPa; cyan = 30–50 GPa; blue = 18–30 GPa; magenta = 5–18 GPa; black = below 5 GPa.

Impact velocity affects impact delivery of organics in two ways: (1) by affecting the fraction of projectile escaping Mars gravity and (2) by affecting the impact energy, thus the intensity of the shock and the amount of postimpact internal energy available for expansion. We investigated the role of impact velocity for impacts on Mars by carrying out two more simulations of a 45° impact, bracketing the velocity range between 12 and 22 km/s, corresponding to 25% and 75% of the impacts on Mars, respectively (Olsson-Steel, 1987). The results are also shown in Table 5.4. The range in velocity results in an uncertainty of ±10% in the fraction of projectile escaping from Mars and affects the overall survival of organics. Over the range of velocities investigated, we find that the surviving fraction of amino acids delivered to the martian surface can vary by a factor of 2 for aspartic acid to about 50 for glycine.

A final integration of these results to estimate the overall delivery of amino acids to the Martian surface requires a more complete investigation of the role of impact velocity as well as of projectile size for varying impact angle.

5.6 Europa: Impactor Loss

Strong evidence that a liquid water ocean exists beneath the surface of Jupiter's moon Europa (Pappalardo et al., 1999; Kivelson et al., 2000; Chyba and Phillips, 2006) fuels speculation about the possibility of life on that world and resulting plans for future spacecraft exploration (Chyba and Phillips, 2001; 2006). But too few biology-related characteristics of Europa are currently understood for firm conclusions to be drawn. We do not know how much organic material is present in its ocean. Even the inventory of elements needed for life (especially the "biogenic" elements C, H, N, O, P, S) in Europa's ocean is nearly entirely unknown. A bulk carbonaceous chondrite (CI) composition is often assumed (e.g., Kargel et al., 2000). However, Europa's formation conditions within the circum-Jovian nebula (Lunine and Stevenson, 1982; Prinn and Fegley, 1989) are poorly known. Thermochemical models predict that the most stable phase for carbon in the proto-Jovian nebula is CH_4, in contrast to CO in the solar nebula (e.g., Prinn and Fegley, 1989). In the region where Europa formed the temperature may have been too high for CH_4 to condense out (e.g., Lunine and Stevenson, 1982), pointing to a carbon-depleted Europa. Unless the bulk of proto-Europa originated from solid planetesimals that accreted in the solar nebula without undergoing further modification, it is difficult to feel confident in a bulk CI composition for Europa, at least for C. This suggests that Europa might have formed largely bereft of organic material.

We investigated the exogenous contribution to Europa's biogenic inventory through high-resolution 2D simulations with CSQ (coupled to ANEOS) to model cometary impacts on Europa (Pierazzo and Chyba, 2002). More than 90% of the craters on the Galilean satellites are estimated to be due to impact by Jupiter-family comets (Zahnle et al. 1998), with long period comets and Trojan asteroids making up the rest of impactors. The distribution of the cumulative impact velocity given by Zahnle et al. (1998) suggests that the median impact velocity of these comets on Europa is around 26.5 km/s. We modeled cometary projectiles 0.5 and 1 km in diameter, and impact velocities of 16, 21.5, 26.5, and 30.5 km/s. Based on Zahnle et al. (1998), these velocities correspond to the 10, 25, 50, and 75% levels (i.e., 10% of impacts occur at impact velocities below 16 km/s). The typical density of comets is unknown. Estimates of cometary nuclei densities in the literature have ranged between 0.2 and 1.2 g/cm^3 (Rahe et al., 1994). To assess the effect of porosity, we used cometary densities of 1.1, 0.8, and 0.6 g/cm^3, which correspond to porosities of 0, 27, and 45%, respectively. The latter value of 0.6 g/cm^3 corresponds to the best estimate of comet Shoemaker-Levy 9's density, based on tidal physics (Asphaug and Benz, 1996).

Europa's surface was treated as pure nonporous ice with a surface temperature of 110 K and a temperature gradient of 32 K/km (equivalent to the linear temperature gradient of an ice shell about 5 km thick). Temperature gradients in Europa's ice shell depend not only on ice thickness but on tidal heating within the shell and whether the ice is convecting or conducting (Chyba et al., 1998); however, these uncertainties for the upper few kilometers of the ice (the depth relevant to the impacts simulated here) do not strongly affect the fate of the projectile, which is the focus of this study.

The velocity evolution recorded by the tracers allowed us to determine the percentage of the postimpact projectile that would exceed Europa's escape velocity (about 2 km/s); according to our adopted escape criterion, we treat all escaped material as gone from Europa forever, consistent with estimating a lower limit for accreted mass. While some of this material might be subsequently reaccreted by Europa, much of it could be lost because of ionization and subsequent acceleration in Jupiter's magnetic field. Because CSQ overestimates shock temperatures and underestimates shock pressures, the results of this study should be considered conservative.

The results of the various simulations, shown in Table 5.5 and Fig. 5.7, indicate that a large fraction of most impacting comets reaches escape velocity after colliding with Europa's surface. For a nonporous comet some fraction of the projectile is retained by Europa even at the highest impact velocity modeled, 30.5 km/s. However, for porous comets a significant fraction of the projectile is retained only for impact velocities below 16 km/s. Tracers from porous projectiles have a consistently higher velocity, suggesting that comet porosity strongly affects the fraction of material that escapes after the impact. Porosity affects the partitioning of the impact energy between target and impactor (extra PdV work must be done to close the pore in the projectile). The higher the projectile's porosity the more impact energy is partitioned to it rather than to the target, causing a hotter and faster expansion of the vaporized projectile material. (At the velocities of Jupiter-family comets on Europa nearly all of the comet is vaporized in the impact.) Overall, the retention of a nonnegligible amount of the impactor differs from the conclusions of Melosh and Vickery (1989) for planetary escape of impact-produced vapor. Their intentionally simple analytical model indicates that at typical Europan impact velocities (above about 5 km/s) all of the postimpact vapor plume, which for an icy impactor includes the vaporized projectile, should exceed escape velocity. Our hydrodynamic simulations suggest instead that significant retention,

Table 5.5. Fraction of projectile that escapes from Europa (V_{esc}) and fraction (relative to the initial amount in the projectile) of amino acids surviving impact in 2D hydrocode simulations of impacts of comets 1 km in diameter on Europa. ρ_{pr} is the projectile density; v_{imp}= impact velocity.

ρ_{pr} (g/cm^3)	v_{imp} (km/s)	V_{esc} (%)	Glycine (%)	Aspartic acid (%)	Glutamic acid (%)
1.1	16	15.9	0.86	0.83	3.50
1.1	21.5	44.9	0.02	0.54	0.27
1.1	26.5	69.4	5×10^{-4}	0.31	0.02
1.1	30.5	80.1	10^{-5}	0.13	0.002
0.8	16	46.9	0.76	0.75	2.36
0.8	21.5	88.7	0.001	0.12	0.02
0.8	26.5	100	–	–	–
0.6	16	73.3	0.83	0.45	0.61
0.6	21.5	100	–	–	–

at the 10% level, of impactor material occurs for impacts at the lower end of the velocity distribution of Jupiter-family comets on Europa.

Impact angle is another factor that influences the retention of impactor material. The dramatic increase in organic survivability with decreasing impact angle (Pierazzo and Chyba, 1999a) is counteracted by the increase in projectile material ejection velocity for decreasing impact angle. This effect is negligible for impact angles above 60°, and becomes significant below that. On Europa, where the escape velocity is very low, projectile escape dominates increased survival, as even in a vertical impact over 2/3 of the projectile escapes for median impact velocities. We thus extrapolated to Europan impacts by assuming that for impact angles below 60° all of the projectile will escape Europa's gravity, regardless of impact velocity. According to impact probability theory, 25% of randomly distributed impactors will strike within this angle of the normal (Shoemaker, 1962); the results from the 2D simulations can then be generalized to represent this fraction of near-vertical impacts.

Using the estimates of Zanhle et al. (1998; 1999) and Levison et al. (2000), we estimated an Europan average impactor flux of 5.5×10^7 g/year (see Pierazzo and Chyba, 2002). Holman and Wisdom (1993) argued that the comet

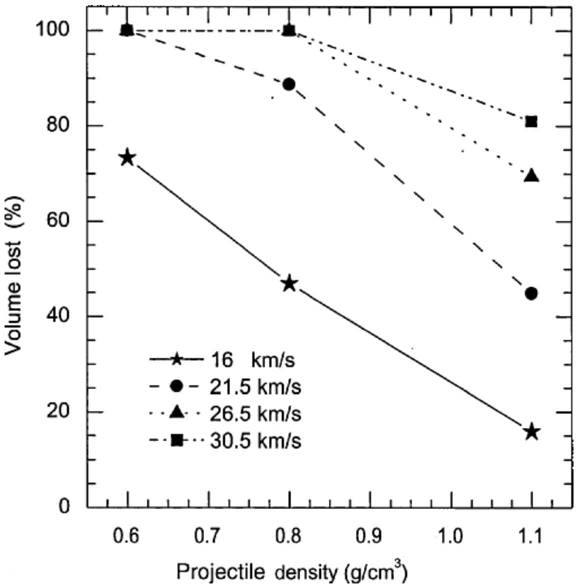

Fig. 5.7. Fraction of projectile material reaching Europa's escape velocity in 2D impact simulations (with CSQ) as a function of projectile bulk density (x-axis) and impact velocity (various lines/symbols) for a comet 1 km in diameter. From Pierazzo and Chyba (2002).

flux has decreased with time due to the depletion of the Kuiper belt. Integrating the current flux backwards in time with this assumption, the integrated flux over 4.4 Gyr is 8.2×10^{17} g, 3.4 times greater than if the flux had been constant (Pierazzo and Chyba, 2002). The total cometary mass accreted on Europa over 4.4 Gyr, M_{acc}, assuming a given comet density is thus given by

$$M_{acc} = 8.2 \times 10^{17} \times F(\Theta) \times \left[\sum_{\mathrm{i}} F(< v_{\mathrm{i}}) \times F_{\mathrm{p}}^{i}\right] \tag{5.3}$$

where $F(\Theta) = 0.25$ is the fraction of comets impacting within 30° of the normal; $F(< v_i)$ is the fraction of comets impacting with velocities in that velocity bin (e.g., 10% for $v_i < 16$ km/s; 15% for $16 < v_i < 21.5$ km/s; and so on); and F_p^i is the fraction of the projectile that is retained on Europa, given in Table 5.5. For a 1.1 g/cm^3 comet density, the total cometary mass accreted over 4.4 Gyr is: $M_{acc} = 8.2 \times 10^{17} \times 0.25 \times [0.1 \times 0.84 + 0.15 \times 0.55 + 0.35 \times 0.30] = 6.0 \times 10^{16}$ g. This decreases to 1.4×10^{16} g for a 0.8 g/cm^3 comet density, and down to 5×10^{15} g for a comet density of 0.6 g/ cm^3.

The fraction of surviving amino acids delivered in the impact is determined by integrating Eq. (5.1) over the component of the projectile that does not exceed Europa's escape velocity. We obtain substantial survival fractions for some amino acids at all the impact speeds modeled. However, because a large fraction of the projectile is lost to space, only part of the surviving organics will be deposited on the surface of Europa (Table 5.5). We also find that the survival of the retained amino acids increases from 30% for a nonporous comet 1 km in diameter to about 55% for a nonporous comet 0.5 km in diameter. However, when integrated over the mass of the projectile, the overall contribution to the Europan inventory is about the same for the two cases, indicating that smaller comet sizes are not any more favorable than the case examined. In the end, the total amount of amino acids delivered to Europa's surface is several orders of magnitude lower than that estimated for Earth. While some fraction of these organics may be cycled into the ocean, some may be lost by sputtering, but much may be mixed into the regolith by impact gardening (Chyba and Phillips, 2001; 2006).

Although delivery of complex organics is inefficient, cometary impact could still prove important for providing, over the age of the Solar System, an inventory of biogenic elements that may be scarce on Europa. We used mass abundances for C (16.8 wt%), N (4.3 wt%), and S (2.8 wt%) estimated for comet Halley for a dust/gas ratio of 0.8 (Delsemme, 1991). The (as yet unknown) cometary phosphorus abundance (taken to be 0.5 wt%) is estimated by scaling from the C abundance assuming a CI-chondrite P/C ratio (Lodders and Fegley, 1998). Cometary accretion by Europa over 4.4 Gyr should have provided between 0.9 and 10 Gt of C (where 1 Gt=10^{15} g), 0.2–3 Gt of N, 0.2–2 Gt of S, and 0.02–0.3 Gt of P (Pierazzo and Chyba, 2002). This material would be initially deposited on Europa's surface after the initially vaporized projectile condenses out. The young appearance of Europa's icy surface suggests a geological resurfacing timescale of about 50 Myr (Zahnle et al., 1998; Levison et al., 2000). If resurfacing leads to the biogenic elements accumulated on the surface being recycled to the ocean beneath, cometary delivery could provide the raw material to support a biosphere on Europa. (Direct delivery of projectile material, with its inventory of biogenic elements, to the Europan ocean is highly improbable even if the projectile could plunge through the moon's several km-thick icy surface – Turtle and Pierazzo, 2001 – since most of the projectile is vaporized by the impact and entrained in the expansion plume.) These values are about eight orders of magnitude lower than those given by an assumption of a CI bulk composition for Europa (Kargel et al., 2000). Alternatively, they may be compared to estimates of the prokaryotic biomass in the Earth's oceans today (Whitman et al., 1998), which contains 300 Gt of C, 70 Gt of N, and 8 Gt of P. Since Europa's ocean is expected to have a mass about twice that of Earth's oceans (Chyba and Phillips, 2001), this suggests that even if comets were the only source of biogenic elements to Europa's oceans, microorganism densities could in principle be as high as $\sim$1% that of the Earth's oceans, assuming otherwise favorable conditions.

5.7 Amino Acids on the Moon: Impact Delivery?

The Moon is the planetary body closest to the Earth. Therefore, since its formation the Moon must have experienced an impact history similar to that of the Earth (although scaled by the different cross sections of the two bodies). If asteroid and comet impacts delivered a significant source of amino acids to the Earth, it is reasonable to expect that it may have happened on the Moon as well, although of course the different escape velocities of the two worlds must be taken into account. The late 60s and the 70s witnessed intensive analyses of amino acids in lunar soils (Hamilton, 1965; Hare et al., 1970; Harada et al., 1971; Nagy et al., 1971; Gehrke et al., 1972; 1975; Hamilton and Nagy, 1972; 1975; Modzeleski et al., 1973; Fox et al., 1973; 1976). Results range from no obvious evidence of amino acid presence above background levels in the lunar regolith (Gehrke et al., 1975) to findings of amino acid kinds and amounts similar to those found in meteorites (e.g., Fox et al., 1975). Differences in analyses and sample preparation methods may be the causes of such disagreement (e.g., Fox et al., 1981). These studies were unable to clearly characterize the possibility of terrestrial contamination of the samples.

More recently, Brinton and Bada (1996) reexamined amino acids in lunar soils. In particular, they tried to address the question of possible terrestrial contamination, by assuming that any excess of L-enantiomers over a racemic mixture represent terrestrial contamination. Once corrected for contamination, they found that the distribution of amino acids in lunar soils differs significantly from that of carbonaceous chondrites. In terms of abundance, the concentration of AIB is ±0.3 ppb. Based on the flux of carbonaceous material to the Moon, they estimated the impact survivability of AIB acid on the lunar surface to be ±0.8%.

To evaluate the importance of cometary impact delivery of amino acids on the Moon, we modeled the impact of a 2-km-diameter comet on the lunar surface at 45°. We used an impact velocity of 20 km/s, which corresponds to the median impact velocity on the Moon for short-period comets (Chyba, 1991). Results are shown in Table 5.4: Because of the low lunar escape velocity, almost 70% of the projectile reaches the Moon escape velocity soon after impact, and is thus lost. The outcome does not appear to improve much for a more favorable case of a 90° (vertical) impact, as over 50% of the projectile reaches escape soon after impact. This result is similar to the case of Europa, where we reached the conclusion that impact delivery is not a significant source of complex organic molecules (Pierazzo and Chyba, 2002). Furthermore, even in the case that some amino acids will eventually condense on the lunar surface, the high day-time temperatures on the lunar surface will cause those not in permanently shadowed regions to quickly decompose, unless they are quickly deposited and buried on the night side of the Moon before the day-time temperature excursion begins.

This result suggests that although cometary impacts did occur on the Moon, it is improbable that significant impact-delivered concentrations of amino acids are contained in the lunar regolith.

5.8 Summary and Conclusions

Previous modeling studies indicated that most organics would be entirely destroyed in large comet and asteroid impacts on the Earth. However, the availability of new kinetic parameters for the thermal degradation of amino acids in the solid phase has made it possible to readdress this question, and extend it to the case of other planetary bodies of the solar system that may have harbored life. We recognize that the kinetic parameters so far available are far from ideal for this type of modeling, and that parameters based on impact experiments (Blank et al., 2001) would be superior. This work summarizes the results of several high-resolution hydrocode simulations of asteroid and comet impact coupled with recent experimental data for amino acid pyrolysis in the solid phase. Differences due to impact velocity and projectile material, as well as effects of impact angle, have been investigated. The results suggest that some amino acids would survive the shock heating of large (kilometer size) cometary impacts. We find that a significant fraction of the Earth's prebiotic volatile inventory may have been delivered by asteroidal and cometary impacts during the period of heavy bombardment. At the time of the origin of life on the Earth, the steady-state oceanic concentration of certain amino acids (like aspartic and glutamic acid) delivered by comets could have equaled or substantially exceeded that due to Miller–Urey synthesis in a CO_2-rich atmosphere. Furthermore, in the unlikely case of a grazing impact (impact angle around 5° from the surface) an amount of some amino acids comparable to the background steady-state production would be instantaneously delivered to the early Earth.

The grazing impact hypothesis does not seem to work for Mars. Because of the lower escape velocity, large fractions of the projectile ends up escaping Mars gravity, ranging from a few percent in vertical impacts to almost 100% in low angle impacts ($<15°$). Overall, however, a significant fraction of organic material appears to be delivered to Mars by cometary impacts.

Although subject to the same impact history of the Earth, the Moon has a very different fate. The very low escape velocity causes most of the projectile to escape after cometary impacts on the lunar surface, while the very large daily temperatures excursions will be detrimental for any fragile organics exposed at the lunar surface. Thus, we should not expect to find significant abundances of amino acids in the lunar regolith. This is in agreement with experimental studies of amino acid concentrations in lunar soils.

Impact delivery of cometary material to Europa over 4.4 Gyr (even without taking into account any destructive effect of sputtering) would provide amino acid concentrations in Europa's oceans that are several orders of magnitude below those estimated for cometary delivery to Earth's oceans. Therefore, cometary delivery of intact prebiotic organics appears unimportant for Europa. However, over solar system history, cometary impacts may well have delivered to Europa gigatons of carbon and nitrogen, and somewhat less sulfur and phosphorous. If these biogenic elements could be recycled to the ocean beneath, they could provide the raw material to support a biosphere on Europa.

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References

Anders, E. (1989), Pre-biotic organic matter from comets and asteroids. *Nature*, **342**, 255–257.

Asano, T. and LeNoble, W.J. (1978), Activation and reaction volumes in solution. *Chem. Rev.*, **78**, 407–489.

Asphaug, E., and Benz W. (1996), Size, Density, and Structure of Comet Shoemaker-Levy 9 Inferred from the Physics of Tidal Breakup. *Icarus*, **121**, 225–248.

Bada, J.L. (1991), Amino acid cosmogeochemistry. *Phil. Trans. R. Soc. Lond. B*, **333**, 349–358.

Barak, I. and Bar-Nun, A. (1975), The mechanism of amino acid synthesis by high temperature shock-waves. *Origins Life*, **6**, 483–506.

Basiuk, V.A. and Navarro-Gonzales, R. (1998), Pyrolytic behavior of amino acids and nucleic acid bases: Implications for their survival during extraterrestrial delivery. *Icarus*,**134**, 269–278.

Basiuk, V.A., Douda, J. and Navarro-Gonzales, R. (1999), Transport of extraterrestrial biomolecules to the Earth: Problem of thermal stability. *Adv. Space Res.*, **24**, 505–514.

Benz, W., Cameron, A.G. and Melosh, H.J. (1989), The origin of the Moon and the single impact hypothesis. *Icarus*, **81**, 113–131.

Bernstein, M.P., Dworkin, J.P., Sanford, S.A., Cooper, G.W. and Allamandola, L.J. (2002), Racemic amino acids from the ultraviolet photolysis of interstellar ice analogues. *Nature*, **416**, 401–403.

Blank, J.G. and Miller, G.H. (1998), The fate of organic compounds in cometary impacts. In A.F.P. Houwing, A. Paull, R.R. Boyce, P.M. Danehy, M. Hannemann, J.J. Kurtz, T.J. McIntyre, S.J. McMahon, D.J. Mee, R.J. Sandeman and H. Tanno (eds.), Proceedings of the *21st International Symposium on Shock Waves* (Panther Press, Fyshwick, Australia), pp. 1467–1572.

Blank, J.G., Miller, G.H., Ahrens, M.J. and Winans, R.E. (2001), Experimental Shock Chemistry of Aqueous Amino Acid Solutions and the Cometary Delivery of Prebiotic Compounds. *Origins Life Evol. Biosph.*, **31**, 15–51.

Bockelée-Morvan, D. and 11 co-authors (1998), Deuterated water in comet C/1996 B2 (Hyakutake) and its implications for the origins of comets. *Icarus*, **133**, 147–162.

Brinton, K.L.F. and Bada, J.L. (1996), A reexamination of amino acids in lunar soils: Implications for the survival of exogenous organic material during impact delivery. *Geochim. Cosmochim. Acta*, **60**, 349–354.

Brinton, K.L., Engrand, C., Glavin, D.P., Bada, J.L. and Maurette, M. (1998), A search for extraterrestrial amino acids in carbonaceous antarctic micrometeorites. *Origins Life Evol. Biosph.*, **28**, 413–424.

Chamberlin, T.C. and Chamberlin, R.T. (1908), Early terrestrial conditions that may have favored organic synthesis. *Science 28*, 897–910.

Chang, S. (1993), Prebiotic synthesis in planetary environments. In J.M. Greenberg, C.X. Mendoza-Gomez, V. Pirroncello (eds.) *The Chemistry of Life's Origins*, (Kluwer Academic, Boston), 259–300.

Chyba, C.F. (1991), Terrestrial mantle siderophiles and the lunar impact record. *Icarus*, **92**, 217–233.

Chyba, C.F., and Phillips, C.B. (2001), Possible Ecosystems and the Search for Life on Europa. *Proc. Natl. Acad. Sci. USA*, **98**, 801–804.

Chyba, C.F., and Phillips, C.B. (2006). In *Planets and Life: The Emerging Science of Astrobiology*, (eds.) W Sullivan, J Baross. Cambridge: Cambridge University Press, to be published.

Chyba, C.F. and Sagan, C. (1992), Endogenous production, exogenous delivery and impact-shock synthesis of organic molecules: an inventory for the origins of life. *Nature*, **355**, 125–132.

Chyba, C.F., Ostro, S.J., and Edwards, B.C. (1998), Radar Detectability of a Subsurface Ocean on Europa. *Icarus*, **134**, 292–302.

Chyba, C.F., Thomas, P.J. and Zahnle, K.J. (1993), The 1908 Tunguska explosion: atmospheric disruption of a stony asteroid. *Nature*, **361**, 40–44.

Chyba, C.F., Thomas, P.J., Brookshaw, L. and Sagan, C. (1990), Cometary delivery of organic molecules to the early Earth. *Science*, **249**, 366–373.

Clark, B.C. (1988), Primeval procreative comet pond. *Origins Life*, **18**, 209–238.

Cronin, J.R. (1976), Acid-labile amino acid precursors in the Murchison meteorite. *Origins Life*, **7**, 337–342.

Cronin, J.R. (1998), Organic molecules on the early Earth. Clues from the origin of the Solar System: Meteorites. In Brack A. (ed.) *The molecular origins of life: Assembling pieces of the puzzle* (Cambridge Univ. Press, Cambridge, UK), 119–146.

Cronin, J.R. and Pizzarello, S. (1983), Amino acids in meteorites. *Adv. Space Res.*, **3(9)**, 5–18.

Cronin, J.R., Pizzarello, S. and Cruikshank, D.P. (1988), Organic matter in carbonaceous chondrites, planetary satellites, asteroids, and comets. In J.F. Kerridge and M.S. Matthews (eds.) *Meteorites and the Early Solar System* (Univ. of Arizona Press, Tucson, AZ), 819–857.

Delsemme, A.H. (1988), The Chemistry of comets. *Phil. Trans. R. Soc. London Ser. A*, **325**, 509–523.

Delsemme, A.H. (1991), Nature and History of the Organic Compounds in Comets: An Astrophysical View. In R.L. Newburn, M. Neugenbauer, J. Rahe (eds.) *Comets in the Post-Halley Era. Vol. 1* (Kluwer, Dordrecht), 377–428..

Edmond, J.M., Von Damm, K.L. and McDuff, R.E. (1982), Measures, C.I., Chemistry of hot springs on the East Pacific Rise and their effluent dispersal. *Nature*, **297**, 187–191.

Fox, S.W., Harada, K. and Hare, P.E. (1973), Accumulated analyses of amino acid precursors in returned lunar samples. *Proc. 4th Lunar Sci. Conf.; Geochim. Cosmochim. Acta* Suppl.4 (Pergamon Press), 2241–2248.

Fox, S.W., Harada, K. and Hare, P.E. (1975), Amino acids precursors in returnaed lunar samples from Apollo 17: Further evaluations of contamination. *Lunar Planet. Sci. Conf.*, **6**, 271.

Fox, S.W., Harada, K. and Hare, P.E. (1976), Amino acid precursors in lunar fines: Limits to the contribution of jet exhaust. *Geochim. Cosmochim. Acta*, **40**, 1069–1071.

Fox, S.W., Harada, K. and Hare, P.E. (1981), Amino acids from the moon – Notes on meteorites. In *Subcellular biochemistry.* Vol. 8 (Plenum Publishing), 357–373.

Gehrke, C.W., Zumwalt, R.W., Kuo, K., Rash, J.J., Aue, W.A., Stalling, D.L., Kvenvolden, K.A., Ponnamperuma, C. (1972) Research for amino acids in lunar samples. *Space Life Sci.*, **3**, 439–449.

Gehrke, C.W., Zumwalt, R.W., Kuo, K., Ponnamperuma, C. and Shimoyama, A. (1975), Search for amino acids in Apollo returned lunar soil. *Orig. Life*, **6** 541–550.

Gilbert, G.K. (1893), The Moon's face, a study of the origin of its features. *Bull. Philos. Cos. Wash (D.C.)*, **12**, 241–292.

Glavin, D.P. and Bada, J.L. (2001), Survival of amino acids in micrometeorites during atmospheric entry. *Astrobiology*, **1**, 259–269.

Hamilton, P.B. (1965), Amino acids on hands. *Nature*, **205**, 284–285.

Hamilton, P.B. and Nagy, B. (1972), Problems in the search for amino acids in lunar fines. *Space Life Sci.*, **3**, 439–449.

Hamilton, P.B. and Nagy, B. (1975), Comments on the search for amino acids in Apollo 15, 16, and 17 lunar samples. A study in contamination control. *Anal. Chem.*, **47**, 1718–1720.

Harada, K. Hare, P.E., Windsor, C.R. and Fox, S.W. (1971), Evidence for compounds hydrolyzable to amino acids in aqueous extracts of Apollo 11 and Apollo 12 lunar fines. *Science*, **173**, 433–435.

Hare, P.E., Harada, K. and Fox, S.W. (1970), Analyses for amino acids in lunar fines. *Proc. Apollo 11 Lunar Sci. Conf.; Geochim. Cosmochim. Acta* Suppl. 1, Vol. 2 (Pergamon Press), 1799–1803.

Hennet, R.J.-C., Holm, N.G., and Engel, M.H. (1992) Abiotic synthesis of amino acids under hydrothermal conditions and the origin of life: A perpetual phenomenon? *Naturwiss.*, **79**, 361–365.

Holm, N.G., and Anderson, E.M. (1995) Abiotic synthesis of organic compounds under the conditions of submarine hydrothermal systems: A perspective. *Planet. Space Sci.*, **43**, 153–159.

Holm, N.G., and Anderson, E.M. (1998) Organic molecules on the early Earth: Hydrothermal systems. In A. Brack (ed.) *The molecular origins of life: Assembling pieces of the puzzle*, Cambridge Univ. Press (Cambridge, UK), pp. 86–89.

Holman, M.J., and Wisdom, J. (1993), Dynamical Stability in the Outer Solar System and the Delivery of Short Period Comets. *Astronom. J.*, **105**, 1987–1999.

Imai, E.-i., Honda, H., Hatori, K., Brack, A., and Matsuno, K. (1999) Elongation of oligopeptides in a simulated submarine hydrothermal system. *Science*, **283**, 831–833.

Kargel, J.S., Kaye, J.Z., Head, J.W., III, Marion, G.M., Sassen, R., Crowley, J.K., Ballesteros, O.P., Grant, S.A., and Hogenboom, D.L. (2000), Europa's Crust and Ocean: Origin, Composition, and the Prospects for Life. *Icarus*, **148**, 226–265.

Kasting, J.F. (1993), Earth's early atmosphere. *Science*, **259**, 920–925.

Kasting, J.F. and Brown, L.L. (1998), The early atmosphere as a source of biogenic compounds. In Brack A. (ed.) *The molecular origins of life: Assembling pieces of the puzzle* (Cambridge Univ. Press, Cambridge, UK), pp. 35–56.

Kivelson, M.G., Khurana, K.K., Russel, C.T., Volwerk, M., Walker, R.J., and Zimmer, C. (2000), Galileo Magnetometer Measurements: A Stronger Case for a Subsurface Ocean at Europa. *Science*, **289**, 1340–1343.

Kring, D.A., and Cohen, B.A. (2002), Cataclysmic bombardment throughout the inner solar system 3.9–4.0 Ga. *J. Geophys. Res.*, **107(E2)**, doi:10.1029/2001JE001529.

Krueger, F.R. and Kissel, J. (1987), The chemical composition of the dust of comet P/Halley as measured by "PUMA" on board VEGA-1. *Naturwiss.*, **74**, 312–316.

Levison, H.F., Duncan, M.J., Zahnle, K., Holman, M., and Dones, L. (2000), Planetary Impact Rates from Ecliptic Comets. *Icarus*, **143**, 415–420.

Lodders, K., and Fegley, B. (1998), *The Planetary Scientist's Companion* (Oxford Univ. Press, New York).

Lunine, J.I., and Stevenson, D.J. (1982) Formation of the Galilean Satellites in a Gaseous Nebula. *Icarus*, **52**, 14–39.

McCollom, T.M. (1999) Methanogenesis as a potential source of chemical energy for primary biomass production by autotrophic organisms in hydrothermal systems on Europa. *J. Geophys. Res.*, **104(E12)**, 30,729–30,742.

McGlaun, J.M., Thompson, S.L. and Elrick, M.G. (1990), CTH: A three-dimensional shock wave physics code. *Int. J. Impact Eng.*, **10**, 351–360.

McKay, C.P. (1997), The search for life on Mars. *Origins Life Evol. Biosph.*, **27**, 263–289.

McKay, C.P. and Borucki, W.J. (1997), Organic synthesis in experimental impact shocks. *Science*, **276**, 390–392.

Melosh, H.J. (1989), *Impact Cratering: A Geologic Process.* (Oxford University Press, New York).

Melosh, H.J. and Vickery, A.M. (1989), Impact erosion of the primordial atmosphere of Mars. *Nature*, **338**, 487–489.

Miller, S.L. (1953), The production of amino acids under possible primitive Earth conditions. *Science*, **117**, 528–529.

Miller, S.L. (1998), The endogenous synthesis of organic compounds. In A. Brack (ed.) *The Molecular Origin of Life* (Cambridge Univ. Press, Cambridge, UK), 59–85.

Modzeleski, V.E., Modzeleski, J.E., Mohammed, M.A.J., Nagy, L.A., Nagy, B., McEwan, W.S., Urey, H.C., and Hamilton, P.B. (1973) Carbon compounds in pyrolysates and amino acids in extracts of Apollo 24 lunar samples. *Nature (Phys. Sci.)*, **242**, 50–52.

Monnard, P.-A., Apel, C.L., Kanavarioti, A. and Deamer, D. W. (2002). Influence of ionic solutes on self-assembly and polymerization processes related to early forms of life: Implications for a prebiotic qaueous medium. *Astrobiology*, **2**, 213–219.

Muñoz Caro, G.M., Melerhenrich, U.J., Schutte, W.A., Barbier, B., Arcones Segovia, A., Rosenbauer, H., Thiemann, W.H.-P., Brack, A. and Greenberg, J.M. (2002), Amino acids from ultraviolet irradiation of interstellar ice analogues. *Nature*, **416**, 403–405.

Nagy, B. and 10 others (1971), Carbon compounds in Apollo 12 lunar samples. *Nature*, **232**, 94–98.

Oberbeck, V.R. and Aggarwal, H. (1992), Comet impacts and chemical evolution of the bombarded Earth. *Origins Life Evol. Biosph.*, **21**, 317–338.

Olsson-Steel, D. (1987), Collisions in the Solar System – IV. Cometary impacts upon the planets. *Mon. Not. R. Ast. Soc.*, **227**, 501–524.

Oró, J. (1961), Comets and the formation of biochemical compounds on the primitive Earth. *Nature*, **190**, 389–390.

Pappalardo, R.T., and 31 others (1999), Does Europa have a subsurface ocean? Evaluation of the geological evidence. *J. Geophys. Res.*, **104**, 24015–24056.

Peterson, E., Hörz, F. and Chang, S. (1997), Modification of amino acids at shock pressures of 3.5 to 32 GPa. *Geochim. Cosmochim. Acta*, **61**, 3937–3950.

Pierazzo, E., and Chyba, C.F. (1999a), Amino Acid Survival in Large Cometary Impacts. *Meteoritics Planet. Sci.*, **34**, 909–918.

Pierazzo, E., and Chyba, C.F. (1999b), Impact Delivery of Organics to Mars. *Bull. Am. Astron. Soc.*, **31(4)**, 1183.

Pierazzo, E. and Chyba, C.F. (2002), Cometary delivery of biogenic elements to Europa. *Icarus*, **157**, 120–127.

Pierazzo, E. and Chyba, C.F. (2003), Impact delivery of organics to Mars: Oblique Impacts. *Lunar Planet. Sci. Conf.*, **34**, Abst. #1645.

Pierazzo, E., and Melosh, H.J. (2000) Hydrocode Modeling of Oblique Impacts: The Fate of the Projectile. *Meteoritics Planet. Sci.*, **35**, 117–130.

Pierazzo, E., Vickery, A.M. and Melosh, H.J. (1997), A re-evaluation of impact melt production. *Icarus*, **127**, 408–423.

Pierazzo, E., Artemieva, N.A. and Spitale, J.N. (2001), The Ries impact event: A tale of two hydrocodes (Abstract). In F. Martinez-Ruis, M. Ortera-Huertas and I. Palomo (eds.) *Impact markers in the stratigraphic record. Abstracts from the 6th ESF IMPACT Workshop* (ESF, Granada, Spain), pp. 87–88.

Pohorille, A. (2002), From organic molecules in space to the origins of life and back. *Adv. Space Res.*, **30**, 1509–1520.

Pollack, J.B. (1979), Climate change on the terrestrial planets. *Icarus*, **37**, 479–553.

Pollack, J.B., Kasting, J.F., Richardson, S.M. and Poliakoff, K. (1987), The case for a wet, warm climate on early Mars. *Icarus*, **71**, 203–224.

Prinn, R.G., and Fegley, B. (1989), Solar Nebula Chemistry: Origin of Planetary, Satellite and Cometary Volatiles. In S.K. Atreya, J.B. Pollack and M.S. Matthews, (eds.) *Origin and Evolution of Planetary and Satellite Astmospheres* (Univ. of Arizona Press, Tucson), pp. 78–136.

Rahe, J., Vanysek, V. and Weissman, P.R. (1994), Properties of cometary nuclei. In T. Gehrels (ed.) *Hazards Due to Comets and Asteroids* (Univ. of Arizona Press, Tucson), pp. 597–634.

Rodante, F. (1992), Thermodynamics and kinetics of decomposition processes for standard α-amino acids and some of their dipeptides in the solid state. *Thermochim. Acta*, **200**, 47–61.

Schlesinger, G. and Miller, S.L. (1983), Prebiotic syntheses in atmospheres containing CH_4, CO, and CO_2. I. Amino acids. *J. Mol. Evol.*, **19**, 376–382.

Segura, T.L., Toon, O.B., Colaprete, A. and Zahnle, K. (2002), Environmental effects of large impacts on Mars. *Science*, **298**, 1977–1980.

Shock, E.L. and Schulte, M.D. (1990), Summary and implications of reported amino acid concentrations in the Murchison meteorite. *Geochim. Cosmochim. Acta*, **54**, 3159–3173.

Shock, E.L. and Schulte, M.D. (1998), Organic synthesis during fluid mixing in hydrothermal systems. *J. Geophys. Res.*, **103(E12)**, 28,513–28,527.

Shoemaker, E.M. (1962), Interpretations of lunar craters. In Z. Kopal (ed.) *Physics and Astronomy of the Moon* (Academic Press, New York), pp. 283–359.

Shuvalov, V.V. (1999), Multi-dimensional hydrodynamic code SOVA for interfacial flows: Application to the thermal layer effect. *Shock Waves*, **9**, 381–390.

Snyder, L. (1997), The search for interstellar glycine. *Origins Life Evol. Biosph.* **27**, 115–133.

Stevenson, D. (2000), Europa's Ocean – the Case Strengthens. *Science*, **289**, 1305–1307.

Stöffer, D., Artemieva, N.A. and Pierazzo, E. (2002), Modeling the Ries-Steinheim impact event and the formation of the Moldavite strewn field. *Meteoritics Planet. Sci.*, **37**, 1893–1907.

Stribling, R. and Miller, S.L. (1987), Energy yields for hydrogen cyanide and formaldehyde synthesis: the HCN and amino acid concentrations in the primitive ocean. *Origins Life*, **17**, 261–273.

Thomas, P.J. and Brookshaw, L. (1997), Numerical models of comets and asteroid impacts. In P.J. Thomas, C.F. Chyba, C.P. Mckay (eds.) *Comets and the Origin and Evolution of Life.* (Springer-Verlag, New York), pp. 131–145.

Thompson, S.L. (1979), CSQII. An Eulerian finite differences program for two-dimensional material response. Part I. Material Section. *Rep. SAND77-1339* (Sandia National Laboratories, Albuquerque,NM).

Thompson, S.L. (1985), CSQIII An Eulerian Finite Difference Program for Two-Dimensional Material Response: Users Manual. *Rep. SAND87-2763* (Sandia Natl. Lab., Albuquerque, NM), 87 pp.

Thompson, S.L. and Lauson, H.S. (1972), Improvements in the Chart D radiation-hydrodynamic code III: Revised analytical equation of state. *Rep. SC-RK-61 0714* (Sandia National Laboratories, Albuquerque, NM).

Tingle, T.N., Tyburczy, J.A., Ahrens, T.J. and Becker, C.H. (1992), The fate of organic matter during planetary accretion: Preliminary studies of the organic chemistry of experimentally shocked Murchison meteorite. *Origins Life Evol. Biosph.*, **21**, 385–397.

Turtle, E.P., and Pierazzo, E. (2001), Constraints on the Thickness of an Europan Ice Shell from Impact Crater Simulations. *Science*, **234**, 1326–1328.

Vallentyne, J.R. (1964), Biogeochemistry of organic matter II. Thermal reaction kinetics and transformation products of amino compounds. *Geochim. Cosmochim. Acta*, **28**, 157–188 .

Walker, J.C.G. (1986), Carbon dioxide on the early Earth. *Origins Life*, **16**, 117–127.

Whitman, W.B., Coleman, D.C. and Wiebe, W.J. (1998), Prokaryotes: The Unseen Majority. *Proc. Natl. Acad. Sci. USA*, **95**, 6578–6583.

Yanagawa, H., and Kobayashi, K. (1992) An experimental approach to chemical evolution in submarine hydrothermal systems. *Origins Life Evol. Biosph.*, **22**, 147–159.

Zahnle, K.J. (1986), Photochemistry of methane and the formation of hydrocyanic acid (HCN) in the Earth's early atmosphere. *J. Geophys. Res.*, **91**, 2819–2834.

Zahnle, K., Dones, L. and Levison, H.F. (1998), Cratering Rates on the Galilean Satellites. *Icarus*, **136**, 202–222.

Zahnle, K., Levison, H., Dones, L. and Schenk, P. (1999), Cratering rates in the outer Solar System (CD-ROM). *Lunar Planet. Sci. Conf.*, **30**, Abst. #1770.

Zhao, M. and Bada, J. (1989), Extraterrestrial amino acids in Cretaceous/Tertiary boundary sediments at Stevns Klint, Denmark. *Nature*, **339**, 463–465.

6

Comets and Prebiotic Organic Molecules on Early Earth

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Summary. Life on the Earth may have originated in the final throes of the heavy bombardment, although the evidence for this conclusion is uncertain. This bombardment could have rendered the Earth's surface inhospitable for life for hundreds of millions of years subsequent to terrestrial formation. It may also have delivered to the Earth's surface prebiotic organic molecules of relevance to the origin of life. The quantitative importance of these exogenous sources, in comparison with endogenous production, depends largely on the nature of the early atmosphere. This chapter reviews current controversies in these areas and presents the current best, albeit still tentative, estimates of endogenous and exogenous sources of organics, and resulting concentrations of organics in the Earth's early oceans, for a range of early Earth models.

6.1 The Uninhabitable Habitable Zone

Life on the Earth depends critically on a handful of "biogenic" elements, such as carbon, hydrogen, nitrogen, oxygen, phosphorous, sulfur, and others. These elements are abundant in the outer Solar System, but comparatively rare in the region of the terrestrial planets. McKay (1991) has illustrated this graphically for the case of carbon. Figure 6.1 shows the ratio of carbon atoms to heavy atoms (i.e., all atoms heavier than helium) throughout the Solar System. The inner Solar System is extremely depleted in carbon, compared to solar abundances. Moving outward from the Sun, it is not until we reach the C-type asteroids in the main asteroid belt that the carbon abundance begins to approach that of the Sun.

Yet it is only at heliocentric distances less than the distance to the asteroid belt that planetary surface temperatures are high enough for the existence of surface liquid water (although subsurface liquid water oceans may be common

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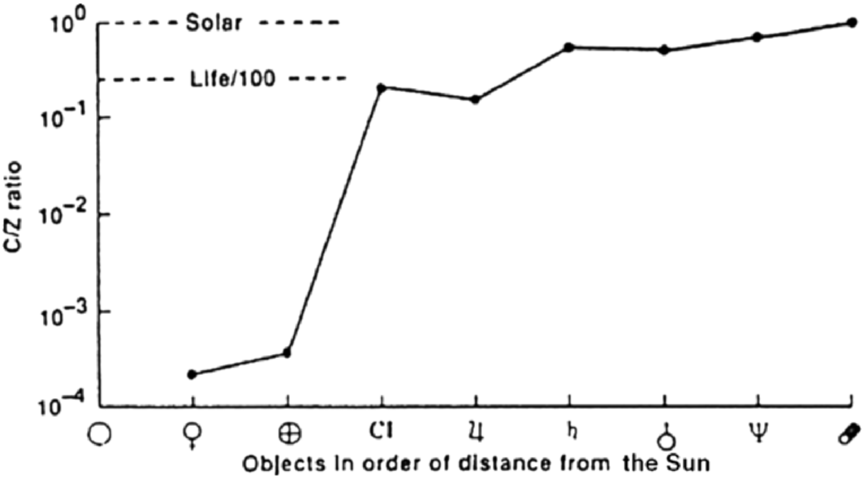

Fig. 6.1. Ratio of carbon (C) atoms to heavy (Z) atoms (atoms heavier than He) throughout the Solar System. The relative abundances of C in the Sun and in life on the Earth are shown for comparison. From McKay (1991).

on icy moons). Liquid water is the sine qua non of life as we know it (Horowitz, 1986; Mazur, 1980) and those terrestrial environments in which liquid water is most rare are those closest to being sterile. (For a review of what is now known about life in extreme environments on the Earth, including liquid–water–poor environments, see National Research Council, 2006.)

6.1.1 The Habitable Zone and Liquid Water

The circumstellar habitable zone is defined as the volume of space around a star (or around a multiple-star system) within which an Earth-like planet could support surface liquid water. An Earth-like planet is one comparable in mass to the Earth and having similar surface inventories of CO_2, H_2O, and N_2 (Kasting et al., 1993; Chyba et al., 2000). The zone's inner boundary is that distance at which a moist or runaway greenhouse effect occurs (as in the case of Venus in our Solar System). The outer boundary is that distance at which CO_2 condenses out of an atmosphere and is no longer available as a greenhouse gas (in our Solar System, somewhere around the orbit of Mars). In the context of the solar habitable zone, the distribution of biogenic elements presents an apparent dilemma: the elements essential to life are comparatively rare exactly where the temperatures make surface liquid water possible. (For the prospects for life in liquid water subsurface oceans on icy moons, see, e.g., Chyba and Phillips, 2002).

The dilemma worsens only when Solar System formation models are taken into account. The problem is that many of the biogenic elements are among the most volatile elements. Delsemme (1997; and this volume) has reviewed progress in thermochemical equilibrium and chemical kinetics models of the accretion disk out of which our planetary system formed. Such models have consistently found temperatures around 1,000 K in the region of terrestrial accretion, too high for the Earth to be provided with its observed inventories of water, nitrogen, and carbon (Cameron, 1983; Lewis, 1974; Lewis et al., 1979; Prinn and Fegley, 1989). Delsemme finds similar temperatures by using the transition between volatile-poor S-type asteroids and comparatively volatile-rich C-type asteroids to peg the accretion disk's temperature to 450 ± 50 K at 2.6 AU, then extrapolating inward to the region of the terrestrial planets. At temperatures near 1,000 K, water, carbon, nitrogen, and other volatiles remain almost entirely in the gas phase over the range of pressures likely to have existed in the accretion disk. Volatiles are therefore almost entirely absent from the dust grains out of which the planet-forming planetesimals aggregate. From the point of view of the biogenic elements, the habitable zone would seem, initially at least, uninhabitable. However, Campins et al. (2004) argue that with the Earth's total water inventory (including very uncertain quantities of water in the mantle) amounting to less than 1% of the Earth's mass, only small amounts of water would need be present in Earth-region planetesimals for a significant contribution to the Earth's water inventory to have been made. We face the dilemma that small deviations from average conditions could be sufficient to account for the terrestrial volatiles; this makes confident modeling of the origin of the oceans or other volatiles difficult.

6.1.2 Are the Earth's Oceans Extraterrestrial?

There are several plausible sources of water for early Earth, of which comets are but one. Wetherill (1990, 1994) showed that the latter stages of planetary formation were marked by collisions of large planetary embryos scattered across considerable heliocentric distances, and this result is borne out by subsequent simulations (Morbidelli et al., 2000). Thus, the Earth may have acquired an initial complement of volatiles though early radial mixing. The later stages of outer planet formation should have led to the scattering of volatile-rich planetesimals from the Jupiter–Saturn region (both asteroids and comets; Morbidelli et al., 2000; Campins et al., 2004), and comets from the Uranus–Neptune region (Fernandez and Ip, 1983; Shoemaker and Wolfe, 1984) and Kuiper belt (Morbidelli et al., 2000). Hartmann (1987, 1990) has argued that spectral observations of solar system satellites, as well as the preponderance of CM clasts among the foreign fragments in polymict meteoritic breccias, provide evidence for an intense scattering of C-type asteroids during the first $\sim 10^8$ years of solar system history.

But it is unclear whether volatiles accreted by the Earth prior to approximately 4.4 Gyr ago would have been retained. The hypothesized Moon-forming impact may have stripped the Earth of whatever terrestrial atmosphere existed prior to that event (Cameron, 1986). Terrestrial water present prior to core formation around 4.45 ($\sim 10^8$ years after the Earth's formation; Stevenson, 1983; Stevenson, 1990; Swindle et al., 1986; Tilton, 1988) should have been efficiently destroyed by reacting with metallic iron according to $Fe + H_2O \rightarrow FeO + H_2$; large quantities of hydrogen produced in this way may have removed other degassed volatiles by hydrodynamic escape (Dreibus and Wänke, 1987, 1989). It is possible that only those volatiles accreted by the Earth subsequent to core formation would have contributed to the Earth's extant volatile inventory. Icy planetesimals scattered from the accretion regions of Uranus and Neptune, with scattering timescales of hundreds of Myr, may in this case have been more likely contributors to the present terrestrial volatile inventory than icy planetesimals scattered from the jovian and saturnian regions, whose scattering timescales were perhaps as short as tens of Myr (Fernandez, 1985; Ip, 1977).

Isolated zircon crystals eroded from 4.3-to 4.4-Gyr-old igneous rocks (Mojzsis et al., 2001; Wilde et al., 2001) suggest that a hydrosphere may have existed on the Earth as early as 4.4 Gyr ago. Zircons imply that liquid water was involved in the genesis of their source rock, and oxygen isotopes in the zircon grains reveal that they formed in a crust that was interacting with a hydrosphere (Mojzsis et al., 2001; Wilde et al., 2001; see also Campins et al., 2004).

Comets are more than 40% water by mass (Delsemme, 1992); only approximately 10% of the observed cratering record on the Moon needs to have been cometary in origin for the Earth to have acquired its entire oceanic inventory of 1.4×10^{21} kg water from comet impacts (Chyba, 1987; Chyba, 1990). Estimates of water in the Earth's crust suggest that the crustal inventory of water is small compared to that in the oceans; however, it is possible that much more water is present in the Earth's mantle (Campins et al., 2004). Alternatively, if the heavy bombardment responsible for the observed lunar cratering record were primarily due to CI carbonaceous chondrites, the Earth could have acquired its oceans entirely from an asteroidal source (Chyba 1991; Chyba et al., 1994). It now seems likely that there were, in fact, multiple source regions for the Earth's oceans (Morbidelli et al., 2000; Campins et al., 2004).

6.1.3 D/H Ratios and Noble Gas Evidence

Isotopic ratios and noble gas abundances may constrain the relative contributions of some of the reservoirs that contributed to the Earth's oceans (Ehrenfreund et al., 2002; Campins et al., 2004). The deuterium-to-hydrogen (D/H) ratio has been measured (via HDO/H_2O) in three comets: Halley (Balsiger et al., 1995; Eberhardt et al., 1995), Hale-Bopp (Meier et al., 1998), and Hyakutake (Bockelée-Morvan et al., 1998). All three comets have D/H ratios about twice as high as that in the Earth's oceans (Standard Mean Ocean Water, or SMOW) and about 12 times higher than the protosolar value. Some authors have argued that this excludes comets as a source for more than a small fraction of the Earth's ocean water (e.g., Meier et al., 1998; Robert, 2001), although in an extreme model a 50% contribution can still not be ruled out

(Ehrenfreund et al., 2002). However, comets that formed in the Jupiter–Saturn region could have incorporated water with the same D/H ratio as that of the Earth (Delsemme, 1999 and this volume; Drouart et al., 1999). The D/H ratio in carbonaceous chondrites also overlaps with SMOW (Ehrenfreund et al., 2002). The three comets for which D/H has been observed are all thought to have come from the Oort cloud, which should be populated primarily by comets that originated in the Uranus–Neptune and Kuiper belt regions (Fernandez and Ip, 1983; Duncan et al., 1987). That is, the D/H ratios of comets that formed in the jovian or saturnian regions of the early Solar System have probably not yet been empirically sampled.

In principle, one could use abundances of noble gases or their isotopes in asteroids, comets, and planetary atmospheres to determine the relative contributions of different impactor types to the volatile inventories of Venus, Earth, and Mars (Owen et al., 1992; Chyba et al., 1994). These constraints have been recently reviewed (Campins et al., 2004). If comets with a solar abundance ratio of Ar/H_2O had contributed to the Earth's oceans, the Earth's atmosphere would be expected to have approximately 10^4 times as much Ar than is in fact present (Swindle and Kring, 2001), which might imply that comets contributed but a small fraction of the Earth's ocean water. There are, however, two reasons why this argument must be treated with caution. The first is the model-dependent result that the heavy bombardment is expected preferentially to remove gas-phase elements (e.g., the noble gases, N_2, and any other volatiles that are significantly partitioned into the Earth's atmosphere) due to substantial atmospheric erosion, whereas little removal of condensed-phase volatiles (such as H_2O in the oceans) is expected (Chyba, 1990). So preferential removal of Ar, other noble gases, and N is just what is to be expected. Second, a search for Ar in three comets using the Far Ultraviolet Spectroscopic Explorer satellite failed to detect Ar, placing an upper limit on Ar/O abundance at least an order of magnitude below solar abundance (Weaver et al., 2002). Evidently comets are, in fact, depleted in Ar with respect to solar abundance; determining how great the depletion of Ar and other noble gases in comets truly is will obviously elucidate the constraints on the possible contribution of comets to the Earth's oceans.

6.2 The Time Window for the Origin of Life[1]

To assess the importance of comets for the origin of life on the Earth, we must have some sense of the window in time in which that origin occurred. For example, comet impacts on the Earth today are rare, and it is likely that this has been the case at least since the heavy bombardment, evidence for which is preserved in the lunar cratering record, ended around 3.8 Gyr ago. Therefore the role of comets would seem very different if the origin of life

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[1] Much of Sect. 6.2 is based on Chyba and Hand (2005).

occurred 3.0 Gyr ago rather than 4.0 Gyr ago. What is the evidence for the timing of the origin of life?

6.2.1 Frustration of the Origin of Life

The origin of life on the Earth presumably occurred after the solidification of the Earth's magma ocean about 10^8 years after terrestrial accretion (Solomatov, 2000). Subsequent to that time, impacts of objects large enough to have vaporized the Earth's oceans may have frustrated the origins of life until approximately 3.8–3.9 Gya (Sagan, 1974; Maher and Stevenson, 1988). Trying to specify the precise cutoff date is hampered by the necessity to extrapolate from small numbers, so that there are large statistical uncertainties (Sleep et al., 1989; Chyba et al., 1994; Zahnle and Sleep, this volume).

The other side of the time window for life's origin is given by signatures of ancient life in the Earth's geological record. Evidence based on microfossils and stromatolites,[2] or carbon isotopic fractionation, has led to arguments that life on the Earth might have been well established 3.5 Gyr ago (Schopf, 1993) or 3.8–3.9 Gyr ago (Mojzsis et al., 1996; Rosing, 1999), respectively. However, these lines of evidence have become increasingly controversial (Brasier et al., 2002; van Zuilen et al., 2002; see also Westall, 2005), and we review those controversies here.

6.2.2 Microfossils and Stromatolites

Strong fossil evidence for ancient microscopic life is present in ∼3-Gyr-old rocks, less-certain fossil evidence exists in 3.5-Gyr-old rocks, and substantially more controversial isotopic evidence exists in 3.8-Gyr-old rocks. Carbonate deposits in ∼3-Gyr-old South African sedimentary rocks show well-preserved stromatolites that match well with similar, known biogenic structures seen in much younger rocks and even in modern aqueous sedimentary environments (Beukes and Lowe, 1989). Similar structures are also seen in the ∼3.0-Gyr-old rocks of Steep Rock, Ontario (Wilks and Nisbet, 1985). Stromatolites have been found in 3.5-Gyr-old rocks, but modeling work has shown that such sedimentary structures might also be produced without biology (Grotzinger and Rothman, 1996), and it is difficult to be certain that these stromatolites are of biological origin (Knoll, 2003).

The evidence becomes more difficult to assess the further back in time one goes. There are ∼3.5-Gyr-old filamentous structures in both the Apex cherts (granular, sedimentary silica (SiO_2)) of the Warrawoona Group of Western Australia (Schopf, 1993; Schopf and Packer, 1987); and the Onverwacht Group, Barberton Mountain Land, South Africa (Walsh and Lowe, 1985).

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[2] Stromatolites are microbial mat communities consisting of phototactic or photosynthetic bacteria, other microorganisms, and sediments, often domical in shape and with a laminar structure.

These represent the most ancient credible morphological microfossils, although the question of their biogenicity remains to be entirely resolved. In particular, the Apex microfossils are the focus of some controversy (Brasier et al., 2002). Originally it was claimed that the proposed microfossils represented ancient cyanobacteria within a sedimentary, stromatolitic environment, but it now appears that the Apex chert may be hydrothermal in origin, opening the possibility that the structures might also be explained by physical processes resulting in chains of crystal formation. Schopf and Packer (1987) and Schopf (1993) argue for a biological origin with photomicrographs of apparently discrete, cellular structures aligned in chains of curving filaments. Brasier et al. (2002) reinterpret the microscopic structures as the result of amorphous graphite mixing with metal-rich hydrothermal vein cherts and volcanic glass, and cite examples of branched filamentous structures in rebuttal to the morphological claim that these derive from ancient bacteria. They find δ^{13}C values[3] of –30‰ to –26‰, consistent with biogenic fractionation of the carbon, but argue that such fractionation could also occur when volcanic CO_2 interacts with high temperature (250–350°C) hydrothermal fluids. In reply, Schopf et al. (2002) utilize Laser–Raman imagery of the filaments to argue that they are indeed carbonaceous structures.

Recent work demonstrating the nonbiological synthesis of complex filamentous silica–carbonate structures blurs the line segregating biogenic morphologies from nonbiologically produced structures (Garcia-Ruiz et al., 2003). But one line of evidence that could prove compelling is that of the discrete cellular compartmentalization of the mineralized carbon. Many of the abiogenic structures of Garcia-Ruiz et al. (2003) are continuous, spiraling filaments that give only the appearance of being lines of discrete cells.

6.2.3 Molecular Biomarkers

Biomarker molecules such as terpanoids, hopanes, and steranes,[4] derived from cellular and membrane lipids, can provide strong evidence for the past presence of life in ancient sediments. This approach has been used to argue for the advent of cyanobacteria, and therefore oxgenic photosynthesis, by 2.5 Gyr ago, and for the emergence of eukaryotes at 2.7 Gyr ago (Brocks et al., 1999; Summons et al., 1999). However, such tests are increasingly difficult to perform on increasingly ancient rocks. In particular, the 3.5-Gyr-old Warrawoona rocks

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[3] Carbon-13 isotope geochemistry is based on the difference of ^{13}C isotopes in the sample relative to the ^{13}C in a standard from the Cretaceous known as the Peedee Belemnite ($^{13}C_{PDB}$). Certain differences are indicative of biological isotope fractionation. For example, photosynthesis creates a δ^{13}C fractionation of about -25‰, because it kinetically favors the ^{12}C atom. The formal definition of δ^{13}C is $\delta^{13}C \equiv 1000[(^{13}C/^{12}C)_{\mathrm{sample}}/(^{13}C/^{12}C)_{\mathrm{PDB}} - 1]$.

[4] These molecules, stable over geologic timescales, consist of linked carbon ring structures. Terpanes are characteristic of cell membranes present in the archea, hopanes in bacteria, and steranes in eukaryotes.

have been too metamorphosed to permit such biomarkers to have survived (Knoll, 2003).

6.2.4 Carbon Isotope Fractionation

Carbon isotope fractionation is the only technique that provides evidence for life in 3.8–3.9-Gyr-old rocks (Mojzsis et al., 1996; Rosing, 1999; Schidlowski, 1988), because these ancient rocks have been so heavily metamorphosed that fossil evidence could not have survived to the present day. Graphite in the 3.8-Gyr-old highly metamorphosed sedimentary rocks (metasediments) of Western Greenland was found to have an isotopic signature of $\delta^{13}\mathrm{C} \approx -28‰$, seemingly indicative of biology early in the Earth's history (Schidlowski, 1988). Mojzsis et al. (1996) claimed that graphite particles were found within a banded iron formation and in apatite grains in the oldest, Akilia, metasediments, providing a reasonable geological context for the proposed biosignature.[5] In this picture, the graphite would have formed from carbonaceous material originally derived from microbial life.

However, some have since argued against the biogenic nature of the graphite (Fedo and Whitehouse, 2002; van Zuilen et al., 2002). A $\delta^{13}\mathrm{C}$ value of $-10‰$ to $-12‰$ in graphite can be obtained when the mineral siderite ($\mathrm{FeCO_3}$) is thermally decomposed at temperatures above 450°C (van Zuilen et al., 2002) according to $6\mathrm{FeCO_3} \rightarrow 2\mathrm{Fe_3O_4} + 5\mathrm{CO_2} + \mathrm{C}$. The resulting magnetite ($\mathrm{Fe_3O_4}$) and istopically light graphite (C) remain in the rock while the $\mathrm{CO_2}$ escapes. Van Zuilen et al. (2002) also suggest that recent organic material possibly emplaced by percolating ground water may also play a role in the especially light graphite values. The original claims for life reported $\delta^{13}\mathrm{C} \approx -28‰$ (Mojzsis et al., 1996; Schidlowski, 1988), but more recent analysis of the graphite particles with a larger number of samples has found the signature to be more varied, ranging from $\delta^{13}\mathrm{C}$ of $-18‰$ to $+2‰$ (Ueno et al., 2002). This could be in agreement with the abiogenic fractionation process just described. The observed carbonates would then not be sedimentary, but rather metasomatic in origin (van Zuilen et al., 2002). That is, they would result from high-temperature fluids interacting with iron-rich material, rather than from iron precipitation and sedimentation, as is often associated with microbial communities. Worse is the claim that the apatite crystals do not, in fact, contain graphite inclusions (Lepland et al., 2005). Moorbath (2005) concludes a brief review by saying that there is only one site left in the Isua region where an argument for an isotopic biosignature older than 3.7 Gyr remains possible (Rosing and Frei, 2004).

It is therefore at least possible that the short-time windows ($\leq 10^8$ years) for the origin of life once posited to be bounded by the last ocean-vaporizing

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[5] Banded iron formations are sedimentary rocks rich in oxidized iron that may therefore be indicative of the onset of oxygenic photosynthesis. Apatite, a form of calcium phosphate, is a mineral often found in association with microbial activity.

impact and the earliest (~3.8–3.9 Gyr ago) evidence for life on the Earth will need to be relaxed by hundreds of millions of years. If the origin of life occurred closer to 3.5 Gyr ago than to 3.9 Gyr ago, exogenous input of organics from comets would be substantially less at the time of life's origin. Here we continue to use 4.0 Gyr ago as our time of comparison; moving this date to 3.5 Gyr ago would reduce our estimates of exogenous input by about an order of magnitude.

6.3 Endogenous Production of Prebiotic Organic Molecules

Before proceeding to a discussion of exogenous sources of prebiotic organic molecules on early Earth, we first examine organic production *in situ*. Only those exogenous sources that deliver organics in quantities comparable to or greater than endogenous production, or that deliver types or mixtures (e.g., amino acids with a preference for a particular "handedness" or chirality) of molecules not readily made *in situ*, need be considered as potentially important contributors to the origin of life on the Earth.

6.3.1 Nature of the Early Atmosphere[6]

Chyba and Sagan (1992, 1997) summarize a number of endogenous sources of organics on early Earth. Critical to these estimates is the nature of the early atmosphere (Chyba, 2005).

In 1952, graduate student Stanley Miller, working with his thesis advisor Harold Urey, simulated the putative atmosphere of early Earth (e.g., Urey, 1952a,b) with a mixture of methane (CH_4), ammonia (NH_3), molecular hydrogen (H_2), and water (Miller, 1953, 1974). When he introduced an electrical spark to represent lightning (we now know that electrical sparks are intermediate in character between lightning (which generate hot plasmas) and coronal discharges (which generate cold plasmas); see Chyba and Sagan (1991)), Miller observed the formation of amino acids, the building blocks of proteins. Subsequent work showed that the amino acids were the result of reactions in liquid water (representing the Earth's ocean) of simple organic molecules such as hydrogen cyanide (HCN) and aldehydes (RHCO, where R stands for some chemical group) formed in the gas mixture (Miller, 1957). For example, when R = H, the aldehyde in question is formaldehyde (H_2CO) and the amino acid glycine results.

But by the 1960s the validity of hydrogen-rich (and hence reducing) model atmospheres for early Earth, such as the CH_4–NH_3 Miller–Urey atmosphere, began to be questioned (Abelson, 1966). Carbon dioxide- (CO_2)- rich atmospheres have been favored since the 1970s (e.g., Walker, 1977). Schlesinger

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[6] Much of Sect. 6.3.1 is based on Chyba (2005).

and Miller (1983a, b) and Stribling and Miller (1987) have shown that the production of amino acids and other organic molecules is orders of magnitude less efficient in such atmospheres, depending on the ratio $[H_2]/[CO_2]$ (see Fig. 6.2).

Early models of the Earth's evolution held the planet's iron-rich core to have formed slowly over hundreds of millions of years. Prior to core formation, metallic iron would have been abundant in the Earth's mantle, in effect providing a huge oxygen sink. (More carefully, pressure, temperature, and the oxygen fugacity of the mantle all play a role; for a review of these factors, see, e.g., Kasting, 2000.) Consequently, carbon and nitrogen compounds that outgassed into the atmosphere would have been saturated with hydrogen (CH_4 and NH_3). Early life would have been heterotrophic, making use of the abundant organic molecules produced by Miller–Urey synthesis in a reducing atmosphere. Subsequently, core formation would have greatly increased the mantle's oxygen fugacity, leading to carbon outgassing as CO_2 rather than as CH_4. (The classic statement of this scenario for early Earth is that of Holland, 1962.) Abiotic organic production would then have plummeted, forcing life to evolve to cope with this change, perhaps driving the evolution of autotrophy whereby life would develop the ability to fix carbon from CO_2, since nonbiological organic carbon would now be rare.

This is an appealing picture, elegantly tying major events in the evolution of life to planetary evolution – but it is probably largely incorrect. It is now thought that the Earth must have been hot at the time of its formation, because it accreted from fast-colliding planetesimals. It seems likely that the core therefore formed virtually simultaneously with the Earth itself (Stevenson, 1983; see also Rushmer et al., 2000). But with the iron largely sequestered in the core from the start, there never would have been a Miller–Urey atmosphere. Most current models for the early Earth atmosphere predict an atmosphere rich in CO_2 (like those of Mars and Venus today), with H_2 mixing ratios as low as approximately 10^{-3} (Kasting, 1990; see also Kasting and Catling, 2003), implying low $[H_2]/[CO_2]$ ratios.

Even if there ever had been a Miller–Urey atmosphere, modeling in the late 1970s suggested that it would be destroyed by solar ultraviolet (UV) light too quickly (over geologically very short timescales) for plausible outgassing rates to maintain the putative NH_3- and CH_4-rich atmosphere (Yung and Pinto, 1978; Kuhn and Atreya, 1979; Owen et al., 1979; Kasting, 1982; Levine and Augustsson 1985). It was subsequently suggested that for a prebiotic Miller–Urey atmosphere, this problem might be circumvented by the photolysis-driven formation of a high-altitude organic haze, similar to that in the atmosphere of Saturn's moon Titan (Sagan and Chyba, 1997; Miller et al., 1998). Pavlov et al. (2001) found that a negative feedback linking visible optical depth to *biogenic* methane production limited possible UV shielding via this mechanism to a factor of 2–3.

Tian et al. (2005) have proposed an alternate model for the early Earth atmosphere that may permit $[H_2]/[CO_2]\approx 1$. In their model, the atmosphere is CO_2-rich, not CH_4-rich, but it contains as much as 30% H_2, an abundance orders of magnitude higher than those in previous models. Tian et al. use the current hydrogen outgassing rate, increased by at most a small factor (between 1 and 5) to account for the geologically more active early Earth. In a previous picture, hydrogen loss by Jeans escape was very rapid so that hydrogen loss was diffusion-limited; i.e., it depended on the flux of hydrogen diffusing up to the atmosphere's exobase, above which it is then lost from the atmosphere. In the Tian et al. model, Jeans escape is much slower on early Earth than is the case today due to a much lower exobase temperature on an early Earth that lacked the UV-absorbing (so exobase-heating) ozone that is present today due to O_2 in the Earth's atmophere. In their model, hydrogen loss is limited by the availability of extreme ultraviolet light from the Sun. They find an H_2 escape rate two orders of magnitude lower than that previously found. Because the H_2 escapes much more slowly, if the Earth ever had an H_2-rich atmosphere, it could be sustained.

Tian et al.'s (2005) arguments for a low exobase temperature on early Earth, as well as their argument for the unimportance of nonthermal escape mechanisms for H_2, have been attacked by Catling (2006). Tian et al. have responded (Tian et al., 2006).

Figure 6.2 shows the potential impact of this hydrogen-rich Tian et al. atmosphere for the origin of life. HCN and H_2CO are produced at much lower yields in CO_2-rich atmospheres than in CH_4-rich ones, but production is particularly low in CO_2-rich atmospheres when H_2/C ratios fall below 1. Production also falls when $[H_2]/[CO_2]$ rises above 5 or so; in this case there is so much hydrogen that C—H bonds re-form too rapidly for further chemistry (e.g., the production of C—C bonds) to take place. Tian et al. (2005) suggest that they can keep $H_2/C > 1$ in their model (and, presumably, below $\sim$5), although this also obviously depends on the poorly known CO_2 abundance.

6.3.2 Energy Sources and Atmospheric Organic Production

Chyba and Sagan (1992, 1997) have summarized a number of endogenous sources of organics on early Earth, in effect updating the decades-earlier compilation of Miller and Urey (1959). The approach of these estimates is to multiply an experimentally derived efficiency for organic molecule production (e.g., in moles or kg organic production per joule of a particular energy source inputted into the candidate atmosphere) by an estimate of the globally averaged amount of that type of energy available on early Earth. Obviously critical to these estimates is the nature of the early atmosphere. As long as the exact nature of the early atmosphere is unknown, comparisons are best made for a variety of atmospheric models (Chyba and Sagan, 1992).

Chyba and Sagan (1991) updated the Miller and Urey (1959) estimates for global and electrical discharge on early Earth. Miller and Urey (1959) had used the best estimates then available for global coronal and lightning discharges – estimates that derived from Schonland (1953) from his pioneering

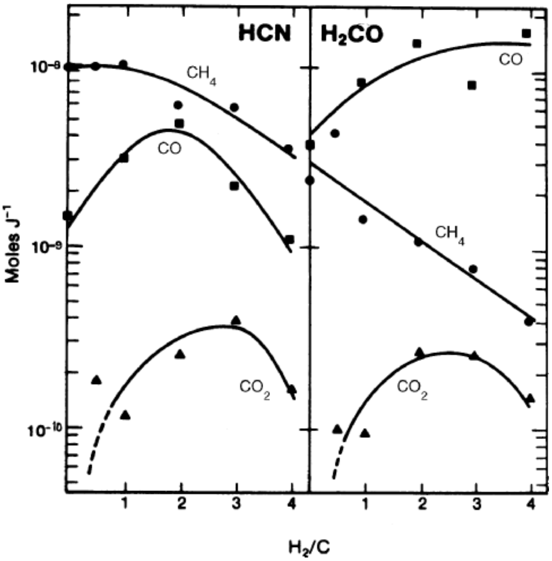

Fig. 6.2. Yields (mol J^{-1}) of organic molecules produced by input spark discharge energy, as a function of atmospheric composition and H_2 abundance. From Stribling and Miller (1987).

experimental work in 1928 (Schonland, 1928). Of course, such estimates could be made more reliably by 1991, subsequent to the advent of global monitoring – yet, remarkably, up until that date the field of the origin of life continued to base estimates of organic production on early Earth by coronal discharge on experiments dating to 1928. Chyba and Sagan (1991), in their review of contemporary data for lightning and coronal energy dissipation, found values about 20 and 120 times smaller, respectively, than those suggested by Miller and Urey (1959). However, the greatest uncertainty in these estimates remains the extrapolation from contemporary rates of electrical energy discharge back to the primitive Earth – an "extrapolation" that amounts to the assumption that the rates 4 Gyr ago were simply the same as those today (Miller and Urey, 1959; Chyba and Sagan, 1991).

Apart from electrical energy sources, a principal source of energy for organic production in the early Earth atmosphere would have been ultraviolet light from the Sun. Chyba and Sagan (1992) used earlier work by Zahnle and Walker (1982) on young solar analogue stars to estimate the evolution of solar ultraviolet energy at the Earth as a function of wavelength interval and time. These results are shown in Fig. 6.3. Production of organics from UV energy can then be estimated. These results assume that there is no significant UV shielding in the atmosphere; a UV shield would act to reduce organic production.

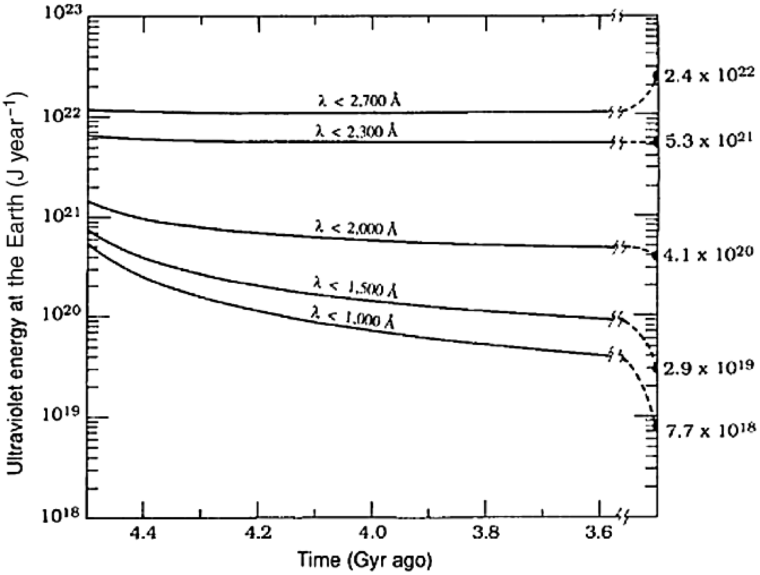

Fig. 6.3. Evolution of the Sun's ultraviolet luminosity through time, beginning with a $\sim 10^8$-yr-old Sun at 4.5 Gyr ago, and extending to today. Dashed lines beyond 3.6 Gyr ago indicate qualitative evolution to current values. From Chyba and Sagan (1992).

Results for organic production in reducing (Miller–Urey) and neutral ($[H_2]/[CO_2] = 0.1$) atmospheres are given in Table 6.1. The case $[H_2]/[CO_2] = 0.1$ may overestimate the H_2 abundance implied by most early Earth models, but the available data (see, e.g., Fig. 6.2) do not extend to much lower values so we choose this level, even at the risk of exaggerating endogenous production for this "end-member" atmosphere. Except where indicated, these data are taken from the compilation in Chyba and Sagan (1997), which updates Chyba and Sagan (1992). (Chyba and Sagan (1992) do, however, consider a number of production mechanisms not included here.)

For comparison, we also include a Tian et al. (2005) atmosphere for which we set $[H_2]/[CO_2] = 3$, the optimum case for organic production (see Fig. 6.2) in a CO_2-rich atmosphere. Results for electrical discharge synthesis in this atmosphere are scaled from that for the Miller–Urey atmosphere according to Fig. 6.2; on the basis of these data, we estimate organic synthesis by electrical discharge to be a factor of 10 lower for the Tian et al. atmosphere than for the Miller–Urey atmosphere. Tian et al. (2005) present results for UV-driven synthesis in their model atmosphere as a function of changing $[H_2]/[CO_2]$ ratio; we cite their value (about 1×10^{10} kg year^{-1}) here.

6.3.3 Organic Production at Hydrothermal Vents

Production of organic molecules may occur at hydrothermal vent sites (e.g., Shock and Schulte, 1998). In Table 6.1, we include an estimate for this production following Ehrenfreund et al. (2002), from Elderfield and Schultz (1996). These authors give a global flux of CH_4 in hydrothermal fluids into the oceans of $1–4 \times 10^8$ kg year^{-1}. This production would depend on the oxidation state of carbon outgassed from the mantle, and thus is not unrelated to atmospheric composition, but it is hard to know how to extrapolate it to early Earth. As with the other endogenous sources considered here, future research should allow better estimates of organic production at hydrothermal vents on early Earth to be made; here we take early Earth production to be identical to today.

6.4 The Lunar Cratering Record

Because of the near absence of a terrestrial geological record of the period prior to 3.5 Gyr ago, we look to other worlds in the Solar System for insights. The Moon is by far the most useful for this purpose, for it alone has been sufficiently sampled to allow a tentative – though still controversial – history of its cratering record to be developed, based on radiometric dating of returned lunar samples.

Our goal is to make use of the observed lunar cratering record to estimate the mass incident upon the Moon as a function of time prior to around 3.5 Gyr ago. This mass flux may then be extrapolated to the Earth, using the ratio of the two worlds' gravitational cross sections to determine how much larger the impactor flux was on Earth compared with that of the Moon. At the high-mass end of this extrapolation (Chyba et al., 1994), this calculation must be modified to take into account the fact that nearly all of the largest objects impacting the Earth–Moon system should have impacted Earth (Zahnle and Sleep, this volume). This need not concern us here since, as described below, organic survivability in impacts is dominated by comets approximately 1 km in size, rather than by the largest, basin-forming impactors. Ultimately we will be interested in the fraction of mass accreted by Earth that consisted of intact organic molecules. These would have represented an exogenous contribution to the terrestrial prebiotic organic inventory.

Melosh (1989) comprehensively reviews the physics of impact cratering. Chyba and Sagan (1992, 1997) review the application of cratering physics to the lunar impact record, shown in Fig. 6.4, to derive estimates of mass flux accreted by the Earth through time. For their smooth monotonic "procrustean fit" to the lunar impact record (Fig. 6.4), they derive an expression for the mass flux on the Earth at time t, $\dot{m}(t)$, in terms of the contemporary mass flux, $\dot{m}(0)$:

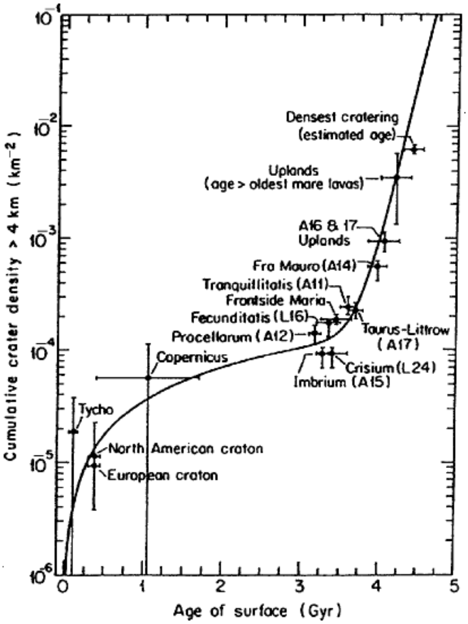

Fig. 6.4. Analytical monotonic fit to cumulative lunar crater density as a function of surface age, with a decay time constant τ=144 Myr (100 Myr half-life). From Chyba (1991). No attempt is made in this figure to model a possible terminal lunar cataclysm, but see the discussion in Sect. 6.4 of the text.

$$\dot{m}(t) = \dot{m}(0) f(t) \tag{6.1}$$

where

$$f(t) = (1 + 1.6 \times 10^{-10} e^{t/\tau}) \tag{6.2}$$

In this model, the decay constant τ is 144 Myr. The relevant value for $\dot{m}(0)$ may be chosen to be the mass flux appropriate for any particular impact population, be they interplanetary dust particles (IDPs), km-diameter comets, or asteroids. This assumes that the time variation of each subpopulation varies as this model for the overall impactor flux. Of course, this may not have been the case. Chyba and Sagan (1992) discussed this concern for IDPs in particular. At various points in the discussion below, we examine this assumption for particular potential impactor populations.

6.4.1 A Terminal Lunar Cataclysm?

The model presented in (6.1) and (6.2) assumes a monotonically falling lunar cratering curve–viz., that of Fig. 6.4. But this model for the lunar cratering history is under considerable debate. Recent evidence, in the form of accurate dating for impact melts within the breccia of lunar meteorites, is consistent with the hypothesis that a brief, intense period of bombardment occurred approximately 3.9 Gyr ago, prior to which the Earth–Moon system was in a relatively "quiet" impact period (Cohen et al., 2000). This hypothesis, first suggested in the early 1970s after analysis of returned Apollo and Luna samples (Tera et al., 1974; Turner et al., 1973; see Hartmann et al. (2000) and Ryder (2002) for reviews), is commonly referred to as the "lunar cataclysm" hypothesis. Though difficult to explain dynamically (but see Gomes et al., 2005), several lines of evidence now appear to support it (Kring and Cohen, 2002). Here we summarize the recent debate, and then turn to its implications for exogenous delivery and the origin of life on the Earth.

Results of ^{40}Ar-^{39}Ar and U-Pb analysis of Apollo and Luna samples suggested that three, and perhaps as many as six, of the impact basins on the nearside of the Moon were produced in the relatively short interval between 3.88 and 4.05 Gyr ago (Tera et al., 1974; Turner et al., 1973). This led to the "lunar cataclysm hypothesis"; i.e., that at $\sim$3.9 Ga a brief (perhaps $<$0.2 Gyr), intense period of bombardment occurred in the Earth–Moon system. Given the nearside selection bias, however (since all returned lunar samples had originated on the lunar nearside), it was argued that the cataclysm hypothesis was premature, and that perhaps the observed age distribution was indicative of just a few large-scale events on the nearside of the Moon and, in particular, the Imbrium event (Hartmann, 1975). Simple models (Grinspoon, 1989; Hartmann et al., 2000) showed how a misleading appearance of a cataclysm could be naturally generated, in principle, by the resetting of radioactive clocks in the course of an exponentially decaying bombardment.

Hoping to overcome the geographic limitations of the Apollo and Luna samples, Cohen et al., (2000) analyzed lunar meteorites, presumed to represent a geographically random sample. Forty-three samples were extracted from the lunar highlands regolith breccias contained within four lunar meteorites. Of these samples, 31 yielded useful ^{40}Ar-^{39}Ar spectra, all of which indicated ages between 2.76 and 3.92 Ga. A 4.45-Gyr-old clast from the H-chondrite Ourique was analyzed simultaneously to eliminate any systematic errors. On the basis of clustering of the measured ages, Cohen et al. (2000) argue that at least seven and perhaps as many as nine impacts are represented, two of which fall in the range 3.8–4.0 Ga. The authors claim that the fact that no melts older than 3.92 Gyr old were found supports the hypothesis that a short, intense period of bombardment occurred around $\sim$3.9 Ga. In short, why are there no impact melts prior to $\sim$4 Gyr ago?

Consistent with this are impact-induced shock-degassing ages (^{40}Ar/^{39}Ar) of some meteorites believed to be representative of the early asteroid belt. Kring and Cohen (2002), following Hartmann (1987), argue that the proposed lunar cataclysm was just a subset of an impact period that took place throughout the inner Solar System and was seeded by material from the asteroid belt. If this were true, then meteorites from the asteroid belt should also contain a record of increased impact activity. In their analysis of compiled datasets for meteorite impact-degassing ages, Kring and Cohen (2002) see a sharp peak at

3.9 Gyr ago for mesosiderites (stony-iron composition resulting from incomplete differentiation in a planetesimal), a broad peak centered around ~3.9 Gyr ago for HED achondrites (howardites, eucrites, and diogenites, silicate-rich crustal rock from differentiated planetesimals), and a secondary peak in ordinary chondrite degassing ages centered around ~3.9 Ga (the primary peak in this spectrum is at ~500 Ma, perhaps corresponding to the disruption of a planetesimal). Finally, they note that the martian meteorite ALH84001, known to have crystallized 4.5±0.13 Ga, contains carbonates formed during a subsequent event that have Rb–Sr ages of 3.90±0.04 Gyr ago and Pb–Pb ages of 4.04±0.10 Ga. Taken all together, Kring and Cohen interpret this as the signature of a cataclysmic event that spanned the inner solar system approximately 3.9 Gyr ago.

Chyba (1987) summarized earlier work that used siderophile element signatures claimed to be identifiable with different projectiles responsible for lunar basin-forming events to argue that most of the sampled basin-forming projectiles did not have what is anticipated to be cometary composition. Kring and Cohen (2002) extend these arguments, and conclude that at least three of the projectiles thought to have been sampled could not have been comets. Of course, asteroids alone could have delivered a substantial volatile inventory to early Earth (Chyba, 1991; Chyba et al., 2000; Kring and Cohen, 2002).

6.4.2 Implications for the Mass Flux on Early Earth

The uncertainties in the time evolution of the lunar cratering flux, and hence the impactor flux incident on early Earth, emphasize that it is wise in assessments of the role of exogenous sources in the origins of life on the Earth to focus on mass flux at a particular time in Earth history (Chyba and Sagan, 1992; Chyba and Sagan, 1997). This flux need not carry with it the requirement that the full-time evolution of any given model be accepted, and allows a straightforward (multiplicative) scaling to the value appropriate for that particular time under other assumptions.

We wish to update the Miller–Urey (1959) table to include the mass of organics per year that were provided to the Earth by exogenous sources. Our previous work chose 4 Gyr ago as the point in time to make these comparisons, based on estimates of the timing of the origin of life on the Earth. Obviously, current uncertainties permit the choice of some other date. There are many other uncertainties in these type of calculations – both for estimating endogenous inputs and exogenous inputs – and we have considered these systematically elsewhere (Chyba, 1993b), a discussion we have updated here.

The mass flux given by a model for a continuously decaying flux (as in (6.2)) might be very different from that predicted by a model that includes a terminal lunar cataclysm.[7] Chyba and Sagan (1997) found the total mass flux at a time t (in Gyr ago) to be given by

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[7] Armstrong et al. (2002) have provided two models for the lunar impacting flux, using the data shown in Fig. (6.4) – one a simple exponential decay, like that

$$\dot{m}(t) = 9.4(1 + 1.6 \times 10^{-10} e^{t/\tau})(m_{\max}^{(1-b)} - m_{\min}^{(1-b)})\mathrm{kg}^{b}\,\mathrm{year}^{-1} \qquad (6.3)$$

Here τ=144 Myr is the decay constant of heavy bombardment. Choosing $m_{\max}$ (in kg) to correspond to the largest known lunar impactor, that which formed the South Pole-Aitken basin, gives $\dot{m}(t = 4.0) = 1\times10^{12}$ kg year^{-1} (180 times today's average flux) and $\dot{m}(t = 3.9) = 5\times10^{11}$ kg year^{-1} (94 times today's average flux).

How do these numbers compare with predictions of terminal cataclysm models? Ryder (2002) presents a variety of models; his preferred model (his Fig. 4d) gives a mass flux of 7×10^{10} kg year^{-1} at his proposed 3.9 Gyr peak for the putative lunar cataclysm. In Ryder's model, this flux is much higher than the adjacent off-peak mass fluxes. However, it is below the flux at 3.9 Gyr ago found in our noncataclysm model–a counterintuitive result. Ryder argues for low fluxes subsequent to crustal solidification 4.4 Gyr ago, lest geochemical inconsistencies manifest themselves. However, our model provides only approximately 1×10^{20} kg of extralunar material incident on the Moon subsequent to 4.4 Gyr ago – only about half of which is actually retained by the Moon (Chyba and Sagan, 1997). This is only approximately 0.1% of the total lunar mass of 7.35×10^{22} kg, violating no lunar geochemical constraint. In this chapter, we continue to use the model of Chyba and Sagan (1997), but the reader should bear in mind that under Ryder's terminal cataclysm model, exogenous mass fluxes suggested here (e.g., in Table 6.1) should be scaled down by about an order of magnitude.

6.5 Impact Delivery of Intact Exogenous Organics

Organic molecules are being delivered to the Earth today from a variety of exogenous sources. These include those interplanetary dust particles (IDPs) small enough to be decelerated slowly enough in the upper atmosphere for organic molecules to survive the resulting heating, and meteorites small enough to be substantially decelerated during their fall, but large enough to avoid complete ablation (Anders, 1989). Impactors in the 1–100-m range often catastrophically airburst in the atmosphere (Chyba, 1993a), as was the case with the Tunguska asteroid of 1908 (Chyba et al., 1993). More recently, a CI carbonaceous chondrite exploded with an energy of ~20 kilotons over Revelstoke, Canada, in 1965; photomicrographs of recovered millimeter-sized fragments reveal unheated interiors (Folinsbee et al., 1967), within which organics should have survived. Finally, the discovery of apparently extraterrestrial amino acids in Cretaceous/Tertiary (K/T) boundary sediments at Stevens Klint, Denmark (Zhao and Bada, 1989), suggests that large asteroid or comet

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of (6.2), the second a model that attempts to incorporate a terminal cataclysm. Both build on the modeling of Chyba et al. (1994). However, we have been unable to make use of their work, because they treated our cumulative cratering model, fit to the data of Fig. 6.4, as a differential flux model.

impacts with the Earth can result in the deposition of large quantities of organics. Each of these exogenous sources of organics would have been more abundant on early Earth than is the case today. Here we estimate their quantitative importance. The results may be compared with the estimates of endogenous production just cited; these comparisons are summarized in Table 6.1.

6.5.1 Interplanetary Dust Particles and Micrometeorites

Anders (1989) has estimated the flux of intact organic matter reaching the Earth's surface in the form of interplanetary dust particles (IDPs). Particles in the mass range 10^{-15}–10^{-9} kg (or about 0.6–60 μm in radius for a typical density of 1 g cm^{-3}) are sufficiently gently decelerated in the upper atmosphere to avoid being heated to temperatures where their organics are pyrolyzed. With a terrestrial mass flux of 3.2×10^6 kg yr^{-1} of IDPs in this size range, and an average IDP organic mass fraction of 10%, Anders found $\dot{m}(0) = 3 \times 10^5$ kg year^{-1} of organics from the contemporary IDP source. Long Duration Exposure Facility (LDEF) data subsequently showed the IDP mass flux to be approximately three times higher than the estimate used by Anders (Love and Brownlee, 1993), giving an improved estimate of the contemporary organic carbon flux from IDPs of $\dot{m}(0) = 1 \times 10^6$ kg year^{-1}. At 4 Gyr ago, the Earth would then have been accreting $\sim 2 \times 10^8$ kg year^{-1} of organics from IDPs, according to (6.1). This would be a flux some 5,000 times smaller than that due to photolysis in an early Miller–Urey atmosphere, but would be comparable to that produced by UV photolysis in a CO_2-rich atmosphere (see Table 6.1).

Whether today's IDP flux can reliably be scaled back according to (6.1) and (6.2), i.e., according to the lunar cratering record, is questionable. Chyba and Sagan (1992) discussed the issue at some length, with reference (their Table 1) to the available data that bore on this question. As they pointed out, if IDPs are the product of cometary sublimation or of asteroid–asteroid collisions, one might expect their production to scale linearly or as the square, respectively, of the number of such objects in the inner Solar System. How loss mechanisms scale must also be considered; for dust whose loss rate is collisionally dominated, terrestrial accretion will scale as the square root of the cometary flux (Whipple, 1976). But those IDPs with masses below $\sim 10^{-9}$ kg have lifetimes dominated by Poynting–Robertson drag, not by collisions (Grün et al., 1985). The comparative importance of these two mechanisms could have changed in an early Solar System in which the IDP flux was higher. Production of particles with masses below 10^{-9} kg would have increased as the square of the number of larger colliding particles. To our knowledge, a model that self-consistently takes into account the production and loss of IDPs in the early Solar System has not been attempted. We therefore note the importance of this issue, but simply scale the IDP flux back in time linearly with the lunar impact record until a better treatment is available.

Micrometeorites in the range of 50–500 μm provide a contemporary global flux of approximately 1.5×10^6 to 4×10^7 kg of extraterrestrial material per year (Maurette et al., 2000; see also Maurette, this volume). The low-end value was derived from collections at a South Pole water well (Taylor et al., 1997), while the upper bound is from an estimate based on LDEF cratering (Love and Brownlee, 1993). In a recent study of Antarctic micrometeorites (AMMs) collected from five different sampling points in the blue ice around the Yamato Mountains of East Antarctica, Yada et al. (2004) calculated that the global micrometeorite accretion rate 27–33 kyr before present was approximately 1.4×10^7 kg year^{-1}. This is consistent with five different estimates of terrestrial meteorite mass accretion for the present, the past few decades, the past $\sim 10^6$ year, 33–67 Myr ago, and the past $\sim$ 3.6 Gyr; see Table 1 of Chyba and Sagan (1992). Because these are direct empirical data that do not depend on crater scaling, plus the fact that that the Yada et al. (2004) results fall within the above range, we use this value for subsequent estimates. Based on the particles collected in Greenland and Antarctica, the bulk of the micrometeorite flux is found to be in the size range of 100–200 μm, with the peak occurring at approximately 200 μm (Engrand and Maurette, 1998).

The micrometeorites most closely match CM- and CR-type carbonaceous chondrites (Maurette, 1998). However, bulk C/O ratios for the micrometeorites (C/O = 0.62 for 100–400-μm particles) indicate values 2.5–3 times higher than Orgueil (C/O = 0.27) and Murchison (C/O = 0.20) (Maurette, 1998). Individual micrometeorites are not well differentiated and are depleted in chondrules. This, coupled with the carbon chemistry and mineralogy, has led some to suggest that at least the larger micrometeorites might be of cometary origin (Maurette, 1998). Measurement of the D/H ratios, however, makes this identification more ambiguous; antarctic micrometeorite D/H ratios agree well with Standard Mean Ocean Water (SMOW) values, leading to a hypothesized link between the formation of Earth's ocean and the micrometeorite flux (Maurette et al., 2000), whatever its origin.

Complex organics such as amino acids and PAHs are found in the micrometeorites. The most abundant amino acids found are α-aminoisobutyric acid (AIB) and alanine, respectively, with the AIB concentration being, on average, roughly an order of magnitude greater than that found in Murchison (Maurette, 1998). The average PAH content of micrometeorites is comparable to that of Murchison, but a greater diversity of PAHs was found in the micrometeorites, including some not previously found in meteorites (Maurette et al., 2000).

Maurette et al. (2000) measured an average carbon content of 2.5 wt% in the AMMs. Therefore, the contemporary carbon flux from this source is approximately 3.5×10^5 kg year^{-1}. If we assume that the micrometeorite flux scales back in time in the same way that we have scaled for IDPs, then at 4 Gyr ago, micrometeorites were delivering approximately 7×10^7 kg year^{-1} of carbon to the Earth's surface. This source of carbon is comparable to that of IDPs and therefore could have played a comparably significant role in the origins of life.

Extending the size range to even larger particles, Matrajt et al. (2004) have examined micrometeorites in the size range 25 μm to 2 mm that survived atmospheric entry and were collected in Antarctic ice. They determined that approximately 14% of those samples contained the extraterrestrial amino acid α-aminoisobutyric acid (AIB). AIB was used to minimize the chance that any amino acid found was due to terrestrial contamination. Evidently at least some objects in the IDP size range (and larger) deliver organic molecules of interest for the origin of life, despite heating during atmospheric entry – an important empirical confirmation of this organic delivery mechanism.

Anbar et al. (2001) examined ~3.9-Gyr-old rocks from Akilia in Greenland that they interpreted as metasediments, looking for iridium and platinum, which could provide signatures of the extraterrestrial mass flux on the Earth during the heavy bombardment. However, their observed concentrations of Ir and Pt were extremely low. Schoenberg et al. (2002) subsequently found tungsten isotope evidence in approximately 3.8-Gyr-old metasediments in Isua, Greenland, and northern Labrador, Canada, suggesting that these ancient sediments do, in fact, contain an extraterrestrial signature. It has now been argued that the Akilia "banded iron formation" (BIF) rocks used by Anbar et al. (2001) are not metasediments (as BIFs would be), but are in fact strongly metamorphosed, metasomatized, and deformed igneous rocks misidentified as sedimentary in origin (Fedo and Whitehouse, 2002; Moorbath, 2005). If this is correct, such rocks could not, therefore, carry a sedimentary record of extraterrestrial infall.

6.5.2 Interstellar Dust

The Earth accretes interstellar dust whenever the Solar System passes through interstellar clouds. Obviously this source of exogenous material is independent of models for the heavy bombardment. Greenberg (1981) estimates that during its first 700 Myr, the Earth would have passed through four or five such clouds, accreting 10^6–10^7 kg year^{-1} of organic molecules during each 6×10^5 year-long passage. Even during cloud passage, this source would have been quantitatively unimportant compared with the accretion of Solar System IDPs.

6.5.3 Meteorites

Anders (1989) estimates that contemporary Earth accretes organic material from meteorites at a rate of approximately 8 kg year^{-1}, quantitatively negligible compared with the accretion of organics from IDPs.

6.5.4 Catastrophic Airbursts

Chyba and Sagan (1992, 1997) reviewed organic delivery to the Earth due to explosions of comets and asteroids in the 1–100-m size range in the Earth's atmosphere. Earth currently experiences several Revelstoke-magnitude explosions per year, and a megaton-scale explosion every approximately 20 years. The mass influx from objects in this size range is approximately 10^7 kg year^{-1} (Chyba 1993a), comparable to the net annual mass influx from IDPs. Airbursts, however, likely deliver a much smaller fraction of their organics intact, because of heating caused by their high explosion energies, so this source is probably small compared with IDPs.

6.5.5 Big Impacts

Clark (1988) suggested the possibility of a rare, soft landing of a comet on the Earth, leading to a rich local mix of exogenous water and organics. However, comets and asteroids small enough to be significantly decelerated by the atmosphere are likely to airburst (Chyba, 1993b), whereas objects larger than several hundred meters in diameter typically pass through the atmosphere and impact the surface at hypervelocities.

Chyba et al. (1990) modelled such cometary impacts quite conservatively, using a two-dimensional smoothed particle hydrodynamics (SPH) simulation of shock heating during normal (vertical) impacts, and found that it was difficult for organic molecules to survive, though possible for ~100-m impactors in dense atmospheres. Their modeling was hampered by a lack of relevant kinetics data for high-temperature pyrolysis of organic molecules, an issue that they discussed at length. As with most subsequent work, Chyba et al. (1990) assumed that only 10% of the impactor flux on early Earth was cometary; results could be easily scaled to other assumptions.

Subsequent work for some time suggested that Chyba et al. (1990) had been overly conservative. Thomas and Brookshaw (1997) extended these numerical simulations to three dimensions, and found lower temperatures than in the two-dimensional models. Two-dimensional simulations may overestimate temperatures by a factor of 2 compared with three-dimensional simulations of comparable resolution (Pierazzo and Melosh, 2000). Impacts at decreasing angles (measured from the horizontal) are characterized by weaker shocks and therefore also increase the chances for organic survival. Pierazzo and Melosh (2000) found that peak shock temperatures in impacts decline like the 3/2 power of the sine of the impact angle.

Blank and Miller (1997) suggested that the high pressures experienced in impacts should offset the effects of shock temperatures and reduce the pyrolysis of organic material, an effect seemingly borne out in their experiments with velocities up to 1.9 km s^{-1}. While the best experimental impact work to date, their impact velocities remained low compared to typical short-period comet impact velocities on the Earth of 25 km s^{-1} (Chyba, 1991). Pierazzo and Chyba (1999, and Chap. 5, this volume) simulated amino acid survival in cometary impacts with a high-resolution two-dimensional hydrocode, making use of more recent kinetics data for amino acid decomposition – though still data that had been obtained at temperatures below 900 K (Rodante, 1992). They found substantial survival of certain amino acids, especially at low impact angles – but repeated earlier cautions (e.g., Chyba et al., 1990) about the inadequacy of the pyrolysis data available for the modeling. Pierazzo and Chyba also found that organic survivability fell rapidly for comets larger than ∼1 km in diameter; estimates of cometary organic mass influx therefore depend only on the flux of objects in this size range, not the flux of the giant basin-forming objects.

Ross (2006) has considered the kinetics of organic (butane) decomposition in much greater detail than was the case in the earlier studies, and employed a time-temperature profile from the two-dimensional comet impact simulations of Pierazzo and Chyba. He was able to show why survival was to be expected in the range of conditions used in the Blank and Miller (1997) simulations, but found that given the temperature–time history of the Pierazzo and Chyba (1999) simulation used, "survival is not possible" for organic molecules in the impact. In particular, the stabilizing effects of higher pressures persist for too short a period of time to enhance survival.

Becker et al. (1996) announced the discovery of extraterrestrial helium trapped in fullerenes at the Sudbury impact site, arguing that this requires those fullerenes to have experienced temperatures below 1,000°C throughout the impact. But since this is a kinetics issue, time and temperature play off against each other, and both must be specified.

Since a two-dimensional simulation of a vertical cometary impact at 20 km s^{-1} found regions of the impactor where temperature remained below 6,000 K, it seems possible that further work investigating three-dimensional impactors in off-vertical impacts might indeed reveal much lower temperature conditions to hold for a fraction of impacting material. Scaling from the effects found in previous work, we would expect a 30° impact in a three-dimensional simulation to reduce a peak shock temperature of just under 6,000 K in a vertical two-dimensional simulation down to a temperature of about 1,000 K. It will therefore be critical to repeat Ross' (2006) analysis with a range of temperature–time curves generated in these more realistic simulations, although he is skeptical of the prospects for amino acid survival even in this lower temperature case. (The presence of extraterrestrial amino acids at the Cretaceous/Tertiary boundary, discussed in Sect. 6.9, might suggest that some amino acids may, in fact survive such impacts, although this conclusion is also controversial.) In light of these uncertainties, we refrain from estimating exogenous input from large comet impacts in this chapter, and look forward to future work illuminating these issues further.

6.6 Atmospheric Shock Synthesis of Organic Molecules

The suggestion that atmospheric shock waves from meteoroids could have synthesized organics on early Earth was first made by Gilvarry and Hochstim (1963) and Hochstim (1963). The production of amino acids via shock chemistry was experimentally demonstrated by Bar-Nun, Bar-Nun, Bauer and Sagan (1970), and subsequently revised and elaborated (Bar-Nun and Shaviv, 1975; Barak and Bar-Nun, 1975). Atmospheric organic shock synthesis is proportional to the organic synthesis efficiency (here expressed in kg organic carbon produced per joule of shock energy applied). It is strongly dependent on atmospheric composition. As summarized by Chyba and Sagan (1992), we estimate the net efficiency for organic carbon production in reducing atmospheres to be $\eta \approx 1 \times 10^{-8}$ kg J^{-1}, and that for intermediate (CO_2-rich) oxidation state atmospheres to be much lower, $\eta \approx 3 \times 10^{-16}$ kg J^{-1}. To our knowledge, there are no experimental data available for $H_2/CO_2/N_2$ atmospheres, and we do not hazard an estimate for the case $[H_2]/[CO_2] \approx 3$. Therefore we are unable to assess shock production in a Tian et al. (2005) atmosphere. It would be especially valuable to have systematic results from shock-tube experiments spanning the range of $[H_2]/[CO_2]$ values from 0.001 to 10.

6.6.1 Shocks from Meteors

The small particle accretion rate of the Earth's current atmosphere is about 4×10^7 kg year^{-1} (Love and Brownlee, 1993). These objects deposit 100% of their kinetic energy into the atmosphere. Taking their initial velocity to be 17 km s^{-1} (Love and Brownlee, 1993), the annual deposition of energy by meteors to the atmosphere is then $\sim 6 \times 10^{15}$ J year^{-1}. Following Pollack et al. (1986) and McKay et al. (1988), taking the fraction of this kinetic energy converted into atmospheric shock heating to be approximately 30%, we have a total organic production in the atmosphere due to meteors of $\dot{m}(0) = \eta(2 \times 10^{15}\ \text{J year}^{-1})$. Assuming meteor flux to scale in time as the lunar cratering record (see the discussion in Sect. 6.5.1), a reducing atmosphere at time t would have experienced an organic production rate by this mechanism of $\dot{m}(t) = (2 \times 10^7\ \text{kg year}^{-1}) f(t)$. A CO_2-rich atmosphere would have experienced a negligible organic production nearly eight orders of magnitude smaller.

6.6.2 Shocks from Airburst

As discussed in Sect. 6.5.4, the mass influx from small asteroids and comets in the 1–100-m range is $\sim 10^7$ kg year^{-1}. For a median terrestrial impact velocity of 13 km s^{-1} for these objects (Chyba, 1993a), we have a net deposition of energy into the atmosphere of 8×10^{14} J year^{-1}, or nearly an order of magnitude below that for meteors. Whether this production rate may be extrapolated back in time according to (6.1) and (6.2) depends on the origin of the small asteroid population. Rabinowitz (1993) notes that the power-law dependence for this population is inconsistent with its evolution from the main-belt population. Perhaps these objects are remnants of short-period comets (Rabinowitz, 1993) or impact ejecta from the Moon. The latter at least would be expected to scale in time according to the lunar cratering record. On the other hand, if these objects are instead debris from recent collisions of larger asteroids with perihelia near Earth (Rabinowitz, 1993), they represent a transient event and the flux cannot be reliably scaled back in time.

6.6.3 Shocks from Giant Impact Plumes

Large impactors shock process the atmosphere primarily through the rapidly expanding postimpact vapor plumes that result from their impacts with the terrestrial surface. Shock processing by big impactors during atmospheric passage is comparatively negligible (Chyba and Sagan, 1992). Taking into account that plumes from the largest impacts rise far above the atmosphere, so that the shock processing yield per unit of impact energy decreases as the energy of impact increases (Kasting, 1990; Zahnle, 1990), one can attempt to calculate net organic production from impactors of sizes ranging all the way up to that of the South Pole-Aitken basin former; one finds $\dot{m}(t) \approx \eta(10^{16} \text{ J year}^{-1}) f(t)$ (Chyba and Sagan, 1992), or about a factor of 5 greater than that due to meteors.

Of course, the effects of the two sources over short timescales are very different; whereas shock processing of the atmosphere by meteors is constant but at a comparatively low level, shock processing by large impacts is dominated by the largest, most infrequent events. Large impacts would have produced large quantities of organics in very short pulses (see, e.g., Oberbeck and Aggarwal, 1992).

6.7 Postimpact Recombination

A number of authors have suggested that organics may have been synthesized on early Earth by recombination of reducing mixtures of gases resulting from the shock vaporization of asteroids or comets on impact (Oró, 1961; McKay et al., 1989; Mukhin et al., 1989; Oberbeck and Aggarwal 1992; Oberbeck et al., 1989; Chyba and Sagan, 1992). The outcome is complicated by possible entrainment of target material and background atmosphere into the vapor plume, effects that are difficult to model and have often not been taken into account. Kasting (1990) argues that organic carbon in the hot rock vapor resulting from a large impact would be almost entirely converted to carbon monoxide.

There are some relevant, though limited, experimental data. Barak and Bar-Nun (1975) have demonstrated the shock synthesis of amino acids even when the initial gas mixtures contain large quantities of water and air. Shock vaporization and organic recombination by laser pulse heating of terrestrial rocks and meteorite samples (Mukhin et al., 1989) yield a wide variety of carbon products of varying oxidation states. These experiments have been discussed critically by Chyba and Sagan (1992). The Mukhin et al. (1989) experiments suggest that some 4% of impactor carbon is incorporated into organics in the vapor plume formed subsequent to impact. If these experimental results may in fact be scaled up over the many orders of magnitude required to reach the energies of large impact events, (6.3) could simply be multiplied by 0.004 to obtain the organic flux on early Earth due to postimpact recombination, assuming 10% of the impactors to be carbon. The resulting numbers would be very large, but it seems unlikely that the proper scaling is simple, so we do not include this extrapolation in Table 6.1.

6.8 Amino Acids at the K/T Boundary

Zhao and Bada (1989) discovered nonbiological amino acids, racemic isovaline and AIB, immediately above and below the clay layer marking the Cretaceous-Tertiary (K/T) boundary. Oberbeck and Aggarwal (1992) suggest that these amino acids might represent material synthesized in the postimpact fireball. But in light of recent work simulating amino acid survival in large impacts (e.g., Pierazzo and Chyba (2002), see Sect. 6.5.5), it is not out of the question that these molecules are extraterrestrial organics that survived the impact of the K/T object. Chyba and Sagan (1997) discussed the possible use of these amino acid abundances as a kind of "ground truth" for extrapolating organic survival or shock-induced production from large impacts back to early Earth, suggesting $\dot{m}(t) = 1 \times 10^6 f(t)$ kg year^{-1}, or 2×10^8 kg year^{-1} 4 Gyr ago.

6.9 An Inventory of Organic Production on Early Earth

The results of the preceding sections are summarized in Table 6.1, which shows delivery or production of organic molecules on Earth 4 Gyr ago (in kg year^{-1}) from the quantitatively most important sources. Table 6.1 gives these results (where possible) for three candidate early atmospheres, a Miller–Urey reducing atmosphere, an "intermediate" oxidation state CO_2-rich atmosphere with $[H_2]/[CO_2]=0.1$, and a Tian et al. (2005) atmosphere, with $[H_2]/[CO_2]=3$, the optimum value for organic production in an H_2/CO_2 atmosphere (Fig. 6.2). Endogenous production drops precipitously as $[H_2]/[CO_2]$ falls below 1. The results in Table 6.1 assume that exogenous inputs scale as the heavy bombardment cratering flux shown in Fig. 6.3; see Sects. 6.4.2, 6.5.1, and 6.6.2 for cautions about this assumption.

The discussion of exogenous inputs so far has ignored the effects of atmospheric erosion. But only ~10% of asteroid, and ~50% of comet, collisions

Table 6.1. Major sources of prebiotic organics for three candidate early Earth atmospheres.

Source	Miller–Urey atmosphere (kg year^{-1})	H_2-rich CO_2 atmosphere (kg year^{-1})[a]	Intermediate oxidation-state atmosphere (kg year^{-1})[b]
UV Photolysis[c]	1×10^{12}	1×10^{10}	3×10^{8}
Electric discharge	3×10^{9}	3×10^{8}	3×10^{7}
Hydrothermal Vents[d]	2×10^{8}	2×10^{8}	2×10^{8}
IDPs	2×10^{8}	2×10^{8}	2×10^{8}
Micrometeorites	7×10^{7}	7×10^{7}	7×10^{7}
Comet impacts[e]	?	?	?
K/T extrapolation[f]	2×10^{8}	2×10^{8}	2×10^{8}
Shocks from impacts[g]	2×10^{10}	?	4×10^{2}
Shocks from meteors[g]	4×10^{9}	?	8×10^{1}
Totals	1×10^{12}	1×10^{10}	9×10^{8}

[a] $[H_2]/[CO_2]=3.0$.
[b] $[H_2]/[CO_2]=0.1$.
[c] These results assume that there is no substantial UV-absorbing haze in the atmosphere. See Sect. 6.3.2.
[d] After Ehrenfreund et al. (2002); see Sect. 6.3.3 for discussion.
[e] Organic survivability in large comet impacts remains highly uncertain; see Sect. 6.5.5 for discussion.
[f] Likely a lower limit since K/T event occurred in an oxygen-rich atmosphere; all candidate atmospheres in Table 6.1 are more favorable to organic synthesis.
[g] Data unavailable for organic shock synthesis in H_2/CO_2 atmospheres; value for $[H_2]/[CO_2]=0.1$ case estimated (Chyba and Sagan, 1993) from $CO_2/N_2/H_2O$ atmosphere experiments. Systematic experimental results for shock synthesis in a range of H_2/CO_2 atmospheres are badly needed.

with Earth occur at velocities high enough to cause erosion (Chyba, 1991), effects small compared with other uncertainties in the problem – even if comets were to make up the bulk of the heavy bombardment impactors.

Table 6.1 shows that net organic production and delivery on early Earth could have been about three orders of magnitude higher in the case of a reducing atmosphere than for an atmosphere of intermediate oxidation state, assuming no significant formation of a UV-shielding haze layer in the Miller–Urey atmosphere. For an early Miller–Urey atmosphere, exogenous sources would have been quantitatively swamped by UV photolysis. In the case of a CO_2-rich atmosphere 4 Gyr ago, however, exogenous sources from IDPs, micrometeorites, and comet impacts (based on the K/T extrapolation) would have been comparable to those produced by UV photolysis. How these results would scale backward in time depends on the role of the putative terminal cataclysm in impacting these results (see Sect. 6.4.2).

There would have been qualitative differences as well; for example, amino acid production in CO_2-rich atmospheres appears to be almost limited to glycine (Schlesinger and Miller, 1983a). On the other hand, IDPs are radiation-hardened from their stay in interplanetary space, and undergo some heating during atmospheric entry, both of which may decrease their complement of the more fragile organics (Chyba, 1990b).

6.10 Organic Sinks and Concentrations

A common way of assessing the importance of different endogenous sources of organics on early Earth is to calculate resulting concentrations of particular organics in the early ocean (e.g., Stribling and Miller, 1987). This is much more difficult to do in the case of exogenous sources, as the nature of organics in IDPs, or delivered or produced in impact events, remains poorly known. Calculation of concentrations requires knowledge of sink, as well as source, terms. It is difficult to assess sinks when one has little idea of which organics one has to consider. Thermal decomposition rates, for example, vary greatly among different types of simple, prebiotically relevant organics (Chyba et al., 1990).

For these reasons, Chyba and Sagan (1992) considered only the simplest sink model, that of the entire ocean cycling through hydrothermal vents on a timescale of $\sim 10^7$ years, as is the case for the contemporary ocean. If one assumes that all organics thereby are destroyed – a debatable assumption – one is freed from the necessity of knowing thermal decomposition rates for the different relevant molecules. However, some organics (such as some of those in IDPs) are likely to sink in the oceans and be buried in abyssal clays (e.g., Kyte and Wasson, 1986), while others will float on the ocean surface, forming a kind of primordial "oil slick" (Lasaga et al., 1971), and remaining protected against vent passage.

Nevertheless, if all the organic products in the reducing and intermediate oxidation state atmospheres considered above (Table 6.1) were fully soluble in an early ocean of contemporary mass (1.4×10^{21} kg), and had a mean lifetime of 10 Myr against destruction in mid-ocean vents or subducted plates, the steady-state organic abundance in the ocean 4 Gyr ago could have been as high as $\sim 10^{-2}$ g per g for a Miller–Urey atmosphere – an extraordinary concentration – and $\sim 10^{-5}$ g per g for an intermediate oxidation state atmosphere. Of course, many concentration mechanisms for organics in solution can be envisioned and undoubtedly existed, but more reducing atmospheres clearly seem more favorable for the origin of life by this reckoning.

To evaluate organic concentrations in more detail for particular species, a more careful treatment is needed (Pierazzo and Chyba, 1999). Concentrations in the ocean are given by

$$d[C]/dt = S/V - k[C] \tag{6.4}$$

where $[C]$ is the concentration (mol L^{-1}), S is the source term (mol yr^{-1}), V is the ocean volume (1.4×10^{21} L), and k is the destruction rate (year^{-1}). Equation (6.4) is readily integrated; in the limit of large t, $[C]$ attains a steady-state value:

$$[C]_\infty = S/(Vk) \tag{6.5}$$

A variety of destruction mechanisms can be quantified for particular molecules, e.g., destruction by ultraviolet light (Dose, 1974), adsorption onto clays (Hedges and Hare, 1987; Oberbeck and Aggarwal, 1992; Chang, 1993), thermal decomposition (Vallentyne, 1964), and passage through hydrothermal vents (Stribling and Miller, 1987). These sinks are discussed in more detail by Pierazzo and Chyba (1999). Taking the ocean to circulate through 300°C vents in 5 Myr gives $k = 1.4 \times 10^{-8}\ \mathrm{yr}^{-1}$, allowing calculations for $[C]_\infty$ via (6.5). Pierazzo and Chyba (1999) present some results for particular amino acids, but this work is subject to the uncertainties discussed in Sect. 6.5.5.

6.11 Prebiotic Organics on the Early Earth

One way to put the prebiotic organic production or delivery rates summarized in Table 6.1 into context is to ask how long would be required to produce a contemporary terrestrial biomass worth of organics. The terrestrial biomass is $\sim 10^{15}$ kg carbon (Whitman et al., 1998). For an early Miller–Urey atmosphere, we have the extraordinary result that a terrestrial biomass of organics could be produced abiotically every $\sim 10^3$ years! At the other extreme, for an intermediate oxidation state atmosphere, about $\sim 10^6$ years are required to produce and deliver a biomass worth of organics. In either case, early Earth hardly seems at a loss for organic molecules.

Indeed, the organic production rate for an early unshielded Miller–Urey atmosphere might appear almost too high to be sustained. At 4 Gyr ago, the timescale for the complete UV processing of a 1-bar CH_4 atmosphere would have been only $\sim 10^7$ year. The situation is complicated, however, by the expected formation of a high-altitude UV-shielding organic haze (Sagan and Chyba, 1997).

How much is enough? Given our continuing lack of understanding of many of the details of the origin of life on the Earth (e.g., Chyba and McDonald, 1995), the difficulty in quantifying the likelihood and effectiveness of possible concentration mechanisms, and the uncertainty over whether the entire "heterotrophic" approach to the origins of life considered in this chapter should instead be replaced by an altogether different autotrophic approach (Wächtershäuser, 1988), it is difficult to assess what rate of organic production or delivery would have been too little for the origin of life. It is possible that exogenous sources provided amino acids with a preference for the left-handed chirality to early Earth (Cronin and Pizzarello, 1997; Engel and Macko, 1997; Chyba 1997; Bailey et al., 1998), imaginably solving the long-standing puzzle of chiral preference. Regardless of the nature of the early atmosphere, a variety of sources dependent on the heavy bombardment would have maintained a significant production or delivery level of prebiotic organics on the early Earth.

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References

Abelson, P.H. (1966), Chemical events on the primitive Earth. *Proc. Natl. Acad. Sci. U.S.A.*, **55**, 1365–1372.

Anders, E. (1989), Pre-biotic organic matter from comets and asteroids. *Nature*, **342**, 255–57.

Armstrong, J.C., Wells, L.E., Gonzalez, G.J. (2002), Rummaging through Earth's Attic for Remains of Ancient Life. *Icarus*, **160**, 183–96.

Bailey, J., Chrysostomou, A., Hough, J.H., Gledhill, T.M., McCall, A., Clark, S., Ménard, F. and Tamura, M. (1998), Circular polarization in star-formation regions: Implications for biomolecular homochirality. *Science*, **281**, 672–74.

Balsiger, H., Altwegg, K., and Geiss, J. (1995), D/H and 18O/16O ratio in hydronium ion and in neutral water from *in situ* ion measurements in Comet P/Halley. *J. Geophys. Res.*, **100**, 5834–40.

Bar-Nun, A., Bar-Nun, N., Bauer, S.H., Sagan, C. (1970), Shock synthesis of amino acids in simulated primitive environments. *Science*, **168**, 470–3.

Bar-Nun, A., Shaviv, A. (1975), Dynamics of the chemical evolution of Earth's primitive atmosphere. *Icarus*, **24**, 197–210.

Barak, I., Bar-Nun, A. (1975), The mechanisms of amino acids synthesis by high temperature shock-waves. *Orig. Life Evol. Biosphere*, **6**, 483–506.

Beukes, N.J., Lowe, D.R. (1989), Environmental control on diverse stromatolite morphologies in the 3000 Myr Pongola Supergroup, South Africa. *Sedimentology*, **36**, 383–97.

Bockelée-Morvan, D.,Gautier, D., Lis, D.C., Young, K., Keene, J., Phillips, T., Owen, T., Crovisier, J., Goldsmith, P.F., Berginet, E.A., et al. (1998), Deuterated water in comter C/1996 B2 (Hyakutake) and its implications for the origin of comets. *Icarus*, **133**, 147–62.

Brasier, M.D., Green, O.R., Jephcoat, A.P., Kleppe, A.K., Van Kranendonk, M.J., et al. (2002), Questioning the evidence for Earth's oldest fossils. *Nature*, **416**, 76–81.

Brocks, J.J., Logan, G.A., Buick, R., Summons, R.E. (1999), Archean molecular fossils and the early rise of eukaryotes. *Science*, **285**, 1033–6.

Cameron, A.G.W. (1983), Origin of the atmospheres of the terrestrial planets. *Icarus*, **56**, 195–201.

Cameron, A.G.W. (1986), The impact theory for the origin of the Moon. In *Origin of the Moon* (W.K. Hartmann, R.J. Phillips, G.J. Taylor, eds.), Lunar and Planetary Institute, Houston, p. 609.

Campins, H., Swindle, T.D., Kring, D.A. (2004), Evaluating comets as a source of Earth's water. In *Genesis, Evolution and Diversity of Life* (J. Seckbach, ed.), Kluwer, Dordrecht, pp. 569–91.

Catling, D.C. (2006), Comment on "A hydrogen-rich early Earth atmosphere". *Science*, **311**, 38a.

Chyba, C.F. (1987), The cometary contribution to the oceans of primitive Earth. *Nature*, **330**, 632–5.

Chyba, C.F. (1990), Impact delivery and erosion of planetary oceans in the early inner solar system. *Nature*, **343**, 129–33.

Chyba, C.F. (1991), Terrestrial Mantle Siderophiles and the Lunar Impact record. *Icarus*, **92**, 217–33.

Chyba, C.F. (1993a), Explosions of small Spacewatch objects in the Earth's atmosphere. *Nature*, **363**, 701–3.

Chyba, C.F. (1993b), The violent environment of the origins of life: Progress and uncertainties. *Geochemica et Cosmochimica Acta*, **57**, 3351–8.

Chyba, C.F. (1997), A left-handed Solar System? *Nature*, **389**, 234–35.

Chyba, C.F. (2005), Rethinking Earth's early atmosphere. *Science*, **308**, 962–3

Chyba, C.F. and Hand, K.P. (2005), Astrobiology: The study of the living universe. *Annu. Rev. Astron. Astrophysics.*, **43**, 31-74, doi: 10.1146/annurev.astro.43.051804.102202.

Chyba, C.F. and McDonald, G.D. (1995), The origin of life in the Solar System: current issues. *Annu. Rev. Earth Planet. Sci.*, **24**, 215–49.

Chyba, C.F., Phillips, C.B. (2002), Europa as an abode for life. *Orig. Life Evol. Biosphere*, **32**, 47–68.

Chyba, C.F., Sagan, C. (1991), Electrical energy sources for organnic synthesis on the early Earth. *Orig. Life Evol. Biosphere*, **21**, 3–17.

Chyba, C.F., Sagan, C. (1992), Endogenous production, exogenous delivery and impact-shock synthesis: An inventory for the origins of life. *Nature*, **355**, 125–132.

Chyba, C.F., Sagan, C. (1997), Comets as a source of Prebiotic Organic Molecules for the Early Earth. In *Comets and the Origin and Evolution of Life* (P.J. Thomas, C.F. Chyba, C.P. McKay, eds.), Springer, New York, pp. 147–73.

Chyba, C.F., Thomas, P.J., Zahnle, K. (1993), The 1908 Tunguska explosion: Atmospheric disruption of a stony asteroid. *Nature*, **361**, 40–4.

Chyba, C.F., Owen, T.C., Ip, W-H. (1994), Impact delivery of volatiles and organic molecules to Earth. In *Hazards Due to Comets and Asteroids* (T. Gehrels, ed.), University of Arizona Press, Tucson, pp. 9–58.

Chyba, C.F., Whitmire, D.P., Reynolds, R. (2000), Planetary habitability and the origins of life. In *Protostars and Planets IV* (A.P.B.V. Mannings, S.S. Russell, eds.), University of Arizona Press, Tucson, pp. 1365–1393.

Clark, B.C. (1988), Primeval procreative comet pond. *Origins of Life*, **18**, 209–38.

Cohen, B.A., Swindle, T.D., Kring, D.A. (2000), Support for the Lunar Cataclysm Hypothesis from Lunar Meteorite Impact Melt Ages. *Science*, **290**, 1754–6.

Cronin, J. and Pizzarello, S. (1997), Enantiometric excesses in meteroritic amino acids. *Science*, **275**, 951–955.

Delsemme, A. (1992), Cometary origin of carbon, nitrogen and water on the Earth. *Origins of Life*, **21**, 279–98.

Delsemme, A.H. (1997), The Origin of the Atmosphere and of the Oceans. In *Comets and the Origin and Evolution of Life* (P.J. Thomas, C.F. Chyba, C.P. McKay, eds.), Springer, New York, pp. 29–67.

Delsemme, A.H. (1999), The deuterium enrichment observed in recent comets is consistent with the cometary origin of seawater. *Planet. Space Sci.*, **47**, 125–31.

Dreibus, G., Wanke, H. (1987), Volatiles on Earth and Mars: A comparison. *Icarus*, **71**, 225–40.

Dreibus, G., Wanke, H. (1989), Supply and loss of volatile constituents during the accretion of terrestrial planets. In *Origin and Evolution of Planetary annd Satellite Atmospheres* (S.K. Atreya, J.B. Pollack, M.S. Matthews, eds.), University of Arizona Press, Tucson, pp. 268–88.

Drouart, A., Dubrulle, B., Gautier, D. and Robert, F. (1999), Structure and transport in the solar nebula from constraints on deuterium enrichment and giant planets formation. *Icarus*, **14**, 129–55.

Duncan, M.J., Quinn, T.R. and Tremaine, S. (1987), The formation and extent of the solar system comet cloud. *Astron. J.*, **94**, 1330–38.

Eberhardt, P., Reber, M., Krankowsi, D. and Hodges, R.R. (1995), The D/H and ^{18}O/^{16}O ratios in water from Comet P/Halley. *Astron. Astrophys.*, **302**, 301–16.

Elderfield, H., Schultz, A. (1996), Mid-Ocean Ridge Hydrothermal Fluxes and the Chemical Composition of the Ocean. *Annu. Rev. Earth Planet Sci.*, **24**, 191–224.

Ehrenfreund, P., Irvine, W., Becker, L., Blank, J., Brucato, J.R., Colangeli, L., Derenne, S., Despois, D., Dutrey, A., Fraaije, H., Lazcano, A., Owen, T., Robert, F. (2002), Astrophysical and astrochemical insights into the origin of life. *Rep. Prog. Phys.*, **65**, 1427–1487.

Engel, M.H. and Macko, S.A. (1997), Isotopic evidence for extraterrestrial non-reacemic amino acids in the Murchison meterorite. *Nature*, **389**, 265–268.

Engrand, C. and Maurette, M. (1998), Carbonaceous micrometeorites from Antarctica. *Meteoritics and Planetary Science*, **33**, 565–580.

Fedo, C.M., Whitehouse, M.J. (2002), Metasomatic origin of quartz-pyroxene rock, Akilia, Greenland, and implications for Earth's earliest life. *Science*, **296**, 1448–52.

Fernandez, J.A. (1985), The formation and dynamical survival of the comet cloud. In *Dynamics of Comets: Their Origin and Evolutionn* (A. Carusi, G.B. Valsecchi, eds.), Reidel, Dordrecht, pp. 45–70.

Fernandez, J.A., Ip, W-H. (1983), On the time evolution of the cometary influx in the region of the terrestrial planets. *Icarus*, **54**, 377–387.

Folinsbee, R.E., Douglas, J.A.V., Maxwell, J.A. (1967), Revelstoke, a new Type I carbonaceous chondrite. *Geochemica et Cosmochimica Acta*, **31**, 1625–35.

Garcia-Ruiz, J.M., Hyde, S.T., Carnerup, A.M., Christy, A.G., Van Kranendonk, M.J., Welham, N.J. (2003), Self-Assembled Silica-Carbonate Structures and Detection of Ancient Microfossils. *Science*, **302**, 1194–1197.

Gilvarry, J.J., Hochstim, A.R. (1963), Possible role of meteorites in the origin of life. *Nature*, **197**, 624–626.

Gomes, R., Levison, H.F., Tsiganis, K., and Morbidelli, A. (2005), Origin of the cataclysmic Late Heavy Bombardment period of the terrestrial planets. *Nature*, **435**, 466–469.

Greenberg, M.J. (1981), Chemical evolution of interstellar dust – a source of prebiotic material? In *Comets and the Origin of Life* (C. Ponnamperuma, ed.), Reidel, Dordrecht, pp. 111–27.

Grinspoon, D.H. (1989), Large impact events and atmospheric evolution on the terrestrial planets. Ph.D. thesis, University of Arizona, Tucson. 209pp.

Grotzinger, J., Rothman, D.H. (1996), An abiotic model for stromatolite morphogenesis. *Nature*, **383**, 423–425.

Grün, E., Zook, H.A., Fechtig, H. and Giese, R.H. (1985), Collisional balance of the meteoritic complex. *Icarus*, **62**, 244–272.

Hartmann, W.K. (1975), Lunar "Cataclysm": A Misconception? *Icarus*, **24**, 181–187.

Hartmann, W.K. (1987), A satellite-asteroid mystery and a possible early flux of scattered C-class asteroids. *Icarus*, **71**, 57–68.

Hartmann, W.K. (1990), Additional evidence about an early intense flux of C asteroids and the origin of Phobos. *Icarus*, **87**, 236–240.

Hartmann, W.K., Ryder, G., Dones, L., Grinspoon, D. (2000), The time-dependent intense bombardment of the primordial Earth/Moon system. In *Origin of the Earth and Moon* (R.M. Canup, K. Righter, eds.), University Arizona Press. Tucson, pp. 493–512.

Hochstim, A.R. (1963), Hypersonic chemosynthesis and possible formation of organic compounds from impact of meteorites on water. Proc. Natl. Acad. Sci. U.S.A., **50**, 200–208.

Holland, H.D. (1962), Models for the evolution of the Earth's atmosphere. In *Petrologic Studies: A Volume to Honor A.F. Buddington* (A.E.J. Engel, H.L. James, B.F. Leonard, eds.), Geological Society of America, Washington, D.C., pp. 447–477.

Horowitz, N.H. (1986), *To Utopia and Back: The Search for Life in the Solar System.* W.H. Freeman and Co., New York.

Ip, W-H. (1977), On the early scattering processes of the outer planets. In *Comets-Asteroids-Meteorites: Interrelations, Evolution and Origin* (A.H. Delsemme, ed.), University of Toledo Press, Toledo, pp. 485–490.

Kasting, J.F. (1982), Stability of ammonia in the primitive terrestrial atmosphere. *J. Geophys. Res.*, **87**, 3091–3098.

Kasting, J.F. (1990), Bolide impacts and the oxidation state of carbon in the Earth's early atmosphere. *Orig. Life Evol. Biosphere*, **20**, 199–231.

Kasting, J.F. (2000), Environmental constraints on the origin of life. In *The Origins of Life* (D. Baltimore, R. Dulbecco, F. Jacob, R. Levi-Montalcini, eds.), Academic Press, New York, pp. 193–200.

Kasting, J.F., Catling, D. (2003), Evolution of a Habitable Planet. *Annual Review of Astronomy and Astrophysics*, **41**, 429–463.

Kasting, J.F., Whtimire, D.P., and Reynolds, R.T. (1993), Habitable zones around main sequence stars. *Icarus*, **101**, 108–128.

Knoll, A. (2003), *Life on a Young Planet.* Princeton University Press, Princeton, p. 277.

Kring, D.A., Cohen, B.A. (2002), Cataclysmic bombardment throughout the inner solar system 3.9–4.0 Ga. *Journal of Geophysical Research*, **107**, No. E2, 10.1029/2001JE001529.

Kuhn, W.R., Atreya, S.K. (1979), Ammonia photolysis and the greehouse effect in the primordial atmosphere of the Earth. *Icarus*, **37**, 207–213.

Lepland, A., van Zuilen, M.A., Arrhenius, G., Whitehouse, M.J., Fredo, C.M. (2005), Questioning the evidence for Earth's earliest life – Akilia revisited. *Geology*, **33**, 77–79.

Levine, J.S., Augustsson, T.R. (1985), The photochemistry of biogenic gases in the early and present atmosphere. *Orig. Life Evol. Biosphere*, **15**, 299–318.

Lewis, J. (1974), The temperature gradient in the solar nebula. *Science*, **186**, 440–443.

Lewis, J., Barshay, S.S., Noyes, B. (1979), Primordial retention of carbon by the terrestrial planets. *Icarus*, **37**, 190–206.

Love, S.G., Brownlee, D.E. (1993), A direct measurement of the terrestrial mass accretion rate of cosmic dust. *Science*, **262**, 550–553.

Maher, K.A., Stevenson, D.J. (1988), Impact frustration and the origin of life. *Nature*, **331**, 612–614.

Maurette, M. (1998), Carbonaceous micrometeorites and the origin of life, *Orig. Life Evol. Biosphere*, **28**, 385-412.

Maurette, M., Duprat, J., Engrand, C., Gounelle, M., Kurat, G., Matrajt, G. and Toppani, A. (2000), Accretion of neon, organics, CO_2, nitrogen and water from large interplanetary dust particles on early Earth. *Planetary and Space Science*, **48**, 1117-1137.

Matrajt, G., Pizzarello, S., Taylor, S. and Brownlee, D. (2004), Concentration and variability of the AIB amino acid in polar micrometeorites: Implications for the exogenous delivery of amino acids to the primitive Earth. *Meteoritics and Planet. Sci.*, **39**, 1849–1858.

Mazur, P. (1980), Limits to life at low temperatures and at reduced water contents and water activities. *Orig. Life Evol. Biosphere*, **10**, 137–159.

McKay, C.P. (1991), Urey Prize lecture: planetary evolution and the origin of life. *Icarus*, **91**, 93–100.

McKay, C.P., Borucki, W.J., Kojiro, K.R., Church, F. (1989), Shock production of organics during cometary impact. *Lunar Planet. Sci. Conf.*, **20**, 671–672.

McKay, C.P., Scattergood, T.W., Pollack, J.B., Borucki, W.J., Van Ghyseghem, H.T. (1988), High-temperature shock formation by N_2 and organics on primordial Titan. *Nature*, **332**, 520–522.

Meier, R., Owen, T.C., Matthews, H.E., Jewitt, D.C., Bockelée-Morvan, D., Biver, N., Crovisier, J. and Gautier, D. (1998), A determination of the DHO/H_2O ratio in Comet C/1995 O1 (Hale-Bopp). *Science*, **279**, 842–844.

Melosh, H.J. (1989), *Impact Cratering: A Geologic Process.* Oxford University Press, New York.

Miller, S.L. (1953), A production of amino acids under possible primitive Earth conditions. *Science*, **117**, 528–529.

Miller, S.L. (1957), The formation of organic compounds on the primitive Earth. *Ann. N.Y. Acad. Sci.*, **69**, 123–135.

Miller, S.L., Urey, H.C. (1959), Organic compound synthesis on the primitive Earth. *Science*, **130**, 245–251.

Miller, S.L. (1974), The first laboratory synthesis of organic compounds under primitive Earth conditions. In *The Heritage of Copernicus: Theories "Pleasing to the Mind"* (J. Neyman, ed.), MIT Press, Cambridge, pp. 228–242.

Miller, S.L., Lyons, J.R., Chyba, C.F. (1998), Organic shielding of greenhouse gases on early Earth. *Science*, **279**, 779a.

Mojzsis, S.J., Arrhenius, G., McKeegan, K.D., Harrison, T.M., Nutman, A.P., Friend. C.R.L. (1996), Evidence for Life on Earth before 3,800 million years ago. *Nature*, **384**, 55–59.

Mojzsis, S.J., Harrison, T.M., Pidgeon, R.T. (2001), Oxygen-isotope evidence from ancient zircons for liquid water at the Earth's surface 4,300 Myr ago. *Nature*, **409**, 178–181.

Moorbath, S. (2005), Dating earliest life. *Nature*, **434**, 154–155.

Morbidelli, A., Chambers, J., Lunine, J.I., Petit, J.M., Robert, F., Valsecchi, G.B., and Cyr, K.E. (2000), Source regions and timescales for the delivery of water to the Earth. *Meteorites and Planetary Science*, **35**, 1309–1320.

Mukhin, L.M., Gerasimov, M.V., Safonova, E.N. (1989), Origin of precursors of organic molecules during evaporation of meteorites and mafic terrestrial rocks. *Nature*, **340**, 46–48.

National Research Council (2006), Preventing the Forward Contamination of Mars. National Academy of Sciences Press, Washington, DC.

Oberbeck, V.R., Aggarwal, H. (1992), Comet impacts and chemical evolution on the bombarded Earth. *Orig. Life Evol. Biosphere*, **21**, 317–338.

Oberbeck, V.R., McKay, C.P., Scattergood, T.W., Carle, G.C., Valentin, J.R. (1989), The role of cometary particle coalescence in chemical evolution. *Orig. Life Evol. Biosphere*, **19**, 39–55.

Oró, J. (1961), Comets and the formation of biochemical compounds on the primitive Earth. *Nature*, **190**, 389–390.

Owen, T.C., Bar-Nun, A., Kleinfeld, I. (1992), The photochemistry of biogenic gases in the early and present atmosphere. *Nature*, **358**, 43–46.

Owen, T.C., Cess, R.D., Ramanathan, V. (1979), Enhanced $C0_2$ greehouse to compensate for reduced solar luminosity on early Earth. *Nature*, **277**, 640–642.

Pavlov, A.A., Brown, L.L., and Kasting, J.F. (2001), UV shielding of NH_3 and O_2 by organic hazes in the Archean atmosphere. *J. Geophys. Res.*, **106**, 23,267–23,288.

Pierazzo, E. and Chyba, C.F. (2002), Cometary delivery of biogenic elements to Europa. *Icarus*, **157**, 120–127.

Pierazzo, E., Chyba, C.F. (2002), Cometary delivery of biogenic elements to Europa. *Icarus*, **157**, 120–127.

Pollack, J.B., Podolak, M., Bodenheimer, P., Christofferson, B. (1986), Planetesimal dissolution in the envelopes of the forming, giant planets. *Icarus*, **67**, 409–443.

Prinn, R.G., Fegley, B. (1989), Solar nebula chemistry: Origin of planetary, satellite and cometary volatiles. In *Origin and Evolution of Planetary and Satellite Atmospheres* (S.K. Atreya, J.B. Pollack, M.S. Matthews, eds.), University of Arizona Press, Tucson, pp. 78–136.

Rabinowitz, D.L. (1993), The size distribution of the Earth-approaching asteroids. *Astrophys. J.*, **407**, 412–427.

Robert, F. (2001), Isotope geochemistry: the origin of water on Earth. *Science*, **293**, 1056–1058.

Rodante, F. (1992), Thermodynamics and kinetics of decomposition processes for standard α-amino acids and some of their defeptides in the solid state. *Thermochim. Acta*, **200**, 47–61.

Rosing, M.T. (1999), ^{13}C-Depleted Carbon microparticles in $>$3700-Ma sea-floor sedimentary rocks from West Greenland. *Science*, **28**, 674–676.

Rosing, M.T., Frei, R. (2004), U-rich Archaean sea-floor sediments from Greenland – indications of $>$3700 Ma oxygenic photosynthesis. *Earth Planet Sci. Lett.*, **217**, 237–244.

Ross, D. (2006), Cometary impact and amino acid survival – chemical kinetics and thermochemistry. *J. Phys. Chem.*, **110**, No. 21, 6633–37.

Rushmer, T., Minarik, W.G., Taylor, G.J. (2000), Physical processes of core formation. In *Origin of the Earth and Moon* (R.M. Canup, K. Righter, eds.), University of Arizona Press, Tucson, pp. 227–243.

Ryder, G. (2002), Mass flux in the ancient Earth–Moon system and benign implications for the origin of life on Earth. *J. Geophys. Res.*, **107**, 10.1029/2001JE001583.

Sagan, C. (1974), The origin of life in a cosmic context. *Orig. Life Evol. Biosphere*, **5**, 497–505.

Sagan, C., Chyba, C.F. (1997), The Early Faint Sun Paradox: Organic Shielding of Ultraviolet-Labile Greenhouse Gases. *Science*, **276**, 1217–1221.

Schidlowski, M. (1988), A 3,800 million-year isotopic record of life from carbon in sedimentary rocks. *Nature*, **333**, 313–318.

Schlesinger, G., Miller, S.L. (1983a), Prebiotic synthesis in atmospheres containing CH_4, CO, and CO_2. Hydrogen cyanide, formaldehyde, and ammonia. *J. Molec. Evol.*, **19**, 383–390.

Schlesinger, G., Miller, S.L. (1983b), Prebiotic synthesis in atmospheres containing CH_4, CO, CO_2. I. Amino Acids. *J. Molec. Evol.*, **19**, 376–382.

Schonland, B.F.J. (1928), The interchange of electricity between thunderclouds and the Earth. *Proc. Roy. Soc. A*, **118**, 252–262.

Schonland, B.F.J. (1953), *Atmospheric Electricity.* Methuen, London.

Schopf, J.W. (1993), Microfossils of the Early Archean Apex Chert: new evidence of the antiquity of life. *Science*, **260**, 640–646.

Schopf, J.W., Kudryavtsev, A.B., Agresti, D.G., Wdowiak, T.J., Czaja, A.D. (2002), Laser-Raman imagery of Earth's earliest fossils. *Nature*, **416**, 73–76.

Schopf, J.W., Packer, B.M. (1987), Early Archean (3.3 to 3.5 billion-year-old) microfossils from Warrawoona Group, Australia. *Science*, **237**, 70–3.

Shock, E.L., and Schulte, M.D. (1998), Organic sysnthesis during fluid mixing in hydrothermal systems. *Journal of Geophysical Research*, **103**, E12, 28513–28528.

Shoemaker, E.M., Wolfe, R.F. (1984), Evolution of the Uranus-Neptune planetesimal swarm. *Lunar Planet. Sci. Conf.*, **15**, 780–781.

Sleep, N.H., Zahnle, K.J., Kasting, J.F., Morowitz, H.J. (1989), Annihilation of ecosystems by large asteroid impacts on the early Earth. *Nature*, **342**, 139–142.

Solomatov, V.S. (2000), Fluid dynamics of a terrestrial magma ocean. In *Origin of the Earth and Moon* (R.M. Canup, K. Righter, eds.), University of Arizona Press, Tucson, pp. 323–338.

Stevenson, D.J. (1983), The nature of the Earth prior to the oldest known rock record: The Hadean Earth. In *Earth's Earliest Biosphere: Its Origin and Evolution* (J.W. Schopf, ed.), Princeton University Press, Princeton, pp. 32–40.

Stevenson, D.J. (1990), Fluid dynamics of core formation. In *Origin of the Earth* (H.E. Newsom, J.H. Jones, eds.), Oxford University Press, New York, pp. 231–249.

Stribling, R., Miller, S.L. (1987), Electric discharge synthesis of HCN in simulated Jovian atmospheres. *Icarus*, **72**, 48–52.

Summons, R.E., Jahnke, L.L., Hope, J.M., Logan, G.A. (1999), 2-Methylhopanoids as biomarkers for cyanobacterial oxygenic photosythesis. *Nature*, **400**, 554–557.

Swindle, T.D., Caffee, M.W., Hohenberg, C.M., Taylor, S. R. (1986), I-Pu-Xe dating and the relative ages of the Earth and Moon. In *Origin of the Moon* (W.K. Hartmann, R.J. Phillips, G.J. Taylor, eds.), Lunar and Planetary Institute, Houston, pp. 331–357.

Taylor, S., Lever, J.H. and Harvey, R.P. (1997), Terrestrial flux rates of micrometeorites determined from the south pole water well (abstract). *Meteoritics and Space Science*, **31**, A140.

Tera, F., Papanastassiou, D., Wasserburg, G.J. (1974), Isotopic evidence for a terminal lunar cataclysm. *Earth Planet Sci. Lett.*, **22**, 1–21.

Tian, F., Toon, O.B., Pavlov, A.A., De Sterck, H. (2005), A Hydrogen-Rich Early Earth Atmosphere. *Science*, **308**, 1014–1018.

Tian, F., Toon, O.B., Pavlov, A.A. (2006), Response to Comment on "A hydrogen-rich early Earth atmosphere". *Science*, **311**, 38b.

Thomas, P.J. and Brookshaw, L. (1997), Numerical models of comet and asteroid impacts. In *Comets and the Origin and Evolution of Life* (P.J. Thomas, C.F. Chyba, and C.P. McKay, eds.), Springer, New York, pp. 131–45.

Tilton, G.R. (1988), Age of the Solar System. In *Meteoritics and the Early Solar System* (J.F. Kerridge, M.S. Matthews, eds.), University of Arizona Press, Tucson, pp. 259–275.

Turner, G., Cadogan, P.H., Yonge, C.J. (1973), Argon selenochronology. Proceedings of the Fourth Lunar Planetary Science conference (Supplement 4, *Geochimica et Cosmochimica Acta*), **2**, 1889–1914.

Ueno, Y., Yurimoto, H., Yoshioka, H., Komiya, T., Maruyama, S. (2002), Ion microprobe analysis of graphite from ca. 3.8 Ga metasediments, Isua supracrustal belt, West Greenland: Relationship between metamorphism and carbon isotopic composition. *Geochemica et Cosmochimica Acta*, **66**, 1257–1268.

Urey, H.C. (1952a), On the Early Chemical History of the Earth and the Origin of Life. *Proc. Natl. Acad. Sci. U.S.A.*, **38**, 351–363.

Urey, H.C. (1952b), *The Planets: Their Origin and Development.* Yale University Press, New Haven.

Yada, T., Nakamura, T., Takaoka, N., Terada, K., Yano, H., Nakazawa, T. and Kojima, H. (2004), The global accretion rate of extraterrestrial materials in the last glacial period estimated from the abundance of micrometeorites in antarctic glacier ice. *Earth Planets Space*, **56**, 67-79.

van Zuilen, M.A., Lepland, A., Arrhenius, G. (2002), Reassessing the evidence for the earliest traces of life. *Nature*, **418**, 627–630.

Wächtershäuser, G. (1988), Before Enzymes and Templates: Theory of Surface Metabolism. *Microbiol. Rev.*, **52**, 452–484.

Walker, J.C.G. (1977), *Evolution of the Atmosphere.* Macmillan, New York. p. 318.

Walsh, M.M., Lowe, D.R. (1985). Filamentous microfossils from the 3,500-Myr-old Onverwacht Group, Barberton Mountain Land, South Africa. *Nature*, **314**, 530–532.

Weaver, H.A., Feldman, P.D., Combi, M.R., Krasnopolsky, V.A., Lisse, C.M., Shemansky, D.E. (2002), A search for Argon and O VI in the comets using the Far Ultraviolet Spectroscopic Explorer. *Astrophys. J.*, **576**, L95–L8.

Westall, F. (2005), Life on the early Earth: a sedimentary view. *Science*, **308**, 366-367.

Wetherill, G.W. (1990), Formation of the Earth. *Annu. Rev. Earth Planet Sci.*, **18**, 205–256.

Wetherill, G.W. (1994), Possible consequences of absence of "Jupiters" in planetary systems. *Astrophys. Space Sci.*, **212**, 23–32.

Whipple, F.L. (1976), A speculation about comets and the Earth. *Mém. Soc. R. Liège 6eme Série*, **9**, 101–111.

Whitman, W.B., Coleman, D.C., and Wiebe, W.J. (1998), Prokaryotes: the unseen majority. *Proc. Natl. Acad. Sci. USA*, **95**, 6578–6583.

Wilde, S.A., Valley, J.W., Peck, W.H. and Graham, C.M. (2001), Evidence from detrital zircons for the existence of continental crust and oceans on Earth 4.4 Gyr ago. *Nature*, **409**, 175–178.

Wilks, M.E., Nisbet, E.G. (1985), Archean stromatolites from the Steep Rock Group, N.W. Ontario, Canada. *Can. J. Earth Sci.*, **22**, 792–799.

Yung, Y.L., Pinto, J.P. (1978), Primitive atmosphere and implications for the formation of channels on Mars. *Nature*, **273**, 730–732.

Zahnle, K.J. (1990), Atmospheric chemistry by large impacts. In *Global Catastrophes in Earth History* (V.I. Sharpton, P.D. Ward, eds.) Geological Society of America, Boulder, pp. 271–288.

Zahnle, K.J. Walker J.C.G. (1982), The evolution of solar ultraviolet luminosity. *Rev. Geophys. Space Phys.*, **20**, 280-292.

Zhao, M., Bada, J.L. (1989), Extraterrestrial amino acids in Cretaceous/Tertiary boundary sediments at Stevns Klint, Denmark. *Nature*, **339**, 463–465.

7

Impacts and the Early Evolution of Life

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Summary. The K/T event shows that, even today, biospheric cratering is an important process. Impacts were much larger and more frequent on the early Earth. In all likelihood impacts posed the greatest challenge to the survival of early life.

7.1 Prologue

The comet Chiron may be the most dangerous object in the solar system. Chiron is a ∼180-km-diameter comet (Lebofsky et al., 1984; Hartmann et al., 1990) that presently resides in an unstable Saturn-crossing orbit (Scholl, 1979; Oikawa and Everhart, 1979; Hahn and Bailey, 1990). Conventional wisdom has Chiron randomly walking into the inner solar system, in manner if not in mass like any short period comet (Duncan et al., 1987; 1988). Its chances of actually colliding with the Earth are low, probably less than 1 in a million. It is far more likely that Saturn or Jupiter will eject it from the solar system. Yet the worst could happen. If Chiron were to strike Earth, the impact would release on the order of 10^{34} ergs. The Earth would be enveloped by a thick rock vapor atmosphere. The upper few hundred meters of the ocean would boil and evaporate. On land the heat pulse would sterilize soild and rock to depths of 50 m. Life would survive, but it would be thrown back into the oceans or buried in caves.

Since its formation the Earth has been subject to collisions with other celestial bodies. An almost inescapable inference is that the Earth and the other planets accumulated by collisions of myriads of smaller objects present in the early solar system (Safronov, 1972). By now the solar system is an almost empty place. Major collisions are rare. But there do occur occasional collisions of note. The impact of a ∼10-km comet or asteroid into the Yucatan peninsula 65 million years ago left a 180-km-diameter hole in the ground (Hildebrand et al., 1991; Swisher et al., 1992) and an even larger hole in the fossil record. This impact, which was originally inferred from the presence of extraordinary amounts of exogenous iridium in a thin global clay layer,

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happens to coincide with the most famous mass extinction (Alvarez et al., 1980). Although the obvious has been resisted by some, there can be little doubt that the Cretaceous-Tertiary (K/T) impact caused the death of most living things on Earth, and the extinction of a fair fraction of the species that had been living thereon, including, famously, the dinosaurs (see Silver and Schultz, 1982; Sharpton and Ward, 1990).

As one looks back toward the beginning of the solar system, collisions become more frequent and the largest among them commensurately greater. Very large events, releasing tens or hundreds of times more energy than the K/T impact, were carving the face of the Moon 3.9 Ga. The Moon suffered at least 10 such collisions between 3.7 and ~4.1 Ga (Taylor, 1982; Wilhelms, 1987). The Earth would have been struck by hundreds of similar objects over the same period, and by tens of objects much larger still. To order of magnitude, the energy released by the largest would have been enough to vaporize the Earth's oceans (Sleep et al., 1989).

Looking still further back, the very existence of the Moon is evidence for a truly colossal collision: a collision of two planets the size of Venus and Mars to form the Earth and Moon (Hartmann et al., 1986; Stevenson 1987; Newsom and Jones, 1990). Such an impact would probably have melted the planet. If life had arisen on the Earth before the Moon-forming impact, it would not have survived here. Indeed, no organic material would have survived. Biogenesis would need to start again.

Evidently life's hold on the Earth would seem increasingly precarious at earlier times, with only the most protective niches, e.g., the mid-ocean ridge hydrothermal vents or deep aquifers, being in any sense continuously habitable (Maher and Stevenson, 1988; Oberbeck and Fogleman, 1989; Sleep et al., 1989). At some point there must have occurred a last collision that life could not survive. The Moon-forming impact may not have been the last of these. The last planet-sterilizing impact presents what is effectively a "biological event horizon" (C.P. McKay, personal communication, 2004), since none of the biochemical events that may have occurred before this impact can bear on the origin of life as it exists now.

7.2 Introduction

The modern science of impact eschatology began when Maher and Stevenson (1988) asked whether frequent large impacts may have frustrated the origin of life. Their approach was to compare the time interval between lethal impacts in a given environment with the presumptive time period required for biogenesis. They argued that chemical evolution at the surface would have suffered frequent devastating setbacks because of frequent big impacts. By contrast the deep sea and especially deep-sea hydrothermal systems would have gone undisturbed for much longer times. Maher and Stevenson argued that the safety of the deep more than offset the chance that biochemistry might evolve faster at the surface. They therefore suggested that life probably originated in hydrothermal systems; they even dated Genesis to 4.2–4.3 Ga, based on their estimate of when such systems became continuously habitable and their presumption that the impact rate declined exponentially with a 70-Ma decay time before 3.5 Ga.

Sleep et al. (1989) altered the question to ask what ecosystems were best suited to survive very large impacts. That is, we assumed that life had already originated in some unspecified manner, and then asked what it would have taken to annihilate it. We discussed in particular the threshold for evaporating the oceans, how often this occurred (rarely, if at all), and the consequences of doing so. We concluded that survival of the fittest favored thermophiles that normally dwelt in the rocks and sediments underneath the oceans. An important technical difference between Sleep et al. (1989) and Maher and Stevenson (1987) was that Sleep et al., opted for a much milder late heavy bombardment; the chief philosophical difference was that Sleep et al., did not address the origin of life. We have elaborated on our point of view in the first edition of this book (Zahnle and Sleep, 1997) and in a later study comparing hazards on Mars and Earth (Sleep and Zahnle, 1998).

Oberbeck and Fogleman (1989, 1990) closely followed Maher and Stevenson but they emphasized the biggest impacts, those large enough to sterilize the globe. This threshold they equated to evaporating the oceans, which they took from Sleep et al., Oberbeck and Fogleman (1989, 1990) argued that ocean vaporizing impacts were frequent. They deduced upper limits for the time available for the origin of life that ranged from 133 million years at 3.5 Ga to just 11 million years at 3.8 Ga. Their results differ substantially from those given by Sleep et al. (1989), who estimated that there were no more than a few, and possibly no, sterilizing impacts; or those of Chyba (1991), who estimates approximately 4 ocean evaporating events between 3.8 and 4.4 Ga; or the estimate we gave in the first edition of this book (2 ± 4 ocean-vaporizing events between 3.8 and 4.1). The difference between our results and Chyba's, on the one hand, and Oberbeck and Fogleman's on the other appears mostly to be the result of using different expressions to relate crater diameters to impact energies. We provide a detailed discussion of how these differences arose in the first edition of this book (Zahnle and Sleep, 1997) that we will not repeat here.

At about the same time that planetary science was rediscovering its power to wreak havoc to the globe, molecular phylogeny, in the form of comparative 16-S ribosomal RNA-sequencing (Pace et al., 1986; Lake, 1988), was pointing towards a sulfur-metabolizing thermophile as the probable identity of the universal ancestor. The universal ancestor should not be confused with the first living organism. At the deepest level of molecular biology, a sulfur-metabolizing thermophile differs little from turnips, humans, or cyanobacteria (how else could 16-S ribosomal RNAs be compared?). The gap between between a rock and a bacterium is incomparably greater. It is the enormity of this gap that defines life; it makes a quantitative difference in complexity appear to be a qualitative difference. Our descent from a sulfur-metabolizing thermophile might mean only that a sulfur-metabolizing thermophile survived what others did not. The mid-ocean ridge hydrothermal systems are one of the habitats favored by these organisms today.

There are some notable differences between this chapter and its predecessor in the first edition. The chapter has been reorganized to address topics in a more conventional but less pleasing order. It has also been largely rewritten in subtle ways to correct errors on our part or to update arguments that have evolved over the past decade. In particular, we address arguments raised by Graham Ryder (2002, 2003) in support of a catastrophic yet mild lunar bombardment history. In the end we do not change our conclusions very much, not because we discount Ryder's arguments but because (1) there are factors going in the other direction that we neglected; (2) our conclusions do not depend on the detailed chronology of events; and (3) we had advocated a relatively mild lunar impact history in the first place. We have also expanded the discussion on the generation and propagation of impact-generated thermal waves into the subsurface, added a section addressing impact-driven mass extinctions on Mars, and deleted some old material because we have nothing new to say to those topics.

7.3 The Lunar Record

No direct record of the earliest impacts exists on the Earth. In contrast, the lunar record is well preserved and well studied. The Moon records an early period (ca. 3.8 Ga and probably earlier) of high impact flux, often called the late bombardment, followed by some 3 to 3.5 billion years rather like the present. The intensity and chronology of the bombardment have been controversial since its discovery in the *Apollo* era.

Hartmann et al. (2000) provide a balanced but inconclusive recent review of the history of space age interpretations of the lunar cratering record and the origin of the concept of the "late heavy bombardment." Chyba (1991) reviews the lunar record in greater detail from a perspective similar to our own. Although there are some differences, Chyba's general conclusions are also similar to ours. By contrast, Ryder (2002, 2003) favors a total impact burden about an order of magnitude smaller. Ryder's methods are similar to ours, and he uses essentially the same raw data, but he makes different assumptions. In particular Ryder limits his assessment to just the craters and basins that survive today. Thus Ryder's estimates define an extreme lower bound. We will return to this issue below.

At the other extreme, Hartmann (1980) and Wilhelms (1987) presume that the observed basins and craters are just the tail end of a monotonically declining impact flux that extrapolates smoothly back in time to the Moon-forming impact. Such exuberant impact fluxes present serious observational (e.g., How did Vesta survive? How did ALH84001 survive 4.5 Gyr on Mars?)

and theoretical (Where in the solar system did the impactors come from?) challenges (Hartmann et al., 2000); moreover, it is difficult to point to any observational data that would be explained by extremely high impact fluxes predating the observable crater record. For the present we will emphasize relatively mild lunar bombardments; perhaps in a future third edition of this book we will have a chance to admit that we were wrong again.

7.3.1 Energies of Basin-Forming Impacts

Impressive multiringed basins formed on the Moon as recently as 3.7–3.8 Ga (Wilhelms, 1987). The Imbrium basin dates to $3.83^{+0.03}_{-0.06}$ Ga; a young age of 3.77 Ga is a relatively recent suggestion by Stadermann et al. (1991). The spectacular Orientale basin is younger but of uncertain age; it is usually put at ∼3.8 Ga; it is older than the 3.72 Ga mare site visited by *Apollo* 17. Nectaris is the oldest basin dated by the *Apollo* program, but the age has been controversial. Most authorities argue that samples dated at 3.92 Ga were generated by Nectaris (e.g., Tera et al., 1974; Wilhelms, 1987; Spudis, 1993; Ryder, 2002). Others have argued that samples of age ∼4.15 Ga were cast by Nectaris, and that the more ancient date is more consistent with other evidence constraining the impact flux at still earlier times (e.g., Wetherill, 1981; Taylor, 1982; Baldwin, 1987). It is of course possible that Nectaris is older still, and that we have no sample that dates it. This possibility is rarely acknowledged. If the young age for Nectaris is adopted than the impact flux had a characteristic fall time of less than 70 Ma (the timescale used by Stevenson and Maher (1988)). With this rapid rate of decline it is likely that the late bombardment was a short-lived event, perhaps even a "terminal cataclysm" (Tera et al., 1974), preceeded by a few hundred million years of lower impact flux (see below for more discussion on this). An old age for Nectaris can be consistent with a monotonic decline in the impact flux. The Moon experienced another half-dozen similar impacts dating between Nectaris and Orientale (Baldwin, 1987; Wilhelms, 1987). Approximately 30 basins older than Nectaris have been identified. The largest confirmed remaining basin, South Pole-Aitken, formed early and has been nearly obliterated by later features. The older age implies a characteristic decay time greater than 144 Ma,[1] the timescale recommended by Ivanov and Neukum (1994) and accepted by Chyba (1991).

Orientale is the youngest and best preserved of the lunar basins. It features four prominent rings in a bulls-eye pattern, with diameters of 320, 480, 620, and 930 km (Wilhelms, 1987). Bratt et al. (1985a, 1985b) used geophysical modelling of thermal contraction and of the gravitational anomaly created by the lunar mantle rising to fill the hole to estimate that the Orientale impact expelled 2.4×10^{22} g of ejecta. Based both on laboratory experiments in wet sand and on much larger scale chemical explosions of known yield in known

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[1] An e-folding time of 144 Myr is the same as a 100-Myr half-life.

targets, Schmidt and Housen (1987) recommend two slightly discordant scaling relations for apparent volume and apparent diameter of simple craters in rock. The apparent crater volume is

$$V_{\mathrm{ej}} = 0.23\,(\rho_{\mathrm{i}}/\rho_{\mathrm{t}})^{0.22}\,(E/\rho_{\mathrm{t}})^{0.78}\,v^{-0.26}g^{-0.65}\sin\theta \tag{7.1}$$

where ρ_{i} and ρ_{t} are the densities of the impactor and the crust; m is the mass of the impactor and v is the impact; and g is the surface gravity. The ejecta mass is $\rho_{\mathrm{t}}V_{\mathrm{ej}}$. We use $\rho_{\mathrm{i}} = 2.4$ and $\rho_{\mathrm{t}} = 2.6$ g/cm^3, respectively. We have supplemented Schmidt and Housen's relation with dependence on the incidence angle θ (Melosh, 1989, p. 121). The most probable incidence angle is 45°. At $v = 13$ km/s, Eq. (7.1) implies that to generate 2.4×10^{22} g of ejecta, the Orientale impact released $\sim 3 \times 10^{33}$ ergs.

The diameter of the simple (transient) crater is

$$D_t = 1.6\,(\rho_{\mathrm{i}}/\rho_{\mathrm{t}})^{.07}\,(E/\rho_{\mathrm{t}})^{.26}\,v^{-0.08}g^{-0.22}\sin^{0.33}\theta \text{ cm} \tag{7.2}$$

This expression is derived from Eq. 7.1 and applies to small bowl-shaped craters. Big craters and basins take on complex forms that are shallower and broader than the transient crater. The process is known as "slumping" and appears to be an integral aspect of the late stages of crater formation. Following Chyba (1991), we adopt the crater slumping prescription employed by McKinnon et al. (1990). The final complex crater has diameter

$$D = 1.2 D_t^{1.13} D_c^{-0.13} \tag{7.3}$$

Equation (7.3) implies that a 930-km-diameter complex crater (i.e., the outer ring of Orientale) corresponds to an impact energy of $\sim 2 \times 10^{33}$ ergs. The corresponding 500-km transient crater coincides approximately to the ring defined by the inner Rook mountains. It exceeds Melosh's (1989, p. 165) estimate that Orientale's transient crater was no larger than ~ 400 km, which corresponds to $< 7 \times 10^{32}$ ergs. Bratt et al., estimated that Orientale released between 4×10^{32} and 3×10^{33} ergs.

Imbrium is estimated to have ejected some 3.6×10^{22} g (Spudis et al., 1988). It has a nominal but uncertain outer diameter of 1,160 km (Wilhelms, 1987). Both of these imply that Imbrium was about twice as energetic as Orientale.

A different approach is to consider the excavation depth. Melosh (1989, p. 78) notes that impacts typically excavate material from a depth equal to about 10% of the transient crater diameter. Neither Imbrium nor Orientale dredged up mantle samples, but Imbrium did dredge up KREEP,[2] which is thought to have formed at the base of the crust (Spudis, 1993, p. 147).

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[2] KREEP is a memorable acronym composed of potassium, rare-earth elements, and phosphorus, all of which are enriched in this peculiar basalt. Because KREEP is rich in radioactive elements K, Th, and U, it can be detected remotely by an orbiting cousin of the geiger counter.

Assuming that the crust under Imbrium was 50–60 km thick (Spudis, 1993, pp. 131, 162), it follows from Eq. 7.2 that Imbrium released between $1 \times 10^{33} - 3 \times 10^{33}$ ergs. Orientale appears to have excavated only anorthosite-rich crust, which sets an upper limit of 60 km on the depth of excavation (the crust is thicker under Orientale than under Imbrium, Spudis, 1993, p. 64) and an upper limit of $\sim 3 \times 10^{33}$ ergs on the energy released by the impact. Bratt et al., estimated that the mantle under Orientale was uplifted some 50 km, which implies an energy in the range of $1 \times 10^{33} - 2 \times 10^{33}$ ergs.

The far side South Pole-Aitken basin is the largest and probably oldest confirmed lunar basin (Wilhelms, 1987; Belton et al., 1992). The basin itself has a nominal diameter of 2,500 km, which according to Eq. (7.3) implies an energy of 5×10^{34} ergs. There is ambiguous spectral evidence obtained on the *Galileo* flyby of the Moon (Belton et al., 1992) that this event might have reached the mantle. More recent *Clementine* data are consistent with some mantle rock on the basin floor but fall short of proving the hypothesis (Lucey et al., 1998). It therefore appears that S. Pole-Aitken did not reach deep into the mantle, else the signature would be clear and undebated. If the crust under S. Pole-Aitken is 70 km thick, and excavation dipped no more than 10 km into the mantle, the S. Pole-Aitken impactor would have released $\sim 1 \times 10^{34}$ ergs.

In assessing these estimates, one should also consider the underlying statistical distribution. Impacts do not follow a bell curve. There are many more small impacts than large impacts in any size range. This applies also to broad windows of uncertainty. The true ejecta mass or the true crater diameter is considerably more likely to be at the small end of a range of estimates than toward the middle. We conclude that the best present estimates for the energies released by Orientale, Imbrium, and S. Pole-Aitken are the conservative estimates 1×10^{33}, 2×10^{33}, and 1×10^{34} ergs, respectively, with considerable uncertainty attending all. Our estimate for Imbrium corresponds to an asteroid of mass $5 \times 10^{20} - 2 \times 10^{21}$ g. For comparison, Baldwin (1987) estimated that Imbrium was 2×10^{21} g and Wetherill (1981) estimated 4×10^{21} g. Ryder (2002) estimated that Imbrium released 1.6×10^{33} ergs, but he chose a smaller mass, 8×10^{20} g, and a higher impact velocity of 20 km/s. From this he deduces a total influx of $\sim 10^{22}$ g to produce all the visible basins and craters on the Moon.

7.3.2 Crustal Contamination by Chondrites

A different approach is to use the lunar crust as an integrating detector. In the Earth, the mantle and crust are highly depleted in siderophile elements, which enter the metallic iron core in preference to the silicate mantle or crust. Platinum group elements like Ir and Os are extremely siderophilic and therefore extremely depleted in the mantle and crust. The Ir and Os content of the Earth's mantle therefore puts an upper limit on what the Earth accreted after the mantle and core were last in effective contact. The Earth's core and mantle did not become fully independent until after the Moon-forming impact (Newsom and Taylor, 1989). On the other hand, the Hf-W isotope system indicates that some siderophile elements have been stranded in the Earth's mantle from ∼11 Ma (Halliday, 1904). There is enough Ir and Os stranded in the Earth's mantle, if well mixed, to require the equivalent of a 17-km-thick chondritic veneer (Anders, 1989). The late veneer could be as thin as 4 km if contamination is limited to the upper mantle (Dauphas and Marty, 1902). We favor whole mantle mixing over geologic time, and so we favor the higher estimate. On the other hand much of the 17-km of the late veneer on the Earth could predate the moon-forming impact or date to the moon-forming impact itself (Newsom and Taylor, 1989). Hence the 17-km veneer appears to be a generous upper limit.

The Moon puts a much tighter limit on the late veneer (Sleep et al., 1989; Ryder, 1902). The Moon presented a suitable collection surface soon after it formed. The initial magma (or mush) ocean froze from the top down while being stirred by impacts (Hartmann, 1980). The date at which a mostly solid crust existed at any depth defines the start of the time interval for Ir and Ni retention in the lunar regolith. The oldest lunar rocks approach 4.5 Ga and indicate that a crust existed early in the history of the Moon (Swindle et al., 1986). The upper part of the lunar crust, ferroan anorthosite, solidified as early as 4.44 Ga (Carlson and Lugmair, 1988). The lunar crust was largely solid by 4.36 Ga (the model age of KREEP), which is believed to mark the final solidification of the base of the crust (Carlson and Lugmair, 1979).

The Moon makes a good meteorite detector because the lunar mantle and crustal melts derived from it are highly depleted in siderophile elements (Drake, 1986). The presence of siderophiles like Ir and Ni in the lunar crust therefore indicates meteoritic contamination. Rocks exposed in the lunar highlands, which are believed to be typical of the lunar upper crust, are breccias composed of pristine rocks, impact melts, and still older breccias. It is generally agreed that Ir abundances indicate a meteoritic component of 1–2%. A slightly higher but broadly consistent estimate of 2–4% is obtained from Ni (Ni is not as siderophilic as Ir). Studies of lunar meteorites indicate that the excess nickel is local to the nearside landing sites and that the planetwide meteoritic component is between 1 and 2% (Warren et al., 1989).

To convert a surficial 1–2% contamination into an equivalent late veneer requires defining an effective mixing depth of the lunar regolith. In our earlier work (Sleep et al., 1989; Zahnle and Sleep, 1997), we interpreted siderophile-rich 4.26 Ga lunar "granulite" samples (Lindstrom and Lindstrom, 1986) as breccias that had become deeply buried and were later exhumed. Our interpretation implied a deep well-mixed crust, and it implied that much of the meteoritic flux predates 4.26 Ga. However, these rocks probably formed at much shallower depths, hundreds of meters (Cushing et al., 1999). Ryder (2002) attributes the granulites to metamorphism within relatively small craters at shallow depths following Cushing et al. (1999). (Lunar scientists apply the term "granulite" in a way that is misleading to those used to terrestrial rocks. Lunar granulites are actually fine-grained.) If shallow, all that the granulites tell us is that there were impacts before 4.26 Ga.

The megaregolith thickness from seismic studies provides a more defensible estimate of the mixing depth. Spudis and Davis (1986) give 35 km as the half-thickness of the lunar crust. This is best regarded as an upper limit on the mixing depth because, for big impacts especially, impact-generated shock waves propagate to depths well below the excavated crater. *In situ* damage by shock waves rather than redistribution of ejecta can account for the megaregolith. This is most important for big impacts because the damaged volume scales as the energy of the impact, while the ejecta volume scales as $E^{0.78}$. If we take the Hugoniot elastic limit ($\sim 3 \times 10^{10}$ dynes/cm^2 for lunar rocks) as the threshold for significant damage, and presume that the peak shock pressure decays as r^{-3} from a peak impact shock pressure of $\sim 2 \times 10^{12}$ dynes/cm^2 over a volume comparable to that of the impactor centered an impactor diameter below the original surface, we would conclude that significant damage extends to a depth ~ 3 impactor diameters. With these assumptions a 35-km damage depth corresponds to an 80-km transient crater, which in turn corresponds to a mixing depth of 16 km.

A fraction of the impacting material is lost to space. If the impact velocity is high enough, a large part of the impactor escapes to space either as vapor or within ejecta (Melosh and Vickery, 1989). Complete vaporization of rock impactors is expected to occur when the normal component of the impact velocity is greater than about 16 km/s. (Sleep and Zahnle, 1998); 50% vaporization occurs at 13 km/s. Given the low 2.4 km/s lunar escape velocity, such vapors mostly escape. Unvaporized material may not escape as easily. Typical maximum ejecta velocities are of order 1/6th to 1/10th of the impact velocity (Melosh, 1989 p. 57). For impact velocities below 12 km/s, maximum ejection velocities should be no more than 1.2–2.0 km/s, lower than the lunar escape velocity. For asteroids, which hit the Moon with a median velocity of 13 km/s, escape is a factor 2 correction (Chyba, 1991).

In contrast, the Moon rarely retains cometary material as the impact velocity typically exceeds 20 km/s (Olsson-Steele, 1987). Icy bodies striking rock vaporize at ∼10 km/s. The absence of lunar polar caps confirms only that cometary vapors are hard to retain. Whether cometary Ir is swept away with the cometary volatiles is uncertain, but the mass fraction of Ir in comets is also smaller than that in asteroids. The siderophile component on the Moon provides no useful constraint on cometary flux.

If the meteoritic component is between 1% and 2%, a 16-km mixing depth and a 50% asteroid retention rate implies a total incident veneer 0.32–0.64-km thick. For a crustal density of 3 g/cm^3, the higher estimate (our preference) is equivalent to 7×10^{22} g. This is comparable to estimates of the same quantity by Chyba (1991), who gives $4 \times 10^{22} - 15 \times 10^{22}$ g, and Morgan et al. (2001), who give 10×10^{22} g. It is larger than Ryder's (2002) estimate of 1×10^{22} g, but Ryder neglects escape and he assumes that the mixed regolith layer is cleaner than we have taken it to be.

A different window on these matters is to consider the direct evidence for impact stirring of the lunar surface. Large impacts were rare enough that regional heterogeneities, primary stratification, and even local igneous bodies have not been obliterated (Pieters, 1986; Davis and Spudis, 1987, Ryder, 1902). We would see the effects of any Imbrium-sized or larger impacts after the upper crust froze at 4.44 Ga and definitely after the whole crust froze at 4.36 Ga because lower crust rocks would outcrop. In fact, only the largest of the known lunar impacts, S. Pole-Aitken, shows any hint of having excavated mantle. Similarly troctolite, an expected constituent of the lower crust, which was excavated by Imbrium, is quite rare (Marvin et al., 1989). These arguments against a large number of cryptic impacts apply to comets as well as asteroids. A massive flux of large comets on the Moon is precluded by the data, but some of the large basins could have been excavated by comets.

7.3.3 Chronology of the Late Bombardment

The timing of the lunar impacts is poorly constrained as the ages of many of the lunar basins are unknown. In particular, the impact flux may not have declined monotonically (e.g., Ryder, 2002, 2003). Rather, the impact flux between 3.8 and 4.0 Ga may have been significantly higher than the impact flux before then. This terminal cataclysm is consistent with what is known about lunar basin ages, but the age of the largest basin, South Pole-Aiken, is unknown and the age of Nectaris has been subject to controversy.

The strongest evidence for a cataclysm involves impact melts whose ages give times that the Moon was hit. As expected from the cataclysm hypothesis, most of these ages fall within the interval of the postulated cataclysm. There are few older ages, which Ryder (2002, 2003) attributes to a peaceful period of low impact flux between the formation of the Moon and the cataclysm. He contends that this is not an artifact of poor preservation of impact melts older than the cataclysm because grossly similar igneous melts that are older than the putative cataclysm are well preserved and well sampled. Ryder's perspective is not universally accepted. Lunar argon–argon ages are spread between 3.7 and 4.1 Ga and older dates are present; they do not generally show a tight clustering in time (Bogard, 1995). Lunar Sr-Rb ages show a similar age distribution. Moreover, radiometric ages of the eucrite parent body show no sign of the cataclysm (Bogard, 1995) that should have affected Vesta at the same time that it affected the Moon.

Figure 7.1 compares various concepts of the lunar bombardment. The curve denoted "Wilhelms" is adapted from the recommended chronology based on *Apollo* dated surfaces as given by Wilhelms (1987, p. 160). It is illustrative of the aggressively extrapolated lunar cratering history favored by Shoemaker and others. For this curve the e-folding decay time of the late bombardment is 100 Ma. Shown for comparison is Neukum's standard lunar

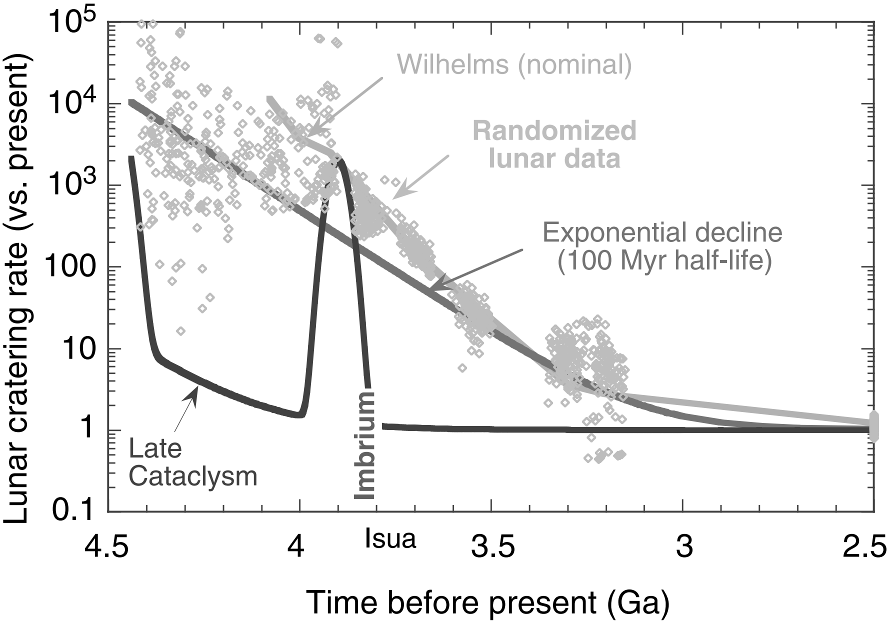

Fig. 7.1. Four concepts of the lunar bombardment. The curve denoted "Wilhelms (nominal)" illustrates the data-driven but extrapolated history favored by Wilhlems (1987). It has an e-folding time of 100 Ma (70 Ma half-life). Neukum's standard lunar crater curve (Ivanov and Neukum, 1994) is labeled "Exponential Decline (100 Myr half-life)." Third is a schematic but quantitatively representative late cataclysm as advocated by Ryder (2002, 2003). Fourth – the clouds of diamonds – are our own Monte Carlo construct, generated by choosing random values consistent with the quoted range of uncertainties in the surface ages and crater counts.

crater curve, which has a 144 Ma e-folding timescale (Ivanov and Neukum, 1994). Also shown for comparison is a schematic but quantitatively representative illustration of the late cataclysm as it was advocated by Ryder (2002, 2003). (It accurately represents both the magnitude and duration of the event and the placid times that preceded it according to Ryder's teachings.)

The clouds of diamonds are our own Monte Carlo construct. They were generated by choosing random values within the full range of uncertainties in the crater counts and the ages of surfaces (Table 11.1 and Figure 8.16 in Wilhelms, 1987). The range of the error bars (Table 7.1) corresponds to the range of random values. The oldest impact fluxes are essentially unconstained. The relative flux F at a time $t_1 < t < t_2$ is computed to second order from crater densities $N_1 < N < N_2$ by

$$F(t) = \frac{25}{17}\frac{(N_2 - N)(t_1 - t)^2 - (N_1 - N)(t_2 - t)^2}{(t_2 - t)(t_1 - t)^2 - (t_1 - t)(t_2 - t)^2}. \tag{7.4}$$

Table 7.1. Random lunar bombardment

	Wilhelms ranges		Model ranges	
	Time (GA)	Crater Density[a]	Time (GA)	Crater Density[a]
Apollo 12	3.16	$2.4^{+0.3}_{0.4}$	3.2 ± 0.06	$2.4^{+0.4}_{0.5}$
Apollo 15	3.25	$2.6^{+0.6}_{0.4}$	3.3 ± 0.06	$2.6^{+0.7}_{0.5}$
Apollo 11	3.57	$3.4^{+3.6}_{1.6}$	3.55 ± 0.06	$3.5^{+4}_{1.5}$
Apollo 17	3.72	$9^{+2.3}_{3.0}$	3.7 ± 0.06	$9^{+2.5}_{3.5}$
Imbrium	3.86	25-48	3.83 ± 0.03	30^{+5}_{-3}
Nectaris	$3.92^{+0.23}_{-0.02}$	100^{+10}_{-20}	$3.92^{+0.23}_{-0.02}$	100^{+20}_{-30}
S.P.-A.[b]	$t_{\mathrm{Nec}} < t < 4.3$	300^{+150}_{-100}	$t_{\mathrm{Nec}} < t < 4.4$	300^{+100}_{-100}
pre-SPA		> 700	$t_{\mathrm{SPA}} < t < 4.44$	$< 10N_{\mathrm{SPA}}$

[a] Units: number of craters wider than 1 km diameter per 10^3 km^2.

[b] Actually Al-Khwarizmi/King.

The factor 25/17 is a normalizing factor that represents a modern cratering rate of 1.7 craters wider than 1-km diameter per 10^3 km^2 over the past 2.5 Gyr. The resulting random fluxes plotted against their corresponding random times.

7.4 The Late Bombardment on the Earth

The Earth and Moon are subject to collisions with the same impactors. One expects the Earth to be hit more often and to greater consequence, for two reasons. The first is that the Earth's cross section is larger and it is enhanced by gravitational focusing. The second reason is statistical. The mass spectra of smaller solar system objects appear to obey power laws in which most of the mass is concentrated in the few largest objects (e.g., Dohnanyi, 1972; Chapman et al., 1979). Because the Earth's effective collisional cross section greatly exceeds the Moon's, in most trials the Earth will accrete *all* of the largest objects in a population of Earth/Moon impactors (Sleep et al., 1989). As these carry most of the mass and energy, in most trials the Earth is much more heavily impacted.

The greatest uncertainty in scaling the lunar impact record to the early Earth lies in the mass distribution of the impactors. We will proceed on the assumption that the population of late Earth impacting objects was a scale-invariant (power law) distribution of collisional fragments resembling the population of asteroids and comets today. If the mass distribution obeyed by the smaller objects that formed lunar craters and basins can be extrapolated to larger impactors, then the masses of the largest impactors can be estimated with some confidence. The most important residual uncertainties are the inevitable uncertainties associated with small number statistics.

7.4.1 Impactor Mass Distribution

The mass distributions of asteroids and comets are usefully described by power laws of form

$$N(>m) = Cm^{1-q} \approx \left(\frac{m_1}{m}\right)^{q-1} , \tag{7.5}$$

where $N(>m)$ is the cumulative number of objects with mass greater than m, q is the exponent of the differential mass distribution $\partial N/\partial m$, and C is a constant related to m_1, the largest object in the distribution. The differential form

$$\frac{\partial N}{\partial m} \approx \frac{q-1}{m_1}\left(\frac{m}{m_1}\right)^{-q} , \tag{7.6}$$

is useful for integations. The most important properties of the power law are that it is scale-free and that, for $q < 2$, most of the mass is in the largest objects. The latter ensures that the cumulative effects of impacts are always dominated by small-number statistics at all scales. The probable origin of the power law is a self-similar fragmentation cascade.

Reported values of q range from about 1.3 to 2.2, with the extreme values associated with comets. According to Safronov et al. (1986), $q \approx 1.6$ in a swarm of planetesimals dominated by coalescence; fragmentation increases q to $\sim$1.8. Dohnanyi (1972) calculated that in a collisionally evolved distribution $q \to 11/6$. Essentially the same result has also been obtained by Williams and Wetherill (1994) and by Tanaka et al. (1996). Asteroids with diameters between 100 and 250 km have $q \approx 2$ (Hughes, 1982; Donnison and Sugden, 1984). The best sample of a modern crater production population, that of Venus, is well matched by $q = 1.8$ (Zahnle, 1992; McKinnon et al., 1997).

Comets do not appear to obey a single power law. Familiar comets (1–10 km) seem to be described by $q \leq 1.7$ (Donnison, 1986; Hughes, 1988; Zahnle et al., 2003), but bigger and smaller comets are rarer than this. Weissman (1990) suggests that $q \approx 2.2$ for long period comets bigger than 10 km. The Kuiper Belt, the probable source of the short period comets, seems to be telling the same story: Kuiper Belt Objects bigger than 50 km across apparently obey a $q \approx 2.1$ power law distribution (Gladman et al., 2001; Trujillo et al., 2001). In the other direction, Zahnle et al. (2003) argue from the discovery history of comets and from the paucity of small impact craters on the Galilean satellites that $q \approx 1.3$ for comets smaller than 0.5 km.

Lunar craters and basins of the late bombardment appear to demand low values of q. The consensus size distribution of lunar highland craters is $N(> D) \propto D^{-b}$, with $b = 1.8$, fit to craters between 10 and 80 km diameters (Wilhelms, 1987, p. 257). Because these craters date from the end of the late heavy bombardment they are directly relevant. Crater-diameter scaling relations like Eq. (7.2) or (7.3) are then inverted to obtain $q = 1 + 0.26b \approx 1.5$ (Maher and Stevenson, 1988, Melosh and Vickery, 1989, Chyba, 1991). Chyba (1991) includes slumping by using Eq. (7.3) to get $q = 1.54$.

The late large lunar basins are consistent with the crater distribution. Wilhelms lists 14 lunar basins from Nectaris to the present. (Lunar "basins" are defined as craters bigger than 300 km diameter.) The largest of these is Imbrium, for which we have estimated a nominal energy release of 2×10^{33} ergs (see above). The smallest, call it Schrödinger, is essentially a big crater; if treated as a crater its impact energy would be $\sim 4 \times 10^{31}$ ergs. For similar impact velocities, Eq. (7.5) implies that

$$q = 1 + \frac{\log\{N(>m_{\mathrm{Sc}}) \div N(>m_{\mathrm{Im}})\}}{\log\{m_{\mathrm{Im}} \div m_{\mathrm{Sc}}\}} = 1 + \frac{\log(14)}{\log(50)} = 1.67. \tag{7.7}$$

This q is consistent with the record for smaller craters and consistent with a cometary source. The same argument applied to the 45+ basins postdating S. Pole Aitken gives the same result

$$q > 1 + \frac{\log(45)}{\log(300)} = 1.67. \tag{7.8}$$

This is considerably uncertain in either direction because (i) S. Pole-Aitken may have been much bigger than we have assumed, and (ii) many of the basins postdating S. Pole-Aitken have been obliterated.

In our opinion, $q = 1.54$ should be viewed as a lower limit because (i) large craters retain their "youthful" appearance longer than do small craters, skewing frequency estimates for craters of a given age; and (ii) large lunar craters do not look like small craters, which violates the assumption of self-similarity by which impactor mass is deduced from crater diameter. We will use $q = 1.7$ unless otherwise noted. Raising q to 1.7 requires raising b to 2.4.

The total mass M_{T} accumulated by the Earth or the Moon is on average directly proportional to the mass of the largest impactor, although the statistical relation between M_{T} and m_1 is very broad. The median value of M_{T}/m_1 is (Tremaine and Dones, 1993)

$$\frac{M_{\mathrm{T}}}{m_1} \approx \frac{4q - q^2 - 2}{2(2-q)(3-q)} \ln\left(\frac{2}{q-1}\right), \tag{7.9}$$

where $1 < q < 2$. The paucity of obvious mantle samples suggests that S. Pole-Aitken could be the largest lunar basin to postdate the solidification of the lunar crust. The low estimate of its impact energy implies a mass of $m_1 \approx 1 \times 10^{22}$ g. This is about one seventh of the total integrated flux required for our nominal 0.64 km late chondritic veneer. Equation (7.9) then implies that $q \approx 1.9$. Reversing the argument, $q = 1.67$ implies that $m_1 \approx 3 \times 10^{22}$ g.

Because power law distributions with $1.3 < q < 1.9$ are dominated by a few large bodies, the predictive value of Eq. (7.9) is necessarily limited by small number statistics: there is a 20% chance that a ratio of m_1/M_{T} as small as 1/8 could fall from a $q = 1.8$ distribution and a 5% chance that it could fall from a $q = 1.7$ distribution. It is also plausible that SPA was bigger than we estimate. A third alternative is to invoke a hidden, larger impact than SPA.

An obvious candidate would be the putative Procellarum basin (Wilhelms, 1987). This impact would be responsible for much of M_{T}.

A dominant cometary source is more difficult to reconcile with the lunar record. There are three reasons: (i) Like asteroids, comets make basins, but for a given basin they leave much less iridium behind. For asteroids the Moon's retention of 0.32 km of chondritic matter corresponds to an energy flux of 6×10^{34} ergs; for comets the same amount of iridium corresponds to an energy flux at least an order of magnitude greater. Evidence for this much greater flux is missing. There should be a half-dozen basins as big as or bigger than S. Pole-Aitken. Mantle samples should be ubiquitous; they're not. (ii) Big comets appear subject to a relatively high value of q. High q is not consistent with the size–number distribution of the lunar basins. (iii) Comets are unpromising candidates for the LHB on dynamical grounds (Zahnle, 1998, Hartmann et al., 2000). Only about one comet in a million hits the Earth; it is much easier for asteroids to hit the Earth. Figure 7.2 shows the relative likelihood that a stray body from a given part of the solar system will hit Earth.

The relative cometary impact rates on Jupiter to the Earth is about 10, 000 to 1 for Jupiter-family comets and about a hundred, to one for long period or Halley-type comets. To deliver a 0.32-km chondritic veneer to the Moon with Jupiter-family comets with 10% Ir retention requires delivering about 10 Earth masses of comet to Jupiter. To deliver a 0.32-km chondritic veneer to the Moon with long period comets with 1% Ir retention requires delivering about an Earth mass to Jupiter. Obviously these estimates do not prove anything; they merely illustrate the magnitude of the problem.

7.4.2 Scaling the Lunar Impact Record to the Earth

The larger gravity of the Earth attracts more impactors and gives them greater energy than if they had hit the Moon. The energy of an object in solar orbit hitting a planet is

$$E = \frac{m v_\infty^2}{2} \left(1 + \frac{v_{\mathrm{esc}}^2}{v_\infty^2}\right) \tag{7.10}$$

where v_{esc} is the escape velocity and v_∞ the approach velocity far from the planet. Similarly, the effective capture cross-section is

$$A = \pi R_p^2 \left(1 + \frac{v_{\mathrm{esc}}^2}{v_\infty^2}\right) \tag{7.11}$$

The escape velocity from the Earth is 11.2 km/s and from the Moon is 2.4 km/s. The average impact velocity on the Earth of the present population of asteroids in Earth-crossing orbits is 16.1 km/s, weighted by the probability of impact (computed using Öpik's formulae (Shoemaker et al., 1982) from near-Earth asteroids tabulated by Shoemaker et al. (1990)). The average impact velocity on the Moon, also weighted by collision probability, is 13.0 km/s. The latter is effectively also the average approach velocity to the Earth. With

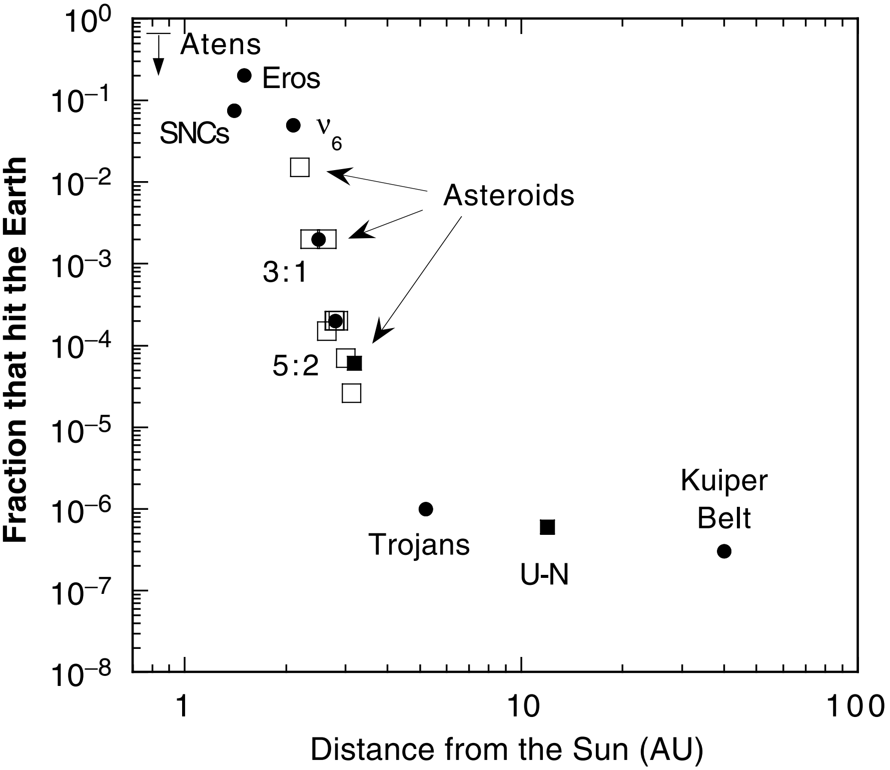

Fig. 7.2. The relative likelihood that a stray body from a given part of the solar system will hit the Earth. Computational results are taken from Levison and Duncan (1997) for the Kuiper Belt; Levison et al. (2002) for the Uranus–Neptune region; Levison et al. (1997) for the Trojan asteroids; main belt asteroids from Zappala et al. (1997); key resonances from Gladman et al. (1996); martian meteorites (SNCs) from Gladman (1997); and Luke Dones (personal communication, 2004) for Eros and the Aten asteroids.

$v_\infty = 13$ km/s, the total impact probability on the Earth is 23 times that on the Moon, which corresponds to a relative accretion rate per unit area by the Earth 1.7 times that of the Moon. The ratios of impact velocity and impact probability do not scale precisely as predicted by Eqs. (7.10) and (7.11) because gravitational focusing has its greatest effect on the slowest bodies; thus the Earth's cross-sectional advantage over the Moon is greatest for the objects with the lowest encounter velocities. For comets the gravitational enhancements are unimportant.

The second factor that affects scaling the impact record from the Moon to the Earth is the value of the power law exponent q. This stems from the rarity of the largest impacts in scale-invariant distributions. For a total impact probability 23 times higher on the Earth than the Moon, the Moon is hit by 4.2% of the impactors and Earth by the remaining 95.8%. Over a large number of trials the Moon will, on average, accrete 4.2% of the total mass, since in a few trials it will get hit by one of the two or three largest bodies. But in half the trials the Moon is not hit by any of the 16 largest objects, since $(0.958)^{16} > 0.5$. In most trials the Moon significantly undersamples the total mass of the impactors. The degree of undersampling is greater the more strongly the total mass of the swarm is concentrated in the largest objects; hence the dependence on q.

From a scale-invariant distribution of potential impactors the cumulative number $N_{\mathrm{e}}(>m)$ of objects greater than mass m striking the Earth is

$$N_{\mathrm{e}}(>m) = A_{\mathrm{e}} C m^{1-q} \tag{7.12}$$

and the cumulative number of objects striking the Moon is (Eq. (7.5))

$$N_{\mathrm{m}}(>m) = A_{\mathrm{m}} C m^{1-q} \tag{7.13}$$

where A_{e} and A_{m} are the effective cross-sectional areas of the Earth and Moon as given by Eq. (7.11). The ratio of the largest objects striking the Earth and the Moon is

$$\frac{N_{\mathrm{e}}(>m_{\mathrm{e}}) \approx 1}{N_{\mathrm{m}}(>m_{\mathrm{m}}) \approx 1} = 1 = \frac{A_{\mathrm{e}} m_{\mathrm{e}}^{1-q}}{A_{\mathrm{m}} m_{\mathrm{m}}^{1-q}} \tag{7.14}$$

Hence the largest object hitting Earth exceeds the largest object hitting the Moon by the factor

$$m_{\mathrm{e}}/m_{\mathrm{m}} = (A_{\mathrm{e}}/A_{\mathrm{m}})^{1/(q-1)} . \tag{7.15}$$

Depending on q, this ratio can easily reach 100. The same arguments also apply to different time intervals, so that a 10 times longer window in time would correspond to $10^{1/(q-1)}$ times more impact flux (Anbar et al., 2001). If 2×10^{33} ergs is taken as the energy of the Imbrium impact, Eq. (7.15) implies that it is quite reasonable for the Earth to have suffered a more or less contemporaneous impact releasing more than 10^{35} ergs, potentially enough energy to vaporize the oceans (see below).

In the median case the Earth accretes $23^{1/(q-1)}$ times more material than does the Moon. For $q = 11/6$, the median case is for ~40 times as much mass to hit the Earth as hits the Moon. For $q = 1.5$, this rises to ~500 times the mass hitting the moon. The bias disappears as $q \to 2$ because most of the mass is then in a large number of small objects. When this bias is taken into account, the inferred 0.64-km blanket of incident material on the Moon (of which 50% is retained by the Moon) inflates to 1.1 km on the Earth for $q = 2$, 2.0 km ($q = 11/6$), 5.2 km ($q = 5/3$), or even 25 km ($q = 1.5$). Thus, if q were small enough, it is possible that a 17-km late chondritic veneer supplying the excess siderophiles in the Earth's mantle could be the Earth's expected complement of the same veneer that left some 320 m of chondritic material in the lunar crust (Chyba, 1991). If so, most of that 17 km would necessarily have been delivered by a single object in a collision releasing $> 10^{37}$ ergs. On

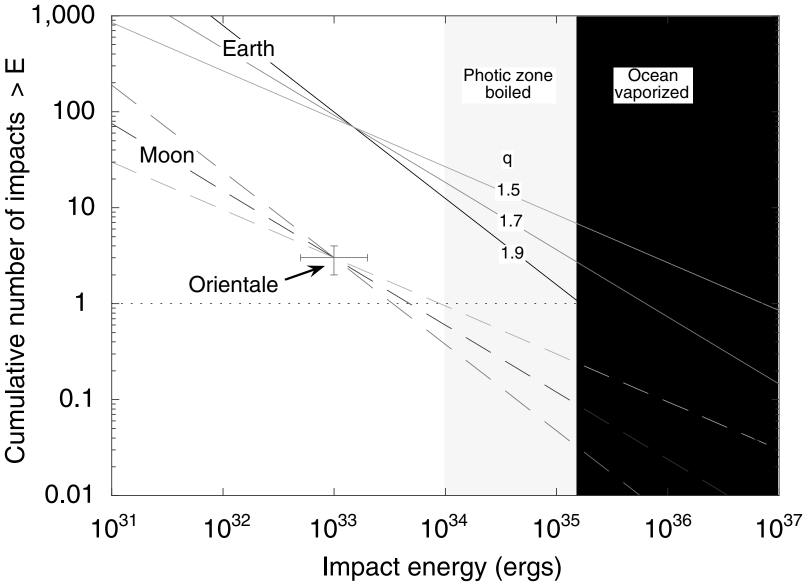

Fig. 7.3. Predicted numbers and energies of terrestrial impacts, scaled from the lunar record at the time of Orientale, Imbrium, and Nectaris. This addresses the period between 3.7 and 4.1 Ga. If extended earlier to include South Pole-Aitken the numbers would be shifted upward by about a factor of 4. The figure shows the number of impacts on the Earth with energies greater than a given energy E as scaled from the energies of the lunar Orientale and Imbrium basins. In this scaling a given object is 23 times more likely to strike the Earth than the Moon, and releases about 50% more energy on the impact. The different curves are labeled by the power law index q, where the cumulative number of impactors with mass greater than m is given by $N(> m) \propto m^{1-q}$. Distributions with smaller values of q are characterized by markedly more enormous impacts.

the other hand, it is not necessary that the Earth accrete its 17 km while the Moon accreted its 320 m, since much or most of this 17 km may have predated the freezing of the lunar crust.

Figure 7.3 illustrates how the lunar basin-forming events ca. 4 billion years ago scale to the Earth. The time interval is approximately 3.7–4.1 Ga, corresponding to impacts after Nectaris. The point marked “Orientale” ranks Orientale third among lunar basins, the ranking given to it by Wilhelms (1987). For specificity the energy released by the Orientale impact is taken to be $1^{+1}_{-.5} \times 10^{33}$ ergs. Cumulative distributions with different plausible slopes are then drawn through the Orientale point. The error bars around “Orientale” should be understood as broadening each line into a diffuse band.

Parallel to, but offset in number and energy, are the corresponding cumulative distributions for impacts on the Earth. The offset in energy is the relatively small factor of 1.5 that results from the Earth’s gravity. The offset in number is the Earth's higher effective cross section, here a factor 23. Marked also is the energy required to vaporize the oceans. Extrapolation to the largest terrestrial impacts illustrates graphically what Eq. (7.15) illustrates algebraically: the chance that one or two impacts of ocean-vaporizing scale occurred on the Earth during the late heavy bombardment is considerable. There is a high probability that during this same interval several impacts occurred that were large enough to vaporize several hundred meters of the top of the oceans; a few of these events would have occurred every hundred million years. The difficulties these would have presented for the continuous habitability of the photic zone are obvious. These matters will be discussed in more detail below.

Another view of the impact history of early Earth is given in Fig. 7.4. This figure shows the largest impacts at given times in the Earth's and Moon's history. The curve for the Earth is mostly scaled from the lunar record, although the Earth has independently recorded some distinctly large events. We have included in the scaling to the Earth the one larger, hypothetical impact predating S. Pole-Aitken that is implied by $q < 1.8$. The energies of smaller craters were estimated using Eqs. (7.2) and (7.3). Errors are indicated by the spans of the ovals. The relative error may be smaller, but the absolute error may be larger – there are many potential sources of systematic error that can affect extrapolation of laboratory cratering relationships to 200-km impact craters.

7.5 Environmental Effects of Large Impacts on the Earth

We begin this section by recounting the events that follow an ocean-vaporizing impact.

7.5.1 An Ocean Vaporizing Impact

The mass of the oceans is 1.4×10^{24} g. When evaporated, the oceans transform into a 270-bar steam atmosphere. Because this exceeds water's critical pressure of 220 bars, what is meant by evaporating the oceans is not entirely clear, since above the critical point there is no distinction between liquid and vapor. For specificity we will regard water's critical temperature of 647 K as the definition of total evaporation. The latent heat of vaporization of water at 273 K is 2.5×10^{10} ergs/g and the specific heat of water vapor is 1.9×10^{7} ergs/g. Therefore it takes a minimum of 4.4×10^{34} ergs to evaporate the oceans.

To illustrate the magnitude of an ocean-vaporizing impact, as a first approximation assume that roughly a quarter of the energy released by the impact is spent evaporating water, with the balance buried in the crust and mantle or radiated to space (Sleep et al., 1989). This corresponds to the impact

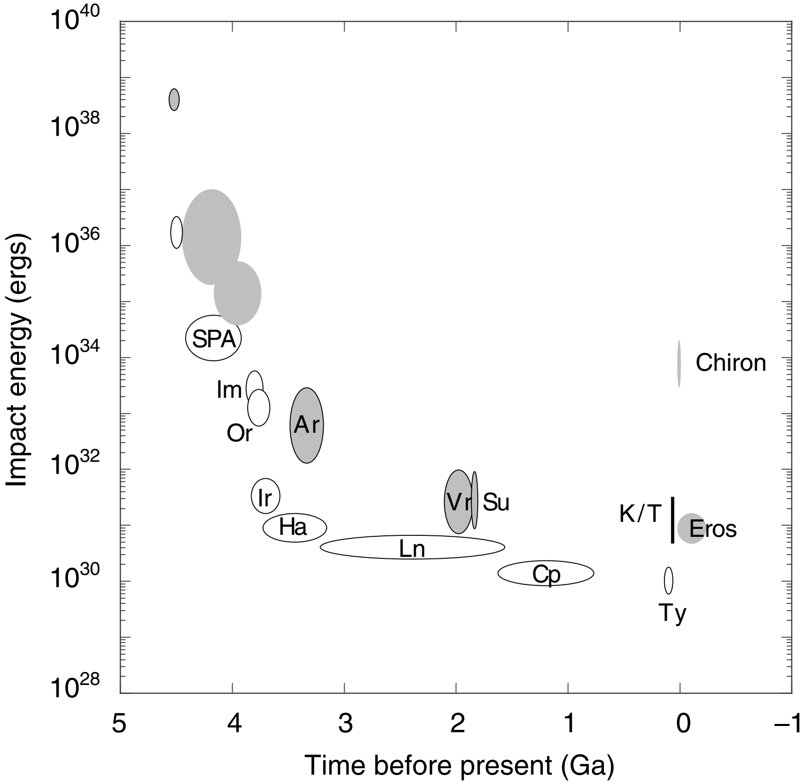

Fig. 7.4. The largest impacts before the present for Moon and the Earth. Open boxes are lunar, and shaded boxes are terrestrial. The dimensions of the boxes indicate uncertainties. The stipled region shows the inferred largest impacts on the Earth. The right-hand axis is the depth of ocean vaporized by the impact. The three earliest events (4.5 BY) shown are the energies of the Earth and Moon formation and the moon-forming impact. Energies and dates of basin-forming impacts are discussed in the text. The lunar craters are Tycho, Copernicus, Langrenus, Hausen, and Iridum; diameters and approximate ages are adapted from Wilhelms (1987). Size and dates of terrestrial impacts at Sudbury and Vredevort are taken from Grieve (1982). Energies of the impacts generating 4 Archean spherule beds between 3.2 and 3.5 Ga are estimated following Kyte et al. (2003). The Chicxulub crater (the K/T crater, 65 Ma) is at least 180 km diameter (Hildebrand et al., 1991). Eros and Chiron remain potential sources of future troubles.

of a 1.2×10^{23} g asteroid at a typical collision velocity of 17 km/s. This asteroid would be 450 km diameter, smaller than Ceres or Texas, but comparable to Vesta and Pallas.

At least a few impactor masses of ejecta are expected. For example, when applied to a 1.2×10^{23} g body striking at 17 km/s, Eqs. (7.2), (7.3), and (7.1) imply a crater diameter of about ~ 2500 km, and some $\sim 2 \times 10^{23}$ g of ejecta from the target and another ~1.2×10^{23} g from the impactor. The former is an underestimate for an impact on this scale because it excludes rock vapor that Eq. (7.1) would leave inside the crater. Much of the ejecta would be hot rock vapor created on impact; most of the rest would be melt droplets and grains destined eventually to be evaporated by later events, such as mixing with hotter vapors or atmospheric re-entry heating (Sleep et al., 1989; Zahnle, 1990; Melosh et al., 1990; Sleep and Zahnle, 1998). The ejecta produce a ~60-bar rock vapor atmosphere with an energy of 5×10^{34} ergs that displaces any preexisting thin atmosphere. After a few sound crossing times – a day or three – the rock vapor atmosphere should smooth out globally and settle into hydrostatic equilibrium. It is through the rock vapor that much of the impact's energy is globally distributed.

Rock Vapor

Panel (*a*) of Fig. 7.5 begins at this point. The rock vapor atmosphere radiates to space with an effective temperature of order ~2,000 K. The saturation vapor pressure of rock is sensitive to temperature, and therefore the cloudtop temperature is relatively insensitive to details.

The high radiating temperature demands rapid condensation and corresponding very strong updrafts. In addition to the updrafts associated with weather, there is a net updraft of $w = 0.4\,(T_{\mathrm{rad}}/2000\ \mathrm{K})^4\,(p/60\ \mathrm{bars})$ cm/s below the photosphere, driven by silicate condensation (assumes a latent heat of condensation of 1.4×10^{11} ergs/g for silicates). This gets large at low pressures. One speculates that local, weather-driven velocities may approach the sound speed, given the enormous energy fluxes present.

These winds must strongly influence the pressure level and droplet size at the cloudtops. Rayleigh–Taylor instability suggests that liquid drops get no larger than $\sim\sqrt{T/g\rho_{\mathrm{drop}}}$ ~0.2 cm (radius), for reasonable surface tensions of silicate drops in a silicate vapor, where T is the surface tension and g the acceleration (we have assumed that surface tensions of silicates in a silicate vapor are ~100 dynes/cm, a few-fold smaller than what they are in air (Walker and Mullins, 1981)). When unstable, the hydrodynamic instabilites have fast growth rates on the order of 10 s^{-1}. Comparing terminal velocity for 0.2-cm drops to the updraft velocity suggests that rock rain can fall at pressures above (altitudes below) ~0.1 bars. At higher altitudes, solitary drops cannot get big enough to fall; they must be transported by convective eddies, freeze (hailstones), or fall collectively. Silicates vary in their triple point pressures. Some have a much stronger preference to be liquid than water. We speculate that the photosphere is defined by a mist of wind-whipped, wind-sheared spray, the size of the drops determined by the aerodynamic accelerations.

As an illustrative example, consider cloudtops in which 0.1% of the mass is condensed as 100-μm droplets. Such a cloud becomes optically thick at 40 mbars, comparable to the altitude where raindrops can get large enough to fall. The saturation vapor pressure of a mixture of forsterite (Mg_2SiO_4) and

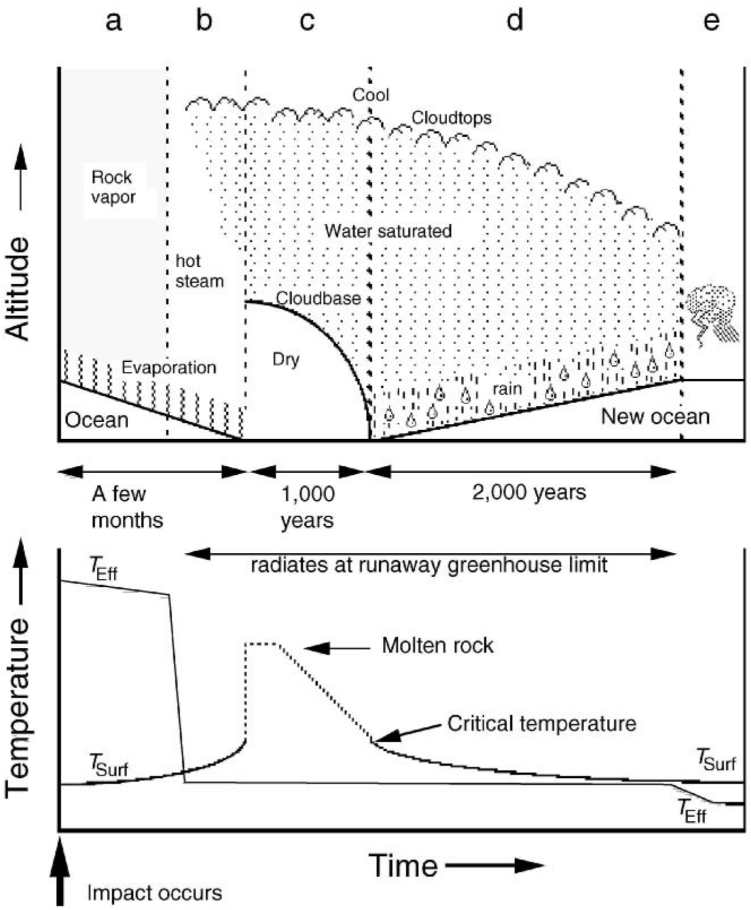

Fig. 7.5. History of an ocean vaporizing impact. (a, b) An impact on this scale produces about 100 atmospheres of rock vapor. Somewhat more than half the energy initially present in the rock vapor is spent boiling water off the surface of the ocean, the rest is radiated to space at an effective temperature of order 2,300 K. (c) Once the rock vapor has condensed the steam cools and forms clouds. (c, d) Thereafter cool cloudtops ensure that the Earth cools no faster than the runaway greenhouse threshold, with an effective radiating temperature of order 300 K. In the minimal ocean vaporizing impact the last brine pools are evaporated as the first raindrops fall. For somewhat larger impacts a transient runaway greenhouse results, with the surface temperature reaching the melting point.

silica at $T \approx 2,000$ K can be approximated by (Mysen and Kushiro, 1988)

$$p_{\mathrm{rv}} = 3.6 \times 10^{10} \exp\left(-68{,}900/T\right) \text{ bars}. \tag{7.16}$$

The vapor consists mostly of Mg, SiO_2, SiO, and O_2, with a mean molecular weight of ∼40. The scale height at 2,500 K is ∼50 km. Equation (7.16) implies a temperature at 40 mbars of 2,500 K. If the droplets were increased to 1 mm, the saturation vapor pressure at optical depth unity would rise to 0.4 bars and the temperature to 2,700 K; if the mass fraction in condensates were increased to 1% or the droplets shrunk to 10 μm, the saturation vapor pressure at optical depth unity would fall to 4 mbars and the temperature to 2,300 K.

Even radiating as a 2,300 K blackbody, it would take a few months to radiate away the energy ($>10^{35}$ ergs) initially present in the rock vapor. At least as much energy is radiated down onto the oceans as is radiated directly to space, because the temperature at the bottom of the atmosphere will be higher than at the top. The high opacity of seawater to infrared radiation (Suits, 1979) concentrates radiative heating in a thin surface layer. Boiling is confined to this layer. In a sense, thermal radiation from the rock vapor ablates the surface of the ocean, leaving the ocean depths cool. The depth of the boiled layer is determined by compositional convection; the hot but extremely saline surface waters mix with enough of the relatively cool and less saline waters below to leave the surface waters at worst neutrally bouyant. In general, the density decrease from thermal expansion outweighs the density increase from higher salinity, so that boiling is limited to surface waters. This is described in more detail in the first edition of this book (Zahnle and Sleep, 1997).

Just above the surface there is a thin boundary layer where the temperature rises rapidly from the relatively cool boiling waters at the surface to the much hotter rock vapors above. Since water vapor is somewhat transparent to $> 2,000$ K thermal radiation (Kasting, 1988), the oceans are not effectively shielded from the hot rock above; yet the water vapor is sufficiently opaque that it is quickly heated to the atmospheric temperature. Once heated the bouyant water vapor rises through and mixes with the denser rock vapor, stirring and homogenizing the atmosphere. The atmosphere is doubtless vigorously convective, driven at the top by radiative cooling at the cloudtops and at the bottom by rising plumes of low density, water-rich gases. The temperature profile is effectively set by the saturation vapor pressure of rock. For a 60-bar rock vapor atmosphere, Eq. (7.16) implies a temperature near the surface of $\sim 3,400$ K. The radiative heat flux onto the oceans exceeds that to space by a factor of order $(3400/2300)^4 \approx 5$. This factor applies only to the oceans. On dry land the surface quickly heats to reach radiative equilibrium, and rocks begin to selectively melt and evaporate. As the oceans shrink, the relative importance of radiation to space grows. While the oceans remain, most of the energy in the atmosphere goes to evaporating sea water and heating water vapor. To evaporate and heat water vapor to 3,400 K takes some 8.2×10^{10} ergs/g; to do this to the oceans requires $\sim 1.2 \times 10^{35}$ ergs (This would require an impact ~ 3 times bigger than the minimal ocean vaporizing impact that we have been considering.) At an effective radiating temperature of 3,400 K, the cooling time of the atmosphere reduces to about a fortnight. The actual cooling time would be somewhere between a fortnight and a few months, depending on the relative surface areas of dry land and open seas.

Throughout this period a hot rock rain or hail falls into the ocean at a rate of meters per day. In the minimal ocean-vaporizing impact 200 m of precipitated rock eventually accumulate on the ocean floor. The thermal energy in the rain is considerable. The rainout of a 60-bar rock vapor atmosphere delivers about 1×10^{34} ergs, or roughly 20% of the energy assumed initially present in the ejecta. The raindrops are quenched near the surface, and so contribute to boiling (with a thermal diffusivity $\kappa = 0.01$ cm^2/s it takes about a second to cool a millimeter-size drop and about a minute to cool a centimeter-size drop).

Other heat sinks are probably unimportant. It takes less than 2×10^{32} ergs to heat a 1 bar N_2 atmosphere to 3,500 K. Even a 60-bar CO_2 atmosphere (if all the CO_2 in all the Earth's carbonates were put into the atmosphere) requires less than 10^{34} ergs to reach 3,500 K. In all likelihood the preexisting atmosphere is quickly raised to the temperature of the rock vapor, either by radiative heating or by mixing with the rock vapor.

The heat capacity of the crust on a timescale of months is also limited because the depth of heating is limited by thermal conduction. The problem is somewhat akin to ablation of meteors. Exposed surfaces would melt and flow downhill, exposing fresh rock. Low spots would also accumulate rock rain at a rate of meters per day. We expect that the net effect is that the original surface would heat to a depth comparable to the 200-m thickness of the ejecta blanket. Assuming a heat capacity of 1.4×10^7 ergs/g/K and a heat of fusion of 4×10^9 ergs/g, and an exposed surface covering 40% of the globe, the crust would absorb about 3×10^{33} ergs while heating to 1,500 K. This is small compared to the energy released by the impact.

Steam

After a month or two the rock vapor has fully condensed and fallen from the sky. Here begins panel (*b*) of Fig. 7.5. There remains behind a hot steam atmosphere, and if the impact were small enough, a hot salty ocean of considerable depth. The top of the steam atmosphere soon cools and condenses water clouds, and the effective radiating temperature drops to ∼300 K. Once a cool upper atmosphere is established radiative cooling to space falls off precipitously, but the flow of energy to the oceans does not. Hence most of the thermal energy that remains in the steam is used to evaporate water until either the oceans are gone or the atmosphere reaches saturation vapor pressure equilibrium at the surface of any remaining seas. For the minimal ocean-vaporizing impact, about half the ocean remains as liquid when the rock vapor has fallen out. The rest of the ocean is afterward evaporated by excess thermal energy present in the hot steam. Put figuratively, in the minimal ocean-vaporizing impact the last brine pools evaporate as the first rains fall on the mountains.

The properties of water vapor atmospheres in quasi-steady state have been studied in detail by Kasting (1988), Abe and Matsui (1988), and Nakajima et al., 1992. The central result of their work is that there is maximum rate at which a water atmosphere over a liquid ocean can radiate to space. This maximum is only some ∼40% higher than the Earth's present infrared flux. This is the "runaway greenhouse" threshold often encountered in comparative planetology.[3] Higher rates of radiative cooling correspond to atmospheres under which no liquid water is present at the surface. The threshold is reached when the infrared optical depth of the cool, moist cloudtops (the uppermost few bars of water vapor) becomes so great that no thermal radiation from the surface or lower atmosphere can escape to space. The planet's radiative cooling rate is then determined solely by the opacity and saturation vapor profiles of water at the cloudtops, and is effectively decoupled from conditions in the lower atmosphere or at the surface. For a mass of water vapor equal to a terrestrial ocean the surface temperature must reach at least approximately 1,500 K for the planetary infrared radiative flux to significantly exceed the runaway greenhouse threshold. The runaway greenhouse threshold for the Earth is 3.1×10^5 ergs cm^{-2} s^{-1}. This includes re-radiation of any incident sunlight. When the net solar irradiation 4 billion years ago is taken into account, the effective runaway greenhouse cooling rate would have been $\sim 1.5 \times 10^5$ ergs cm^{-2} s^{-1}. This assumes an albedo of 33%. With a higher albedo, the Earth would cool more quickly. But even with an albedo of 100% the effective cooling rate is only doubled.

The lifetime of the transient runaway greenhouse – the time it takes to cool and condense an ocean of hot steam – can be estimated by dividing the energy in the steam, plus the smaller amount of energy in hot crustal rock, by the effective runaway greenhouse cooling rate of 1.5×10^5 ergs cm^{-2} s^{-1}. It takes $\sim 4.5 \times 10^{34}$ ergs to evaporate the ocean, and an additional 2.2×10^{34} ergs to raise the steam to 1,500 K, at which point radiative cooling becomes more effective. It therefore takes about 900 years to cool the steam from 1,500 K to the critical temperature (Fig. 7.5, panel (*c*)), and another approximately 1,900 years to rain out the ocean and cool it to 300 K (panel (*d*)). The net globally averaged rainfall is about 150 cm/year. With allowance for the uncertain albedo, we estimate that it would have taken the Earth some 2,000–3,000 years to return to normalcy after an ocean evaporating impact. Abe (1988) gives somewhat shorter cooling times, but he assumes a 100-bar steam atmosphere.

Survival?

Once the oceans are vaporized, it takes little additional energy for the surface temperature to reach the melting point of rock. Yet there might remain possible refugia hidden deep below the surface, thermally insulated by several hundred meters of rock and sediment. The approximate depth of the extinc-

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[3] In the usual runaway greenhouse, as applied to ancient Venus or future Earth, the planet absorbs more sunlight than the atmosphere can radiate, and so the oceans evaporate.

tion horizon can be estimated by considering the propagation of the thermal pulse into the Earth.

We present a model based on the work of Sleep and Zahnle (1997) to illustrate the propagation of the heat pulse from an ocean-boiling impact on the Earth. We consider a subsurface oceanic environment. The heat flow from below is 0.125 W m^{-2}, approximately that through 16 Ma oceanic crust. We intend this to represent a relatively safe environment on the early Earth. The initial condition boils off the ocean and buries the original surface under 300 m of warm (300°C) ejecta. The surface temperature is set to 1300°C. Thereafter it is presumed to decrease linearly to 400°C over the next thousand years and then to 0°C over the next 3000 years.

Figure 7.6 shows the propagation of the thermal pulse into the crust. At 1,000 years temperatures have increased significantly down to 600-m depth.

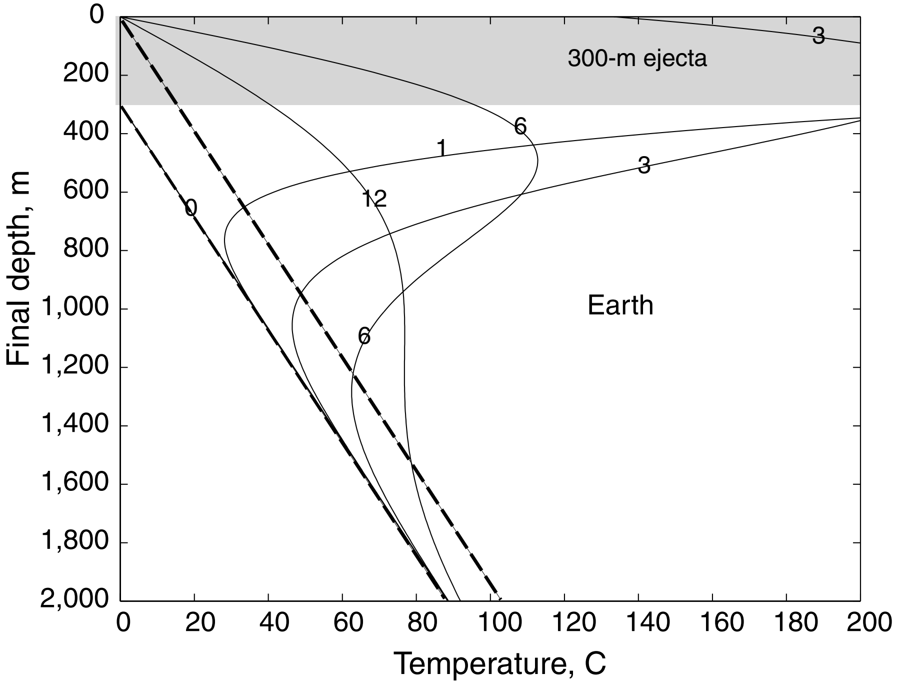

Fig. 7.6. Propagation of the thermal pulse produced by an ocean-vaporizing impact into the oceanic crust at a point far away from the impact. Times are marked in thousands of years. The initial condition is a warm (300°C) blanket of impact ejecta and a 1300°C surface temperature; the surface temperature cools to 0°C over the next 4,000 years. The heavy dashed lines denote the background temperature gradient maintained by a heat flow of 0.125 mW/m^2 through basalt. (Equivalent would be a heat flow of 0.04 mW/m^2 and a thermal conductivity appropriate to deep sea sediment.) The lower line is the initial (pre-impact) condition, the upper line shows the asymptotic state when the thermal pulse has died away.

The safest depths are around 1 km, where temperatures of around 90°C persist for 10^4 years. Only thermophiles could have survived.

After the surface temperature returns to normal (4,000 years in this example), the sterilized but clement surface is at first separated from the deeper habitable region by a region of high temperatures. At this time any mesophiles that survived can reclaim the surface. After 6,000 years committed thermophiles can cross the hot zone to reach the surface. The timescale is long enough for microbes to die selectively, but it is quite short for any biological innovations. We expect that microbial diversity remained low for a geologically significant time after such an impact.

Figure 7.7 generalizes the considerations addressed by Fig. 7.6 to different heat flows. The figure also indicates the corresponding age of the oceanic crust. We plot the maximum temperature reached after the impact at any depth for the minimal ocean-vaporizing impact. This gives a broader picture of the subsurface thermal effects. Only for low heat flows appropriate to old crust can mesophiles survive. They survive best at depths of around 2 km, where a 2×10^{35} erg impact has little effect on temperatures. In the range of heat flows appropriate for the early Earth (unknown; our estimate is shaded) thermophiles survive the heat pulse.

If photosynthetic organisms were to survive on the Earth, they would need to be mixed to the bottom of the ocean (by tsunamis, say) and rapidly buried by several hundreds of meters of ejecta. They must not get crushed, eaten, or poisoned in the process. They would also need to have been buried in the midst of abundant food, chemicals both oxidized and reduced, and yet not be able to access the food so quickly that they could eat all of it while buried for millenia. They must retain the latent ability to photosynthesize in the face of competition from creatures that had long ago discarded the useless skill. They would then need to be exhumed by erosion, but not so soon that they would be scalded by hot rain as the oceans rescondense. Finally, they would need to find a suitable environment where they could grow, presumably without the aid of those other creatures that had played important roles in the parent ecosystem. To meet any of these requirements would be lucky; to meet them all might be asking too much of luck.

Perhaps the best strategy for surviving such an impact is to go into orbit (Zahnle and Sleep, 1997; Sleep and Zahnle, 1998; Wells et al., 2003). Impacts can lift surface rocks into orbit essentially unshocked and unheated (Melosh, 1989). This process is known to occur, most famously among the SNC meteorites, which have travelled to the Earth from Mars. Rocks ejected from the Earth will mostly reach Earth-like orbits, and so will spend relatively little time in space before they are swept up again, typically tens of thousands of years or less (Wells et al., 2003). It is possible that passengers could survive the journey. It has also been noted that rocks can be exchanged between planets, although transit times are usually much longer and hence the voyage more dangerous (Melosh, 1989, Sleep and Zahnle, 1997, Mileikowsky et al., 2000).

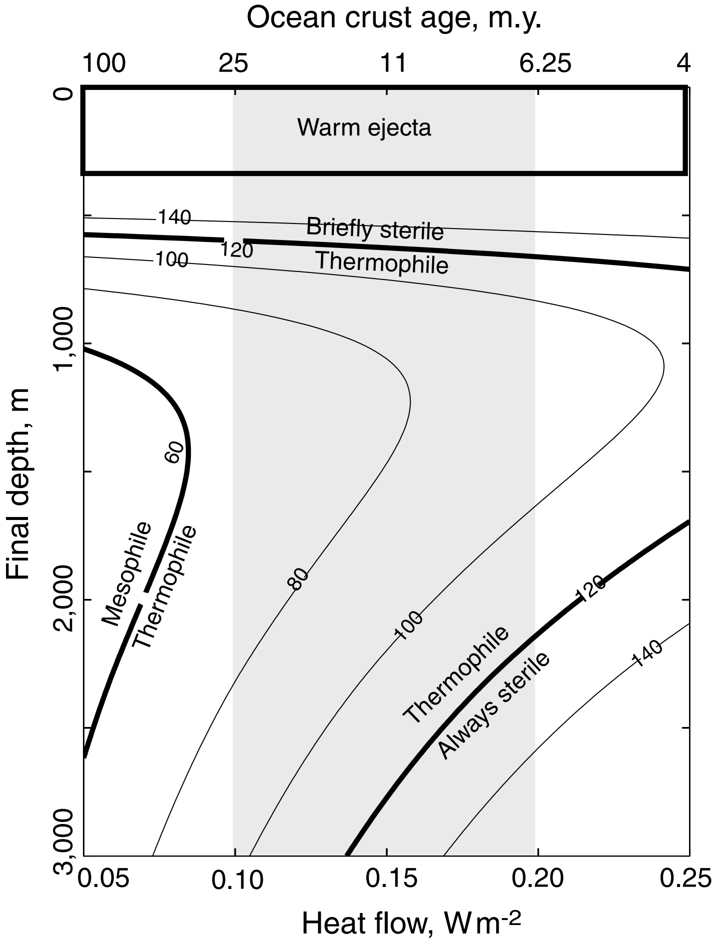

Fig. 7.7. The highest temperature (Celsius) reached beneath the old oceans after an ocean-vaporizing impact. The temperatures are given as a function of depth and heat flow. The crustal age corresponding to a heat flow is also given. Temperatures suitable to hyperthermophiles are widespread, but temperatures suitable to "mesophiles" (here rather liberally equated to thermophiles that thrive or at least survive at 60°C) are found only below 1 km in regions of low heat flow.

7.5.2 Imbrium on the Earth

The Earth must have experienced hundreds of impacts on the scale of the Imbrium and Orientale ($\sim 10^{33}$ ergs) between 3.7 and 4.1 Ga, as we shall see in the next section. These impacts are about 100 times smaller than the ocean-vaporizing event. Consider an "Imbrium-scale" 2×10^{33} erg impact that generated some 5×10^{21} g of ejecta, enough to make a 1-bar silicate atmosphere. The event can be thought of as a scaled-up K/T impact. The ejecta are launched ballistically from the crater, and are thereby distributed globally (Melosh et al., 1990; Zahnle, 1990). Atmospheric reëntry ensures vaporization (Zahnle, 1990). The mixture of rock vapor and multiply shocked air that results sits on top of the original atmosphere, where owing to its high temperature it remains for some time. The layer of rock vapor, rock vapor condensates, and hot air radiates equally to space and the surface at an effective radiating temperature of order 2,000–2,500 K. The cooling time for an Imbrium-scale event is about a day.

The relative transparency of the preexisting atmosphere to 2,000 K infrared radiation prevents it from absorbing a significant fraction of the energy. Hence the impact would boil off some 40 m of sea water, which adds 4 bars of water vapor to the atmosphere. If this event occurred in a 1-bar N_2 atmosphere, there would remain at the surface a hot (150°C), highly saline (15%), boiled layer about 12 m thick. If the event occurred in a 10-bar CO_2 atmosphere, the surface brine layer would be 200°C and 8 m deep. In either case a small part of the extra 4 bars of water vapor in the atmosphere would rain out quickly when mixed with the cool preexisting atmosphere. Raising a 1-bar N_2 atmosphere to 150°C uses only about 1% of the energy in the water vapor; raising a 10-bar CO_2 atmosphere to 200°C uses 10%. The rest of the injected water vapor rains out no faster than the maximum rate permitted by the runaway greenhouse threshold; i.e., 170 cm/year (the average rainout rate is slightly higher than for the ocean-vaporizing impact because the atmosphere is cooler). It takes 24 years to dry out the atmosphere. Because the atmospheric temperature profile would follow the moist adiabat, for the first several years the rain would be hot (>100°C). The result would be a hot stable layer of fresh water some 40 m thick. Obviously there will be some mechanical mixing with the colder saltier water beneath, but the general impression is that normal surface water ecosystems based on photosynthesis would be decimated. Extreme thermophiles and/or extreme halophiles would be much more likely to survive. Indeed, conditions would probably support a global bloom among the photosynthetic halophilic thermophiles. Deep water ecosystems would be relatively unperturbed. In particular, colonies living at hydrothermal vents near the mid-ocean ridges are unlikely to be greatly distressed by the events at the surface.

The largest of the Archean impacts, inferred by Lowe, Byerly, and coworkers from thick layers of what are almost certainly impact-generated spherules (Lowe and Byerly, 1986; Lowe et al., 1989; Byerly et al., 2002; Kyte et al., 2003), may have approached this scale. There are at least four events in the record between 3.2 and 3.5 Ga. Kyte et al. (2003) suggest that the largest were 50–300 times bigger than the K/T; we take this to imply that the biggest one released $3 \times 10^{32} - 3 \times 10^{33}$ ergs. At the high end of the range one expects severe damage even to the simple ecosystems of the day. To our knowledge there is no evidence of such a catastrophe, although the fossil record of the time is scanty and controversy surrounds even the most basic issues.

7.5.3 Evolutionary Filters

The global killing mechanism of any impact large enough to globally decimate microbes is heat, which is readily constrained by conservation of energy. Consider an impactor 10 times larger than that of Imbrium. This is a world comparable to what put the S. Pole-Aitken basin on the Moon or the Hellas basin on Mars. Such an impact on the Earth qualitatively resembles Imbrium but the major untoward effects are proportionately greater. Rather than 40 m of sea water evaporated there are 400; rather than taking 24 years for the steam to rain out, it takes 240. For a preëxisting 1-bar N_2 atmosphere the surface temperature reaches 250°C and the boiled brine layer extends 60 m deep. Over most of the next 240 years hot rainwater pools atop the brine.

It is difficult to see how common surface ecosystems could have survived. Most species of microbes would have become extinct. Still representatives of major clades and major ecological types might have made it through. For example, photosynthetic organisms that could facultatively act as heterotrophs could have survived by being mixed into the deep ocean where conditions remained clement. It is not clear that we would still see clear evidence of this pruning of the tree of life 3.8 B.Y. later.

Raising the energy another factor of 3 would boil about half the ocean and leave the rest as a hot salty brine. Organisms anywhere in the ocean, including hydrothermal vents, would have perished. Only aquifers deeper than 0.5 km would be safe. This impact would have doomed photosynthesis. The inhabitants of the deep aquifers would have ruled the world. It is this scale of event in particular that most strongly suggests that life on the Earth should descend from organisms that either lived in the deep ocean, in hydrothermal systems, or were extremely tolerant of heat and salt. If photosynthesis survived, it would have been preserved among the halophiles and thermophiles. There is no reasonable doubt that events of this scale occurred 4 billion years ago, with perhaps 10 events scattered over the 400 million years interval between 3.7 and 4.1 Ga.

It is widely held that all extant life on the Earth descends from the class of sulfur-metabolizing, thermophilic organisms that populate mid-ocean ridge hydrothermal systems today (Pace et al., 1986; Lake, 1988). In our opinion, the natural story is that such organisms survived because their niche was once the safest one on the Earth. Inhabitants of other environments were filtered out by impact. It is not required that life originate in hydrothermal systems. Life could have arisen at the surface and colonized the mid-ocean ridges. The long intervals between major impacts leave plenty of time for migration. It is simply because deep water hydrothermal systems offered sanctuary from otherwise lethal events that life survived there. We are tempted to invert the argument: because we can trace our descent to thermophiles, we can suggest that life originated before the end of the heavy bombardment.

On the other hand, a hot hydrothermal origin of life is currently a popular hypothesis. If life did originate and evolve to something like its current complexity in hydrothermal systems at the bottoms of oceans, the late bombardment need not have played an important role, and as constrained by other currently available data life need not be as old or older than the Earth's rock record. A hydrothermal origin on the Earth makes the remarkable albeit implicit prediction that life should be widespread in our solar system, independently evolving wherever one finds hydrothermal systems charged with simple C- and N-containing molecules. Several icy moons meet or have met these criteria; probably too have some of the larger asteroids, comets, and Kuiper Belt Objects. Testing the hydrothermal hypothesis by the intensive exploration of, say, Triton ought to be seen as an obvious leading priority of the space program. That it is not seen this way may be a sign that most physical scientists still think of life as magical rather than as a consequence of knowable physical law; we have not quite caught up to Darwin yet.

7.6 The Late Bombardment on Mars

Mars is like the Moon in that great impact basins remain major features of the landscape. The obvious big basins, like Hellas, are as big as the biggest basins on the Moon and the asteroids that made them were probably bigger, given the higher surface gravity and the generally lower impact velocities expected at Mars. In detail, mapping the martian record to the lunar record presents uncertainties that are generally regarded as modest but could be large. It is possible that Mars has been subject to collisions with populations that the Earth and Moon have not. Mars is nearer the asteroid belt, the likely source of most projectiles, and its orbit is crossed by many more Jupiter-family comets (Zahnle, 1993). As with the Earth and the Moon, the specific properties of the late bombardment on Mars depend on the vagaries of small number statistics. Our prejudice is that dangerous impacts were infrequent. Our views on this are strongly colored by the 4.5-Ga age of the Martian meteorite ALH-84001, a presumed sample of the heavily cratered martian uplands. In the interludes between great impacts, life (if any) would have had time enough to colonize any favorable environments.

7.6.1 Environmental Effects of Large Impacts on Mars

The global killing mechanism on Mars, like on the Earth, is heat. However, the smaller size of Mars, its lack of a significant ocean, and its place in the solar system make for significant differences.

The lower gravity of Mars and the lower approach velocities of asteroids cause the typical collision velocity on Mars to be lower than that of the Earth. This changes the nature of typical impact ejecta. The lower impact velocity (∼10/km/s vs. ∼17 km/s) means that the hottest ejecta are forged at energies some three times lower than on the Earth; therefore, less rock vapor forms by the collision itself. Indeed at 10 km/s one expects little vaporization. A second reason is that the lower gravity means that the ejecta carry less specific energy, while the most energetic ejecta escape. For a high velocity impact the specific energy goes as the ratio of the square of the escape velocities. (In a low velocity impact the highest ejection velocities may be significantly less than escape velocity, in which case the event is more localized and the effects on the two planets more alike.) Much of the ejecta from the biggest impacts on Mars is ballistically and unevenly distributed as hot melt, rather than hydrodynamically distributed more or less evently over the entire planet as rock vapor (Sleep and Zahnle, 1997). In a big impact there is not enough time for the ejecta to radiatively cool in transit, so that reëntry (either aerobraking in the atmosphere or lithobraking at the surface) further heats already hot ejecta. Near the impact basin the molten ejecta behave like a large lava flow, ponding in low spots while leaving high spots sparsely covered. More distal ejecta can evaporate. For example, ejecta launched at half the martian escape velocity carry approximately 3×10^{10} ergs/g of kinetic energy, which corresponds to a 2,000 K temperature rise in an already hot material. Although relatively little of the ejecta evaporates, the rock vapors can take up much of the ejecta's energy at points far from the impact site.

From the perspective of life's survival there (given that there was life there), ancient Mars differed from the Earth in at least two important ways. One is that the small amounts of surface water on Mars provided little thermal buffering. An Imbrium-sized projectile would have left the planetary surface covered with on average $\sim$10 m of molten rock. The surface temperature would have been briefly very high. We expect that photosynthetic and other obligate surface organisms would have perished.

A second difference is that molten ejecta, rather than a long-lasting steam atmosphere, governed the duration, depth, and magnitude of subsurface heating. Figure 7.8 follows the propagation into the surface of the heat pulse delivered by a 200-m blanket of molten ejecta. This is the global average generated by a Hellas caliber impact (in the real Hellas the ejecta blanket would be kilometers thick near the basin and on average $\sim$100 m thick over many of the more distant provinces, and probably very patchy if rayed craters provide a useful guide). The Hellas impactor had about 1/3 the mass and released about 1/10 the energy of the hypothetical terrestrial ocean-evaporating event. For the illustration the ejecta pile is given an initial temperature of 1,300°C. The strongly heated region below the original surface is about 50% thicker than the ejecta layer itself. A background heat flow of 0.05 $\mathrm{W\,m^{-2}}$ is assumed. This is equivalent to the heat flow through 100 Ma ocean crust on the Earth; one expects a similar heat flow on Mars through a basaltic crust of similar age. The ancient age of the martian meteorite ALH-84001 implies that stable regions like this have existed on Mars once the planet had aged 100 Myr.

Figures 7.9 and 7.10 show maximum temperatures underground as a function of heat flow for 200- and 500-m ejecta blankets. The figures are analogous to Fig. 7.7 for the Earth. The effects produced by 200 m of hot ejecta resemble

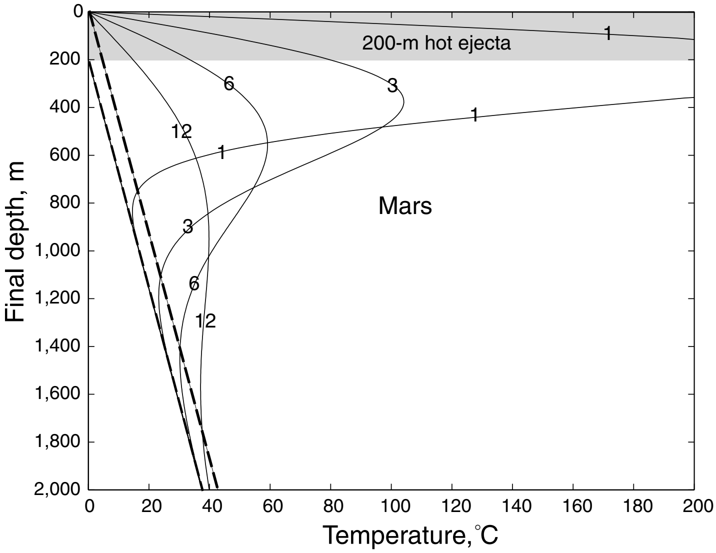

Fig. 7.8. Propagation of the thermal pulse produced by a Hellas-sized impact at a distal location on Mars. Times are marked in thousands of years. The initial condition is a hot (1,300°C) 200-m-thick blanket of impact ejecta and a 1,300°C surface temperature; the surface temperature cools to 0°C over the next 25 years. The heavy dashed lines denote the background temperature gradient maintained by a heat flow of 0.05 mW/m^2 through basalt. The dashed lines have the same meaning as in Fig 7.6.

those produced by evaporating the oceans of the Earth while the 500-m case is much worse.

Differences between Mars and the Earth influence how Figs. 7.8–7.10 should be interpreted. Heat flow is generally lower on the Mars, roughly in proportion to surface gravity. Lower surface gravity on Mars also means that porosity extends commensurately deeper under the surface; this means that, other things being equal, habitable subsurface environments extend 2.6 times deeper than on the Earth. A third point is that Figs. 8–10 presume a 0°C surface before the impact, appropriate to a warm, wet, habitable early Mars. This is a self-consistent choice, given that we are considering the negative effects of impacts on the inhabitants of a habitable early Mars. But given the faint young Sun, a lower surface temperature may seem more likely. To first approximation, save near the surface itself, Figs. 8–10 can be rescaled by adding the original surface temperature in degrees C. A preimpact surface temperature of –60°C would change the "thermophile" fields in Figs. 9 and 10 into "mesophile" fields, and change the "mesophile" fields into "cryophile" fields. Whether a Mars with a –60 °C steady-state surface could have a living subsurface biosphere is a question one may justly ask.

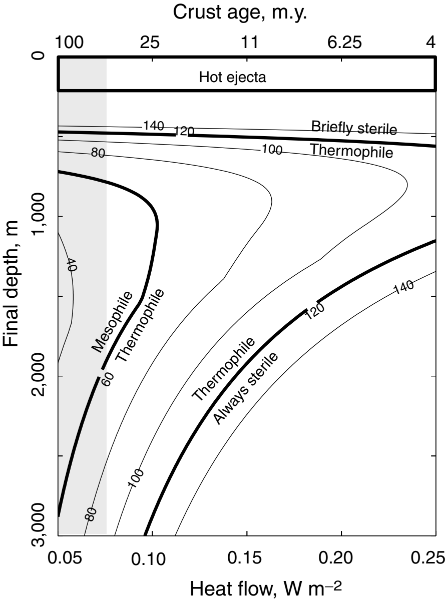

Fig. 7.9. The highest temperature (Celsius) reached beneath the surface after a Hellas-scale impact on Mars. The crustal age corresponding to a heat flow is also given. In general, results resemble those generated by an ocean-vaporizing impact on the Earth, although it should be remembered that Mars is expected to be porous to greater than the Earth in inverse proportion to its gravity, so that a depth of 1 km on Mars is roughly comparable to a depth of 375 m on the Earth. Also, save near the surface, the temperature fields can be rescaled to higher or lower temperatures according to the steady-state surface temperature of Mars. A normally very cold surface (say –60°C) lowers the temperatures at depth by up to 60°C. Thus the martian subsurface can better protect mesophiles.

7.6.2 Local Panspermia

Impacts scatter debris from planet to planet. Some of the debris is remarkably undamaged in the process. The natural speculation is that living organisms might get launched inside these rocks, survive the trip, survive the landing, and once there finds a suitable home, and so innoculate nearby worlds (Melosh, 1989). The lunar and Martian meteorites that hit the Earth indicate the reality of this process and can be used as calibration points (Gladman, 1996; Gladman et al., 1997). Currently about 10 Mars rocks hit the Earth annually (Mileikowsky et al., 2000). The impact rate and hence the rate of rock transfer was 100–1,000 times higher before 3.8 Ga. Roughly a trillion rocks from Mars have hit the Earth over geological time.

Any microbes caught in the ejected rocks faced numerous perils, including high-shock pressures and shock heating from the impact, rapid accelerations, heating again on reëntry, and in between a vacuum laced with cosmic rays.

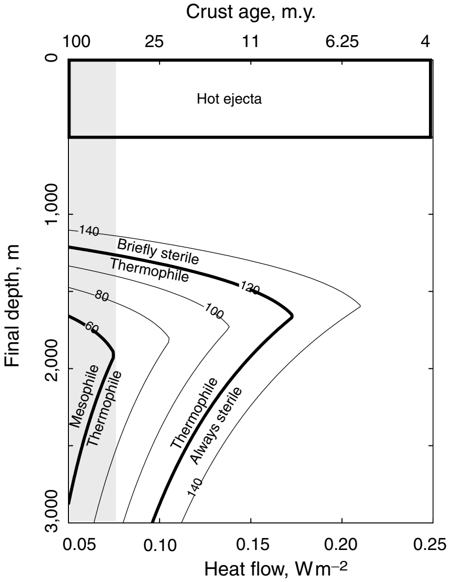

Fig. 7.10. Like Fig. 7.9 but for an impact more directly comparable to an ocean-vaporizing event on the Earth. The range and accessibility of potential refugia are greatly diminished. As with Fig. 9, temperatures at depth rescale with the annual average surface temperature, so that a –60°C surface means that the contour labelled 120°C would correspond to rescaled temperature of 60°C. Although deep survival is promoted by cold surfaces and very low heat flow, one would not expect the corresponding surface environments to be habitable. Climatically warmer or more volcanically active regions that would seem to offer the best ecological options would seem to offer the fewest options for refugia.

While none of these things are good for microbes, studies of Mars rocks and extent terrestrial microbes in the laboratory and in space indicate that they need not be fatal (Mileikowsky et al., 2000). For example, the Mars rock ALH-84001 was never heated above 40°C on its trip to the Earth (Weiss et al., 2000). If the typical rock takes of order 10 million years to transit from Mars to the Earth, we expect that billions of rocks made the trip from Mars to the Earth in less than 10 thousand years, and millions in less than 10 years. These are timescales over which many microbes are likely to survive.

Voyage from the Earth to Mars is more problematic as we have no Earth-derived meteorites to calibrate the process. The thicker atmosphere and higher escape velocity inhibit escape. Nonetheless, we might expect K-T–sized impacts to eject rocks from the Earth and that some of these hit Mars. We might also expect some traffic with an early earthlike Venus, had early Venus been earthlike.

Planetary exchange makes it more difficult to sterilize the whole solar system. The relatively modest impacts that scatter suitable rocks between planets are much more common than dangerous large impactors. Spread over many worlds life would be much less vulnerable to a random event.

Seeding the Earth from another planet creates an evolutionary bottleneck (like a pregnant finch landing on an isolated island) and an evolutionary filter (like large mammals not making it to an isolated island). Some DNA-based microbes may have been able to easily make the trip. The situation for the organisms would have been much like free-living microbes on the modern Earth where similar assemblages inhabit simlar environments globally (Finlay, 2003). For example, the same organisms now inhabit, say, a fjord in Norway and one in New Zealand. It would be meaningless to say whether the ancestors of these modern organisms lived in Norway or New Zealand in the previous interglacial period. Similarly, for some organisms, Mars and the Earth might have been one biosphere.

Other organisms would not have found passage on interplanetary rocks to their liking. This obviously includes any large organism, but also may include molecular organisms that cannot tolerate long periods of stasis in space. In particular, the RNA world may have had to stay home on Mars (Joe Kirshvink, personal communication, 2004).

In contrast to interplanetary panspermia – a testable hypothesis and, as argued above, a possible one – interstellar panspermia is a scientific dead-end. It removes the origin of life to an unknown and unknowable location that will be forever unavailable. It is also extremely unlikely to occur naturally. For example, there is only a slight chance that any rock from a terrestrial planet in our solar system has ever hit a terrestrial planet in another solar system (Melosh, 1903).

An origin of life on Mars is more testable than its origin on the Earth. Mars retains a geological record back to at least 4.5 Ga. Some waterlain sediments are inevitable. Biologists will be able to quickly tell whether any extant organisms found on Mars are related to terrestrial organisms. We will probably be able to do this with molecular fossils. Only the logistics pose difficulties. Similar considerations apply to large asteroids like Ceres. In contrast, the record before 3.5 Ga on the Earth is quite sparse and highly metamorphosed. The early terrestrial record may be gone for good, rather than just being hard to access. The only plausible hope is to find a terrene meteorite on the Moon (Armstrong et al., 2002).

7.7 Conclusions

The K/T impact left a crater that is at least 180-km diameter; from its crater one would deduce an energy release of $\sim 1-2\times 10^{31}$ ergs. This is a considerable amount of energy to release into the biosphere in a short time; a great many bad things could have happened in the aftermath and evidently many did (see Sharpton and Ward (1990) for several lists). To give just one example, the ejecta from the K/T impact would have evaporated about half a meter off the oceans and left about 20 cm of boiled brine on the sea surface. We note that oceanic primary productivity was practically wiped out for thousands of years thereafter. The K/T event had many other influences of which we are all no doubt aware. The survivors were selected, naturally, but not in response to the usual Darwinian competition (although widespread conventionally successful species were doubtless favored in general).

Bigger impacts likely played a bigger role in the evolution of early life. The lunar cratering record implies that hundreds of objects like those that produced the Imbrium and Orientale basins struck Earth between 3.7 and 4.1 Ga. These events were typically about 100 times more energetic than the K/T. Impacts on this scale would have vaporized the topmost tens of meters of the ocean. Surface and shallow water ecosystems would very likely have been destroyed. These impacts posed a serious recurrent hazard to life at the Earth's surface. Impact-generated Archean spherule beds indicate that events on this scale may have occurred ca. 3.2–3.5 Ga, and one or two might be expected on the Earth since, with effect dwarfing that of the K/T.

More important were the tens of events that vaporized hundreds of meters of seawater. It is this scale of event in particular that most strongly suggests that life on the Earth should descend from organisms that lived in the deep ocean, in hydrothermal systems, or were extremely fond of heat and salt. If photosynthesis survived, it would have been preserved among the halophiles and thermophiles.

Impacts large enough to fully vaporize the oceans must also have occurred if one looks early enough. How many times this happened can be extrapolated from the lunar record, although the estimate is sensitive to the mass distribution of large impactors. Reading off Fig. 7.3, one sees an expectation of 2^{+4}_{-2} such events between 3.7 and 4.1 Ga (Nectaris), and about thrice this many if we extend the time period to include South Pole Aitken. What happened before SPA is debatable. The actual number of these events and their timing are mostly a matter of chance. Such events, if they took place, would have strongly biased survival to favor organisms living in mid-ocean ridge hydrothermal systems or comparably deep-protected environments.

In this chapter we have stressed the dark side of impacts. But not all is dark. Implicit in all these mass extinctions are the new radiations that followed: a biology of revolutionary rather than evolutionary change. One of the greatest puzzles in evolution is its slow pace over the 3-plus billion years between life's origin and the Cambrian explosion. Did impacts speed the courses of evolution and so give us form?

Big impacts are also germane to the setting of the origin of life on the Earth. Indeed their influences are likely profound and many beneficial. Impacts significantly influenced the chemistry of the ocean and atmosphere. These influences remained long after the dust settled and the oceans returned.

Impact-induced shock chemistry tends to generate carbon monoxide from carbon dioxide. An impact that vaporizes the oceans is more than large enough to convert much of CO_2 in the atmosphere and oceans into CO and O_2. If the impactor were itself relatively reduced, for example, an olivine shard of a shattered protoplanetary mantle or a free-flying iron core carved from a disintegrated Vesta-like world, the chemical effects would be profound. The injection of $\sim 10^{21}$ moles of metallic iron into the atmosphere and ocean has the potential of reducing 10 bars of CO_2 into CO without generating any O_2. The occasional large iron-rich impactor may have added enough reducing power to generate a transient methane–ammonia atmosphere. The suitability of such an atmosphere for prebiotic chemistry, even if ephemeral, is well-known. Even the background flux of reducing meteors has the power to tip a CO_2 atmosphere into a CO atmosphere by photochemistry alone (Kasting, 1993). Despite its poisonous reputation, carbon monoxide would have been more conducive to the origin of life than CO_2.

Meanwhile the same impacts excavated enormous amounts of mafic and ultramafic material from the mantle, much of which accumulated on the seafloor as warm, glassy, or otherwise damaged sediments (Koster van Groos, 1988). Seawater circulating through the cooling ultramafic sediments would generate H_2 by serpentization, while any carbonate and bicarbonate ions would tend to react to leave carbonate *in situ* and perhaps vent some CH_4 to the air.

It is possible that any preëxisting CO_2 greenhouse would have been lost, but it is also possible that a CH_4 greenhouse might be created to replace it. The eventual postimpact surface temperature could have been very cold and the world an icehouse or very hot and the world a steambath; depending on details and accidents all possibilities may have been realized when one considers the possible histogram of great events.

The world, 3,000 years after the impact, is clearly a rather different place, with an atmosphere and an ocean that for any of several reasons (some listed above) are far out of low-temperature chemical equilibrium. Whether these constitute inviting conditions for prebiotic chemistry or the origin of life we leave to the imagination of the reader.

7.8 Epilogue

We opened this essay with the image of a giant rogue comet astray in the inner solar system. Of known objects in the solar system, only comets are big enough and pass the Earth closely enough to cause mass extinctions in the next million years. As worded, the previous sentence is literally true. Comets big enough to cause K/T level consequences pass the Earth's orbit about twice per decade. Famous examples are P/Halley and C/Hale-Bopp. On average such a comet will hit the Earth on one revolution in 300 million. Thus comets threaten the biosphere on a 1.5-Gyr time scale.

Currently there are no known asteroids that pose a similar near-term threat. However, this line of reasoning contains some tendentious elements. There are resonances in the asteroid belt (the 3:1, the 5:2, and the ν_6 are the important ones; the ratios refer to resonances with the orbital period of

Jupiter, while the ν_6 is a precession resonance with Saturn) from which asteroids can be directed into the Earth in less than a million years (Morbidelli and Gladman, 1998); we know little of the distant asteroids that might tomorrow stumble into one of these resonances.

Also, dangerous known asteroids do exist. When we first set forth the image of Chiron as the most dangerous object in the solar system (an image we have retained in this revision because of the magnitude of what could happen in the geologically near future if it were to find us), George Wetherill (personal communication, 2004) said to us, "I would have thought it was Eros." Indeed. Eros is the most famous of the Near Earth Asteroids. It is a roughly prolate rock or pile of rocks some 11 km wide and 34 km long. Its mass is 6.7×10^{18} g. It is at least as big as the K/T impactor was. It is not currently in an orbit that threatens the Earth, and it cannot reasonably get into such an orbit in the next million years (Michel et al., 1996). Yet its orbit is not stable and there are few options open for its future development. Orbital simulations carried out for 20 Myr indicate that Eros has about a 20% chance of hitting the Earth (Luke Dones, personal communication, 2004) in the next 100 Myr. By itself, this one asteroid has a threefold greater chance of causing a K/T level event than the sum of all comets known and unknown.

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References

Abe, Y. (1988), Conditions required for sustaining a surface magma ocean, *Proc. 21st ISAS Lun. Planet. Symp.*, 225–231.

Abe, Y. and Matsui, T. (1988), Evolution of an impact-generated H_2O- CO_2 atmosphere and formation of a hot proto-ocean on Earth, *J. Atm. Sci.*, **45**, 3081–3101.

Anders, E. (1989), Prebiotic organic matter from comets and asteroids, *Nature*, **342**, 255–257 (1989).

Alvarez, L.W., Alvarez, W., Asaro, F., and Michel, H.V. (1980), Extraterrestrial cause for the Cretaceous–Tertiary extinction, *Science*, **208**, 1095–1108.

Armstrong, J.C., Wells, L.E., and Gonzalez, G.V. (2002), Rummaging in Earth's Attic for Remains of Ancient Life, *Icarus*, **160**, 183–196.

Baldwin, R.B. (1981), On the origin of the planetesimals that produced the milti-ringed basins. In, *Multi-ring Basins, Proc. Lun. Planet. Sci. 12A*, (Schultz, P. and Merrill, R.B. eds), Pergamon Press, New York, pp. 19–28.

Baldwin, R.B. (1987), On the relative and absolute ages of seven lunar front face basins I, *Icarus*, **71**, 1–18.

Baldwin, R.B. (1987), On the relative and absolute ages of seven lunar front face basins II, *Icarus*, **71**, 19–29.

Belton, M.J.S., Head, J.W., Pieters, C.M., Greeley, R., McEwen, A.S., Neukem, G., Klaasen, K.P., Anger, C.D., Carr, M. H., Chapman, C.R., Davies, M.E., Fanale, F.P., Gierasch, P.J. Greenberg, R., Ingersoll, A.P., Johnson, T., Paczkowski, B., Pilcher, C.B., and Veverka, J. (1992), Lunar impact basins and crustal heterogeneity: New western limb and far side data from Galileo, *Science*, **255**, 570–576.

Bogard, D.D. (1995), Impact ages of meteorites: A synthesis, *Meteoritics*, **30**, 244–268.

Bratt, S.R., Solomon, S.C. and Head, J.W. (1985a), The evolution of impact basins: Cooling, subsidence, and thermal stress, *J. Geophys. Res*, **90**, 12415–12433.

Bratt, S.R., Solomon, S.C., Head, J.W. and Thuber, C.H. (1985b), The deep structure of lunar basins: Implications for basin formation and modification, *J. Geophys. Res*, **90**, 3049–3064.

Brinkman, H. and Philippe, H. (1999), Archaea sister group of Bacteria? Indications from tree reconstruction artifacts in ancient phylogenies, *Mol. Bio. Evol.*, **16**, 817–825.

Byerly, G.R., Lowe, D.R., Wooden, J.L., and Xie, X. (2002), An Archean impact layer from the Pilbara and Kaapvaal cratons. *Science*, **297**, 1325–1327.

Carlson, R.W. and Lugmair, G.W. (1979), Sm-Nd constraints on early lunar differentiation and the evolution of KREEP, *Earth Planet Sci. Lett.*, **45**, 123–132.

Carlson, R.W. and Lugmair, G.W. (1988), The age of ferroan anorthosite 60025 - Oldest crust on a young moon?, *Earth Planet Sci. Lett.*, **90**, 119–130.

Chapman, C.R., Williams, J.G., and Hartmann, W.K. (1978), The Asteroids, *Ann Rev. Astron. Astrophys.*, **16**, 33–75.

Chyba, C. (1991), Terrestrial mantle siderophiles and the lunar impact record, *Icarus*, **92**, 217–233.

Connan, J. (1984), Biodegradation of crude oils in reservoirs, *Adv. Petroleum Geochem.,* **1**, 299–335.

Duaphas, M., and Marty, B. (2002), Inference on the nature and the mass of Earth's late veneer from noble metals and gases, *J. Geophys. Res.*, **107**(E12), 5129.

Davis, P.A. and Spudis, P. (1987), Global petrologic variations on the moon - A ternary-diagram approach, *J. Geophys. Res.*, **92**, E387–E395.

Di Giulio, M. (2003), The universal ancestor was a thermophile or a hyperthermophile: Tests and Evidence, *J. Theor. Biol.*, **221**, 425–436.

Drake, M.J.(1987), Is lunar bulk material similar to Earth's mantle? In *Origin of the Moon*, (Hartmann, W.K., Phillips, R. J. and Taylor, G.J., eds.), Lunar and Planetary Institute, Houston, pp. 105–143.

Donnison, J.R. and Sugden, R.A. (1984), The distribution of asteroidal diameters, *Mon. Not. Roy. Astron. Soc.*, **210**, 673–682.

Donnison, J.R. (1986), The distribution of cometary magnetudes, *Astron. Astrophys.*, **167**, 359–363.

Dohnanyi, J.S. (1972), Interplanetary objects in review: statistics of their masses and dynamics, *Icarus*, **17**, 1–48.

Duncan, M., Quinn, T., and Tremaine, S. (1987), The formation and extent of the solar system comet cloud, *Astron. J.*, **94**, 1330–1338.

Duncan, M., Quinn, T., and Tremaine, S. (1988), The origin of short period comets, *Astrophys. J.*, **328**, L69–L73.

Finlay, B.J. (2002), Global dispersal of free-living microbial Eukaryote species, *Science*, **296**, 1061-1063.

Forterre, P., de la Tour, C.B., Philippe, H., and Duguet, M. (2000), Reverse gyrase from hyperthermophiles – probable transfer of a thermoadaption trait from Archaea to Bacteria, *Trends Genetics*, **16(4)**, 152–154.

Forterre, P., Brochier, C., and Philippe, H. (2002), Evolution of the Archaea, *Theor. Popul. Biol.*, **61**, 409–422.

Gladman, B. (1997), Destination Earth: Martian meteorite delivery, *Icarus*, **130**, 228–246.

Gladman, B.J., Burns, J.A., Duncan, H., Lee, P., and Levison, H.F. (1996), The exchange of impact ejecta between terrestrial planets, *Science*, **271**, 1387–1392.

Gladman, B., Kavelaars, J.J., Petit, J.-M., Morbidelli, A., Holman, M.J., Loredo, T. (2001), The Structure of the Kuiper Belt: Size Distribution and Radial Extent, *Astron. J.*, **122**, 1051-1066.

Grieve, R.A.F. and Shoemaker, E.M. (1994), The record of past impacts on Earth. In *Hazards Due to Comets and Asteroids*, (Gehrels, T. ed.), Univ. Arizona Press, Tucson, pp. 417–462.

Hahn and Bailey, M. (1990), Rapid dynamical evolution of giant comet Chiron, *Nature*, **348**, 132–136.

Hartmann, W.K. (1980), Dropping stones in magma oceans: Effects of early lunar cratering. In *Proceedings of the Conference on the Lunar Highlands Crust*, (J. Papike and R. Merrill, eds), Pergamon Press, New York, pp. 155–173.

Hartmann, W.K., Phillips, R.J. and Taylor, G.J., eds. (1986), *Origin of the Moon*, Lunar and Planetary Institute, Houston.

Hartmann, W.K., D.J. Tholen, K.J. Meech, and Criukshank, D.P. (1990), 2060 Chiron: Colorimetry and possible cometary behavior, *Icarus*, **83**, 1–15.

Hartmann, W.K., Ryder, G., Dones, L., and Grinspoon, D. (2000), The Time-Dependent Intense Bombardment of the Primordial Earth/Moon System. In *Origin of the Earth and Moon*, (Canup, R.M., and Righter, K. eds.), University of Arizona Press, Tucson, pp. 493–512.

Hildebrand, A.R., Penfield, G.T., King, D.A., Pilkington, M., Camargo, Z.,A., Jacobsen, S.B. and Boynton, W.V. (1991), Chicxulub crater: a possible Cretaceous/Tertiary boundary impact crater on the Yucatan Peninsula, Mexico, *Geology*, **19**, 867–871.

Hughes, D.W. (1982), Asteroidal size distribution, *Mon. Not. R. Astron. Soc.*, **199**, 1149–1157.

Hughes, D.W. (1988), Cometary distribution and the ratio between the numbers of long- and short- period comets, *Icarus*, **73**, 149–162.

Kasting, J.F. (1988), Runaway and moist greenhouse atmospheres and the evolution of Earth and Venus, *Icarus*, **74**, 472–494.

Kasting, J.F. (1990), Bolide impacts and the oxidation state of carbon in the Earth's early atmosphere, *Orig. Life*, **20**, 199–231.

Korotev, R.L. (1987), The nature of the meteoritic components of Apollo 16 soil, as inferred from correlations of iron, cobalt, iridium, and gold with nickel, *J. Geophys. Res.*, **92**, E447–E461.

Koster van Groos, A.F. (1988), Weathering, the carbon cycle, and the differentiation of the continental crust and mantle, *J. Geophys. Res.*, **93**, 8952–8958.

Kyte, F.T., Shukolyukov, A., Lugmair, G.W., Lowe, D.R., and Byerly, G. (2003), Early Archean spherule beds: chromium isotopes confirm origin throguh multiple impacts of projectiles of carbonaceous chondrite type, *Geology*, **31**, 283–286.

Lake, J.A. (1988), Origin of the eukaryotic nucleus determined by rate-invariant analysis of rRNA sequences, *Nature*, **331**, 184–186.

Lebofsky, L.A., Tholen, D.J., Rieke, G.H., and Lebofsky, M.J. (1984), 2060 Chiron: Visual and thermal infrared observations, *Icarus*, **60**, 532–537.

Levison, H.F., L. Dones, C.R. Chapman, S.A. Stern, M.J. Duncan, and Zahnle, K. (2001), Could the late lunar bombardment have been triggered by the formation of Uranus and Neptune? *Nature*, **151**, 286-306.

Lindstrom, M.M. and Lindstrom, D.J. (1986), Lunar granulites and their precursor anorthositic norites of the early lunar crust, *J. Geophys. Res.*, **91**, D263–D276.

Lowe, D.R. and Byerly, G.R. (1986), Early Archean silicate spherules of probable impact origin South Africa and Western Australia, *Geology*, **11**, 668–671.

Lowe, D.R., Byerly, G.R., Asaro, F., and Kyte, F. (1989), Geological and geochemical record of 3400-million-year-old terrestrial meteorite impacts, *Science*, **245**, 959–962.

Lucey, P.G., Taylor, G.J., Hawke, B.R., and Spudis, P.D. (1998), FeO and TiO2 concentrations in the South Pole-Aitken basin - Implications for mantle composition and basin formation, *J. Geophys. Res.*, **103**, 3701–3708.

Maher, K.A. and Stevenson, D.J. (1988), Impact Frustration of the origin of life, *Nature*, **331**, 612–614.

Marvin, U.B., Carey, J.W. and Lindstrom, M.M. (1989), Cordierite-spinel troctolite, a new magnesium-rich lithology from the lunar highlands, *Science*, **243**, 925–931.

Melosh, H.J. (1989), *Impact Cratering: A Geological Process*, Oxford University Press, New York.

Melosh, H.J. (1990), Giant impacts and the thermal state of the Earth. In *Origin of the Earth*, (Newsom, H.E. and Jones, J.H., eds.), Oxford University Press, pp. 69–84.

Melosh, H.J. (2003), Exchange of meteorites (and life?) between stellar systems, *Astrobiology*, **3,** 207–215.

Melosh, H.J., Schneider, N., Zahnle, K., and Latham, D.(1990), Ignition of global wildfires at the Cretaceous/Tertiary boundary, *Nature*, **343**, 251–254.

Melosh, H.J., and Vickery, A.M. (1989), Impact erosion of the primitive atmosphere of Mars, *Nature*, **338**, 487–490.

Michel, P., Farinella, P., and Froeschl'e, C. (1996), The orbital evolution of the asteroid Eros and implications for collision with Earth, *Nature*, **380**, 689–691.

Mileikowsky, C., Cucinotta, F.A., Wilson, J.W., Gladman, B., Horneck, G., Lindgren, L., Melosh, J., Rickman, H., Valtonen, M., and Zheng, J.Q. (2000), Risks threatening transfer of microbes between bodies in our solar system, *Planet. Space Sci.*, **48**, 1107–1115.

Morbidelli, A. and Gladman, B. (1998), Orbital and temporal distributions of meteorites originating in the asteroid belt, *Meteor. and Plan. Sci.*, **33**, 999–1016.

Morgan, J.W., Walker, R.J., Brandon, A.D., and Horan, M. F. (2001), Siderophile elements in the Earth's upper mantle and lunar breccias: Data synthesis suggests manifestations of same late influx, *Meteoritics Planet. Sci.*, **36**, 1257-1275.

Mysen, B.O. and Kushiro, I. (1988), Condensation, evaporation, melting, and crystallization in the primitive solar nebula, *Am. Min.*, **73**, 1–19.

Nakajima, S., Hayashi, Y.-Y., and Abe, Y. (1992), A Study of the 'runaway greenhouse effect' with a one-dimensional radiative-convective equilibrium model, *J. Atm. Sci.*, **49**, 2256–2266.

Newsom, H.E. and Jones, J.H. (1990), *Origin of the Earth*, Oxford University Press.

Newsom, H.E. and Taylor, S.R. (1989), Geochemical implications of the formation of the Moon by a single giant impact, *Nature*, **338**, 29–34.

Oberbeck, V. and Fogleman, G. (1989), Impacts and the origin of life, *Nature*, **339**, 434.

Oberbeck, V. and Fogleman, G. (1990), Estimates of the maximum time required for the origin of life, *Orig. Life Evol. Bio.*, **19**, 549–560.

Oikawa, S. and Everhart, E. (1979), Past and future orbit of 1977 UB, object Chiron, *Astron. J.*, **84**, 134–139.

Olsson-Steel, D. (1987), Collisions in the solar system. IV. Cometary impacts upon the planets, *Mon. Not. Roy. Astron. Soc.*, **227**, 501–524.

Pace, N., Olsen, G.J., and Woese, C.R. (1986), Ribosomal RNA phylogeny and the primary lines of evolutionary descent, *Cell*, 45, 325–326.

Pieters, C.M. (1986), Composition of the lunar highland crust from near-infrared spectroscopy, *Rev. Geophys.*, **24**, 557–578.

Ringwood, A.E. and Seifert, S. (1986), Nickel-cobalt abundance systematics and their bearing on lunar origin. In *Origin of the Moon*, (Hartmann, W.K., Phillips, R.J. and Taylor, G.J., eds.), Lunar and Planetary Institute, Houston, pp. 331–358.

Rivera, M.C. and Lake, J.A. (1992), Evidence that eukaryotes and eocyte prokaryotes are immediate relatives, *Science*, **257**, 74–76.

Ryder, G. (2002), Mass flux in the ancient Earth-Moon system and benign implications for the origin of life, *J. Geophys. Res.*, **107**(E4), 5022.

Ryder, G. (2003), Bombardment of the Hadean Earth: Wholesome or deleterious?, *Astrobiology*, **3**, 3–6.

Safronov, V.S. (1972), *Evolution of the Protoplanetary Cloud and Formation of the Earth and the Planets*, NASA TT F-677.

Safronov, V.S., G.V. Pechernikova, E.I. Ruskol, and Vitjazev, A.V. (1986), Protosatellite swarms, In *Satellites*, (Burns, J. and Matthews, M.S., eds.), The University of Arizona Press, Tucson, pp. 89–116.

Schmidt, R.M., and Holsapple, K.A. (1982), Estimates of crater size for large body impact. In *Geological Implications of Impacts of Large Asteroids and Comets on the Earth*, (Silver, L.T., and Schultz, P.H., eds.), Geological Society of America Special Paper 190, pp. 93–102.

Schmidt, R.M., and Housen, K.R. (1987), Some recent advances in the scaling of impact and explosion cratering, *Int. J. Impact Mech.*, **5**, 543–560.

Scholl, H. (1979), History and evolution of Chiron's orbit, *Icarus*, **40**, 345–349.

Sharpton, V., and Ward, P., eds. (1990), *Global Catastrophes in Earth History*, Geological Society of America Special Paper 247.

Shoemaker, E.M., Wolfe, R.F. , and Shoemaker, C.S. (1982), Cratering timescales for the Galilean satellites. In *Satellites of Jupiter*, (Morrison, D., ed.), The University of Arizona Press, Tucson, pp. 277–339.

Shoemaker, E.M., Wolfe, R.F., and Shoemaker, C.S. (1990), Asteroid and comet flux in the neighborhood of Earth. In *Global Catastrophes in Earth History*, (V.L. Sharpton and P.D. Ward, eds.), Geol. Soc. of Am. Special Paper 247, pp. 155–180.

Silver, L.T., and Schultz, P.H., eds. (1982), *Geological Implications of Impacts of Large Asteroids and Comets on the Earth*, Geological Society of America Special Paper 190.

Sleep, N.S., Zahnle, K., Kasting, J.F., and Morowitz, H. (1989), Annihilation of ecosystems by large asteroid impacts on the early Earth, *Nature*, **342**, 139–142.

Spudis, P.D. (1993), *The Geology of Multi-Ring Impact Basins: The Moon and Other Planets*, Cambridge University Press, New York.

Spudis, P.D. and Davis, P.A. (1986), A Chemical and Petrological Model of the Lunar Crust and Implications for Lunar Crustal Origin, *J. Geophys. Res.*, **91**, E84–E90.

Spudis, P.D., Hawke, B.R. and Lucey, P.G. (1988), Materials and formation of the Imbrium basin, *Proc. Lunar Planet. Sci. Conf.*, **18**, 155–168.

Stadermann, F.J., Heusser, E., Jessberger, E.K., Lingner, S., and Stöffler, D. (1991), The case for a younger Imbrium basin: New ^{40}Ar-^{39}Ar ages of Apollo 14 rocks, *Geochim. Cosmochim. Acta*, **55**, 2339–2349.

Stevenson, D.J. (1987), Origin of the Moon – the Collision Hypothesis, *Ann. Rev. Earth Planet. Sci.*, **15**, 271–315.

Suits, G.W. (1979), Natural Sources. In *The Infrared Handbook*, (Wolfe, W. and Zissis, G., eds.), Office of Naval Research, Washington, D.C., pp. 3-1–3-154.

Swisher, C., Grajales-Nishimura, J., Montanari, A., Margolis, S., Claeys, P., Alvarez, W., Renne, P., Cedillo-Pardo, E., Maurrasse, F., Curtis, G., Smit, J., and McWilliams, M. (1992), Coeval ^{40}Ar/^{39}Ar ages of 65.0 million years ago from Chicxulub crater melt rock and Cretaceous-Tertiary boundary tektites, *Science*, **257**, 954–958.

Swindle, T.D., Caffee, M.W., Hohenberg, C.M. and Taylor, S.R. (1986), I-Pu-Xe dating and the relative ages of the Earth and Moon. In *Origin of the Moon*, (Hartmann, W.K., Phillips R.J. and Taylor, G.J., eds.), Lunar and Planetary Institute, Houston, pp. 331–358.

Tanaka, H., S. Inaba, and Nakazawa, K. (1996), Steady-state size distribution for the self-similar cascade, *Icarus* **123**, 450–455.

Taylor, S.R. (1986), *Planetary Science: A Lunar Perspective*, Lunar and Planetary Institute, Houston.

Tera, F., Papanastassiou, D.A., and Wasserburg, G.J. (1974), Isotopic evidence for a terminal lunar cataclysm, *Earth Planet. Sci. Lett.*, **22**, 1–21.

Tremaine, S. and Dones, L. (1993), On the statistical distribution of massive impactors, *Icarus*, **106**, 335–341.

Trujillo, C.A. Jewitt, D.C., and Luu, J.X. (2001), Properties of the Trans-Neptunian Belt: Statistics from the Canada-France-Hawaii Telescope Survey, *Astron. J.*, **122**, 457–473.

Turcotte, D.L., and Schubert, G. (1982), *Geodynamics*, Wiley, New York.

Walker, D., and Mullins, O. (1981), Surface tension of natural silicate melts from 1200-1500 C and implications for melt structure, *Contrib. Mineral. Petrol.*, **76**, 455-462.

Warren, P.H., Jerde, E.A. and Kallemeyn, G.W. (1989), Lunar meteorites - Siderophile element contents, and implications for the composition and origin of the moon, *Earth Planet. Sci. Lett.*, **91**, 245–260.

Weiss, B.P., Kirshvink, J.L., Baudenbacher, F.J., Vali, H., Peters, N.T., Macdonald, F.A., and Wikswo, J.P. (2000), A low temperature transfer of ALH84001 from Mars to Earth, *Science*, **290**, 791–795.

Weissman, P.R. (1990), The cometary impactor flux at the Earth. In *Global Catastrophes in Earth History*, (Sharpton, V.L., and Ward, P.D., eds.), Geological Society of America Special Paper 247, 171–180.

Wells, L.E., Armstrong, J.C., and Gonzalez, G. (2003), Reseeding of early Earth by impacts of returning ejecta during the late heavy bombardment, *Icarus*, **162**, 38–46.

Wetherill, G.W. (1975), Late heavy bombardment of the moon and terrestrial planets, *Proc. Lunar Sci. Conf.*, **6** 1539–1561.

Wetherill, G.W. (1981), Nature and origin of basin-forming projectiles. In *Multi-ring Basins, Proc. Lun. Planet. Sci. 12A*, (Schultz, P. and Merrill, R.B., eds.), Pergamon Press, New York, pp. 1–18.

Wilhelms, D.E. (1987), *The Geologic History of the Moon*, U.S.G.S. Professional Paper 1348.

Williams, D.R., and Wetherill, G.W. (1994), Size Distribution of Collisionally Evolved Asteroidal Populations: Analytical Solution for Self-Similar Collision Cascades. *Icarus*, **107**, 117–128.

Valley, J.W., Peck, W.H., King, E.M., and Wilde, S.A. (2002), A cool early Earth, *Geology*, **30**, 351–354.

Vickery, A.M., and Melosh, H.J. (1990), Atmospheric erosion and impactor retention in large impacts, with application to mass extinctions. In *Global Catastrophes in Earth History*, (Sharpton, V.L., and Ward, P.D., eds.), Geological Society of America Special Paper 247, pp. 289–300.

Zahnle, K. (1990), Atmospheric chemistry by large impacts. In *Global Catastrophes in Earth History*, (Sharpton, V.L., and Ward, P.D., eds.), Geological Society of America Special Paper 247, pp. 271–288.

Zahnle, K. (1993), Xenological constraints on the impact erosion of the early Martian atmosphere, *J. Geophys. Res.*, **98**, 10899–10913.

Zahnle, K. and Sleep, N. (1996), Impacts and the early evolution of life. In *Comets and the Origin and Evolution of Life*, (Thomas, P., Chyba, C., and McKay, C., eds.), Springer-Verlag, New York, pp. 175–208.

Zappala, V., Cellin o, A., diMartino, M., Migliorini, F., and Paolicci, P. (1997), Maria's family: physical structure and possible implications for the origin of giant NEAs, *Icarus*, **129**, 1–20.

Zel'dovich, Ia. B., and Raizer, Yu. P. (1967), *Physics of Shock Waves and High Temperature Hydrodynamic Phenomena*, Academic Press, New York.

8

Extraterrestrial Impact Episodes and Archaean to Early Proterozoic (3.8–2.4 Ga) Habitats of Life

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Summary. The terrestrial record is punctuated by major clustered asteroid and comet impacts, which affected the appearance, episodic extinction, radiation, and reemergence of biogenic habitats. Here I examine manifest and potential extraterrestrial impact effects on the onset and evolution of Archaean to early Proterozoic (3.8–2.4-Ga) habitats, with reference to the Pilbara (Western Australia) and Kaapvaal (eastern Transvaal) Cratons. The range of extraterrestrial connections of microbial habitats includes cometary contribution of volatiles and amino acids, sterilization by intense asteroid and comet bombardment, supernova and solar flares, and impact-triggered volcanic and hydrothermal activity, tectonic modifications, and tsunami effects. Whereas cometary dusting of planetary atmosphere may contribute little-modified extraterrestrial organic components, large impact effects result in both incineration of organic molecules and shock synthesis of new components. From projected impact incidence, $\sim$1.3% of craters >100 km and $\sim$3.8% of craters >250 km have to date been identified for post–3.8-Ga events, due to the mm-scale of impact spherules and the difficulty in their identification in the field – only the tip of the iceberg is observed regarding the effects of large impacts on the Precambrian biosphere, to date no direct or genetic relations between impacts and the onset or extinction of early Precambrian habitats can be confirmed. However, potential relations include (1) $\sim$3.5–3.43 Ga – intermittent appearance of stromatolite-like structures of possible biogenic origin on felsic volcanic shoals representing intervals between mafic volcanic episodes in rapidly subsiding basins, a period during which asteroid impacts are recorded; (2) $\sim$3.26–3.225 Ga – impact-triggered crustal transformation from mafic–ultramafic volcanic environments to rifted troughs dominated by felsic volcanics and turbidites, marked by a major magmatic peak, resulting in extensive hydrothermal activity and development of sulphate-reducing microbes around anoxic submarine fumarole ("black smoker") environments; (3) $\sim$2.63–2.47 Ga – impact-triggered tsunami effects in oxygenated carbonate-dominated epicontinental and intracratonic environments (Hamersley and Transvaal basins); (4) in at least three instances onset of ferruginous sedimentation closely following major impact events, possibly signifying hydrothermal Fe-enrichment related to impact-triggered volcanic activity. Due to limitations on the phylogenic speciation of Precambrian stromatolite and bacterial populations, major impact–extinction–radiation relations are identified only from the late Proterozoic, beginning with the $\sim$0.59-Ga Acraman

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impact and continuing with major Phanerozoic extinctions and radiations associated with impact and volcanic events in the late Ordovician, late Devonian, late Triassic, late Jurassic, and late Cretaceous.

8.1 Introduction

Davies (1998) highlighted fundamental questions regarding the origin of life in terms of the quantum leap from organic molecules (amino acids, purines, and pyrimidines) to complex information-rich biomolecules (peptides, nucleic acids, proteins, and enzymes) whose genetic information cannot be expressed by mathematical algorithms, and with a probability of $1:10^{120}$ of forming by chance. Intrinsic to this inquiry is the origin of prebiotic molecules, environmental and temporal settings of early microorganisms – questions increasingly amenable to testing in view of cometary components of terrestrial sediments, including α-aminoisobutyric acid (AIB), isovaline (Zhao and Bada, 1989; Zahnle and Grinspoon, 1990) and noble gases such as ^{3}H (Farley et al., 1998). Cometary dusting of planetary atmosphere is capable of contributing little-modified extraterrestrial organic components – which are incinerated upon asteroid and comet impacts – in turn capable of shock synthesis of new organic molecules (Chyba and Sagan, 1992). The identification of 3.8–4.4-Ga zircons (Froude et al., 1983; Wilde et al., 2001) and the near-pristine preservation of ~3.5-Ga-old volcanic-sedimentary records, for example in the Pilbara and Kaapvaal cratons (Van Kranendonk et al., 2002; Poujol et al., 2003), potentially allows the search for earliest life forms to extend to the earliest chapters in terrestrial history. In this section I consider aspects of the Precambrian impact history in terms of the temporal and size frequencies of asteroid and comet impacts and their effects on volcanic and sedimentary environments where early life evolved, with principal reference to the Archaean to early Proterozoic records of the Pilbara and Kaapvaal cratons. Below, a review of Archaean and early Proterozoic asteroid and comet impact units will be followed by a discussion of the role of impacts in biospheric evolution.

8.2 PRE–3.8-Ga Events

In attempting interpretations of the relations between biospheric evolution and terrestrial environments, the polarity between uniformitarian views of terrestrial and biological history (James Hutton: 1726–97; Charles Lyell: 1797–1875) and catastrophic notions (Cuvier: 1769–1832) reemerges in terms of theories that alternatively advocate (1) progressive crustal and biological evolution, and (2) observations of episodic catastrophic events, such as mantle plume pulsations and extraterrestrial bombardments. In the wake of accretion of chondritic fragments and cosmic dust, gravitational collapse, melting and contemporaneous cometary contribution of organic components (Chyba, 1993;

Chyba and Sagan, 1992, 1996; Delsemme, 2000), appearance of sial crustal tracts is indicated by ~4.4-Ga zircons, signifying onset of two-stage mantle melting processes, which require hydrous crust (Ringwood and Green, 1966). From $^{18}O/^{16}O$ evidence at this stage, the Earth may have been cool enough to allow presence of liquid water at the surface (Wilde et al., 2001; Peck et al., 2001; Mojzsis et al., 2001). The earliest replicating cells probably required only 20 or so elements (da Silva and Williams, 1991), available at submarine hot springs, and as many fundamental organic molecular components (Wald, 1964; Eck and Dayhoff., 1968).

Early views of the Late Heavy Bombardment (LHB), defined by an impact incidence of $4–9\times10^{-13}$ km^{-2} year $^{-1}$ on the Moon (for craters >18 km) (Baldwin, 1985), have been questioned by Ryder (1997, 2003) in view of a scarcity of pre-LHB ejecta in the lunar highlands – which may or may not reflect the severe sampling limitations. Despite extensive records of ~3.8–4.4-Ga-old zircons in Archaean gneisses and derived clastic sediments on the Earth (Froude et al., 1983; Wilde et al., 2001), suggesting preexistence of sial crustal domains, no shock metamorphic planar deformation features (PDF) were observed in the zircons to date – a possible result of severe breakdown of shocked grains during erosion – nor have siderophile element anomalies been detected (Koeberl et al., 2000), although Tungsten isotope anomalies miliate for extraterrestrial contribution (B. Kamber, personal Communication 2003). Whether the Earth was affected by the LHB, though very likely, remains a key question.

During a Late Heavy Bombardment of Earth (~3.95–3.85 Ga), still subject to uncertainties (Ryder, 2003), exposure to cosmic radiation, electric and thermal flash associated with large asteroid impacts, solar clouding effects and acid rain would annihilate any photosynthesizing bacterial colonies from the surface (Zahnle and Sleep, 1997; Greenspoon, 1990; Chyba, 1993; Chyba and Sagan, 1993), possibly with the exception of extremophile chemotrophic bacteria residing in faults and fractures of the “deep biosphere.” Traces of isotopically light $^{13}C/^{12}C$ graphite within apatite in 3.85-Ga banded iron formation in southwestern Greenland provide first possible clues for such habitat (Mojzsis et al., 1996; Mojzsis and Harrison, 2000).

8.3 Post–3.8-Ga Extraterrestrial Impacts

Continuous accretion of cosmic dust accretion from about 3.8 Ga, estimated from deep ocean pelagic sediment cores at the rate of 3×10^4 ton year^{-1} (Kyte, 2002), contributed a small fraction of about 0.2×10^{-7} of the Earth mass. The contribution of meteorites, asteroids, and comets can be roughly estimated from the impact frequency/size distribution (Fig. 8.1). Episodic heavy bombardment did not terminate with the LHB, but continued throughout Earth–Moon history at rates of $4.3 \pm 0.4 \times 10^{-15}$km^{-2} year^{-1} (for craters >20 km), i.e., two orders of magnitude less than during the LHB (Shoemaker

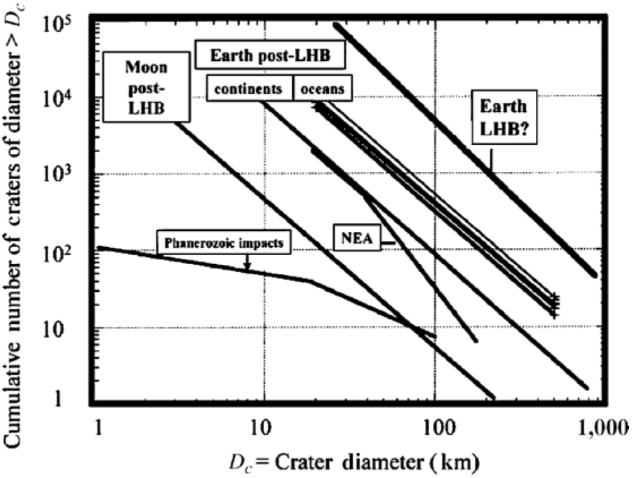

Fig. 8.1. Crater size vs. cumulative frequency plots for post-LHB times in Earth–Moon system. Moon post-LHB – post-LHB lunar maria craters and post-Martian plains craters (after Barlow, 1990). NEA – crater distribution extrapolated from observed Near-Earth Asteroids ($D_c = 20D_p$). PHANEROZOIC – Phanerozoic impact rates (Grieve and Dence, 1979), showing loss of smaller craters. EARTH POST-LHB – average Earth cratering rate based on Table 8.1 and extrapolated to entire Earth surface for 20-km-diameter craters and cumulative crater vs. size–frequency relationships equivalent to lunar impact incidence rates; CONTINENTS – mean cratering rate on time-integrated continental crust (~20% of Earth's surface). OCEANS – mean cratering rate on time-integrated ocean crust (~80% of Earth's surface). E-LHB – Late heavy bombardment of the Earth, extrapolated from lunar data of Barlow (1990).

and Shoemaker, 1996) (Fig. 8.1). This agrees with the cratering rate inferred from the near-Earth asteroid (NEA) flux of $5.9 \pm 3.5 \times 10^{-15}\text{km}^{-2}$ year^{-1} for asteroids >1 km. Based on these estimates, the impact incidence post–3.8-Ga involves some 390±36 craters >100-km-large and 45±4 craters >250-km-large (Table 8.1). Due to Earth–Moon gravity cross section, it is likely that the mean impact incidence exceeded these estimates by ×1.4. Based on the dominantly mafic/ultramafic composition and the lack of shocked quartz grains in Archaean and early Proterozoic impact ejecta (Simonson et al., 1998; Glikson and Allen, 2004), the majority of these impacts occurred in simatic/oceanic regions of the Earth. This conclusion is in agreement with estimates of the growth of continental crust with time based on rare earth elements (Taylor and McLennan, 1981) and Sm-Nd isotopes (McCulloch and Bennett, 1994).

That the projected impacts did not occur as a continuous or random flux is suggested by the clustering of impacts on the Earth and Moon (Fig. 8.2 A–E), corroborated in Precambrian terrains by impact fallout units (Table 8.2) and in Phanerozoic terrains by both impact craters and ejecta fallout units (Table 8.3). Established impact clusters occur at the K-T boundary (Chicxulub, Boltysh) and late Eocene (Popigai, Cheasapeake Bay). Possible, though

Table 8.1. Postterrestrial impact rates and estimated minimum numbers of craters on several crater diameter scales.

Crater diameters[a]	$D_c \geq 20^b$	$D_c \geq 100^b$	$D_c \geq 250^b$	$D_c \geq 500^b$	$D_c \geq 1,000^b$
[A]	$8,300 \pm 770$	390 ± 36	45 ± 4	17 ± 1.6	4 ± 0.3
[B]	$10,630 \pm 5200$	460 ± 225	54 ± 26	19 ± 9.3	5 ± 2.4
(1)	$2,020 \pm 990$	90 ± 44	11 ± 5.4	4 ± 2	1 ± 0.5
(2)	$8,100 \pm 3970$	360 ± 17	42 ± 21	15 ± 7.3	4 ± 2
(3)	40	6	2	NA	NA
(4)		30	10	NA	NA
(5)	0.38	1.3	3.8	NA	NA
(6)	1.9	6.6	18.0	NA	NA

Based on projected cratering incidence for craters $D_c \geq 20$ and empirically observed cumulative crater and asteroid size frequency plots $N \propto D_c^{-1.8}$ (Shoemaker and Shoemaker, 1996). Estimated crater numbers are rounded; [A] Terrestrial cratering rate equivalent to the lunar cratering rate of $R = 4.3 \pm 0.4 \times 10^{-15} \text{km}^{-2} \text{year}^{-1}$ at ~3.2 Ga; asteroid impact velocities assumed (Shoemaker and Shoemaker, 1996). [B] Terrestrial cratering rate of $5.5 \pm 2.7 \times 10^{-15} \text{km}^{-2} \text{year}^{-1}$ for craters of $D_c \geq 20$ km (Grieve and Pesonen, 1996); (1) predicted number of craters formed on continental crust based on a mean cratering rate; (2) predicted number of craters formed on oceanic crust based on a mean cratering rate; (3) number of actually observed continental craters; (4) absolute minimum number of craters deduced for the entire Earth as based on 3; (5) percent observed to predicted craters for entire Earth surface; (6) percent observed to predicted craters for a time-integrated continental crust area.

[a] Estimated cratering rate $R \times 10^{-15}$ km^{-2} year^{-1} craters with $D_c \geq 20$ km.

[b] Estimated number of craters of size $\geq D_c$ (in km) formed < 3.8 Ga from the relation $N \propto D_c^{-1.8}$. (N, number of craters; D_c, diameter).

Table 8.2. Precambrian impact fallout units and associated tsunami deposits.

Formation and impact unit symbol	Symbol	Province	Age (Ga)	Number of units
Apex Basalt	ACM -1 ACM-2	Central Pilbara Craton, Western Australia	3470.1±1.9 Ma	2 <
Hoogenoeg Formation	HF	Barberton greenstone belt, Transvaal, South Africa	3470.4±2.3 Ma	2
Basal Fig Tree Formation	S2, S3, S4	Barberton greenstone belt, Transvaal, South Africa	∼3.24–3.225	3
Top Jeerinah Formation	JIL	Pilbara Craton, Western Australia	>2.629±5	1
Monteville Ghaap Formation	MONT	Griqualand West Basin, Kaapvaal Craton, Transvaal, South Africa	?∼2.63	2
Bee Gorge Member, Wittenoom Formation	SMB-1 SMB-2	Hamersley Basin, northern Western Australia	2561±8	2
Carawine Dolomite	SBMB	East Hamersley Basin, northern Western Australia	?∼2.56	
Dales Gorge S4 Macroband	DGS4	Hamersley Basin, northern Western Australia	∼2.47–2.50	
Base Kuruman Iron Formation	KIF	Kaapvaal Craton Transvaal, South Africa	?2.47	
Graenseso Formation, Ketilidian Orogen	KET	Southern Greenland	∼1.8–2.1	1
Bunyeroo Ejecta	BUN	Flinders Ranges, South Australia	0.58	

Abbreviations: *WA, Western Australia; WTR, Western Transvaal; BTR, Barberton Mountain Land, east Transvaal; SA, South Australia.*

Table 8.3. Listing of Phanerozoic impact clusters and possible impact clusters.

Impact structure and fallout	D_s	Ma
A. late Eocene cluster		
Chesapeake Bay	85	35.5 ± 0.6
Popigai	100	35.5 ± 0.8
Wanapeiti, Ontario	7.5	37.2 ± 1.2
B. late Cretaceous cluster		
Early Danian		~64.9
Boltysh	24	65.17 ± 0.64
Chicxulub	180–280	64.98 ± 0.05
C. Cretaceous split projectiles		
Kara	65	70.3 ± 2.2
Ust Kara	25	70.3 ± 2.2
Tookoonooka,Queensland	55	128 ± 5
Tallunidilli, Queensland	30	128 ± 5
D. late Jurassic possible cluster		
Morokweng	90	145 ± 0.8
Mjolnir	40	143 ± 20
Gosses Bluff	24	142.5 ± 0.8
D. late Triassic possible cluster		
Manicouagan	100	214 ± 1
Saint Martin	40	220 ± 32
Rochechouart	23	214 ± 8
Obolon	15	215 ± 25
Red Wing	9	200 ± 25
E. Late Carboniferous split projectile		
Cleawater East, Quebec	26	290 ± 20
Clearwater West, Quebec	36	290 ± 20
F. late Devonian possible cluster		
Woodleigh, Western Australia	120	359 ± 4
Siljan, Sweden	52	368 ± 1.1
Alamo, Nevada	~100	~367
Charlevoix, Quebec	54	42 ± 15
G. late Ordovician possible cluster		
Pilot, NWT Canada	6	445 ± 2
Calvin, Michigan	8.5	450 ± 10
Ames, Oklahoma	16	470 ± 30
Slate Island, Ontario	~30	450

Based on crater and impact ejecta fallout data after Crater@gsc.nrcan.gc.ca and Glikson (1996, 2001).

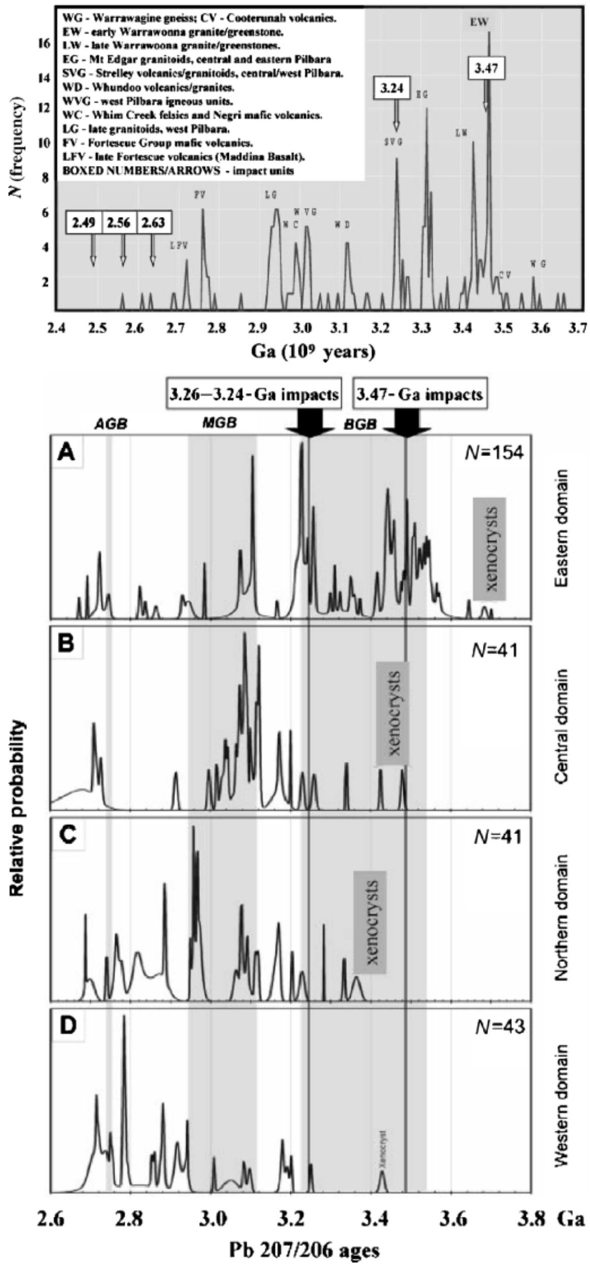

Fig. 8.2A,B. (A) Frequency distribution of U-Pb zircon ages of Archaean igneous rocks in the Pilbara Craton, Western Australia (based on data in Van Kranendonk et al., 2002); (B) Frequency distribution of U-Pb zircon ages of Archaean igneous rocks in the Kaapvaal Craton, South Africa (from Poujol et al., 2003). Asteroid impact ages are marked within frames.

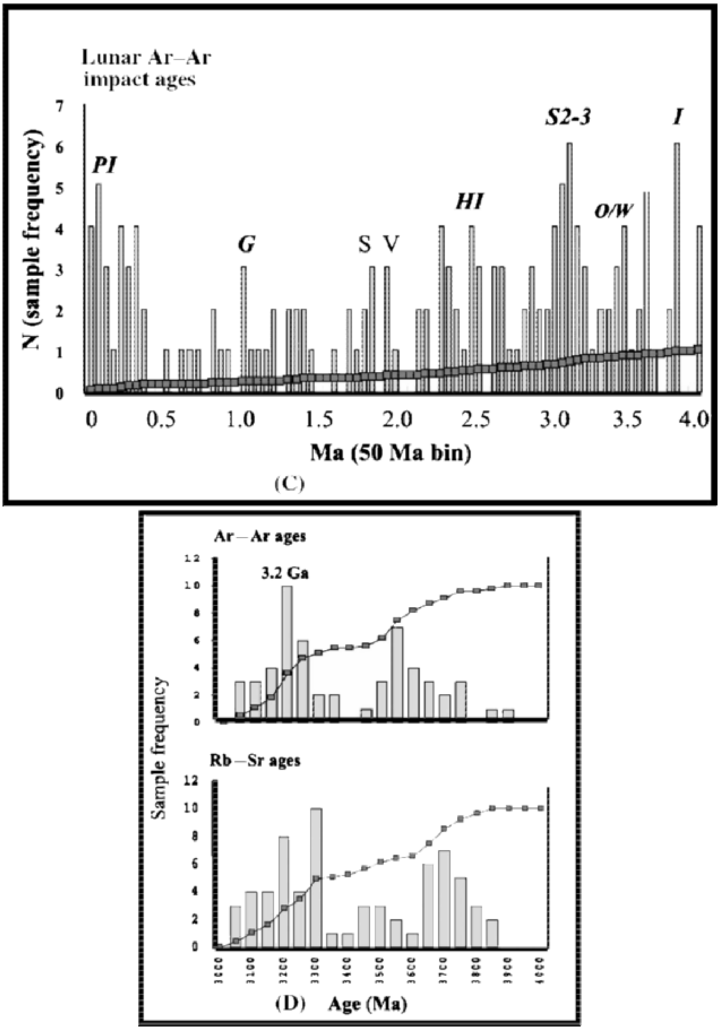

Fig. 8.2C,D. (C) Frequency distribution of Ar–Ar of lunar impact spherules after Culler et al. (2000); (D) Frequency distribution of Ar–Ar ages and Rb–Sr ages of mare baslts (after Basaltic Volcanism of the Terrestrial Planets, 1981).

yet subject to further isotopic age definitions, occur in the late Ordovician, late Devonian, late Triassic, and late Jurassic. Double craters, probably representing split projectiles, are recorded at Tookoonooka–Tallunidilli (Queensland), Kara-Kara-Ust (Ukraine) and Clearwater East-Clearwater West (Quebec) (Table 8.3). Precambrian impact fallout units include multiple impacts at 3.47 Ga (Pilbara and Kaapvaal cratons; Lowe et al., 2003; Byerly et al., 2002; Glikson, 1993, 1996, 1999, 2001; Glikson et al., 2004) and 2.56 Ga in the Hamersley Basin (Glikson, 2004) (Table 8.3). In evaluating the environmental and biological consequences of multiple impacts, the cumulative synergy effect of these events needs to be taken into account – the total effect being greater than the sum of individual events.

8.4 Archaean to Early Proterozoic Impacts, Pilbara, and Kaapvaal Cratons

8.4.1 About 3.5-Ga Impact Cluster

By 3.5 Ga – a period characterized by extensive subaqueous mafic–ultramafic volcanic activity, episodic bombardment by large asteroids (Lowe et al., 2003; Byerly et al., 2002; Glikson et al., 2004) has been closely associated with intermittent felsic volcanic activity in the 3.47-Ga Warrawoona Group (Pilbara Craton) and the Hoogenoeg Formation (Barberton Mountain Land, Transvaal) (Fig. 8.3.A–F). In the Pilbara at least two and possibly a larger number of impacts are represented, including (1) a 0.6–0.8-m-thick microkrystite spherule-bearing diamictite (ACM-S2) with pebble to cobble-size chert-intraclasts; (2) 14-m-thick chert-hosted lenses of impact spherules interlayered with spherule-bearing arenites (ACM-S3). The microkrystite spherules are discriminated from detrital volcanic fragments by their high sphericities, inward-radiating fans of sericite pseudomorphs after K-feldspar, relic quench textures and Ni–Cr–Co anomalies. The Presence of spherule-bearing chert fragments in ACM-S3 may hint at an older spherule-bearing chert (?ACM-S1). The near-perfect sphericities of chert-hosted spherules and arenite-hosted spherules militates against wave corrosion and spherule breakage in high-energy shallow water environment, suggesting the spherules were either protected by rapid burial or, alternatively, disturbance was limited to a short-term high-energy perturbation induced by a deep-amplitude impact-triggered tsunami wave.

Possible equivalents of the ∼3.47-Ga bombardment and volcanic events are suggested from ∼3.5-Ga Ar–Ar ages of lunar impact spherules (Fig. 8.2.A–C). During this period stromatolite-like structures appear in association with hydrothermal barite-chert zones (∼3.49-Ga Dresser Formation) and above barite-bearing submerged or lagunal felsic volcanic shoals and other unconformably underlying units (∼3.34–3.426-Ga Panorama Formation) (Dunlop and Buick, 1981; Van Kranednonk et al., 2003). A prime example for the development of stromatolites is in the Strelley Pool Chert, a 3426–3350 Ma quartz arenite, carbonate, evaporate (?), and conglomerate-bearing succession deposited across a regional unconformity (Hoffman et al., 2001; Van Kranendonk, 2000, Van Kranendonk et al., 2003). Here conical structures show a resemblance, at least in gross morphology, to certain forms of stromatolites known from younger stratigraphic units, and to living stromatolites growing in hot springs, such as at Yellowstone or in New Zealand. Superficially they are similar to laterally linked forms such as *Thyssagetes Vlasov 1977*, and a few cones have lateral branches, a feature common in

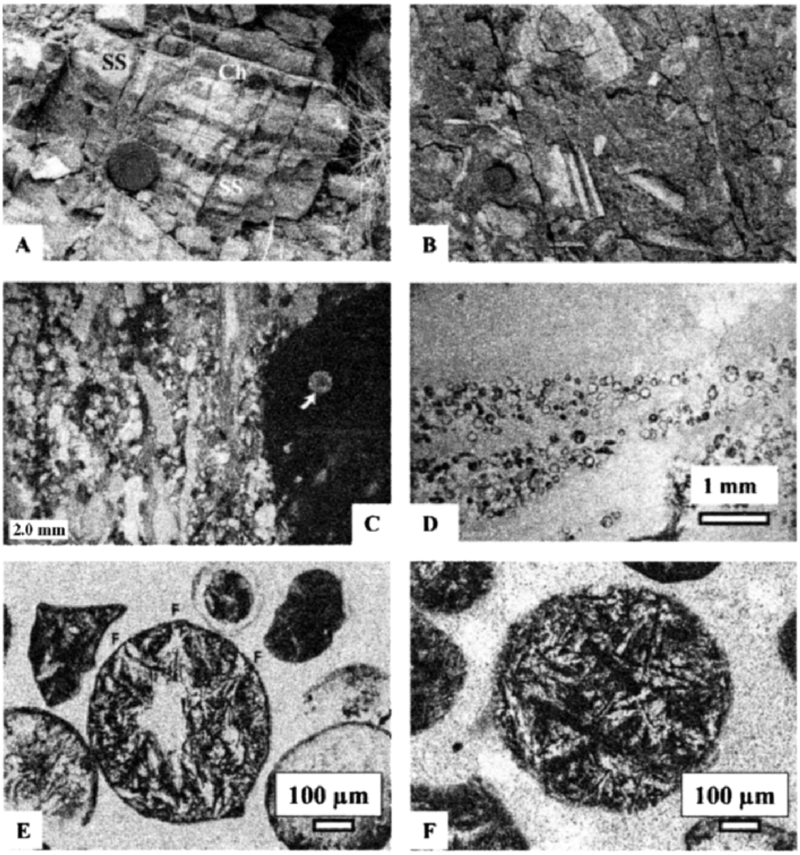

Fig. 8.3. 3.47-Ga impact cluster, Antarctic Chert Member, Apex Basalt, upper Warrawoona Group, central Pilbara Block, Western Australia. (A) Intercalated microkrystite spherule-bearing arenite (ACM-S3) (ss – light colored) and chert (ch – dark colored)(lens cap – 6 cm); (B) impact spherule-bearing chert fragment to boulder-size diamictite (ACM-S2); (C) spherule-bearing intraclast microconglomerate containing a pebble of black chert with an embedded microkrystite spherule, possibly derived from an early microkrystite spherule-bearing unit ACM-S1. Spherules are indicated by arrows; (D) lenses of microkrystite spherules within chert (ACM-S3); (E) microkrystite spherule showing inward-radiating sericite pseudomorphs after K-feldspar [F] devitrification textures, and a centrally offset vesicle; (F) microkrystite spherule showing quench textured pseudomorphs, probably after ferromagnesian phases (olivine, pyroxene).

Jacutophyton Schapovalova 1965. However, details of laminar structures have been lost through recrystallization, and the structures lack an axial zone, a character typically present in most fossil taxa including both *Thyssagetes* and *Jacutophyton*. Moreover, the branches in *Jacutophyton* are much more frequent and reguar in shape. Conical stromatolites also occur in the

2.67-Ga-old Kanowna district, Eastern Goldfields, in the Abitibi greenstone belt, Superior Province, Canada, and as intercalations in the 515 Ma Cambrian, Antrim Plateau Volcanics. The stromatolite units have been deformed by tectonic movements, uplift, and erosion, represented by erosional surfaces preserved within the sequences. In some instances, granitic bodies have reached the surface as small islands or continental nuclei due to local uplift and erosion (Buick et al., 1995).

8.4.2 About 3.26–3.225-Ga Asteroid Bombardment

The most intense meteoritic bombardment identified on the Earth to date is recorded by three 3.26–3.225-Ga multiple impact microkrystite spherule units at the base of the ~3.2-Ga Fig Tree Group, Barberton, eastern Transvaal (Fig. 8.4.A–C). The impact origin of these units is established by their domination by microkrystite spherules, microtektites, Ni-chromites, and ^{53}Cr-^{52}Cr isotope systematics diagnostic of chondrites (Lowe and Byerly, 1986; Lowe et al., 1989; 2003; Shukolyukov et al., 2000; Kyte et al., 2003). As pointed out by Lowe et al. (1989), the location of the impact cluster just above the contact between the mafic–ultramafic volcanic Onverwacht Group and the overlying felsic volcanic and turbidites of the Fig Tree Group may be significant, hinting at major crustal transformation triggered by the impacts. A similar change is recognized in the Pilbara as the transition from the Sulphur Springs Group (Kangaroo Cave Formation) to the Gorge Creek Group (Pincunah Hill Formation). No impact spherules were encountered in the latter unit, whose basal section contains a local olistostrome breccia (Fig. 8.4.C) derived from reactivation bounding faults, possibly as a result of impact-triggered crustal disturbance.

Mass balance calculations based on the Iridium anomalies and spherule size of the impact fallout units (Melosh and Vickery, 1991) indicate asteroids several tens of kilometer in diameter, consistent with impact craters on the scale of 400–600 km (Byerly and Lowe. 1994; Shukloyukov et al., 2000; Kyte et al., 2003; Lowe et al., 2003; Glikson and Allen, 2004). The mafic chlorite-dominated composition of the spherules and the absence of shocked quartz grains militates for derivation of the ejecta from simatic/oceanic loci (Simonson et al., 1998). Siderophile element (Ni, Co), ferrous elements (Cr, V), and Platinum Group Element (PGE) patterns of least-altered microkrystite (impact-condensate) spherules and microtektites are consistent with a mafic/ultramafic composition of impact target crust (Glikson and Allen, 2004). A domination of mafic/oceanic crust during the Archaean, estimated as >80% of the Earth crust from models based on rare earth elements (REE) (Taylor and McLennan, 1981) and Sm-Nd isotopes (McCulloch and Bennett, 1994), and encompassing hundreds of kilometer-scale impact basins, is inconsistent with uniformitarian geodynamic models based exclusively on plate tectonic processes.

The spherule data suggest multiple impacts about 3.26–3.225 Ga (Byerly and Lowe, 1994; Shukloyukov et al., 2000). Deposition of S1, S2, and S3

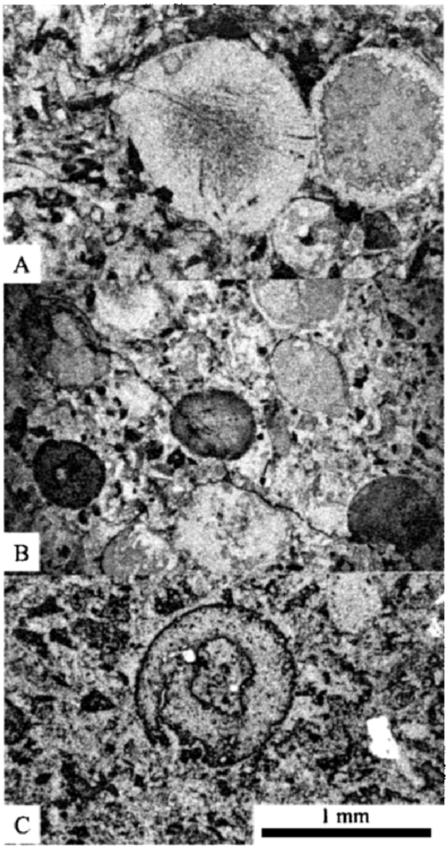

Fig. 8.4A–C. About 3.24-Ga microkrystite spherules of the S3 impact fallout unit, Mapepe Formation, lower Fig Tree Group, Barberton Mountain Land, eastern Transvaal. (A) right hand – carbonate-rimmed chlorite spherule; center spherule – carbonate dominated; groundmass consists of spherule fragments and iron oxides; plane polarized light (ppl); (B) chlorite-dominated spherules (ppl); (C) reflected light microphotograph of a chlorite-dominated spherules containing a central vesicle and Nickel-rich chromites.

spherule units was disturbed by impact-generated tsunami currents, including multiple tsunami wave fronts. These tsunamis may have promoted mixing within a globally stratified ocean, enriching surface waters in nutrients for biological communities (Lowe et al., 2003). This impact period may correlate with a major ^{40}Ar-^{39}Ar 3.18-Ga age distribution peak measured by Culler et al. (2000) in a small sample of lunar impact spherules (Fig. 8.2.C).

Fig. 8.4D. Olistostrome consisting of boulders (OL) of chert and volcanic rocks several tens of meters across within fragmental conglomerate of the Pincunah Formation, overlying a ∼3.24-Ga chert marker that marks the boundary between an underlying volcanic sequence (Sulphur Springs Group) and an overlying turbidite-banded ironstone sequence (Gorge Creek Group) – correlated with the ∼3.24-Ga impact cluster of the lower Fig Tree Group, eastern Transvaal. The olistostrome may represent tectonic movements related to the impact cluster.

8.4.3 About 2.6–2.4-Ga Impact Clusters and Associated Tsunami

The Jeerinah Impact layer (JIL) (Simonson et al., 2000; Glikson, 2004) consists of a sequence of siltstone, chert and mafic volcanics, capped by a ∼40-cm-thick microkrystite spherule-bearing rip-up breccia, a lenticular spherule unit up to about 60 cm thick, with an overlying ∼70-cm-thick boulder-size debris-flow conglomerate. The sequence represents initial current and/or seismic disturbance of the seabed, settling of microkrystite spherules, subsequent slumps and debris flow (Fig. 8.5.A–D). The age of JIL is constrained by U-Pb zircon date of 2629 ± 5 Ma of overlying volcanic tuff (Nelson et al., 1999) and U-Pb ages on zircon from sediments from the base of the Jeerinah Formation (2684 ± 6 Ma, 2690 ± 6 Ma; Arndt et al., 1991). Pending further isotopic age studies, it is possible that the JIL impact occurred close to the late Archaean (∼2.7–2.68 Ga) volcanic peaks that dominate greenstone belts of the Yilgarn, Superior, Brazil, and part of the Kaapvaal cratons. Significantly, by analogy to banded iron formations which overlie the ∼3.26–3.225 impact boundary in the Pilbara and Kaapvaal, the JIL fallout units is located immediately below the banded iron formation of the Marra Mamba Iron Formation.

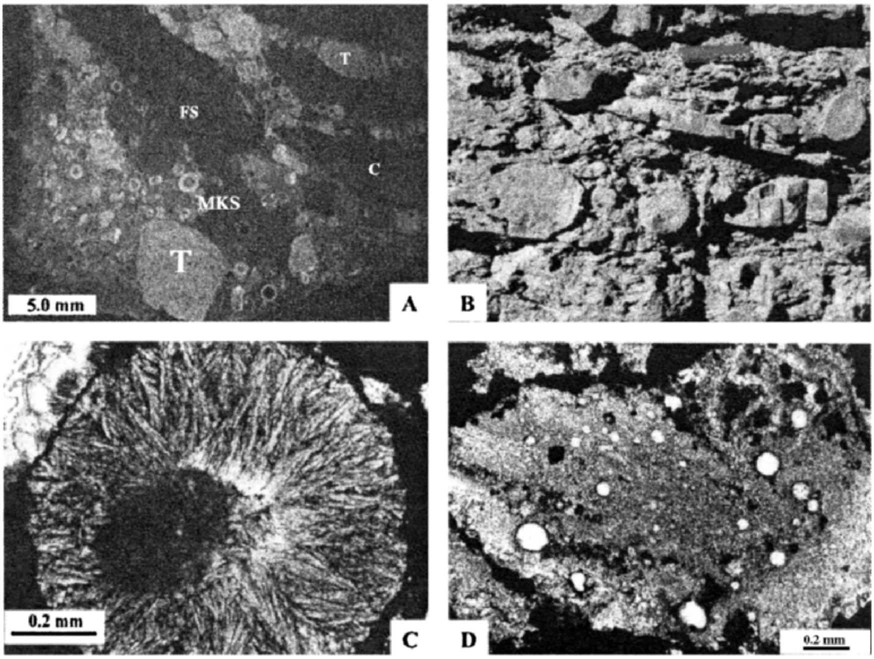

Fig. 8.5. More than 2.63-Ga Jeerinah Impact Layer. (A) Polished section of rip-up ferruginous siltstones (FS) with intervening microtektites (T) and microkrystite spherules (MKS). (B) Boulder breccia-conglomerate overlying the main spherule layer. knife – 8 cm. (C) JIL microkrystite spherule showing inward radiating K-feldspar fans and an offset central vesicle – both hallmarks of condensate spherules. (D). JIL microtektite showing crude flow bands and quartz-filled vesicles.

A microtektite and microkrystite-bearing impact spherule-bearing megabreccia unit (SBMB), possibly correlated with the 2.56-Ga SMB impact fallout unit (Fig. 8.6), consisted of 20–30-m-thick brecciated chert and dolomite fragment-rich carbonate breccia occurs in the lower part of the $\sim$2.54–2.56-Ga Carawine Dolomite over 100-km NW-SE in the eastern outlier of the Hamersley Basin (Simonson, 1992; Hassler et al., 2001; Glikson, 2004). The megabreccia is either excavated into, or conformably overlies, layered carbonate, and consists of chert and dolomite fragments and blocks derived from the underlying carbonates (Fig. 8.7.A–E). The SBMB constitutes a unique time-event marker located below wave base in subbasins between, as well as below, the stromatolite reef. Where stratigraphic relations are established, the stromatolites appear mainly later than the impacts. No impact debris was found to date in the possibly contemporaneous stromatolite reefs, such as in the Gregory Range – a lack attributed to high-energy currents over the shallow reef environment. Preservation of intact spherules within the veins is attributed to dilation of the injected veins under extreme hydraulic pressures caused by

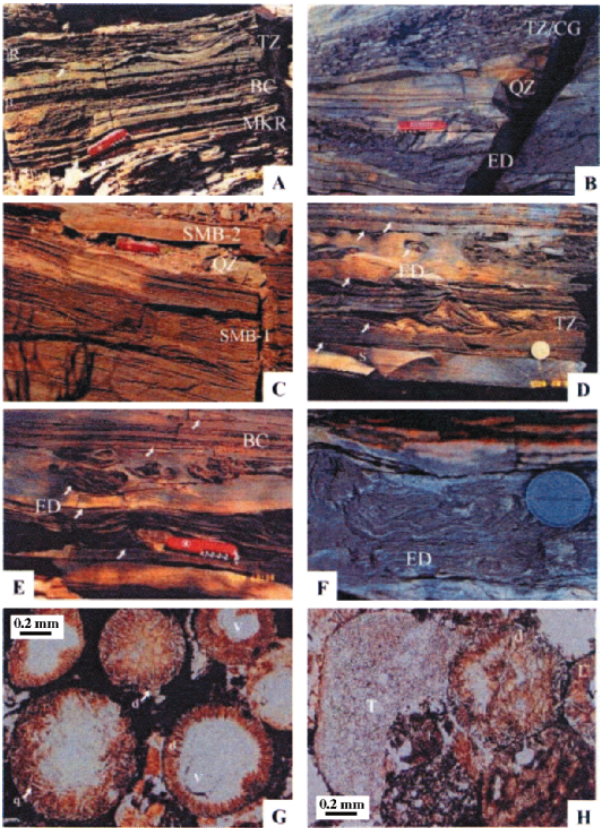

Fig. 8.6. About 2.56-Ga impacts. (A) Classic outcrops of SMB-1, Munjina Gorge, showing a basal microkrystite layer (MKR) (under Swiss knife), Bouma-cycle turbidites (BC), the base of the cross-rippled tsunami zone (TZ) with climbing ripples is indicated by an arrow. Knife is 8 cm. (B) Pocket of chert pebble-conglomerate of SMB-2 overlying silicified siltstone of the “Quiet Zone” (QZ) which, in turn, overlies eddie-structured turbidites of SMB-1 (ED). Bee Gorge; (C) Climbing ripples of SMB-1 overlain by siltstones of the “Quiet Zone” (QZ), overlain by spherule-bearing siltstone of SMB-1. Bee Gorge area; (D) Turbulence flame structures (FS) overlying silicified siltstone (S) which in places contains basal spherule lenses. The FS zone is overlain by siltstone that contains turbulent eddie structures; SMB-1, Crossing Pool, Wittenoom Gorge. Arrows from base to top point to (1) base of SMB-1 turbidite; (2) base of flame structured zone; (3) base of siltstone-hosted eddie zone; (4) turbulence eddie; base of “Quiet Zone”; (E). Turbulence eddies in SMB-1, Crossing Pool, Wittenoom Gorge. Arrows from base to top point to: (1) base of cross-layered zone; (2) top of cross-rippled zone; (3) Siltstone-hosted eddie zone; (4) turbulence eddie; (5) base of Bouma cycle zone; (6) top of Bouma cycle zone; (F) Convoluted turbulence eddie structures, SMB-1, Bee Gorge; (G) Microkrystite spherules from SMB-1, Munjina Gorge, displaying radial inward radiating devitrification features (d) of K-feldspar fans and randomly oriented K-feldspar microlites. Note the offset vesicle (V) in the right-hand spherule; (H) Microtektite (T) consisting of microlitic K-feldspar and located near a microkrystite spherules of similar mineralogy but showing inward-radiating textures and offset vesicles. These textural differences are interpreted, respectively, in terms of derivation from microtektite melt droplets and vapor condensation melt droplets.

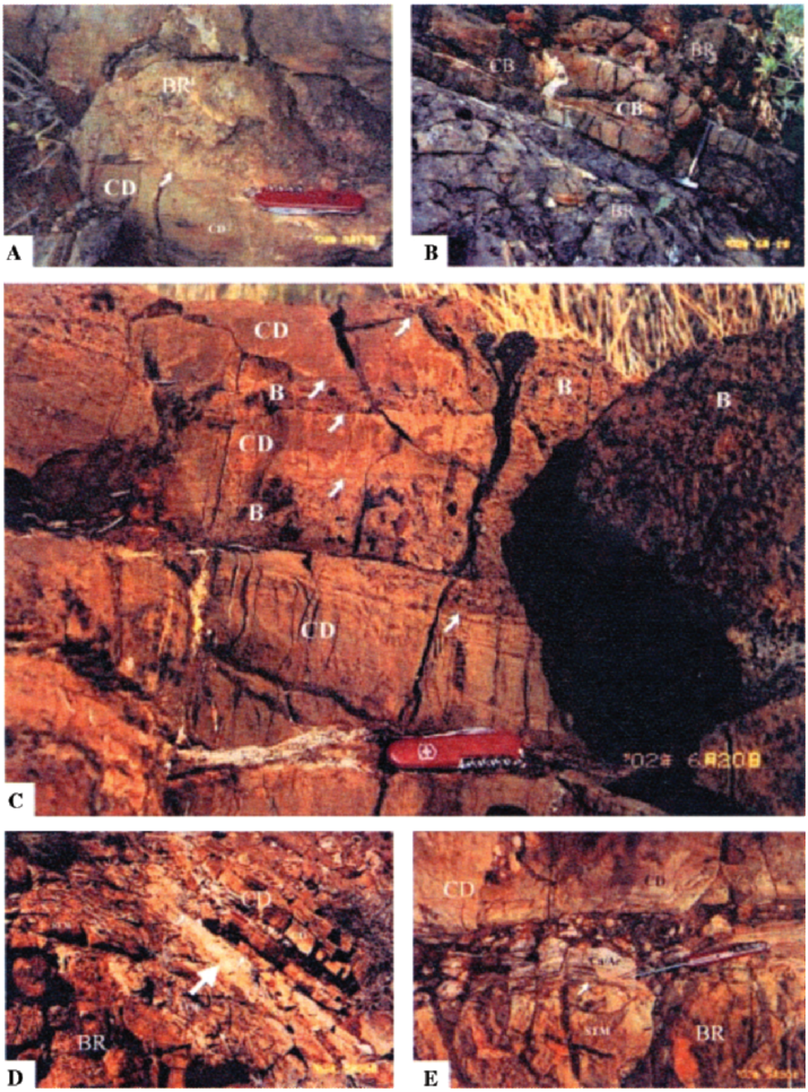

Fig. 8.7. Outcrops of spherule-bearing megabreccia (SBMB) of the Carawine Dolomite. Swiss knife, 8 cm. Hammer, 30 cm. (A) Base of the SBMB showing breccia excavated in relief into underlying carbonates, cutting through bedding planes, Warrie Warrie Creek. BR, breccia; CD, Carawine Dolomite; (B) A 7-m-long (only part shown) detached carbonate layer segment overlying and underlying megabreccia, Ripon Hills; (C) Excavated base of the SBMB showing alternating carbonate blocks of Carawine Dolomite (CD) and layer-parallel injected breccia [B] which contains isolated microkrystite spherules. Warrie Warrie Creek. Swiss knife is 8 cm. (D) Top of the SBMB, showing undisturbed carbonates (CD) capping breccia (BR). Arrows point to contact zone; (E) Top of the SBMB, knife and arrow point to a sharp contact between breccia (BR) and layered carbonate (CD).

the tsunami. The field relations suggest ejecta fallout preceded arrival of the tsunami waves. The tsunami dispersed the upper soft sedimentary layer of the seabed, including the spherule layer, as a subaqueous mud cloud. Disruption of below-wave base sediments and their underlying substratum to depths in the order of over 100 m require tsunami amplitudes on the scale of hundreds of meters. The tsunami did not necessarily originate from impact craters, and could have emanated from faults and plate margins reactivated by impact-triggered seismic activity.

Stratigraphic correlations and isotopic Pb–Pb carbonate ages tentatively support a correlation between the ~2.54–2.56-Ga SBMB megabreccia and the ~2.56-Ga Spherule Marker Bed (SMB) multiple impact unit, Bee Gorge Member, Wittenoom Formation, central Hamersley Basin (Simonson, 1992; Simonson and Hassler, 1997; Glikson, 2004) (Figs 8.6 A–H). The SMB-1 and SMB-2 impact fallout layers each consists of a spherule layer or lenses overlain by Bouma cycle graded turbidites and/or by current perturbed turbidites containing turbulence eddies or conglomerate. The two impact cycles are separated by a stratigraphically consistent little disturbed silicified siltstone layer. A weakening of tsunami effects from the eastern to the central Hamersley Basin (Simonson, 1992; Glikson, 2004) over a distance of about 200 km, suggests a northeast origin of the tsunami and deepening of the basin in the southwest direction.

A stratigraphically consistent <20-cm-thick unit of microkrystite spherules and microtektite-bearing impact fallout ejecta overlies 2.47–2.50-Ga volcanic tuff (DGS4) of the Dales Gorge Member, Hamersley Basin. Locally the unit incorporates up to meter-scale fragments and boulders of banded chert and stromatolite carbonate, suggesting tsunami transport postdating spherule deposition (Fig. 8.8 A–D). The unit displays anomalous platinum group element (PGE), Ni, Cr, and Co abundances and ratios, indicating meteoritic contamination. Mixing calculations suggest a contribution of 2.5–3% projectile component to the impact-generated volatile cloud. Conservative mass balance estimates derived from the Ir and Pt flux, assuming global extent of a 10-cm-thick spherule unit and chondritic projectile composition, suggest an asteroid diameter on the scale of ~30 km. Similar estimates are obtained from spherule sizes, which in DGS4 reach a mean diameter of ~2.0 mm in aerodynamically elongate spherules. The evidence implies formation of an impact basin on the scale of 400 km in simatic/oceanic regions of the early Proterozoic crust (Glikson et al., 2004).

8.5 Possible and Demonstrated Connections Between Extraterrestrial Impacts and Habitats of Life

Of the wide range of physical environmental controls over recorded habitats of stromatolite-like, probable stromatolites and confirmed stromatolite colonies

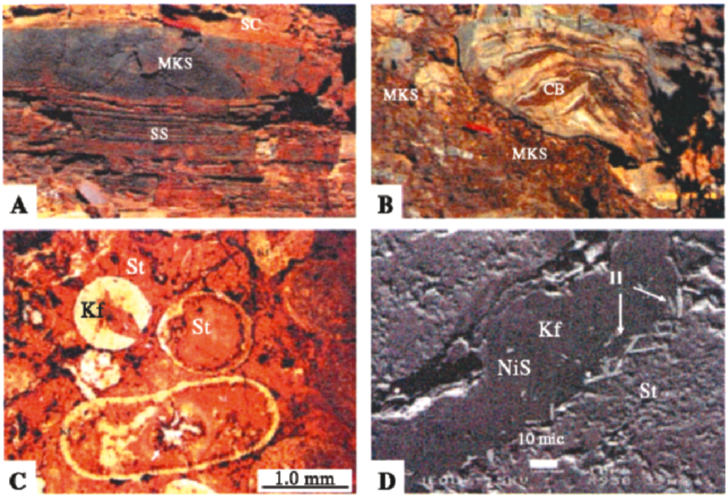

Fig. 8.8. Approximately 2.47–2.50-Ga Dales Gorge Iron Member S4 Macroband (DGS4) impact fallout unit. (A) stilpnomelane-dominated tuff and siltstone (SS) overlain by a 20-cm-thick microkrystite spherule unit (MKR), overlain by siderite chert (SC), Fortescue Falls; (B) Boulder of banded chert (CB) incorporated in the upper part of DGS4, resting in part on spherule-bearing stilpnomelane matrix (MKR) containing chert fragments. (C) Elongate and oval microkrystite spherules consisting of stilpnomelane (st) mantled by K-feldspar (Kf), plane polarized light; (D) scanning electron microscope image showing a K-feldspar rim bordering stilpnomelane spherule (st). The K-feldspar (Kf), showing lower electron contrast, contains ilmenite microlites (Il) and submicron particles of NiS.

in the Pilbara Craton, volcanic and hydrothermal factors are the most manifest, whereas the role of asteroid and comet impacts is more difficult to evaluate due to (1) the paucity of the impact and palaeontological records; (2) the mm scale of microkrystite spherules and of microtektites renders these diagnostic entities difficult to recognize in the field; and (3) the effect of large impact in modifying tectonic environments and triggering volcanic and hydrothermal activity is inherently difficult to ascertain, in view of the preservation worldwide of only a small fraction of well-preserved and exposed Archaean supracrustal volcanic-sedimentary assemblages. However, several lines of evidence point to direct, indirect, and, in some instances, potentially critical controls of the environments in which Archaean and early Proterozoic microorganisms survived extraterrestrial impacts, as in the following examples from the Pilbara and Kaapvaal Cratons.

The appearance of undulating to dome-shaped stromatolite-like structures of possible, yet unproven, biogenic origin in the ∼3.49-Ga Dresser Formation (Figs. 8.9 and 8.10 A), Pilbara Craton, intercalated with black chert, silicified arenite and carbonate (Buick et al., 1981; Dunlop and Buick, 1981; Grove et al., 1981) (Fig. 8.10 B), is characterized by its intimate intercala-

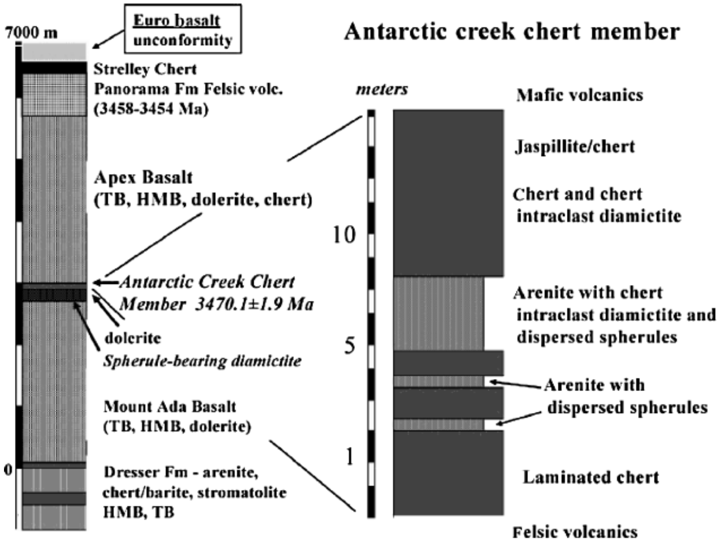

Fig. 8.9. Schematic columnar stratigraphic section through the Warrawoona Group in the eastern part of the North Pole dome, between the Dresser Formation and the Strelley Pool Chert. Schematic stratigraphic column of the upper Warrawoona Group in the eastern part of the North Pole dome, Pilbara Craton, northwestern Australia, including the Dresser Formation, Mount Ada Basalt, Antarctic Creek Chert Member, Apex Basalt and Panorama Formation. Spherule-bearing Antarctic Creek Chert Member in the eastern North Pole dome area. TB, tholeiitic basalt; HMB, high-Mg basalt. Thicknesses in the left-hand column after Van Kranendonk (2000) and in the right-hand column based on the present study.

tion with and injection by stratiform barite, which also occurs in barite-chert veins (T-chert) underlying these units. These commonly brecciated veins contain similar assemblages as the stromatolite-bearing units and are considered hydrothermal feeders of the latter (Farmer, 2000). Barium is typically highly enriched in felsic volcanics of the ∼3.49–3.43-Ga Warrawoona Group, for example in the Duffer Formation (Glikson and Hickman, 1981), representing late hydrothermal activity in felsic volcanic centers. Mafic volcanic units that overlie the Dresser Formation – the Mount Ada Basalt and Apex Basalt (Van Kranendonk, 2000), comprise many kilometer-thick sequences of pillowed basalt, suggesting rapid subaqueous foundering of the sea bed, allowing no foothold for stromatolite development. Intervals between volcanic activity and corresponding subsidence are represented by numerous chert units, signifying mainly colloidal silica precipitation accompanied by minor sedimentary fluxes. At least two of these intercalations, located between the Mount Ada Basalt and the Apex Basalt, includes the 3.47-Ga impact fallout microkrystite spherules described above (Fig. 8.3). The impact fallout unit is succeeded by a unique jaspilite chert unit correlated with the Marble Bar Chert – a distinct stratigraphic marker in the eastern Pilbara.

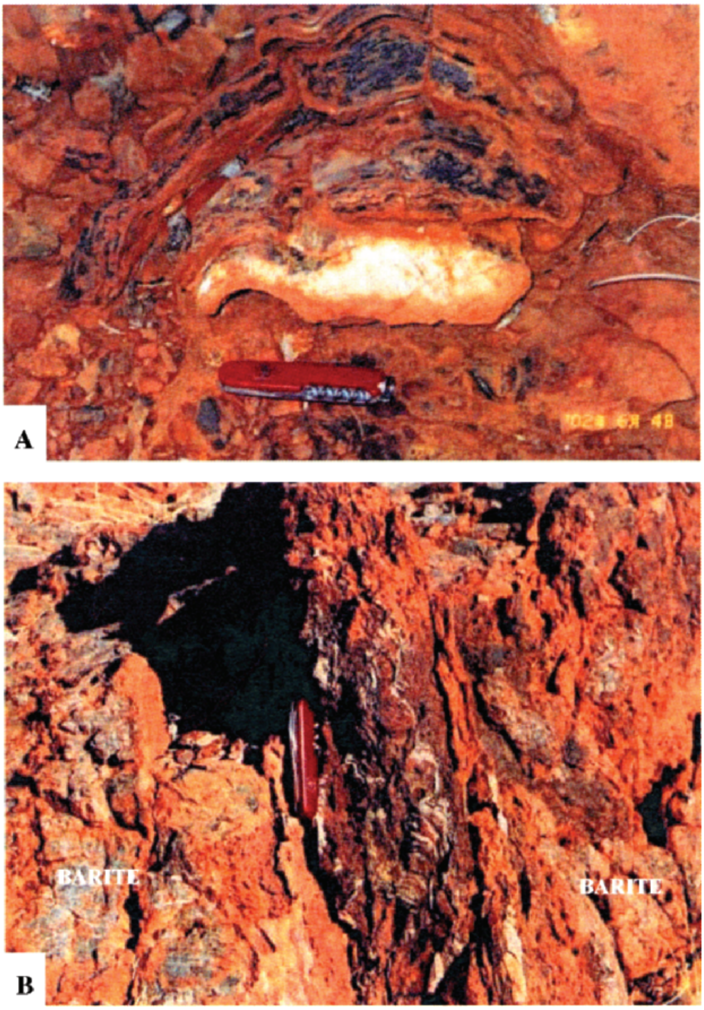

Fig. 8.10A,B. Pilbara stromatolite-like structures, probable stromatolites, and possible microorganisms. (A) 3.49-Ga carbonate-chert stromatolite-like structure intercalated with barite, Dresser Formation, North Pole dome, central Pilbara; (B) carbonate-chert stromatolite-like unit intercalated with barite, Dresser Formation;

Stromatolite-like structures reappear in the wake of a major felsic volcanic phase represented by the 3.434–3.426-Ga Panorama Formation, and are located in the unconformably overlying Strelley Pool Chert, associated with chert, arenite and barite (Fig. 8.10.C,D). The biogenicity of these stromatolites remains the subject of current debate (Hoffman et al., 1999; Brasier et al., 2004).

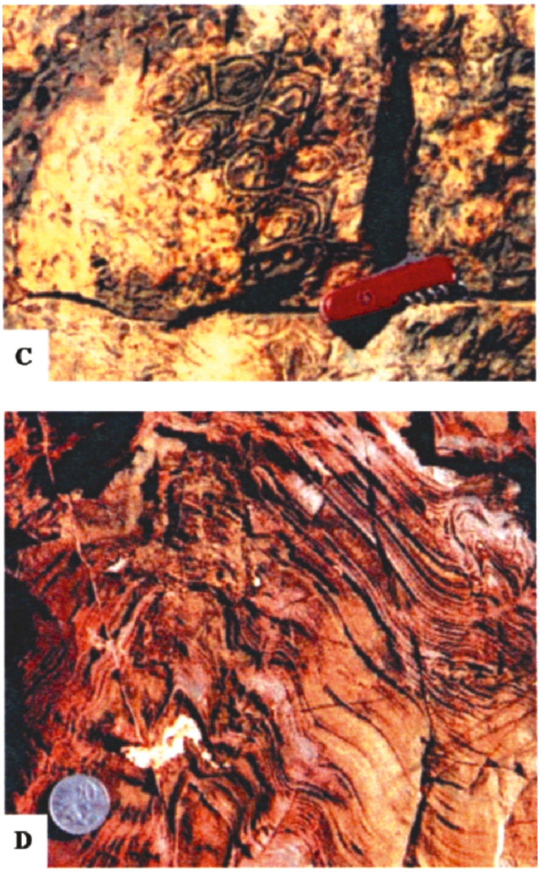

Fig. 8.10C,D. (C) 3.43-Ga Strelley Pool Chert silicified carbonate stromatolite-like structures – planar bedding plane view; (D) Strelley Pool Chert stromatolite-like structures – cross-sectional view, showing branching morphologies.

The fundamental change in crustal environment associated with the 3.26–3.225-Ga impact cluster is succeeded in the Pilbara by an assemblage of turbidites, felsic volcanics, and black shales that contain bundles of tubular microbial remains reminiscent of *Archaeon Pyridictium* (Rieger et al., 1995) from marine hydrothermal environments (Fig. 8.10.G) (M.V. Glikson and L. Duck, personal communication, 2004). It follows that, despite the intense bombardment during the ~3.2-Ga period, extremophile and thermophile microorganisms survived, probably in deep fractures and faults of the "deep hot biosphere" of Gold (1999).

Stromatolite colonies associated with felsic tuffs of the ~2.73-Ga Tumbiana Formation display evolved morphologies (Fig. 8.10 H), where cabbage-like individual bioherms separated by well-defined debris-filled collars can reach meter-scale dimensions. Yet larger stromatolites up to several tens of meter

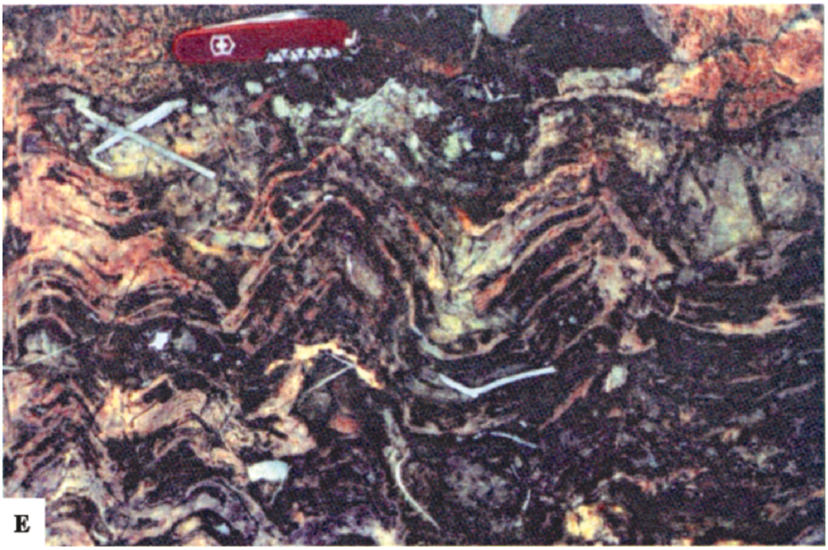

Fig. 8.10E. (E) Strelley Pool Chert stromatolite-like structures, cross-sectional view.

Fig. 8.10F. (F) Strelley Pool Chert carbonate with silicified veins and possible molds of anhydrite or barite.

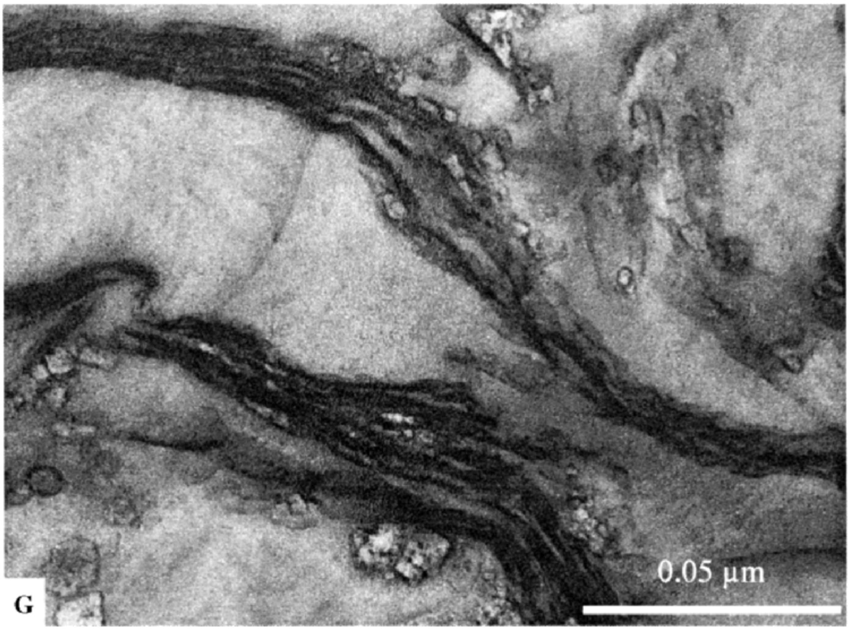

Fig. 8.10G. (G) Tubular bundles of microbial remains in black shale of the ~3.24-Ga Pincunah Formation, Sulphur Springs Group (L. Duck and M. Glikson, personal communication, 2004), reminiscent of the Archaeon Pyridictium reported by Rieger et al. (1995) from marine hydrothermal environments. Microbial remains were isolated from organic matter concentrated from black shales of the Pincunah Formation, Sulphur Springs, central Pilbara Craton, Western Australia.

across occur in the ~2.56–2.54-Ga Carawine Dolomite, where the stromatolites are located stratigraphically higher than the tsunami-generated impact spherule-bearing megabreccia (SBMB) (Fig. 8.7).

Direct potential relations between impacts and biogenic relations occur between the >2.63-Ga Jeerinah Impact Layer and the immediately overlying banded iron formation of the Marra Mamba Iron Member (Fig. 8.5). In so far as a bacterial origin may be attributed to banded iron formations (Morris, 1993; Konhauser et al., 2002), the location of banded iron formation and ferruginous sediments above impact fallout units, also observed in the Antarctic Chert Member and above the ~3.24-Ga impact cluster, may signify Fe enrichment of the hydrosphere following volcanic and hydrothermal input triggered by the impacts.

The increasing diverse nature of marine microplankton observed from the latest Proterozoic (Vendian), allowing detailed speciation, and preservation of amino acids and noble gas species in unmetamorphosed Phanerozoic sediments, opens the way for possible cometary contributions (not yet observed in older sequences). Examples are the identification of extinction/radiation

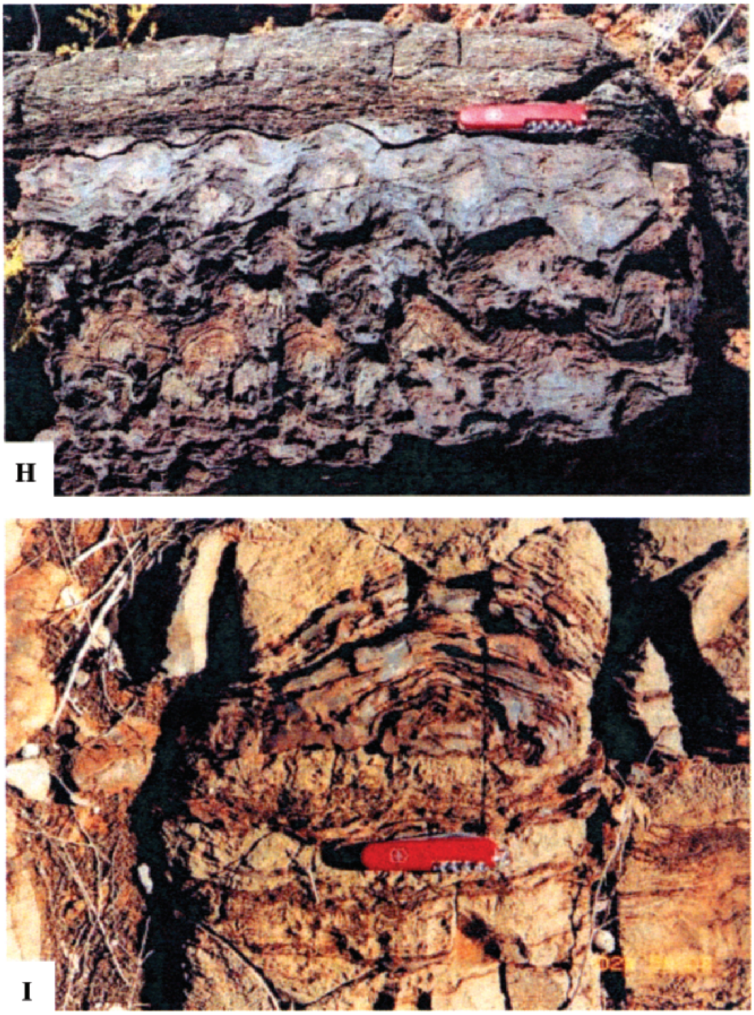

Fig. 8.10H,I. (H) 2.73-Ga carbonate stromatolites of the Tumbiana Formation, Meentheena area; (I) 2.56–2.54-Ga stromatolites in the Carawine Dolomite, Woodie Woodie area, eastern Hamersley Basin.

relations across the a. 580 Ma Acraman impact boundary in South Australia and Western Australia (Grey, 2004) and a number of major impact related, or possibly impact related, extinctions during the Phanerozoic, including the K-T boundary (Alvarez, 1986). The discovery of racemic AIB (α-amino isobutyric acid) and Isovaline halo associated with K-T boundary horizon at Stevns Klint (Zhao and Bada, 1989; Zahnle and Grinspoon, 1990) (Fig. 8.11 A) and anomalous extraterrestrial ^{3}He flux displayed by the late Eocene section at Massignano, Italy (Farley et al., 1998), allows identification

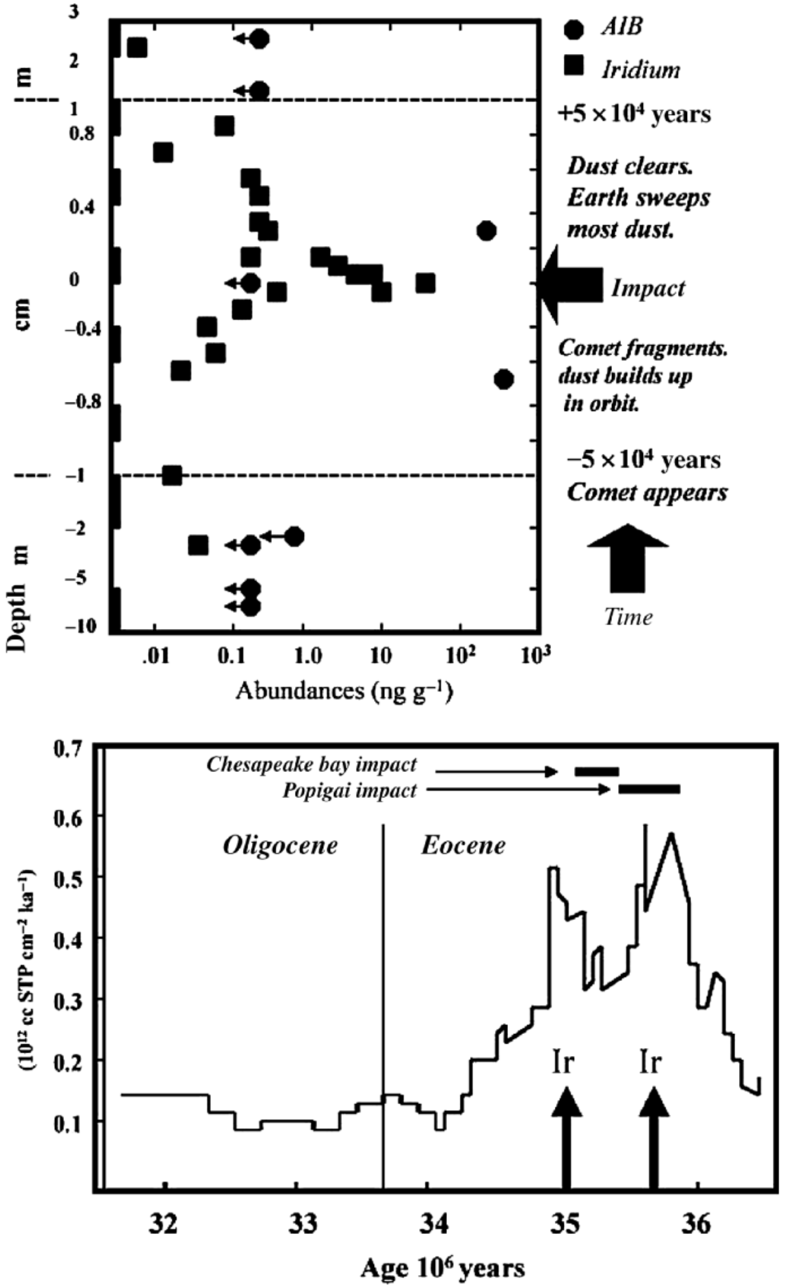

Fig. 8.11. Cometary components associated with impact boundaries. (A) Relations between AIB (α-amino isobutyric acid) and Ir across the K-T boundary at Stevns Klint (from Zhao and Bada, 1989; Zahnle and Grinspoon, 1990); (B) Extraterrestrial ^{3}He flux (10^{12} cc STP cm^{-2} ka^{-1}) displayed by the late Eocene section at Massignano, Macertata, Italy (from Farley et al., 1998).

of cometary components and their discrimination from Ir-rich impact ejecta (Fig. 8.11 B). Another component proposed as of extraterrestrial origin may be fullerenes (Poreda and Becker, 2003). Future extension of these and new methods to least-altered Precambrian sediments may increase knowledge on the role of asteroid and comet impacts on the early Earth.

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References

Alvarez, W. (1986). Toward a theory of impact crises. *Eos*, **67**, 649–658.

Arndt, N.T., Nelson, D.R., Compston, W., Trendall, A.F. and Thorne, A.M. (1991). The age of the Fortescue Group, Hamersley Basin, Western Australia, from ion microprobe zircon U-Pb results. *Aust. J. Earth Sci.*, **38**, 261–281.

Barlow, N.G. (1990). Estimating the terrestrial crater production rate during the late heavy bombardment period. *Lunar Planet. Instit. Contr.*, **746**, 4–7.

Brasier M., Green O., Lindsay J. and Steele A. (2004). Earth's oldest (∼3.5 Ga) fossils and 'early Eden hypothesis': Questioning the evidence. *Origins Life Evol. of Biosphere*, **34**, 257–269.

Kluwer Academic Publishers, The Netherlands. Buick, R., Dunlop, J.S.R. and Groves, D.I. (1981). Stromatolite recognition in ancient rocks: an appraisal of irregularly laminated structures in an Early Archaean chert-barite unit from North Pole, Western Australia. *Alcheringa*, **5**, 161–181.

Buick, R., Thornett, J.R., McNaughton, N.J., Smith, J.B., Barley, M.E. and Savage, M. (1995). Record of emergent continental crust ∼3.5 billion years ago in the Pilbara craton of Australia. *Nature* , **375**, 574–577.

Byerly, G.R. and Lowe, D.R. (1994). Spinels from Archaean impact spherules. *Geochim. Cosmochim. Acta*, **58**, 3469–3486.

Byerly, G.R., Lowe, D.R., Wooden, J.L., Xiaoogang Xie (2002). A meteorite impact layer 3470 Ma from the Pilbara and Kaapvaal Cratons. *Science*, **297**, 1325–1327.

Chyba, C.F. (1993). The violent environment of the origin of life: progress and uncertainties. *Geochim et Cosmochim. Acta*, **57**, 3351–3358.

Chyba, C.F. and Sagan, C. (1996). Comets as the source of prebiotic organic molecules for the early Earth. In: *Comets and the Origin and Evolution of Life* (P.J. Thomas, C.F. Chyba and C.P. McKay, Eds.), pp.147–174. Springer Verlag, New York.

Culler, T.S., Becker, T.A., Muller, R.A. and Renne, P.R. (2000). Lunar impact history from ^{39}Ar/^{40}Ar dating of glass spherules. *Science*, **287**, 1785–1789.

Davies, P. (1998). *The Fifth Miracle.* Penguin Books.

de Silva, J.R.F. and Williams, R.J.P. (1991). *The Biological Chemistry of the Elements.* Clarendon Press, oxford.

Delsemme, A.H. (2000). Cometary origin of the biosphere – 1999 Kuiper prize lecture. *Icarus*, **146**, 313–325.

Dunlop, J.S.R. and Buick, R. (1981). Archaean epiclastic sediments derived from mafic volcanics, North Pole, Pilbara Block, Western Australia. *Geol. Soc. Aust. Sp. Pub.*, **7**, 225–233.

Eck, R.V. and Dayhoff, M.O. (1968). Evolution of the structure of ferredoxin based on living relics of primitive amino acid sequences. *Science*, **152**, 363–366.

Farley, K.A., Montanari, A., Shoemaker, E.M., and Shoemaker, C.S. (1998). Geochemical evidence for a comet shower in the Late Eocene. *Science*, **280**, 1250–1253.

Farmer J.D. (2000). Hydrothermal systems: Doorways to Early Biosphere Evolution. *GSA Today*, **10 (7)**, 1–9.

Froude, D.O., Ireland, T.R., Kinny, P.K., Williams, I.S., Compston, W., Williams, I.R., Myers, J.S. (1983). Ion Microprobe identification of 4,100–4,200 Myr-old terrestrial zircons. *Nature*, **304**, 616–618.

Glikson, A.Y. (1993). Asteroids and early Precambrian crustal evolution. *Earth Sci. Rev.*, **35**, 285–319.

Glikson, A.Y. (1996). Mega-impacts and mantle melting episodes. tests of possible correlations. *Aust. Geol. Surv. Org. J. Aust. Geol. Geophy.*, **16**, 587–608.

Glikson, A.Y. (1999). Oceanic mega-impacts and crustal evolution. *Geology*, **27**, 387–341.

Glikson, A.Y. (2001). The astronomical connection of terrestrial evolution. crustal effects of post-3.8 Ga mega-impact clusters and evidence for major 3.2±0.1 Ga bombardment of the Earth-Moon system. *J. Geodyn.*, **32**, 205–229.

Glikson, A.Y. and Hickman, A.H. (1981). Geochemical stratigraphy of Archaean mafic-ultramafic volcanic successions, eastern Pilbara Block, Western Australia. in. *Archaean Geology* (J.E. Glover and D.I. Groves, Eds) *Geol. Soc. Aust. Sp. Pub.*, **7**, 287–300.

Glikson, A.Y. and Allen, C. (2004). Iridium anomalies and fractionated siderophile element patterns in impact ejecta, Brockman Iron Formation, Hamersley Basin, Western Australia. evidence for a major asteroid impact in simatic crustal regions of the early Proterozoic earth. *Earth Planet. Sci. Lett.*,**220**, 247–264

Glikson, A.Y. (1996). Mega-impacts and mantle melting episodes: tests of possible correlations. *Aust. Geol. Surv. J. Aust. Geol. Geophys.*, **16**, 587–608

Glikson, A.Y. (1999). Oceanic mega-impacts and crustal evolution. *Geology*, **27**, 387–341.

Glikson, A.Y., (2004). Early Precambrian asteroid impact-triggered tsunami: excavated seabed, debris flows, exotic boulders, and turbulence features associated with 3.47–2.47 Ga-old asteroid impact fallout units, Pilbara Craton, Western Australia. *Astrobiology*, **4**, 19–50.

Glikson, A.Y., Allen, C. and Vickers (2004). Multiple ∼3.47 Ga–old asteroid impact fallout units, Pilbara Craton, Western Australia. *Earth Planet. Sci. Lett.*, **7040**, 1–14.

Gold, T. (1999). *The Deep Hot Biosphere.* Berlin, 235 pp.

Gostin, V.A., Keays, R.R. and Wallace, M.W. (1986). Iridium anomaly from the Acraman ejecta horizon. impacts can produce sedimentary Iridium peaks. *Nature*, **340**, 542–544.

Grey, K. (2004). The significance of the ca. 580 Ma impact event (Abstract). *17th Aust. Geol. Conven.*, Hobart, p. 232

Grieve, R.A.F. and Dence, M.R. (1979). The terrestrial cratering record: II. The crater production rate. *Icarus*, **38**, 230–242.

Grieve, R.A.F. and Pesonen, L.J. (1996). Terrestrial impact craters: their spatial and temporal distribution and impacting bodies. *Earth, Moon and Planets*, **72**, 357–376.

Groves D.I., Dunlop J.S.R., and Buick R. (1981). An early habitat of life. *Sci. Am.*, **245**, 64–73.

Hassler, S.W., Robey, H.F., and Simonson, B.M. (2000) Bedforms produced by impact-generated tsunami, ∼2.6 Ga Hamersley basin, Western Australia. *Sedimentary Geology*, **135**, 283–294.

Hassler, S.W. and Simonson, B.M. (2001). The sedimentary record of extraterrestrial impacts in deep shelf environments. Evidence from the early Precambrian. *J. Geology*, **109**, 1–19.

Hoffmann, H.J., Grey, K., Hickman, A.H., and Thorpe, R.I. (1999). Origin of 3.45 Ga coniform stromatolites in Warrawoona Group, Western Australia. *Geol. Soc. Am. Bull.*, **111**, 1256–1262.

Jahn, Bor-ming and Simonson, B.M. (1995). Carbonate Pb-Pb ages of the Wittenoom Formation and Carawine Dolomite, Hamersley Basin, Western Australia (with implications for their correlation with the Transvaal Dolomite of South Africa). *Precamb. Res.*, **72**, 247–261.

Koeberl, C., Reimold, U.W., McDonald, I., and Rosing, M. (2000). Search for petrographic and geochemical evidence for the late heavy bombardment on Earth in Early Archaean rocks from Isua, Greenland. In Eds I. Gilmour and C. Koeberl, *Impacts and the Early Earth*, Springer-Verlag, Berlin, *Lecture Notes in Earth Sciences*, **92**, 73–97.

Konhauser, K.O., Hamade, T., Raiswell, R., Ferris, F.G., Southam, G. And Canfield, D.E. (2002). Could bacteria have formed the Precambrian banded iron formations? *Geology*, **30**, 1079–1082.

Kyte, F.T., Shukolyukov, A., Lugmair, G.W., Lowe, D.R. and Byerly, G.R. (2003). Early Archaean spherule beds. Chromium isotopes confirm origin through multiple impacts of projectiles of carbonaceous chondrite type. *Geology*, **31**, 283–286.

Lowe, D.R. and Byerly, G.R. (1986). Early Archaean silicate spherules of probable impact origin, South Africa and Western Australia. *Geology*, **14**, 83–86.

Lowe, D.R., Byerly, G.R., Asaro, F. and Kyte, F.T. (1989). Geological and geochemical record of 3400 Million years old terrestrial meteorite impacts. *Science*, **245**, 959–962.

Lowe, D.R., Byerly, G.R., Kyte, F.T., Shukolyukov, A., Asaro, F., and Krull, A. (2003) Spherule beds ∼3.47–3.34 Ga-old in the Barberton greenstone belt, South Africa. a record of large meteorite impacts and their influence on early crustal and biological evolution. *Astrobiology*, **3**, 7–48.

McCulloch, M.T.,Bennett, V.C. (1994) Progressive growth of the Earth 's continental crust and depleted mantle:geo-chemical constraints. *Geochim. et Cosmochim. Acta*, **58**, 4717–4738.

Melosh, H.J. and Vickery, A.M. (1991). Melt droplet formation in energetic impact events. *Nature*, **350**, 494–497

Mojzsis, S.J., Arrhenius, G., McKeegan, K.D., Harrison, T.M., Nutman, A.P., and Friend, C.R.L. (1996). Evidence for life on Earth by 3800 million years ago. *Nature*, **384** (6604), 55–59.

Mojzsis, S.J. and Harrison, T.M., (2000). Vestiges of a beginning: Clues to the emergent biosphere recorded in the oldest known rocks. *GSA Today*, **10**, 1–6.

Mojzsis, S.J., Harrison, M.T., and Pidgeon, R.T. (2001). Oxygen isotodpe evidence from ancient zircons for liquid water at the Earth's surface 4300 Myr ago. *Nature*, **409**, 178–180.

Morris, R.C. (1993). Genetic modelling for banded iron formation of the Hamersley Group, Pilbara Craton, Western Australia. *Precamb. Res.*, **60**, 243–286.

Peck, W.H., Valley, J.W., Wilde, S.A. and Graham, C.M. (2001). Oxygen isotope ratios and rare earth elements in 3.3 to 4.4 Ga zircons: Ion microprobe evidence for high d18O continental crust and oceans in the Early Archean. *Geochim. et Cosmochim. Acta*, **65**, 4215–4229.

Poreda, R.J. and Becker, L. (2003) Fullerenes and interplanetary dust at the Permian-Triassic boundary. *Astrobiology*, **3**, 75–90.

Poujol, M., Robb, L.J., Anhaeusser, C.R. and Gericke, B. (2003). A review of the geochronological constraints on the evolution of the Kaapvaal Craton, South Africa. *Precamb. Res*, **127**, 181–213.

Rieger, G., Rachel, R., Hermann, R., and Stetter, K.O. (1995). Ultrastructure of the hyperthermophilic Archaeon Pyrodictium abyssi. *J. Struct. Biol.*, **115**: 78–87.

Ringwood, A.E. and Green, D.H. (1966). An experimental investigation of the gabbro-eclogite transformation and some physical consequences. *Tectonophysics*, **3**, 387–427.

Ryder, G. (1997). Coincidence in the time of the Imbrium Basin impact and Apollo 15 Kreep volcanic series: impact-induced melting? *Lunar Planet. Instit. Contrib.*, **790**, 61–62.

Ryder, G. (2003). Bombardment of the Hadean Earth: wholesome or deleterious? *Astrobiology*, **3**, 3–6.

Shoemaker, E.M. and Shoemaker, C.S. (1996). The Proterozoic impact record of Australia. *Aust. Geol. Surv. Org. J. Aust. Geol. Geophy.*, **16**, 379–398.

Shukolyukov, A., Kyte, F.T., Lugmair, G.W., Lowe, D.R. and Byerly, G.R. (2000). *The oldest impact deposits on Earth. Impacts and the Early Earth* (C. Koeberl and I. Gilmour, Eds) Springer, Berlin, pp. 99–116.

Simonson, B.M. (1992). Geological evidence for an early Precambrian microtektite strewn field in the Hamersley Basin of Western Australia. *Geol. Soc. Am. Bull.*, **104**, 829–839.

Simonson, B.M. (2003). Petrographic criteria for recognizing certain types of impact spherules in well-preserved Precambrian successions. *Astrobiology*, **3**, 49–65.

Simonson, B.M. and Hassler, S.W. (1997). Revised correlations in the early Precambrian Hamersley Basin based on a horizon of resedimented impact spherules. *Aust. J. Earth Sci.*, **44**, 37–48.

Simonson, B.M., Davies, D., Wallace, M., Reeves, S. and Hassler, S.W. (1998). Iridium anomaly but no shocked quartz from Late Archean microkrystite layer: oceanic impact ejecta? *Geology*, **26**, 195–198.

Simonson, B.M., Hornstein, M. and Hassler, S.W. (2000). Particles in late Archean Carawine Dolomite (Western Australia) resemble Muong Nong-type tektites. In: *Impacts and the Early Earth* (I. Gilmour and C. Koeberl, Eds) Springer-Verlag, Berlin, *Lecture Notes in Earth Sciences*, **92**, 181–214.

Simonson, B.M., Davies, D. and Hassler, S.W. (2000). Discovery of a layer of probable impact melt spherules in the late Archean Jeerinah Formation, Fortescue Group, Western Australia. *Aust. J. Earth Sci.*, **47**, 315–325.

Taylor, S.R. and McLennan, S.M. (1981). The rare earth element evidence in Precambrian sedimentary rocks: implications for crustal evolution. In: *Precambrian Plate Tectonics* (A. Kroner, Ed.), *Developments in Precambrian Geology*, **4**, 527–545.

Van Kranendonk, M.J. (2000). Geology of the North Shaw 1:100 000 Sheet. *Geological Survey of Western Australia 1:100 000 Geological Series*, 86.

Van Kranendonk, M.J., Hickman, A.H., Smithies, R.S. and Nelson, D.R. (2002). Geology and tectonic evolution of the Archaean North Pilbarta Terrain, Pilbara Craton, Western Australia. *Econ. Geol.*, **97**, 695–732.

Wald, G., (1964). The origin of life. *Proceeding of the USA National Academy of Science*, **52**, 595–611.

Wallace, M.W., Gostin, V.A. and Keays, R.R. (1996). Sedimentology of the Neoproterozoic Acraman impact ejecta horizon, South Australia. *Aust. Geol. Surv. Org. J. Aust. Geol. Geophy.*, **16**, 443–451.

Wilde, S.A., Valley, J.W., Peck, W.H., and Graham, C.M. (2001). Evidence from detrital zircons for the existence of continental crust and oceans on the Earth 4.4 Ga ago. *Nature*, **409**, 175–178.

Woodhead, J.D., Hergt, J.M., and Simonson, B.M. (1998). Isotopic dating of an Archean bolide impact horizon, Hamersley Basin, Western Australia. *Geology*, **26**, 47–50

Zahnle, K. and Grinspoon, D. (1990). Comet dust as a source of amino acids at the Cretaceous/Tetiary boundary. *Nature*, **348**, 157–160.

Zahnle, K. And Sleep, N.H. (1997). Impacts and the early evolution of life. In: *Comets and the Origin and Evolution of Life* (P.J. Thomas, C.F. Chyba and C.P. McKay, Eds), Springer Verlag, New York, pp. 175–208.

Zhao, M. and Bada, J.L. (1989). Extraterrestrial amino acids in Cretaceous/Tertiary boundary sediments at Stevns Klint, Denmark. *Nature*, **339**, 443–445.

9

The Contemporary Hazard of Comet Impacts

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Summary. Cosmic impacts by asteroids and comets pose a continuing hazard of loss of human life and property. Significant contemporary risk is associated with projectiles in the energy range from about 5 megatons of TNT up to the size of the KT impactor (100 million megatons). The lower threshold for damage is defined by the atmosphere of the Earth, which effectively shields us from smaller projectiles. Up to energies of about a gigaton of TNT, the effects are local or regional for impacts on the land, or coastal for ocean impacts, which can generate large tsunamis. A greater risk is associated with still larger impacts, which are capable of causing global ecological catastrophe, possibly leading to mass mortality from starvation and epidemics. The primary objective of any program to deal with this hazard is to determine whether or not such a near-term impact is likely, which is the objective of the Spaceguard Survey of near-Earth asteroids and short-period comets. Long-period comets, however, pose a different challenge, since they cannot be discovered long in advance of a possible impact, their orbits are harder to predict, and they are significantly more difficult to deflect or destroy.

9.1 Introduction

Recognition of a contemporary impact hazard is a result of changing perceptions of catastrophic influences on evolutionary history. Although a few prescient planetary scientists (e.g., Baldwin, 1949) had recognized that the impact origin for the lunar craters implied a comparable cratering history for the Earth, the majority of scientists first became aware of the importance of impacts in the history of life from the identification of a cosmic impactor as the probable cause of the end-Cretaceous (KT) extinction (Alvarez et al., 1980). The Alvarez paper not only established the presence of an extraterrestrial component in the KT boundary layer, but also suggested a mechanism – short-term global climate change caused by stratospheric dust – whereby an impact could influence the entire ecosphere. Thus an impact of negligible energy or momentum on a geophysical scale could have profound influence on the history of life (e.g., Glikson, this volume).

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It is a relatively short step from recognition of the role of impacts in evolutionary history to the realization that impacts also pose a contemporary hazard. As long as this hazard is limited to the fall of meteorites (which generally strike the ground at terminal velocity for an object falling through air), there is not a major hazard from impacts; indeed, there are few authenticated records of any human having been killed by a meteorite.

Larger impacting objects can penetrate to the lower atmosphere or surface at nearly their initial velocity. The only historic record of such a hypervelocity impact occurred on June 30, 1908, when the atmospheric disruption of a stony impactor released 10–20 megatons of explosive energy near the Tunguska River in Siberia (Krinov, 1963). There were at most two deaths. The best-known impact crater on the Earth, Meteor Crater in Arizona, also represented an explosive energy of 10–20 megatons, but in this case the projectile was metallic rather than stony. There were no casualties, since the impact occurred long before the occupation of North America by humans. This historical record, while limited, confirms our intuitive expectation that large hypervelocity impacts are much rarer than comparably destructive volcanic eruptions or earthquakes, and therefore that the risk they pose is less than that of many other natural hazards.

It is common for older books to state that the Tunguska impactor was a comet, and this “fact” is still occasionally quoted even in texts. However, it is now clear that it was probably a stony asteroid about 60 m in diameter that disintegrated and effectively exploded at an altitude of approximately 8 km, devastating more than 10^5 hectares of Siberian forest. See, e.g.; Chyba et al. (1993), Vasilyev (1998), Sekanina (1988), and Farinella et al. (2001).

In contrast to the low level of danger from smaller (Tunguska-class) impacts, the hazard associated with very large (but exceedingly rare) impacts can be considerable, as a consequence of their global influence. Unlike other natural disasters, which are limited in size by various physical constraints (e.g., an earthquake will relieve crustal stress whenever it approaches some maximum value), there is no practical limit to the magnitude of an impact (Chapman and Morrison, 1989). Comets and asteroids exist today that are substantially larger than the KT impactor. It is not impossible that an object as large as Chiron (approximately 200 km in diameter) could eventually strike the Earth, possibly bringing the history of terrestrial life to an abrupt conclusion, as discussed by Zahnle and Sleep (this volume).

Even at smaller scales than the KT event, an impact could blanket the Earth's atmosphere with dust and precipitate a severe, if brief, environmental catastrophe. This potential for globally catastrophic impacts was recognized in the first conference on the impact hazard, held in 1981 at Snowmass Colorado under NASA sponsorship, with Gene Shoemaker as chairperson. Although the report of that Snowmass Conference was never published (see Chapman and Morrison, 1989), it has influenced all subsequent thinking about the contemporary impact hazard.

The public has also been exposed to vivid accounts of such environmental disasters through the popular science fiction novel *Lucifer's Hammer* (Niven and Pornelle, 1977), the Hollywood films *Meteor*, *Deep Impact* and *Armageddon*, and numerous TV documentaries, as well as by press accounts of the nuclear winter debate of the 1980s.

In addition to its much larger scale, the impact hazard differs from other natural calamities in that we are capable, at least in principle, of avoiding major impacts. We cannot suppress an earthquake or tame a hurricane, but we probably could deflect a cosmic projectile before impact. These possibilities were first evaluated in 1968 by a group of MIT students who were given the assignment of devising a system to protect the planet from a hypothetical impact by the asteroid Icarus. Even today, their Project Icarus Report (Kleiman, 1968) retains its interest.

One reason we are interested in the impact hazard is that, unlike the weather, we can do something about it. In this chapter I discuss the nature of the impact hazard and estimate its magnitude relative to other natural disasters, following previous analyzes published by Chapman and Morrison (1994), Morrison et al. (1994), Toon et al. (1997), Atkinson et al. (2000), Morrison et al. (2003), Stokes et al. (2003), and others. I then summarize possible mitigation schemes, with particular attention to the special problems posed by comets, which are more difficult to deal with than asteroids. The chapter concludes with a brief discussion of public policy issues raised by the impact danger.

9.2 Impactor Population

The first step in analyzing cosmic impacts is to determine the flux of comets and asteroids striking the Earth. The average total impact flux over the past 3 Gyr can be found from the crater density on the lunar maria (Hartmann et al., 1986). Given the absence of significant erosion or geological activity since the end of widespread volcanism on the Moon, these lava plains are a scorecard for the integrated flux of cosmic debris in near-Earth space. With adjustments for the Earth's greater gravity, the average flux at the top of the Earth's atmosphere can be derived from the lunar flux (Zahnle and Sleep, this volume). We can also estimate the contemporary impact rate on the Earth from a census of existing Earth-crossing asteroids and comets together with estimates of their dynamical lifetimes (Shoemaker, 1983; Shoemaker et al., 1990; Bottke et al., 2002, Stuart & Binzel, 2004; Steel, (1997). As surveys reveal more of the present population of near-Earth objects, this latter approach (estimating the current impact flux) has gained in favor over the lunar approach.

The Earth-crossing asteroids are primarily rocky or metallic fragments of main-belt asteroids or extinct comet nuclei (Wetherill, 1988; 1989). In addition, there are impacts from active comets. The bulk properties of the projectiles thus range from metallic (like iron–nickel meteorites) to stony (like chondritic meteorites) to cometary (low-density silicates, organics, and volatiles). The lunar cratering history does not distinguish among stony, metallic, or volatile-rich projectiles, but population estimates based on astronomical observations do, since comets are distinguished by the presence of an extended atmosphere or coma visible in telescopic images.

From the known asteroid discovery statistics and the lunar crater size distribution of 20 years ago, Shoemaker (1983) derived the population and size distribution for Earth-crossing asteroids larger than a given diameter (see also Morrison, 1992). He concluded that long-period and short-period active comets added about 5% of the asteroid flux. However, comets average significantly greater impact velocities than asteroids and, therefore, constitute a larger share (at least 10%) of the impact hazard.

More recent work based on a much larger observed population of both comets and asteroids generally confirms the Shoemaker estimates for the larger comets, those with nucleus diameters greater than a few kilometers (Weissman, 1997). However, we now recognize a significant shortfall in the population of smaller comets, relative to the number expected from a power-law size distribution. Recent surveys have discovered no comets with diameters of less than 1 km, in spite of their high brightness relative to asteroids of the same size, and the comets imaged by spacecraft (Halley, Borrelly, and Wild 2) are all between 4 and 8 km in average dimension. The low population of small craters inferred for the Galilean satellites, especially Europa, also argues for a paucity of small comets. Current arguments for the population of comets in the km and subkm range are summarized by D. Yeomans in Chapter 2 "Population Estimates" in Stokes et al. (2003). Note that in recent population estimates, extinct (nonoutgassing) comet nuclei in Earth-approaching orbits, if they exist, are counted with the population of near-Earth Asteroids (NEAs).

Steel has discussed evidence for possibly significant variations in the impact flux, noting that comet "showers" could lead to major short-term increases in the impact hazard (Steel et al., 1994). However, the current impact rate as derived from the known population of Earth-crossing comets and asteroids is apparently similar to the long-term average flux recorded by the lunar craters, suggesting that we do not live in a special time with respect to possible large-scale variations. For the purposes of this evaluation of the current impact hazard, it is adequate to treat impacts as occurring at their long-term average rate. Figure 9.1 summarizes the average terrestrial impact flux as a function of projectile kinetic energy, measured in megatons (1 MT $= 4.2 \times 10^{15}$ J). Also shown for comparison is the associated diameter for a stony asteroid striking the Earth with a velocity of 20 km/s. Note the steep power-law dependence of size on energy, a relationship equally apparent when we look at the size distribution of small lunar craters (A. Harris, private communication, 2003; Morrison et al., 2003; see also Bottke et al., 2002; Stokes, 2003; Stuart and Binzel, 2004).

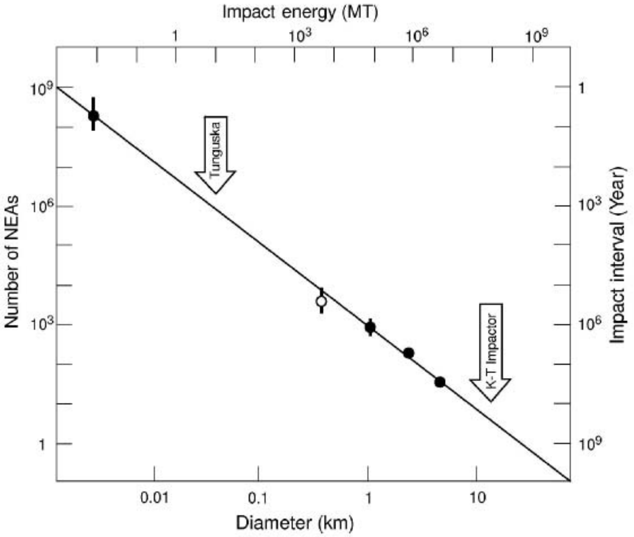

Fig. 9.1. Impactor diameter (and kinectic energy in megatons) vs. Average terrestrial impact flux (1 MT = 4.2×10^{15} J).

9.3 Nature of the Hazard

Based on the average flux of comets and asteroids striking the Earth, we can evaluate the danger posed by impacts of different magnitudes. Of particular interest is the threshold for penetration though the atmosphere, and the threshold at which impacts have major global effects as well as local effects.

9.3.1 Penetration Through the Atmosphere

The atmosphere protects us from smaller projectiles. Figure 9.1 indicates that an impact event with the energy of the Hiroshima nuclear bomb occurs roughly annually, while a megaton event is expected at least once per century. Obviously, however, such relatively common events are not destroying cities or killing people. Even at megaton energies, most bodies break up and are consumed before they reach the lower atmosphere. Unless they are composed of iron, meteors as large as a few tens of meters are subject to aerodynamic stresses during atmospheric entry that cause fragmentation and dispersal at high altitude (Chyba et al., 1993; Hills and Goda, 1993). The height of fragmentation depends primarily on the meteoroid's physical strength, with loose cometary aggregates and carbonaceous meteorites fragmenting at altitudes above 30 km, as observed for most meteors. Stronger stony objects can penetrate to perhaps 20 km, but still cause little or no damage when they explode. Such atmospheric explosions are routinely detected by military surveillance satellites; the largest reported bolide exploded 21 km above the western Pacific Ocean on February 1, 1994 with an estimated energy of 50–100 kilotons (Tagliaferri, 1994; McCord et al., 1995).

If the projectile is large enough and strong enough to penetrate below about 15-km altitude before it explodes, the resulting airburst can be highly destructive. Numerical models of atmospheric fragmentation and dispersal show that rocky objects >50 m in diameter (10 megatons) and cometary objects >100 m (100 megatons) penetrate deep enough to pose significant hazards (Chyba et al., 1993; Hills and Goda, 1993; Chyba, 1994, Morrison et al., 2003; Stokes, 2003). The area of devastation scales approximately as the explosive yield to the two-thirds power and is somewhat greater for an airburst than for a groundburst explosion (Glasstone and Dolan, 1977).

Tunguska provides a calibration, with a shock wave sufficient to fell trees over an area of 10^5 hectares. The yield of the Tunguska blast has been estimated at 10–20 MT from microbarograph measurements in Europe and comparison of the blast damage with later nuclear airbursts. If we assume that the radius of forest devastation would apply also to destruction of many buildings, the area of damage is given by

$$A = 10^4 Y^{2/3} \tag{9.1}$$

where Y is the yield in megatons and A is in hectares (Chyba et al., 1993; Hills and Goda, 1993; Chapman and Morrison, 1994). For example, this formula indicates that at 100 MT, the radius of destruction is 20 km and the fraction of the Earth's surface that is affected is 0.001%. At 100,000 MT, the radius is 200 km and the area is about 0.1%. (For references to more detailed models of damage that also take into account population distributions, see discussions in Stokes, 2003.)

9.3.2 Globally Catastrophic Impacts

At sufficiently great energies, an impact has global consequences. An obvious, if extreme, example is the KT impact 65 million years ago, which disrupted the global ecosystem and led to a major mass extinction. This impact of a 10–15-km object released approximately 10^8 MT of energy and excavated a crater (Chicxulub in Mexico) >200 km in diameter. Among the environmental consequences were devastating wildfires and changes in atmospheric and oceanic chemistry as well as a dramatic short-term perturbation in climate produced by some 10^{16} kg of submicrometer dust injected into the stratosphere (Alvarez et al., 1980; Sharpton and Ward, 1990; Toon et al., 1982, 1994, 1997).

Chapman and Morrison (1994) and Morrison et al. (1994) first argued that even much smaller projectiles can perturb the global climate by injecting dust into the stratosphere, producing climate changes sufficient to reduce crop yields and precipitate mass human starvation (but not a mass extinction). They defined a globally catastrophic impact as one that would lead to the death of more than a quarter of the world's population. The primary cause of such death would probably be starvation and disease caused by crop failures, but such an unprecedented catastrophe might also threaten the stability and future of modern civilization.

To appreciate the scale of the global catastrophe thus defined by Chapman and Morrison, we must be clear what it is not. Such a catastrophe is far larger than the effects of the great World Wars but far smaller than the KT impact. Although it could destabilize modern civilization, it would not threaten the survival of the human species. Nor would such a catastrophe leave any fossil record, although this fact would provide scant comfort to those people who experienced such an impact.

9.3.3 Threshold for a Globally Catastrophic Climate Perturbation

A drop of a few degrees Celsius in surface temperature over many months is sufficient to reduce crop yields dramatically (Harwell and Hutchinson, 1989; Covey et al., 1990; Toon et al., 1997). The energy threshold for a globally catastrophic impact is therefore determined by the explosive yield required to loft sufficient submicrometer dust into the stratosphere to lower the surface temperature by this amount. Models originally developed for nuclear winter (Turco et al., 1991) suggest that a global stratospheric dust layer with an optical depth more than 2 would depress land temperatures by as much as 10°C, and lead to the climatic effects associated with nuclear winter. In the most comprehensive discussions of these effects, Toon et al. (1994, 1997) find that major climate effects would almost certainly follow from an impact with a yield of 10^6 MT, and perhaps from one as much as an order of magnitude less. For a stony object striking at 20 km per second, one million megatons corresponds to a diameter of about 2 km.

For a nominal threshold energy of 3×10^5 MT, corresponding to a diameter for an asteroid of about 1.4 km, there is an average frequency of about twice per million years. Given the many uncertainties in determining this threshold energy, the frequency of such global catastrophes can be estimated only to lie between 10^5 and 10^6 years. Particularly uncertain in this estimate is the response of society to such an "impact winter."

9.4 Hazard Analysis

We now address the scale of destruction and the numerical hazard associated with impacts of various magnitude, still following the analyses published by Chapman and Morrison (1994) and Morrison et al. (1994). By numerical hazard is meant the probability of death for an individual due to this event.

If the average zone of mortality from an impact explosion can be identified roughly with the area of devastation defined earlier from the Tunguska example, then the average number of fatalities per impact can be calculated (using the average world population density of 0.1 person per hectare) as

$$N = 10^3 Y^{2/3} \tag{9.2}$$

Of course, most of the world's population is concentrated in a tiny fraction of the surface area, so most such impacts strike uninhabited parts of the globe and kill few people or none at all, just as in the 1908 example of Tunguska (Chesley and Ward, 2005). Indeed, the average interval between a Tunguska-scale impact on an urban zone is about 10,000 years for the current population distribution, and was much longer in past centuries.

At energies above about 1000 MT, the danger from tsunami damage for ocean impacts dominates the mortality calculations (Pike, 1993; Hills et al., 1994; Morrison et al., 1994; Toon et al., 1997; Ward and Asphaug, 2000; Chesley and Ward, 2004). Tsunamis can project the damage for thousands of kilometers beyond the point of impact, thus blurring the distinction between local and global scales. There are substantial uncertainties in estimating the effects of tsunamis, since their wavelength is intermediate between that of seismic tsunamis and familiar storm surges; the effects have not been measured directly. For a variety of reasons, the hazard of impact tsunamis should be treated separately (as is done in Stokes, 2003), to also allow for population distribution near coasts and the likelihood that target areas will be evacuated given a few hours of warning. As noted by Chesley and Ward (2005), fatalities calculated for impact tsunamis are better thought of as surrogates for property damage, since most of the population is likely to survive – homeless and wet, perhaps, but not dead.

Above the threshold for global catastrophe, the number of fatalities is (by definition) more than one fourth of the Earth's total population. Just above the nominal threshold, the expected average local casualties from the direct blast are tens of millions, while indirect casualties are (by definition of the global threshold) one and a half billion. This difference reflects the different areas affected: less than 1% of the Earth's surface for the direct blast, but the entire surface for the indirect effects.

Is the greatest risk from the smaller, more frequent impacts that cause local or regional destruction, from larger impacts near the global catastrophic threshold, or from the even rarer mass extinction events? Chapman and Morrison (1994) first integrated the cumulative damage over segments of the impactor size-frequency distribution to yield some quantitative estimates, while Stokes (2003) contains a more detained recent analysis focused on subkilometer impacts.

The smaller, frequent events larger than the atmospheric cutoff yield equivalent annual fatality rates of tens of deaths per year for land impacts, up to perhaps a few hundred per year if the tsunami risk (which becomes important only for impactors large than 200 m) is included. In reality, of course, centuries to tens of thousands of years pass with practically no fatalities, followed by an impact that would kill huge numbers if it struck a major urban area or generated a large tsunami. Such risks, while not insignificant, are substantially lower than the mortality associated with many smaller and more frequent natural hazards, such as earthquakes, hurricanes, volcanic eruptions, floods, or mud slides. Programs to retire this risk may be justifiable, but are at a much lower priority than dealing with civilization-threatening impacts.

At the opposite, high-yield extreme, a mass-extinction event would probably kill almost the entire world population, but these impacts are so infrequent that the annual fatality rate is only a few hundred (the world's present population of 5 billion people killed every 10–100 million years). We are relatively certain that no asteroid large enough (diameter >5 km) to cause a disaster of this magnitude exists today in an Earth-crossing orbit. However, we cannot exclude the possibility of a large comet appearing at any time and dealing the Earth a devastating blow that might lead to human extinction. I will return to this issue later when I discuss mitigation strategy.

The greatest risk is associated with impacts near the threshold for global catastrophe, which we have taken as several $\times 10^5$ MT. If one and a half billion people are killed by events that occur every 500,000 years or so, then the fatality rate would be of the order several thousand per year. The annual risk per individual is near 1 in 2 million, with a corresponding lifetime risk of about 1:40,000. This risk is still small compared to many other causes of death, both natural and accidental, but it approaches that associated with other natural disasters, such as earthquakes or severe storms. Furthermore, there is the qualitative difference noted previously between the globally catastrophic impact and all other natural dangers, in that only the impact has the potential to kill billions and destabilize civilization.

Human reaction to such risk estimates varies greatly, especially since the impact hazard represents such an extreme combination of low probability together with high consequence (Slovic, 1987; Morrison et al., 1994; Morrison et al., 2004). Since no one has been killed by an impact in all of recorded history, it is easy to dismiss the risk as negligible and to regard those who express concern as alarmist. Furthermore, the calculated annual risk of about 1 in a million is near the level at which many persons consider risks to be effectively zero. On the other hand, modern industrial societies spend large sums to protect people from even less likely hazards, ranging from hurricanes to terrorist attacks to trace quantities of toxins in food and water.

9.5 Risk Reduction and Mitigation

For most natural hazards, risk reduction or mitigation strategies can deal only with the consequences of the disaster. Thus, for example, we cannot stop an earthquake or even reduce its force, but we can mandate standards in building construction and develop plans to treat casualties and restore public services after the event. If impacts could be predicted weeks or months in advance, similar approaches could be taken, including evacuation of the populace from the target area. In addition, however, the possibility exists of avoiding the impact entirely by deflecting or destroying the projectile before it hits.

Prediction is the key to any strategy of risk reduction. Because impacts are such rare events, it is difficult to justify standing defenses or even civil defense plans to deal with an impact if one takes place. By usual standards of cost-effectiveness, such efforts are nonproductive or even counterproductive, in that the risks inherent in the defense preparations or the opportunity costs represented by preparing to deal with events that are unlikely to happen for centuries or millennia exceed any positive effects of such efforts. (See also discussions by Sagan and Ostro (1994a, b) and Harris et al. (1994) of additional risks that may be associated with development of asteroid defenses.)

9.5.1 Impact Prediction

The source of impacts that is easiest to deal with is the Earth-crossing asteroids and their cousins, the short-period comets; fortunately, this population also represents the primary impact risk. It is possible with current technology to undertake a complete census (down to some size limit) of the asteroids and short-period comets in near-Earth space in order to determine whether any will strike the Earth in the near future. Such an approach, called the Spaceguard Survey, was proposed in 1992 (Morrison, 1992) and endorsed by NASA in 1998, with the acceptance of a "Spaceguard Goal" to find 90% of these objects larger than 1 km in diameter by the end of 2008.

The Spaceguard strategy is to use wide-angle ground-based astronomical telescopes to survey the sky for asteroids and short-period comets. The most successful current system is the Lincoln Laboratory Near Earth Asteroid Research project (LINEAR), which uses a pair of 1-m aperture Air Force telescopes in New Mexico, operated with NASA funding (Stokes, 2000). LINEAR is discovering about one NEA per day, about 1/3 of which are larger than 1 km and the rest smaller. Moving objects are picked out automatically by the search software, and a preliminary orbit can be obtained with data from even a single night. Much of the follow-up necessary to secure more robust orbits is carried out by dedicated amateur astronomers. Lists of new discoveries are posted daily on public web sites (Minor Planet Center <cfa-www.harvard.edu/iau/mpc.html>; NEO Program Office <neo.jpl.nasa.gov>), and this information is used to guide both the ongoing surveys and the follow-up support.

The Spaceguard Survey is intended to identify any potential threat to the Earth by detecting an asteroid on one of the many flybys that precede an actual impact. This approach should normally provide a warning time of at least several decades. The survey is optimized for finding asteroids near 1 km in diameter, which embraces the lower limit in size for a global catastrophe. Halfway into the Spaceguard Survey decade, about 60% of the estimated 1100 ± 100 of the NEAs larger than 1 km had already been found. This is not as positive a result as might seem, however, since the rate of new discoveries falls off as the survey nears completeness. Estimates of when the 90% level will be met vary from 2008 to beyond 2010.

If we focus attention on asteroids larger than 5 km, which may be near the threshold for an extinction event, we are complete today for asteroids (but at this size long period comets may represent a significant contribution to the hazard). Thus astronomers have already assured us that we are not due for an extinction level impact from an asteroid within the next century. The remaining extinction danger is thus from a long-period comet impact.

9.5.2 Deflection or Destruction

The 1968 MIT study of a postulated impact threat from asteroid Icarus (Kleiman, 1968) assumed that there was insufficient time to deflect the asteroid, so the only solution was to destroy it. If, however, a specific impact threat can be identified a decade (or more) in advance, then deflection becomes the strategy of choice.

The most straightforward approach to deflection for an object in a short-period orbit is to change the orbital period. If an impulse is applied several orbits before the threatened collision, only a very small velocity change (a few cm/s) is required (Ahrens and Harris, 1992). A variety of ways have been suggested to nudge an asteroid, ranging from setting surface nuclear charges to pushing with an attached rocket motor. Recently, a group called the B612 Foundation has proposed a specific near-term test in which a nuclear-reactor–powered ion thrust engine (a “space tug”) could be used to demonstrate the technology by making a very small, but measurable, change in the orbit of a 200-m asteroid (Shweickart et al., 2003). While we do not have today the technology to deflect an asteroid, it seems reasonable to expect that if one is discovered on collision course, especially one whose impact could kill a billion people and destabilize world civilization, the space-faring nations would find a way to accomplish the deflection and save the planet.

The alternative approach of destroying a projectile rather than deflecting it requires much larger energy. In order to avoid making the situation worse by converting the incoming projectile from a cannon ball into a cluster bomb, sufficient energy must be applied to disperse the fragments so that very few strike the Earth. Destruction is the strategy of choice only when the warning time is so short that deflection is impractical. This is more likely to be the case for a comet than an asteroid.

9.5.3 The Challenge of Comets

Both active short-period comets and extinct comets discovered by the Spaceguard Survey are equivalent to asteroids for purposes of the present discussion. However, long-period comets pose an entirely different class of problems. Since these comets do not reside in near-Earth space, no survey can hope to discover them decades before they approach the Earth. They might appear at any time, and discovery cannot be expected more than a few months before the possible impact. Furthermore, since no means exists to distinguish a faint object (either comet or asteroid) against the dense stellar background in the Milky Way, it is possible for a comet to "sneak up" on the Earth, escaping detection until it is only a few weeks from impact. Thus a perpetual survey is required to detect long-period comets, and even with such a survey we cannot be sure of success.

If only a few months' warning is available, it may not be possible to deflect an incoming comet. Since such a deflection impulse would have to be applied close to the Earth, a very large energy is required, risking unintentional disruption of the comet unless a series of smaller impulses is possible. Complicating matters further, there would be no time to precede the deflection mission with reconnaissance missions to characterize the target. Indeed, rendezvous (matching orbit) with such a comet is not generally possible. Such cases naturally lead toward a destruction strategy requiring very large nuclear bombs carried on high-energy rockets that can be launched on a few weeks warning and fired with split-second accuracy during a fast flyby.

Additional problems arise from the indeterminacy of the orbit for a long-period comet entering the solar system (Chodas, 1997). In the case of an asteroid, there is ample time to refine the orbit using both optical and radar astrometry in order to determine whether a future impact will take place. In contrast, an incoming comet can be observed over only a short orbital arc, and radar would not be available until it was very close to the Earth. Even if optical observations were sufficient to determine a high probability of impact, nongravitational effects are likely to alter the orbit in unpredictable ways. It is probably impossible to provide reliable information on the trajectory of such a comet in advance of the decision to intercept.

It is easy to imagine various nightmare scenarios for incoming comets. Suppose that a very large comet is discovered near the orbit of Jupiter, and that based on a few weeks of observation, the Earth is found to lie within the error ellipse of the projected orbit. But suppose also that the area of this error ellipse at the Earth is hundreds of times greater than the area of the Earth itself. What should be done? Should a crash program of defense be initiated even though the probability of impact is less than 1%? At what point is action justified? Suppose further that additional tracking does not shrink the ellipse greatly because of the onset of nongravitational forces. Perhaps the comet disappears behind the Sun for a few months and cannot be seen at all (the scenario described in the novel Lucifer's Hammer; Niven and Pournelle, 1977). How would a decision on countermeasures be made? Could a deflection be considered when its unintentional effect might be to cause an impact rather than to avoid one? What organization would take responsibility for dealing with these issues?

The situation described above is of concern for several reasons. Most important, it is the unexpected appearance of a large comet that has the most potential for truly catastrophic results, from which recovery may be impossible. Second, even though the probability of such an event is extremely small, the chances of a false alarm resulting from the indeterminate orbit of the comet are much larger. There are likely to be thousands of such false alarms for every real impact (Chapman, 2000).

As a practical matter, we can expect that the first "threats" that society will have to face will be due to either a cometary false alarm or the detection of a relatively small asteroid (like Tunguska) on a collision course with the Earth. In either case the pressures for an active defense may be overwhelming, in spite of arguments that the probability of significant damage is quite low. The odds of either of these events happening within the lifetimes of ourselves or our grandchildren are fairly large (Chapman, 2000; Morrison et al., 2004).

9.6 Summary and Conclusions

The threat of impacts of asteroids and comets has existed since our planet's birth, but it has only recently been recognized as having practical consequences for modern life. The chances that civilization might be disrupted or destroyed by such an impact are very low, but they are not zero. By some measures, they are comparable to other hazards that society takes very seriously.

It is within our capability to inventory most of the population of larger Earth-crossing asteroids and short-period comets, and the Spaceguard Survey is well on its way to meeting the goal of finding 90% of NEAs larger than 1 km. Unfortunately, there is no similar strategy that will ensure a long warning time for a long period or new comets. The risk of asteroid impacts does not require the development and maintenance of expensive and inherently risky "space defenses" in advance of the discovery of a specific threat. However, a comet might be identified on an impact trajectory with a lead time of only a few months; should we prepare in advance to deal with such a contingency, probably at great expense, even though it is extremely unlikely? Surely we should at least consider how we would deal with the consequences of an impact that could not be prevented and might arrive with little warning (Garshnik et al., 2000)?

Should we develop technologies for deflecting or destroying comets? Many would argue that it is prudent to begin such research before an actual threat is identified. Others argue that since these technologies are unlikely to be needed within the next several decades, it is a waste of resources to do any work at present. The most compelling case is probably to accelerate our scientific study of asteroids and comets (Belton, 2004). The knowledge gained by such scientific exploration is also needed to make plans for future defense efforts, if they are required.

If the society concludes that the impact threat deserves higher priority, who should be in charge of these efforts – both advanced surveys and development of defense systems? Is NASA the correct agency? What should be the role of the Department of Defense? For that matter, are these topics the responsibility of the U.S. government? To date, there is no official position or plan that allocates responsibility within the U.S. government or the international community. This issue is sometimes paraphrased when astronomers ask, "Who should I call if I discover a comet or asteroid on a collision course with the Earth?"

The development of space defenses is an inherently hazardous undertaking. The existence of nuclear weapons and launch vehicles carries its own risk, since these might be used against targets on the Earth rather than in space. In addition, as pointed out by Sagan and Ostro (1994a, b) and Harris et al. (1994), the technology developed to deflect threatening asteroids could also be used to alter the course of a benign asteroid so that it would strike the Earth. The fact that such a suicidal act would require that a government be under the control of a madman does not make it impossible.

As public recognition of the impact hazard grows, such questions will increasingly fuel the hazard-mitigation debate. There may be demands for governmental action to protect the Earth from impacts. However, the impact hazard must be considered in parallel with, and balanced against, debates over the society's priorities of dealing with other potential ecological disasters, many of which appear to be more severe than the impact hazard. Over the very long term, however, impacts must be dealt with to ensure the survival of civilization and the human species itself.

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References

Ahrens, T.J. and A.W. Harris (1992). Deflection and fragmentation of near-Earth asteroids. *Nature*, **360**, 429–443.

Alvarez, L.W., W. Alvarez, F. Asaro, and H.V. Michel (1980). Extraterrestrial cause for the Cretaceous-Tertiary extinction. *Science*, **208**, 1095–1108.

Atkinson, H., C. Tickell and D. Williams (2000). *Report of the Task Force on potentially hazardous Near Earth Objects*, British National Space Center, London. <http:www.nearthearthobject.co.uk>.

Baldwin, R.B. (1949). *The Face of the Moon.* University of Chicago Press, Chicago

Belton, M.J.S. (2004). Towards a national program to remove the threat of hazardous NEOs. In *Mitigation of Hazardous Comets and Asteroids* (M.J.S. Belton, T.H. Morgan, N. Samarashina and D.K. Yeomans, editors), Cambridge University Press, Cambridge (UK), pp. 391–410.

Bottke, W.F., A. Morbidelli, R. Jedicke, J.-M. Petit, H.H. Levinson, P. Michel, and T.S. Metcalf (2002). Debiased orbital and absolute magnitude distribution of the near-Earth Objects. *Icarus*, **156**, 399–433.

Chodas, P.W., (1997). Impact warning times for long period comets (abstract) *Bull. Amer. Astron. Soc.*, **29**, 1102.

Muinonen (1994). Earth-crossing asteroids and comets: Groundbased search strategies. In *Hazards Due to Comets and Asteroids* (T. Gehrels, ed.). University of Arizona Press, Tucson, pp. 149–198.

Canavan, G.H., J. Solem, and J.D.G. Rather (1994). Near-Earth object interception workshop. In *Hazards Due to Comets and Asteroids* (T. Gehrels, ed.). University of Arizona Press, Tucson, pp. 93–126.

Chapman, C.R. (2000). The asteroid/comet impact hazard: Homo sapiens as dinosaur? In *Prediction: Science, Decision Making, and the Future of Nature* (ed. D. Sarewitz, R.A. Pielke, Jr. and R. Byerly); Island Press, Washington DC, pp. 107–134.

Chapman, C.R. and D. Morrison (1989). *Cosmic Catastrophes.* Plenum Press, New York, p. 302.

Chapman, C.R. and D. Morrison (1994). Impacts on the Earth by asteroids and comets: Assessing the hazard. *Nature*, **367**, 33–40.

Chesley, S. and S.W. Ward (2005). Impact-generated tsunami: A quantitative assessment of human and economic hazard, *J. Natural Hazards*, **38**, 355.

Chyba, C.F. (1993). Explosions of small Spacewatch asteroids in the Earth's atmosphere. *Nature*, **363**, 701–703.

Chyba, C.F., P.J. Thomas, and K.J. Zahnle (1993). The 1908 Tunguska explosion: Atmospheric disruption of a stony asteroid. *Nature*, **361**, 40–44.

Covey, C., S.J. Ghan, J.J. Walton, and P.R. Weissman (1990). Global environmental effects of impact-generated aerosols: Results from a general circulation model. In *Global Catastrophes in Earth History* (V.L. Sharpton and P.D. Ward, eds.), Geological Society of America Special Paper 247, 263–270.

Farinella, P., L. Foschini, C. Froeschle, R. Gonczi, T.J. Jopek, G. Longo, and P. Michel (2001). Probable asteroidal origin of the Tunguska cosmic body. *Astron. Astrophys.*, **377**, 1081–1097.

Garshnek, V., D. Morrison, and F.M. Burkle (2000). The mitigation, management, and survivability of asteroid/comet impact with the Earth. *Space Policy*, **16**, 213–222.

Gehrels, T. (1991). Scanning with charge-coupled devices. *Space Sci. Rev.*, **58**, 347–375.

Glasstone, S. and P.J. Dolan (1977). *The Effects of Nuclear Weapons*, 3rd edn. U.S. Government Printing Office, Washington, DC.

Harris, A.W., G.H. Canavan, C. Sagan, and S.J. Ostro (1994). The deflection dilemma: Use versus misuse of technologies for avoiding interplanetary collision hazards. In *Hazards Due to Comets and Asteroids* (T. Gehrels, ed.). University of Arizona Press, Tucson, pp. 1145–1156.

W.K. Hartmann, R.J. Phillips, and G.J. Taylor, editors (1986). *Origin of the Moon.* Lunar and Planetary Institute, Houston, TX.

Harwell, M.A. and T.C. Hutchinson (1989). *Environmental Consequences of Nuclear War ll: Ecological and Agricultural Effects*, 2nd edn. Wiley, New York.

Hills, J.G. and M.P. Goda (1993). The fragmentation of small asteroids in the atmosphere. *Astron. J.*, **105**, 1114–1144.

Hills, J.G., I.V. Nemtchinov, S.P. Popov, and A.V. Teterev (1994). Tsunami generated by small asteroid impacts. In *Hazards Due to Comets and Asteroids* (T. Gehrels, ed.). University of Arizona Press, Tucson, pp. 779–790.

Kleiman, L.A., editor (1968). *Project Icarus.* MIT Press, Cambridge MA, p. 162.

Krinov, E.E. (1963). The Tunguska and Sikhote–Alin meteorites. In *The Moon, Meteorites, and Comets* (B.M. Middlehurst and G.P. Kuiper, eds.). University of Chicago Press, Chicago, pp. 208–234.

McCord, T.B., J. Morris, and D. Persing (1995). Detection of a meteoroid entry into the Earth's atmosphere on February 1, 1994. *J. Geophys. Res.*, **100**, 3245–3250.

Morrison, D., editor (1992). *The Spaceguard Survey: Report of the NASA International Near- Earth-Object Detection Workshop.* Unpublished NASA report. See <http:impact.arc.nasa.gov>.

Morrison, D., C.R. Chapman, and P. Slovic (1994). The impact hazard. In *Hazards Due to Comets and Asteroids* (T. Gehrels, ed.). University of Arizona Press, Tucson, pp. 59–92.

Morrison, D., A.W. Harris, G. Sommer, C.R. Chapman and A. Carusi (2003). Dealing with the impact hazard. In *Asteroids III* (W. Bottke, A. Cellino, P. Paolicchi and R.P. Binzel, eds.), University of Arizona Press, pp. 739–754.

Morrison, D., C.R. Chapman, D. Steel, and R. Binzel (2004). Impacts and the public: Communicating the nature of the impact hazard. In *Mitigation of Hazardous comets and Asteroids* (M.J.S. Belton, T.H. Morgan, N. Samarashina and D.K. Yeomans, editors), Cambridge University Press, Cambridge (UK), pp. 353–390.

Pike, J. (1993). The big splash. Unpublished manuscript.

Niven, L. and J. Pournelle (1977). *Lucifer's Hammer.* Fawcett Crest Books, New York.

Rabinowitz, D.L., E. Bowell, E.M. Shoemaker, and K. Muinonen (1994). The population of Earth-crossing asteroids. In *Hazards Due to Comets and Asteroids* (T. Gehrels, ed.). University of Arizona Press, Tucson, pp. 285–312.

Sagan, C. and S.J. Ostro (1994a). Dangers of asteroid deflection. *Nature*, **368**, 501.

Sagan, C. and S.J. Ostro (1994b). Long-range consequences of interplanetary collisions. *Issues in Sci. & Tech.*, **20**, 67–72.

Schweickart, R.L., E.T. Lu, P. Hut and C.R. Chapman (2003). The asteroid tugboat. *Scientific American*, November 2003, 54–61.

Sekanina, Z. (1998). Evidence for asteroidal origin of the Tunguska object. *Planetary & Space Science*, **46**, 191–204.

Sharpton V.I. and P.D. Ward, editors (1990). *Global Catastrophes in Earth History: An Interdisciplinary Conference on Impacts, Volcanism, and Mass Mortality.* Geological Society of America Special Paper 247, Boulder.

Shoemaker, E.M. (1983). Asteroid and comet bombardment of the Earth. *Annual Rev. Earth Planet. Sci.*, **11**, 461–494.

Shoemaker, E.M, R.F. Wolff, and C.S. Shoemaker (1990). Asteroid and comet flux in the neighborhood of the Earth. In *Global Catastrophes in Earth History* (V.L. Sharpton and P.D. Ward, eds.), Geological Society of America Special Paper 247, 155–170.

Slovic, P. (1987). Perception of risk. *Science*, **236**, 280–285.

Steel, D.I. (1997), The Origin of the Atmosphere and of the Oceans. In *Comets and the Origin and Evolution of Life* (P.J. Thomas, C.F. Chyba, C.P. McKay, eds.), Springer, New York, pp. 209–242.

Steel, D.I., D.J. Asher, W.M. Napier, and S.V.M. Clube (1994). Are impacts correlated in time? In *Hazards Due to Comets and Asteroids* (T. Gehrels, ed.). University of Arizona Press, Tucson, pp. 463–478.

Stokes, G.H., J.B. Evans, H.E.M. Viggh, F.C. Shelly, and E.C. Pearce. Lincoln Near-Earth Asteroid Program (LINEAR). *Icarus*, **148**, 21–28 (2000). See also <www.ll.mit.edu/LINEAR/>.

G. Stokes, editor (2003). *Study to Determine the Feasibility of Extending the Search for Near Earth Objects to Smaller Limiting Diameters* (Report of the NASA NEO Science Definition Team, August 2003). <http:neo.jpl.nasa.gov/neo/report.html>.

Stuart, J.S. and Binzel, R.P. (2004). Bias-corrected population, size distribution, and impact hazard for the near-Earth objects, *Icarus*, **170**, 295–311.

Tagliaferri, E., R. Spalding, C. Jacobs, S.P. Worden, and A. Erlich (1994). Detection of meteoroid impacts by optical sensors in Earth orbit. In *Hazards Due to Comets and Asteroids* (T. Gehrels, ed.). University of Arizona Press, Tucson, pp. 199–220.

Toon, O.B., J.B. Pollack, T.P. Ackerman, R.P. Turco, C.P. McKay, and M.S. Liu (1982). Evolution of an impact-generated dust cloud and its effects on the atmosphere. In *Geological Implications of Impacts of Large Asteroids and Comets with the Earth* (L.T. Silver and P.H. Schultz, eds.), Geological Society of America Special Paper 190, 187-200.

Toon, O.B., K. Zahnle, R.P. Turco, and C. Covey (1994). Environmental perturbations caused by impacts. In *Hazards Due to Comets and Asteroids* (T. Gehrels, ed.). University of Arizona Press, Tucson, pp. 791–826

Toon, O.B., K. Zahnle, D. Morrison, R.P. Turco & C. Covey (1997). Environmental perturbations caused by the impacts of asteroids and comets. *Reviews of Geophysics*, **35**, 41–78.

Turco, R.P., O.B. Toon, T.P. Ackerman, J.B. Pollack and C. Sagan (1991). Nuclear winter: Physics and physical mechanisms. *Annual Rev. Earth Planet. Sci.*, **19**, 383–422.

Vasilyev, N.V. The Tunguska meteorite problem today. *Planetary & Space Sci.*, **46**, 129–150 (1998)

Weissman, P.R. (1982). Terrestrial impact rates for long and short-period comets. In *Geological Implications of Impacts of Large Asteroids and Comets with the Earth* (L.T. Silver and P.H. Schultz, eds.), Geological Society of America Special Paper 190, 15–24.

Weissman, P.R. (1991). The cometary impactor flux at the Earth. In *Global Catastrophes in Earth History* (V.L. Sharpton and P.D. Ward, eds.) Geological Society of America Special Paper 247: 171–180.

Weissman, P.R. (1997). The cometary impact flux at Earth. *Annals New York Academy of Sciences*, **822**, 67–95.

Wetherill, G.W. (1988). Where do the Apollo objects come from? *Icarus*, **76**, 1–18.

Wetherill, G.W. (1989). Cratering of the terrestrial planets by Apollo objects. *Meteoritics*, **24**, 15–22.

10

The Conditions for Liquid Water in Cometary Nuclei

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Summary. Liquid water is considered fundamental for the development of life. Comet nuclei are composed largely of ice, and under the proper conditions, some of that ice may transform into liquid water. We describe the physical processes involved in computing the heat balance in comet nuclei and present the results of numerical models of their thermal evolution. We determine under which conditions liquid water may form.

10.1 Introduction

Comets are usually thought of as being relics from the time of the formation of the solar system, which have preserved their primordial structure and composition. This is not strictly true, since the outer layers of a comet are exposed to thermal and UV-radiation while the comet is near the sun. This results in the formation of the comet's halo and tail, and is the ultimate cause of all of the cometary activity that is observed. These outer layers evaporate while the comet is near the sun. It is, however, generally assumed that the deep interior of the comet retains its pristine nature. An early study of the radioactive heating of cometary interiors (Whipple and Stefanic, 66) seemed to confirm this idea, by showing that, for the expected abundances of radioactive ^{40}K, ^{235}U, ^{238}U, and ^{232}Th, a temperature rise of only 90 K is to be expected. Since the initial temperature in the comet interior is expected to be of the order of 50 K or less, such a moderate temperature rise would not seriously affect the internal structure.

It was probably considerations like this that caused Hoyle and Wickramasinghe (1978) to propose that life could form in the outer layers of comets. They argued that since organic molecules are seen in interstellar clouds, there might be prebiotic molecules formed in interstellar grains. If these grains are eventually incorporated into comets, then each time a comet approaches the sun, those grains on the surface will be exposed to the solar UV-flux, and these molecules would be altered. They suggested that repeated exposure to

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this flux might lead to the formation of life. The difficulty with this picture is that the solar radiation penetrates only into a very thin outer layer of the nucleus, and that layer is quickly lost by sublimation.

One of the most exciting results of recent experiments on organic compounds is the fact that they show self-organizing behavior when exposed to liquid water (see, e.g. Allamandola et al., 1997). If liquid water could form inside a comet, any prebiotic material might be able to advance toward life even without the impetus provided by the solar UV-flux. The issue then becomes to determine under what conditions liquid water can form in a comet interior.

10.2 Reconsidering Internal Heat Sources

10.2.1 Radioactive Heating

In the years since the work of Whipple and Stefanic (1966), our picture of radioactive heating has changed in several ways. One of the most important is the realization that ^{26}Al, an extinct radionuclide, may have been an important heat source. In 1976, Lee et al. presented strong evidence that ^{26}Al had been present in the early solar nebula. Afterwards γ-ray observations from the *HEAO 3* and *Solar Maximum Mission* satellites detected ^{26}Al dispersed throughout the galaxy (Mahoney et al., 1982; Share et al., 1985). A review of more recent measurements of galactic ^{26}Al is given by Diehl et al. (1997), while relevant meteoric work is summarized by MacPhersonet al. (1995). Several sources have been suggested for this isotope, including ordinary novae (Clayton, 84), asymptotic giant branch stars (Cameron, 85), and massive stars (Dearborn and Blake, 85). In any event, it is now believed that the production rate in the galaxy is high enough so that a steady state abundance of ^{26}Al would have existed in the early solar system, and that some of this would have been incorporated into comets when they were formed. ^{26}Al has a half-life of only 7.4×10^5 years, so it could have been active only in the early life of the comet, but, as we shall see, it is a powerful heat source, and can have a strong effect on the further evolution of the body.

Early estimates of the effect of ^{26}Al on cometary interiors (Irvine et al., 1980; Wallis, 1980) indicated that if the thermal diffusivity was sufficiently low, and the body sufficiently large, the internal temperature could be raised to a high enough value to melt water. Recently, additional short-lived radioactive heat sources have been suggested, such as ^{60}Fe (Knie et al., 1999), but ^{26}Al is still the most important radionuclide for internal heating.

10.2.2 Amorphous–Crystalline Transition

An additional heat source is provided by the ice itself. When water vapor condenses at very low temperatures, it forms amorphous ice. Upon heating, this material spontaneously transforms to crystalline ice at a rate given by

$$\frac{\partial \rho_a}{\partial t} = -\lambda\left(T\right)\rho_a \tag{10.1}$$

where ρ_a is the bulk mass density of the amorphous ice, T is the temperature, and t is the time. The rate of crystallization, $\lambda(T)$, has been measured by Schmitt et al. (1989) to be

$$\lambda\left(T\right) = 1.05 \times 10^{13} e^{-5370/T} \qquad \mathrm{s}^{-1} \tag{10.2}$$

This transformation is irreversible, so the latent heat released provides a one-time source of 9×10^8 erg g^{-1} (Klinger, 1981).

Amorphous ice has a conductivity different from that of crystalline ice, so the thermal diffusivity of the medium will undergo a change with time, and this too has to be taken into account in a detailed model. Finally, amorphous ice has the ability to trap other gases (Bar-Nun et al., 1988). When the ice is heated and transforms to crystalline ice, these occluded gases are released. This has important consequences for the structure and heat balance of the nucleus, and will be discussed below.

The formation of crystalline ice via the amorphous–crystalline transition can be described by

$$\frac{\partial \rho_{\mathrm{c}}}{\partial t} = \left(1 - \sum_n f_n\right)\lambda\left(T\right)\rho_a - q_v \tag{10.3}$$

Here ρ_c is the bulk density of the crystalline ice, f_n is the mass fraction of the nth species of trapped gas, and q_v is the rate of sublimation of water vapor. The latter is given by

$$q_v = S\left[P_{\mathrm{vap}}(T) - P\right]\sqrt{\frac{m_{\mathrm{H_2O}}}{2\pi k T}} \tag{10.4}$$

Here S is the surface area of the comet, k is Boltzmann's constant, $m_{\mathrm{H_2O}}$ is the mass of a water molecule, and P and P_{vap} are the partial and vapor pressures of water, respectively. These heat sources provide the energy to drive comet evolution even in the absence of solar radiation.

10.3 Cooling Mechanisms

10.3.1 Thermal Diffusivity

The energy produced by the various heating mechanisms will heat the local neighborhood, but it will also diffuse to other regions of the comet in response to the relevant gradients, and will eventually be lost to space. There are two important heat transfer mechanisms: thermal diffusion and material diffusion. The thermal diffusion rate depends on the thermal diffusion coefficient:

$$\kappa \equiv \frac{K}{\rho C} \tag{10.5}$$

where K is the thermal conductivity, ρ is the density of the material, and C is the heat capacity. These parameters are known for bulk ice, but the ice in comets is believed to be porous. While ρ and C are easily computed for a bulk medium, the relationship between K and the porosity, p, is not simple, and a number of attempts have been made to model it (see Prialnik et al., 2005 for a review). In the models presented here, we have used the simple formulation of Smoluchowski (1982), which is similar to other formulations at low porosity.

A second effect of the pores is to allow for material (gas and dust) transport. This material will carry heat out of the region and can be an efficient cooling mechanism. Thus the porosity reduces diffusive heat transport by lowering the area of contact between adjacent volumes, but increases the mass transport by allowing gas and dust (which is carried by the gas) to flow more efficiently. The net result will depend on the abundance and the volatility of the gases available.

10.4 Simple Physics

The competition between the cooling and heating mechanisms will determine whether a given volume of the comet will reach melting. Heating will release trapped gas, and the pressure of the released gas can cause the pores to grow. As a result, both the gas content and the porosity of different regions of the comet may change during its evolution. This, in turn, will alter the thermal diffusivity, and the cooling and heating rates will all change. To keep track of such changes, a detailed numerical model is necessary. We will present the results of such numerical simulations below. It is useful, however, to first look at the basic physics of the relevant processes.

10.4.1 Energy Considerations

If we assume that the comet interior has an initial temperature 20 K, then the energy required to heat a gram of ice to 260 K can be found by integrating the product of the heat capacity (Klinger, 81)

$$c(T) = 7.49 \times 10^4 T + 9 \times 10^5$$

and the temperature change from 20 to 260 K. The result is 2.73×10^9 erg g^{-1}. Because of the temperature dependence of the heat capacity, an initial temperature of 50 K would reduce this by only 4%. For the radioactive materials that are relevant to the problem, the total energy available per gram of comet are shown in Table 10.1.

Table 10.1. Radioactive heat sources.

Element	**Available energy (erg/g)**	**lifetime (year)**
^{235}U	1.17×10^9	1.03×10^9
^{238}U	4.22×10^9	6.49×10^9
^{232}Th	9.08×10^9	2.00×10^{10}
^{40} K	1.89×10^{10}	1.82×10^9
^{26} Al	7.4×10^9	1.07×10^6

10.4.2 Timescales

As mentioned before, the temperature of a comet interior is determined by the competition between heating and cooling processes. These, in turn, depend, not only on the amount of trapped gas and dust, on the porosity of the ice, and on the nature of the ice (amorphous or crystalline), but also on the way these parameters evolve with time. The heating and cooling rates can be computed only by modelling the detailed evolution of the body. One can, however, gain some insight by considering the relative rates of heating and cooling.

The rate of heat flow to the surface is given by

$$4\pi R^2 K \frac{dT}{dr} \approx 4\pi R^2 K \frac{T}{R} \tag{10.6}$$

where K is the thermal conductivity, T is the temperature, and R is the comet's radius. If ρ is the density of the comet nucleus, and Q is the heat production per unit mass, then we will have a steady state when

$$Q \approx \frac{3KT}{\rho R^2} \tag{10.7}$$

In the absence of ^{26}Al, other radioactive materials give $Q \approx 4 \times 10^{-7}$ erg g^{-1} s^{-1}. The thermal conductivity of crystalline ice is given by (Klinger, 1980) as $K(T) = 5.67 \times 10^7/T$ erg cm^{-1} s^{-1} K^{-1}, so that a steady state is reached only for bodies of the order of a few hundred kilometers in radius, consistent with previous calculations. If ^{26}Al is present with a primordial mass fraction of 5×10^{-8}, then $Q = 2 \times 10^{-4}$ erg g^{-1} s^{-1}, and steady state can be achieved for bodies of the order of 10 km. Thus bodies larger than this will retain energy, heat up, and may reach melting.

An additional complication is due to the fact that when water vapor is deposited at low temperatures, the ice formed is amorphous, and has a lower thermal conductivity than ordinary crystalline ice.

$$K(T) = 2.34 \times 10^2 T + 2.80 \times 10^3 \tag{10.8}$$

At a temperature of 90 K (the significance of which will be explained shortly), $K(T) = 2.39 \times 10^4$ erg cm^{-1} s^{-1} K^{-1}. In this case R is reduced to ~1.8 km. In addition to a lower thermal conductivity, amorphous ice, when heated, transforms, exothermically, to a crystalline phase. This transformation can supply up to 9×10^8 erg g^{-1}, the rate of crystallization being given by Eq. (10.2), above. At a temperature of 90 K, the rate of transformation is fast enough, so that the latent heat released is of the order of that released by ^{26}Al decay. This additional heating will cause the phase transformation to proceed even faster, resulting in runaway heating. In this simple model, ^{26}Al decay will bring bodies larger than about 2 km to high central temperatures for a limited period.

Cooling by the gas depends on the gas diffusion coefficient, which is $\kappa_{\mathrm{gas}} \sim 10$ cm^2 g^{-1} (see, e.g. Prialnik, 1992). From Fig. 10.1, ^{26}Al requires some 10^5 years to heat the interior to 90 K. For a 1-km radius comet the thermal diffusion time is also approximately 10^5 years. Thus heating and cooling are roughly balanced. The inclusion of gas cooling, however, will ensure that the temperature stays well below melting. The gas diffusion timescale will be greater than approximately 10^5 years for comets larger than approximately 30-km radius. This is a good rough estimate of the size needed to produce melting.

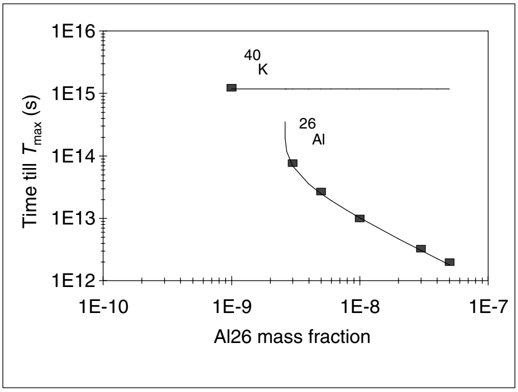

Fig. 10.1. Time to heat to 90 K as a function of ^{26}Al abundance (solid curves). The squares are the results of numerical models.

In Fig. 10.1, the squares show the time it takes to reach a maximum in the central temperature for a series of the models we computed with the standard abundance of radioactive U, Th, and K, and a variable abundance of ^{26}Al. In all cases the maximum temperature equaled or exceeded 260 K, so that melting was possible. The lower curve is the time required for ^{26}Al to produce enough heat to bring the ice to 90 K. As can be seen, the curve follows the squares very closely until an ^{26}Al mass fraction of approximately 3×10^{-9} is reached. Such a low abundance will never produce enough energy to heat the ice to 90 K, and runaway heating will never occur. If ^{26}Al were the only heat source, this abundance would be too low to bring about melting. Melting can still be achieved, however, if additional radioactive heat sources are considered.

The upper line shows the time required to reach 90 K as a result of heating by ^{40}K. As can be seen from Table 10.1, ^{40}K can provide substantial heating, albeit at a much lower rate. When the ^{26}Al abundance is too low to provide the required heating ^{40}K can do the job, but it takes much longer. We see that while the sequence of squares appears to be continuous, it is really the result of two distinct heating mechanisms.

If we require the radioactive heat to be retained in order to raise the internal temperature, we must have a cometary body that is sufficiently large so that the thermal diffusion time is longer than the time required to produce the heat. The two curves in Fig. 10.2 show the required size for thermal diffusivities of $\kappa = 10^{-2}$ and $\kappa = 10^{-3}$, respectively. These values roughly bracket the actual values of κ in the comet. The ×'s in the figure show the minimum depth at which melting occurred in the detailed models. This is a good approximation to the minimum radius body required to achieve melting. The agreement between the simple estimates and the detailed models shows that this simple picture is useful for estimating the effects of additional heat sources.

Clearly, the timescale arguments presented here are only illustrations of the physical principles. A nucleus with zero porosity, or zero volatile gas content, will not undergo gas cooling, so the gas diffusion timescale would be irrelevant.

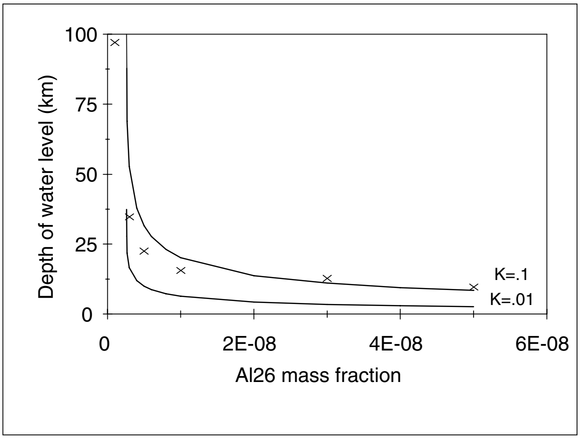

Fig. 10.2. The two curves show the estimated depth of the melting level as a function of ^{26}Al mass fraction based on the simple model described in the text, for two values of the thermal diffusivity. The x's show results of detailed models.

The fine details depend on the porosity and gas content of the nucleus, and on their evolution with time. These must be studied with a full numerical model.

10.5 Numerical Models

We have computed detailed models of comet thermal evolution. The nucleus was assumed to be spherically symmetric, and heated uniformly from all directions. The orbit was taken to be circular, with a semimajor axis (radius) of 100 AU. The actual details of the orbit are not important, other than that they ensure a low surface temperature. The nucleus itself was assumed to be composed of a mixture of ice and dust, with the mass ratio of these two components being 1:1. It was also assumed that 1% CO and 1% CO_2 were originally present, either as ices or as gas occluded in the amorphous ice. The amorphous ice was allowed to crystallize according to Eq. (2) with the resulting release of latent heat. The ice was assumed to be porous.

The baseline model had an initial porosity of 0.1, and an initial pore size of 100 μm. Upon heating, the CO and CO_2 flow through the porous nucleus, along with the water vapor, and contribute to the heat transport. In addition, if their pressure is high enough, these gases can cause the pores to expand, and change the permeability of the medium.

Heating is caused by the radioactive materials ^{40}K, ^{235}U, ^{238}U, ^{232}Th, and ^{26}Al. The first four isotopes are assumed to be present in the dust in their solar ratio to silicon, and the initial ^{26}Al mass fraction in the dust is taken to be 5×10^{-8} in the baseline model. In addition, account is taken of the latent heat released by the amorphous to crystalline phase transition, as well as the phase changes between gases, liquids, and solids. Details of how the various processes are modelled can be found in Prialnik (1992), Prialnik et al. (1987), Mekler et al. (1990), Prialnik et al. (1993), Podolak and Prialnik (1996), and Prialnik et al. (2005).

The actual melting temperature of the ice in the nucleus is somewhat problematic, since it depends on the details of the impurities present. The presence in the ice of 1% ammonia, by mass, for example, will lower the melting temperature of the ice by roughly 1 K. The observed abundance of ammonia in comets is less than this, however. Other materials, such as methanol, though present with a greater abundance, are less effective in lowering the melting point. Finally, the abundance of nonvolatile materials is not known in any detail. In view of this we feel that the ice in the nucleus will almost certainly not melt if the temperature is below 260 K. Above this temperature we will consider the ice liquid, provided there is sufficient pressure to stabilize the liquid state.

Figure 10.3 shows the results of these computations for a series of models starting with the baseline model, and varying only the radius and porosity. As can be seen from the figure, a 1-km comet will never reach melting. The main cooling mechanism is gas diffusion. For such a small radius the gas can

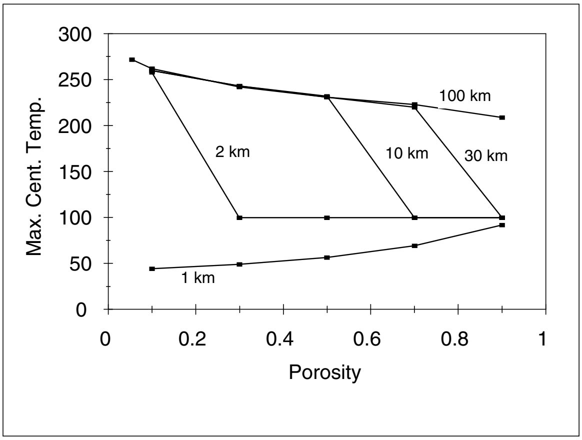

Fig. 10.3. Maximum central temperature for a series of comets of different radii as a function of porosity. Other parameters are like those in the baseline model.

escape easily for any reasonable porosity, and even for very small porosities the heat can escape through thermal diffusion. As the porosity increases, the efficiency of gas diffusion does not change substantially, but the thermal diffusion coefficient decreases somewhat, so that the maximum temperature increases slightly.

As the radius of the comet increases, the time for thermal diffusion quickly exceeds the time for radioactive heat production, and the temperature goes up. However, if the porosity increases sufficiently so that gas cooling becomes effective, the maximum central temperature drops quickly, as can be seen in the figure. For increasing radii, this critical porosity increases until a radius of around 30 km is reached. At this point the gas diffusion timescale is roughly equal to the radioactive heating timescale so that for larger bodies the maximum central temperature is fairly independent of porosity. It does, however, drop as the porosity increases, even for a 100-km body. The maximum central temperature will be in the vicinity of melting only for low porosities ($\sim$0.1).

Figure 10.4 shows the temperature inside a 100-km comet (baseline model) at two particular times: 6.3×10^4 years after formation and 2.3×10^5 years after formation. In both cases the inner 90% of the body is at temperatures above 260 K. High temperature is not sufficient for guaranteeing liquid water, however. An additional requirement is that the ambient pressure be high enough to ensure that the water is in the liquid and not in the gaseous state. Figure 10.5 shows the pressure throughout the comet for the two times shown in Fig. 10.4. As can be seen, the pressures at 6.3×10^4 years are high enough to ensure that water will be present in the liquid phase. By 2.3×10^5 years, however, the pressures have fallen to about 2 mbar throughout most of the volume. At this pressure water at 260 K will be a vapor. Thus, although the

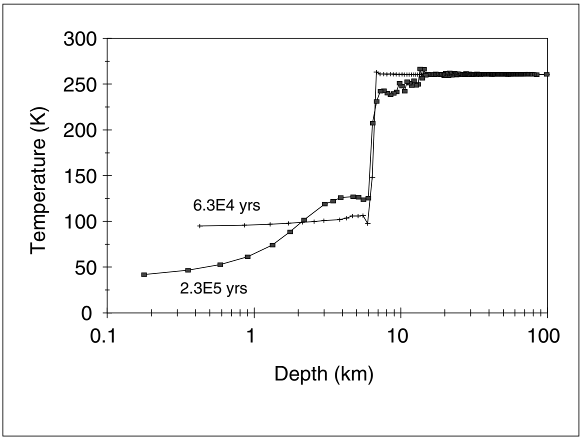

Fig. 10.4. Temperature inside baseline model at 6.3×10^4 years and 2.3×10^5 years after formation as a function of radius.

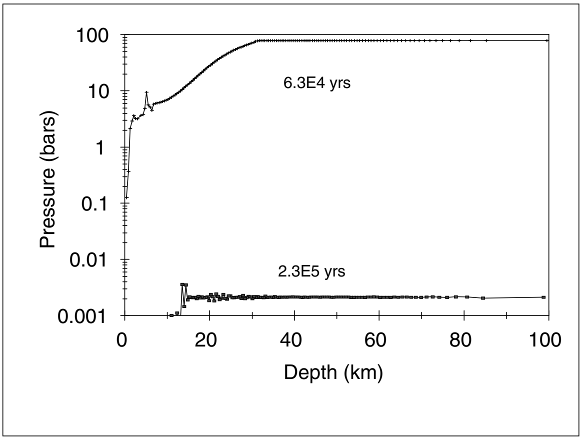

Fig. 10.5. Pressure inside baseline model at 6.3×10^4 years and 2.3×10^5 years after formation as a function of radius.

body of the comet may remain warm for a considerable time, the pressures will be too low to maintain liquid water for much of that time.

The models show that several criteria are needed for the formation of liquid water in a comet interior: The body must have a radius of at least 10 km. It must have a low porosity, of the order of 0.1. The ^{26}Al mass fraction must be around 5×10^{-8}, and occluded gases must be present in amounts less than a few percent. Finally, if the pores themselves are too large, they will allow the gas to cool the comet efficiently. A maximum pore radius of around a millimeter is indicated (Podolak and Prialnik, 2000).

10.6 What Further Studies May Show

Additional heat sources would provide additional energy for melting, and could change these results. Recently, Gudipati and Allamadola (2003) have shown that ions formed by UV radiation or cosmic rays striking polycyclic aromatic hydrocarbons (PAHs) can be trapped in ice. When the ice is heated to temperatures between 50 and 150 K, these ions recombine and release substantial energy. UV radiation will form many ions but they will be concentrated near the surface. When the ice is heated and the ions recombine, the heat can easily diffuse away. But cosmic rays may build up ions in the deeper layers of the comet, where they can be released when the comet heats up due to radioactive heating. This source will soon be included in numerical models. It is possible that if the heat source is sufficiently strong, we may be able to relax some of the requirements set above for a cometary body to have liquid water.

Another effect that must be taken into account is the process of accretion itself, for if a comet accretes very slowly, the effect of ^{26}Al heating can be strongly diminished and vice versa. Recent work by Merk and Prialnik (2003) is an important step toward dealing with this issue. They investigated the simultaneous accretion and thermal evolution of Kuiper belt objects, and found that for the parameter set studied, it is possible to get some liquid water on bodies with radii as small as 4 km. The details depend on the ratio of dust to ice in the body, the heliocentric distance (which affects the accretion rate), as well as the radius of the body itself. These models do not, as yet, include cooling by gas diffusion, so these results will probably need some revision. Nonetheless, based on our understanding of the evolution of icy bodies, it seems likely that liquid water was a component of such bodies in the past.

References

Allamandola, L.J., M.P. Bernstein, and S.A. Sandford (1997). In *Astronomical and Biochemical Origins and the Search for Life in the Universe* (C.B. Cosmovici, S. Bowyer, and D. Werthimer, eds.) p. 23.

Cameron, A.G.W. (1985). Formation and evolution of the primitive solar nebula. In *Protostars and Planets II* (D.C. Black and M.S. Matthews, eds.). University of Arizona, Tucson, pp. 1073-1099.

Clayton, D.D. (1984). ^{26}Al in the interstellar medium. *Astrophys. J.* , **280**, 144-149.

Dearborn, D.S.P. and J.B. Blake (1985). On the source of the ^{26}Al observed in the interstellar medium. *Astrophys. J. Lett.*, **288**, L21-L24.

Diehl, R., U. Oberlack, J. Knodlseder, H. Bloemen, W. Hermsen, D. Morris, J. Ryan, V. Schonfelder, A. Strong, P. von Ballmoos, and C. Winkler (1997). Models for COMPTEL ^{26}Al data. In *Proceedings of the Fourth Compton Symposium*, (C.D. Dermer, M.S. Strickman, and J.D. Kurfess, eds.) AIP Conference Proceedings 410, p. 1114.

Hoyle, F., and N.C. Wickramasinghe (1978). Influenza from space. *New Scientist*, **79**, 946-948.

Gudipati, M.S., and L.J. Allamandola (2003). Facile Generation and Storage of Polycyclic Aromatic Hydrocarbon Ions in Astrophysical Ices. *Ap. J.* **596**, L195–L198

Irvine, W.M., S.B. Leschine, and F.P. Schloerb (1980). Thermal history, chemical composition and relationship of comets to the origin of life. *Nature*, **283**, 748-749.

Klinger, J. (1980). Influence of a phase transition of ice on the heat and mass balance of comets. *Science* (Washington, D.C.), **209**, 634-641.

Klinger, J. (1981). Some consequences of a phase transition in water ice on the heat balance in comet nuclei. *Icarus*, **47**, 320-324.

Knie, K., G. Korschinek, T. Faestermann, C. Wallner, J. Scholten, and W. Hillebrandt (1999). Indication for supernova produced ^{60}Fe activity on Earth. *Phys. Rev. Let.*, **83**, 18-21.

Lee, T., D.A. Papanastassiou, and G.J. Wasserburg (1976). Demonstration of ^{26}Mg excess in Allende and evidence for ^{26}Al. *Geophys. Res. Let.*, **3**, 109-112.

MacPherson, G.J., A.M. Davis, and E.K. Zinner (1995). The distribution of aluminum-26 in the early Solar System - A reappraisal. *Meteorics*, **30**, 365-386.

Mahoney, W.A., J.C. Ling, A.S. Jacobson, and R.E. Lingenfelter (1982). *HEAO 3* discovery of ^{26}Al in the interstellar medium. *Astrophys. J.*, **262**, 578-585.

Mekler, Y., Prialnik, D. and M. Podolak (1990). Evaporation from a porous cometary nucleus. *Astrophys. J.*, **356**, 682-686.

Merk, R. and D. Prialnik (2003). Early thermal and structural evolution of small bodies in the trans-Neptunian zone. *Earth, Moon, and Planets*, **92**, 359–374.

Podolak, M. and D. Prialnik (1996). On the structure and evolution of comet P/Wirtanen. *Planet. and Space Sci.*, **44**, 655-664.

Podolak, M., and D. Prialnik (2000). Conditions for the production of liquid water in comet nuclei. In *Bioastronomy '99: a New Era in Bioastronomy* (G.A. Lemarchand, K.J. Meech, eds.) Sheridan Books, Chelsea, pp. 231-234.

Prialnik, D. (1992). Crystallization, sublimation, and gas release in the interior of a porous comet nucleus. *Astrophys. J.*, **388**, 196-202.

Prialnik, D., A. Bar-Nun, and M. Podolak (1987). Radiogenic heating of comets by ^{26}Al and implications for their time of formation. *Astrophys. J.*, **313**, 893-905.

Prialnik, D., U. Egozi, A. Bar-Nun, M. Podolak, and Y. Greenzweig (1993). On pore size and fracture in gas laden comet nuclei. *Icarus*, **106,** 499-509.

Prialnik, D., J. Benkhoff, and M. Podolak (2005). Modeling the structure and activity of comet nuclei. In *Comets II* (M. Festa, H.V. Keller, and H.A. Weaver, eds.) Univ. of Arizona Press, pp. 359–387.

Schmitt, B., S. Espinasse, R.J.A. Grim, J.M. Greenberg, and J. Klinger (1989). Laboratory studies of cometary ice analogues. *ESA SP*, **302**, 65-69.

Share, G.H., R.L. Kinzer, J.D. Kurfess, D.J. Forrest, E. L. Chupp (1985). *Astrophys. J. Lett.* , **292**, L61.

Smoluchowski R. (1982) Heat transport in porous cometary nuclei. *J. Geophys. Res.* **87**, A422-A424.

Wallis, M.K. (1980). Radiogenic heating of primordial comet interiors. *Nature*, **284**, 431-433.

Whipple, F.L., and R.P. Stefanic (1966). On the physics and splitting of cometary nuclei. *Mem. Roy. Soc. Liege (Ser. 5)*, **12**, 33-52.

11

Spacecraft Missions to Comets

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Summary. Comets have intrigued mankind over centuries. The use of improved astronomical equipment revealed an ever-increasing number of features. It took, however, until the advent of *in situ* measurements by the means of space research until the complexity of cometary physics and chemistry was recognized. Three comets have been visited by spacecrafts up to now, one mission is in progress (*Deep Impact* to Tempel-1, in July 2005) and one is planned (*Rosetta* to Churyumov-Gerasimenko, in 2013), 2 missions failed (CRAF was cancelled in 1992, CONTOUR exploded shortly after launch in 2002). While optical methods give a more global picture of the comet, the analysis of individual dust particles has resulted in the identification of some organic molecules, which may have played an important, steering role in the origin of life processes on the Earth.

11.1 Overview

Even though every some 10 years a bright (i.e., visible to the naked human eye) appears in the sky, amazingly few records are found. Since they appeared to come uncontrolled out of nowhere, comets have been seen as special events, mostly as messengers of good or bad things to happen in the near future. This was changed drastically after Sir Edmond Halley could show that at least one of them is on a closed orbit about the Sun. In 1910, on the return of Halley's comet, the organic material (HCN among others) recently detected in its tail caused a panic among some contemporaries. It has taken almost another half century to comprehend the basic functioning of comets, especially those impressive tails that make up their appearance. The solar wind was postulated by Biermann (1951) to explain why the ion tail was always pointing away from the Sun. Whipple (1950) described the most successful model of a comet nucleus as a "dirty iceball." The action of light pressure could explain the movements of the particles in the dust tail and thereby its shape. Sekanina (e.g., 1991 and references therein) has, in many papers, elaborated this model and could derive rotational states for many comets. So far so good for the most general features, but comets proved to be research resistant for another

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long time. Many comets travel on orbits leading them from the space beyond the orbit of Jupiter to near the Sun and with all inclinations to the ecliptic, including retrograde orbits. Due to celestial mechanics they are hard to reach from the Earth with space probes, except if one accepts high relative flyby speeds of well above several kilometers per second. This leads to a selection of short-period comets, which have already experienced several perihelion passages, and may have thereby lost part of their pristine behavior, i.e., original outgassing properties.

Therefore, it is essentially the high cost and/or the long flight duration, which have made so many mission proposals fail. In the early 1980s, finally, the time has come for in situ measurements triggered by the return of Halley's comet in 1985. Astronomical observations of comets had detected the presence of organic species long before that time and the number of different molecules is still increasing rapidly. Just shortly before that time one had "seen" the nucleus of a comet by radar (see, e.g., Kamoun et al., 1982), but resolution and the small scales involved limited (and still do) the detail which can be reliably observed from the Earth.

11.2 The Relevance for Issues of the Origin of Life

With the evolving field of biochemistry interest came up to find out how the first biochemicals may have come to the Earth. The famous Miller and Urey (1959) experiment had shown that complex organic materials could be formed via electric discharges in a then assumed primordial terrestrial atmosphere. On the other end of the lines of research, astronomers found and find an ever-increasing number of molecules in the gas phase of interstellar clouds. It seems that there is a large inventory available to build up the organic molecules found in living entities on the Earth. Of course just the existence of organic material on the early earth is not a sufficient condition for life to originate, but it may be needed. Undoubtedly, much of the organic material from within interstellar clouds is incorporated into the new born central star(s), planets, and remaining other small bodies, if they are formed, like in our own solar system. While the large bodies experience a thorough thermal alteration during their formation history, it is generally accepted that the smaller bodies, like small asteroids and comets maintain much of their original organic inventory largely unaltered, especially comets, which have been found in the outer reaches of the solar system and kept there for aeons.

During the first few 10 to a hundred million years of the forming solar system, many bodies impacted (and formed) the earth, a process, which continued even after the Earth had a solid surface and water had started to precipitate and form bodies of liquid water. Those small bodies of dust, meteorites and comets arriving late, helped the import of organic material into the cooling earth, the same material, which was largely destroyed by the violent, hot conditions during planet formation.

Even with all the organic material delivered, life would not have emerged without other necessary conditions, we can currently not even formulate in their completeness, despite of the immense progress we have made in understanding more and more of the processes in living entities. When turning to space research, one might hope for two pieces of information, (1) to find out which types of organic chemicals have been deposited on the Earth in which form and "packaging" and (2) to narrow down the enormous variety of conditions, which may have existed, while life formed on the Earth.

11.3 Space Missions to Comets

Among the first proposals for a space mission to a comet was a big NASA/ESA mission sending a probe to a rendezvous with comet Tempel-2 and another probe to flyby Halley's comet, the first comet proven to fly on a closed orbit. While NASA had to drop out of the common project, ESA picked up their end and made it her own flyby mission *Giotto* to 540 km sunward of the comet Halley nucleus. Soon after, a decision was reached to redirect two Venus missions of Interkosmos to Halley's comet too, as VEGA 1 and 2. The fly-by speeds were near 70–80 km/s. When it was found that the Venus missions could be retargeted in a way to intercept comet p/Halley, many dust-related instruments were hastily added to the payload. Among them were dust counters and the impact mass spectrometers PUMA, many of the instruments developed in close cooperation with those flown on *Giotto*. Since no dust protection could be added to the space crafts, they had to stay away from the nucleus quite a bit more than *Giotto* did. Some instruments could be flown only on one of the two sister crafts. VEGA 1 was the first to fly by at 10,000 km and at 79 km/s followed by VEGA 2, next was *Giotto* at 540 km on the sunward side of the nucleus. At a considerably larger distance two Japanese spacecrafts flew by Halley's comet. During its flyby *Giotto* was apparently hit by a large dust particle, while all other spacecrafts seem to have survived unharmed. Even before the first results from these missions were presented, NASA had announced her new Comet Rendezvous and Asteroid Flyby mission (CRAF) in 1985. In the development phase it was the sister spacecraft to Cassini of the new Mariner Mark II class. It was fully equipped for its purpose, with all kinds of imagers for all wavelengths from the infrared to the UV, with a whole suite of instruments to analyze the dust and gas released from the comet. Penetrators would be sent to its nucleus to provide the ground truth for the remote sensing instruments. When the cost for the combined CRAF/Cassini program grew out of bound, CRAF was cancelled in 1992 in favor of the Cassini mission, which took advantage of a rare planetary constellation offering a low energy flight trajectory.

In the wake of the CRAF cancellation two developments evolved, which became important for the further *in situ* investigation of comets: NASA created her Discovery program and ESA redefined her Comet Nucleus Sample

Return mission after NASA had dropped out into a comet rendezvous mission, which was named *Rosetta.*

Since many instruments on CRAF had reached enough maturity, numerous proposals were put forward centering on former CRAF investigations. As many individual missions cannot have the same science return as the combined mission, and all together cost more, none of them made it. Instead, three other comet-related, genuine Discovery proposals were successful. It had taken 12 years after *Giotto* for the first, *Stardust*, to be launched. *Stardust* is a dust-focused mission, which attempts to do *in situ* measurements of both, interstellar and cometary dust by means of the dust impact mass spectrometer CIDA and also to return complementary samples back to the Earth for laboratory analysis. A camera and a dust flux monitor are also on board. The second cometary mission selected was CONTOUR, again with a dust mass spectrometer, dust counters and also a gas mass spectrometer. While *Stardust* is aimed at a very detailed analysis, CONTOUR addressed the diversity of comets when visiting three of them with the identical payload (at different flyby speeds, however). (Unfortunately CONTOUR disappeared after orbit injection and was lost on August 15, 2002). The third cometary mission is *Deep Impact.* This mission is focused on the attempt to observe the subsurface material of a cometary nucleus. While all other missions rely on the dust and gas, which are released from the nucleus under the influence of the Sun's heat input, the 10.2 km/s impact of a daughter probe (largely made of copper) will create a crater of estimated depth and diameter of 25 and 100 m, respectively. The process will be observed from the Earth and from the mother spacecraft on its flyby with optical instruments covering the infrared and visible (4.8–0.3 μm) light.

Yet another NASA mission has visited a comet: Deep Space 1. Its prime purpose, however, is to test a long list of new technologies for interplanetary space research, among them the long-term use of an ion engine for propulsion, autonomous navigation, and attitude control.

By far the most complex mission is ESA's "comet chaser" *Rosetta*, launched on March 2, 2004 to Comet 67P/Churyumov-Gerasimenko. It is built around a spacecraft hosting a grand suite of instruments for remote observations of the comet nucleus during the rendezvous (after a 10-year cruise phase), as well as the plasma environment it creates. The payload includes optical instruments from the UV to the IR as well as mass spectrometers for neutral gas ions as well as for solids (dust). A landing device with a complementary set of instruments will be deposited on the nucleus and will take measurements over several weeks. With an instrument on both the orbiter and the lander, one attempts to investigate the interior structure of the nucleus.

11.4 Results and Expectations

We cannot summarize here all of the results (or expectations) of the cometary missions, but want to concentrate on perspectives related to questions relevant for the origin of life, those concern the organic inventory and the structure of the dust as its carrier. For further details and updates the reader is referred to the home pages of these and future missions on the world wide web.

11.4.1 The Measurements at Halley

The missions to Halley's comet returned a wealth of new data. For the first time a comet nucleus was imaged: while the commonly accepted NASA model had been that of a dirty, but bright spherical icy object, the truth was a rather dark irregularly shaped body, which was essentially seen only against a background of illuminated dust.

At flyby speeds of 70–80 km/s, any micron-sized solid body hitting a solid target is totally vaporized, with a fair percentage of its molecules ending up as singly ionized atomic ions (this ionization actually provides the measuring principle for most dust instruments). Analyzing the mass of the ions gave knowledge of the elemental and some isotopic composition of the dust particles. A very minute fraction ($\sim 10^{-3}$) of the ions turned out to be molecular fragments of the organic material of cometary dust. An analysis of Kissel and Krueger (1987) pointed to highly unsaturated N- and O-containing mostly condensed hydrocarbons. The mineral phase was analyzed by Schulze and Kissel (1992). It was, the first ever, direct analysis of cometary dust. From the results, Maas et al. (1989) concluded that the organic and the mineral components must be intimately mixed in grains, which have mass densities of 1 and below. For technical reasons the PUMA 1 instrument on VEGA 1 gave the most detailed mass spectra, while PIA on *Giotto* gave data much closer to the comet. An analysis by Clark et al. (1987) suggests that the gas released by the dust is the extended source for CO, required to explain the findings by the gas mass spectrometer (Eberhardt et al., 1987).

The wide range of the ratio of ions of the rock forming elements (Mg, Si, S, Fe) to those of the organic component (H, C, N, O, S) found for all mass spectra of individual dust particles points to an intimate mixture of those two components. A feature of the PUMA instruments, allowing an estimate of the initial energy of the ions formed, showed that the C, N, O carried a significantly higher such energy, which leads to the conclusion that they must have originated very near the surface of the dust particle. In total the findings are supporting Greenberg's model (cf. Greenberg, 1984) of a dust grain created around a star, modified through many processes in interstellar space until finally incorporated in the gas and dust cloud from which the solar system was made.

A joint analysis of the dust and gas phase ions by Krueger et al. (1991) data showed that the mean molecular mass needed to be 250–350 Da, far higher than generally assumed before the missions.

11.4.2 Current Missions

Stardust (Brownlee et al., 2003) can use its navigation camera for imaging the comet and it will bring back samples to the Earth. Only two dust instruments complete the scientific payload: a dust flux monitor and a dust impact mass spectrometer CIDA. On its long transit to the comet there are opportunities to watch for interstellar dust and indeed CIDA found 10 events in positive and 35 in negative ion mode. The data were difficult to interpret, since again the results were unexpected: no hints to mineral components, but rather mostly large condensed hydrocarbon molecules with additions of oxygen and a little nitrogen. In a recent paper, Krueger et al. (2004) describe their sophisticated analysis to identify a major organic component in the interstellar dust.

It took 18 years until, on February 2, 2004, the spacecraft carrying CIDA flew by comet Wild-2 at a distance of 236 km (only the crippled *Giotto*'s flyby at p/Giacobini-Zinner in 1992 at 200 km was closer) and new dust measurements became available. At a speed of 6.1 km/s, CIDA measured 27 spectra in positive and 2 in negative ion mode. As expected, the spectra of negative ions were more indicative than those of positive ions. Early results indicate that cometary dust is apparently much richer in N than is interstellar dust. The positive ion spectra also differ significantly between the two populations in that cometary dust shows clearly low mass ions, which did not show up in the interstellar dust.

Apart from dust composition, *Stardust* has sent back 72 images of the comet nucleus with the best resolution of 20 m per pixel so far. As the resolution of a comet nucleus has improved from *Giotto* to Deep Space 1 to *Stardust*, more details of the surface of the nucleus became visible. The surface of comet Wild-2 turns out to be heavily structured and exposes a large variety of geological features (Brownlee et al., 2004). The first results were presented at the 2004 Lunar and Planetary science conference and published in a dedicated issue of *Science* (2004). A first, synoptic interpretation of the dust composition data is given in a separate chapter of this book.

CONTOUR would have passed three different comets at different fly-by speeds and with the same suite of instruments would have allowed a good comparison of their properties. It would have addressed the diversity of different comets. CONTOUR was lost, however, and a reflight is not (yet) in place.

11.4.3 Future Missions

Up to now all "information" we have about comets comes from interpretation of remote *in situ* and earth bound measurements. With *Deep Impact* this should change. The mission attempts to simulate a naturally occurring process, the collision with a meteoroid, by letting a dedicated piece of equipment impact on a comet nucleus at a sufficiently high speed such that a large amount of material is excavated and a residual structure is created. The release of the material and the formation of the crater will be observed by the main spacecraft passing by at a distance of about 500 km. It is indeed the first attempt to look beneath the surface of a comet and it is hard to tell what the results will be. Much will depend on the properties of the expected crust, its thickness, and the physical and chemical state of the material underneath it. Since observations will be done at most all wavelengths from IR to visible light, a synoptic view of this unique event will also yield information on the dynamics of the process, the physics, and the chemistry of the materials involved. The days after July 4, 2005, will be exciting for comet researchers.

After 9 more years, *Rosetta* attempts to deliver more refined studies of a comet, which do require a time period of observation longer than what can be achieved in a fly-by. The *Rosetta* landing craft Philae may be the first beneficiary of the *Deep Impact* results. The spacecraft carries several instruments, dedicated to *in situ* cometary research. For cometary dust there are MIDAS, an atomic force microscope to determine the shape and thereby the mineralogy of individual dust grains, and GIADA, a counter for different-size particles, and last but not least COSIMA, a time-of-flight secondary ion mass spectrometer (TOF-SIMS). COSIMA will allow the analysis of individual dust particles collected on targets that were exposed near the comet in a way which is comparable with the impact spectrometers, but with much more detail, of course. Particles can be selected and positive and negative secondary ions analyzed. Sites previously analyzed can be revisited, and ion etching and heating (up to 160°C) can be used to check the stability and variability of the grains chemistry. The ROSINA investigation, using a complement of gas mass spectrometers, will provide high-sensitivity, high-resolution analyses of cometary gases and ions. Optical devices from microwave (MIRO) through IR (VIRTIS), the visible (OSIRIS) to the UV (ALICE) will scan the nucleus and provide maps of exposed material. Other instruments provide data on the Plasma environment, the detailed motion of the spacecraft. In addition, there is a landing device, which will descend to the nucleus surface and perform many autonomous tests on surface samples and even on samples obtained from up to 1 m below the surface. One major instrument, COSAC, is a GCMS-type spectrometer where samples from the comet nucleus will be heated and the released gas will then be passed through columns of different properties, and (or directly) sent to a time-of-flight mass spectrometer. The *Rosetta* Lander measurements will give the first real and detailed data on a real cometary surface, unfortunately not before 2014. The Lander instrument findings will be complemented by the long-term observation of the comet from the orbiter. The accumulation of 1 year of observations of the nucleus activities will be the most direct clue we can get on the workings of a comet. Even though many models for comets are available, we need those detailed measurements to discriminate between those models as well as to make them more detailed; at least for the *Rosetta* target comet.

11.5 Conclusions

Astronomical observations of comets have delivered a huge amount of data and have been used to derive many global parameters of comets, like their albedo, the rotational state of their nuclei, the position of active zones, the release of dust and gas, and dust grain sizes along with some of their components. They have allowed the deduction of physical properties of the nuclei when they break up. As we are still in need of such observations, especially for fresh comets and data around their aphelion, additional space missions to comets are needed. Only the *in situ* measurements provide the basis for the interpretation and modelling of the astronomical observations. Only through such missions can we learn about the geological phenomena of cometary nuclei. The results from these missions have also proven indispensable with respect to the determination of both the chemical composition and the coexistence of low-temperature organic and high-temperature mineral material, the details of which may ultimately give decisive hints for the origin of life on the Earth and eventually elsewhere.

References

Biermann, L. (1951), Kometenschweife und solare Korpuskularstrahlung. *Zs. f. Astrophysik*, **29**, 274–286.

Brownlee, D.E., Tsou P., Anderson J.D., Hanner M.S., Newburn R.L., Sekanina Z., Clark B.C., Hörz F., Zolensky M.E., Kissel J., McDonnell J.A.M., Sandford S.A., and Tuzzolino A.J. (2003), Stardust: Comet an Interstellar Dust Sample Return Mission. *JGR*, **108**, 8111.

Brownlee D.E., Hörz F., Newburn R.L., ZolenskyM., Duxbury T.C., Sandford S., Sekanina Z., Tsou P., Hanner M.S., Clark B.C, Green S.F., and Kissel J. (2004), Surface of Young Jupiter Family Comet 81/PWild 2: View from the Stardust Spacecraft. *Science*, **304**, 1764–1769.

Clark B., Mason L.W., and Kissel J. (1987), Systematics of The 'CHON' And Other Light-Element Particle Populations in Comet Halley. *Astron. Astrophys*, **187**, 779–784.

Eberhardt P., Krankowsky D., Schulte W., Dolder U., Lämmerzahl P, Berthelier J.J., Woweries J., Stubbemann U., Hodges R.R, Hoffman J.H., and Illiano J.M., (1987), The CO and N_2 Abundance in Comet P/Halley. *Astron. Astrophys.*, **187**, 481–484.

Greenberg J.M. (1984), The Structure and Evolution of Interstellar Grains. *Scientific American*, **250**, 124–135.

Kamoun P.G., Campbell D.B., Ostro S.J., Pettengill G.H., and Shapiro I.I. (1982), Comet Encke - Radar detection of Nucleus. *Science*, **216**, 293–295.

Kissel J. and Krueger F.R. (1987), The Organic Component in Dust From Comet Halley as Measured by the PUMA Mass-Spectrometer on Board VEGA 1. *Nature*, **326**, 755–760.

Krueger F.R., Korth A., and Kissel J. (1991), The Organic Matter of Comet Halley as Inferred by Joint Gas Phase and Solid Phase Analyses. *Space Science Reviews*, **56**, 167–175.

Krueger F.R., Werther W., Kissel J., and Schmid E.J. (2004), Quinone derivatives composing 'interstellar' grains due to both polarity ions detected by the 'Cometary and Interstellar Dust Analyser' (CIDA) onboard the spacecraft Stardust. *Rapid Commun. Mass Spectrom.*, **18**, 103–111.

Maas D., Krueger, F.R., and Kissel, J. (1989), Mass and Density of Silicate- and CHON-Type Dust Particles Released by Comet p/Halley. *Asteroids Comets Meteors III*, 389–392.

Miller, S.L. and Urey, H.C. (1959), Organic Compound Synthesis on the Primitive Earth. *Science*, **130**, 245–251.

Schulze H. and Kissel J. (1992), Chemical Heterogeneity and Mineralogy of Halley's Dust. *Meteoritics*, **27**, 286–287.

Sekanina, Z. (1991), Comprehensive Model for the Nucleus of Periodic Comet Tempel 2 and its Activity. *The Astronomical Journal*, **102**, 350–388 .

Whipple F.L. (1950), A comet model, I: The acceleration of comet Enke. *Astr. J.*, **111**, 375.

12

Interstellar and Cometary Dust in Relation to the Origin of Life

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Summary. Cometary grains are commonly considered to be the precursors of organic materials in early life on the Earth. It is a persistent mystery, however, how chemical evolution within the earliest protocells was triggered. We discuss the type of organics measured from Comet p/Wild-2, using the Cometary and Intersellar Dust Analyzer (CIDA). This instrument is not sensitive to mineralic cores of dust particles due to their low-impact velocities (6 km/s). The CIDA data allows us to analyze the organic fraction of interstellar dust at ∼1 AU from the Sun. Surprisingly, it mainly consists of quinone-type polycyclics, some of them similar to pyrrolo–quinoline–quinone. Strong redox catalysts are apparently required to trigger the earliest chemical evolutionary steps. Our understanding of the thermochemical evolution of accretion from interstellar clouds containing cosmic grains to comets qualitatively and quantitatively requires a comprehensive understanding of the production of water and CO from the comets. The "dirty snowball" model is rejected as a suitable model for "fresh" comets. Apparently the primordial source of water is twofold: (1) a significant fraction of cometary clathrates is contained in the mineralic and the organic fractions, producing water by evaporation; (2) rich oxygen containing PAH's in the organic phase produces water by solar radiation-induced chemical processes.

12.1 First *In Situ* Chemical Analysis of Interstellar Dust

Onboard the NASA spacecraft *Stardust* is installed a dust impact time-of-flight mass spectrometer, CIDA (Cometary and Interstellar Dust Analyzer) (for details, see the previous chapter in this volume). Every dust grain impact producing a certain minimum (trigger) yield of ions generates a mass spectrum, either one of positive ions or of negative ones, depending on the voltages applied. Up to spring 2003, about 10 positive and 35 negative mass spectra from interstellar grains have been recorded. These grains apparently belong to a diffuse interstellar cloud the solar system has been traveling through for about 50 My. In those orbital phases when the instrument has the correct attitude to detect interstellar grains (especially avoiding cometary and

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interplanetary ones) the relative velocity between the spacecraft and the grains is about 20 to 30 km/s. Due to the fact that in the first year after launch (February 1999) only positive mass spectra had been recorded, the chemical assignment was very difficult. After excluding some substance classes, for instance minerals, pure PAHs, or carbon, the remaining substance class was still very unprecisely defined as (at least partly) annealed heterocyclic ring backbone structures (Kissel et al., 2001). Due to the very limited information content of positive ion mass spectra in this impact velocity regime, neither N/C nor O/C atom stochiometric ratios can be determined at this time.

12.1.1 Quinone Derivatives as Main Organic Component

In course of the mission so far a lot of interstellar dust impact negative ion mass spectra have been taken. As already inferred from laboratory test measurements by Kissel and Krueger (2001) and comparison with related ion generation methods, negative ion mass spectra of organic compounds, especially polymers, contain much more specific information than positive ion ones do under these ion generation conditions (i.e., impact speed and grain size). Thus it was possible to elucidate better these ion generation rules and chemically assign the principal component of those interstellar grains. This has been treated already widely by Krueger et al. (2004). Thus it seems sufficient here to summarize the results, omitting the mass spectral arguments given in detail there.

The hydrocarbon polymers are very much dominated by oxygen. The mean atomic ratio O/C can be estimated to be 20%. On the other hand, nitrogen seems to play a minor role only. The mean atomic ratio N/C may be estimated to be $3 \pm 1\%$. The mean degree of saturation can roughly be estimated only as medium: H/C ~ 1 seems to be a fair guess. Sulfur does not play a role (except for possible traces).

However, it seems very interesting that oxygen apparently is much more often bound to carbon only rather than to hydrogen. Thus quinone, furane, and ether moieties are more probable than hydroxyl moieties as present in alcohols, phenoles, or hydroquinones. The nitrogen seems to be fully integrated into (e.g., aromatic) carbon structures, such as pyrroles, pyridines, or quinolines. Also nitriles are possible. There is no hint whatsoever for the substantial presence of amino- or imino-groups, i.e., nitrogen is not bound to hydrogen; a remarkable relation to many of the gas phase molecules found in interstellar clouds (see, e.g., Ehrenfreund and Charnley, 2000).

In negative ion mass spectrometry from stable solids, preferably electronegative, subunits of larger molecules and polymers play the major role. This is in sharp contrast to positive ion mass spectrometry from solids with which generally a large number of reaction and decay products result in, mainly nonradical, daughter ions. Thus, negative ions are much more sensitive to the molecular structure in question than positives are, especially within the impact speed domain we deal with here. Another interesting negative ion species is due to a complete stripping of all (but one, sometimes, a few only) hydrogen atoms from a backbone structure, and cleavage after a charge carrier. This gives rise to ion types, the sum formulae being such as $C_n^-.$, C_nH^-, C_nN^-, $C_nO^-.$, C_nOH^-. ($n = 1, 2, 3, 4$). These are found here, too, with the strong prevalence of oxygen-bearing species.

The smallest structurally more or less intact and intense ions from apparently molecular substructures are due to $C_6OH_x^-$ ($x = 0, 1, 2, ...$). An aromatic (like phenole) or a quinoic source is very probable. Moreover, the whole redox-system benzoquinone/ hydroquinone shows up in the spectra. The anions of benzopyrane and benzopyranone (chromone) are also present. Here we have apparently the basic structures for a lot of quinones. However, although there is a lot of evidence for higher quinones (see next section), for flavones indications are poor. A further basic structure may be $C_{14}H_6O_3$, benzo-naphthalin-(ortho)-quinone with furan ring closure (Fig. 12.1).

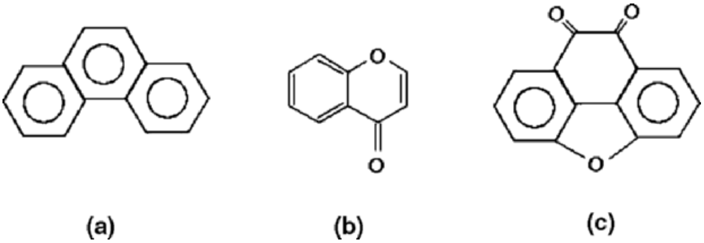

Fig. 12.1. (a) An example of phenanthrene. Due to its low polarity, it cannot be directly measured by CIDA. However, pure PAH's are very probable in interstellar grains by indirect conclusions. (b) The first oxygen, containing species of a series of larger homologues, directly found. (c) A very probable (sub)-structure found in interstellar dust.

As mentioned above, a probability (although small) is given that N-heterocyclic compounds may play an additional role. Just removing some CH-moieties in rings, and with some reorder, we end up with the basic structure of pyrrolo–quinoline–quinone. There is some evidence for carboxylic groups, too. Thus, the famous “PQQ” (see Sect. 12.3.5, and Duine (1999)) and relatives thereof could easily have been built up in diffuse interstellar dust as such, or by further hydrolysis in liquid water.

As pure PAHs have not been found, but, in contrary, strong evidence for quinoic (nonaromatic, nonaliphatic) ring structures and some hetero-aromates was found, we like to call this stuff “dirty PAHs” (O and N being the “dirt” in the overwhelming majority of C backbone atoms in the molecules).

12.1.2 Hydrated "Dirty" PAHs as Products of Radiative Chemistry in Nebulae

Bernstein et al. (1999) found very similar products in the laboratory when strongly irradiating PAH – water mixture ices: Hydrated PAHs as preferably quinones, ethers (also forming furane like ring structures), and (some) alcohols. In interstellar clouds PAH and water was found. First reactions, however, must have happened at polar grains, the simplest readily to be formed being LiH. The light chemical elements of exploded stars are H, C, O, (He?), Li (in that abundance order), however, C and O always come with some N, although in minor abundance. Thus an additional "dirtification" with some N is probable.

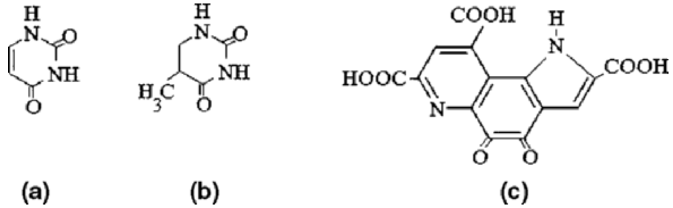

Fig. 12.2. (a) Uracile; primordially probable (sub)-structure with the quinoic property of pyrimidine. (b) Thymine; primordially UNprobable due to its methyl group. Probably developed on the Earth from precursors like uracile. (c) PQQ – pyrroloquinolinequinone with three carboxy substitutes. The formic acid residue is found by CIDA in interstellar dust. PQQ-similar molecules are most important catalysts, as they can act as electron donors and acceptors in (at least) three oxidation states.

Furthermore, we have to point out that over the entire time of production and journey to other stars, the grains take up a lot of radiation dose (some 100 Mrad is an order of magnitude estimate). Thus it is obvious that not only the end-product polymers have to be very stable against radiation; moreover, it is radiative, i.e., epithermal, chemistry that builds up these products at first. Especially these quinoic annealed substances can stabilize free electrons very well (see Sect. 12.3.5). Thus they are the best candidates for organic interstellar dust to enter into our solar system. By the way, there are certainly also a lot of mineral grains in cosmic dust. However, Landgraf et al. (1999) have shown that those microsized particles cannot enter the interior of our solar system for electromagnetic–optical reasons. Thus it is no surprise that we did not detect them.

It seems to be an open question whether in some distances from the active Sun's proton irradiation (not being too energetic) may play a role in reducing the organic matter by proton capture. In this case quinoic systems could be reduced to aromatic (quinol) systems. There is a hint for *o*-hydroquinone there with the 218-nm UV bump. Later irradiation, in contrary, has an oxidizing effect by dehydrogenation via free radicals. Further polymerization stabilizes its chemical structure against decay and vaporization.

12.1.3 Possible Thermochemical Implications for the Accretion Process to Comets

The diffuse interstellar clouds are certainly quite different from dense interstellar clouds from which accretion disks toward proto-planetary systems are formed. Nevertheless, once stochiometric ratios of the basic elements are given in the order of magnitude we find them in our solar system, the organic grain chemistry of the pristine material cannot be much different, just due to the radiation chemistry as treated above.

As a consequence, interstellar grains with mineral cores and organic mantles, similar to the Greenberg (1984) ones, can be baked together to comets. Far away from the central sun, respectively, they stay at very low temperatures for some Gy, but accumulate further cosmic radiation, at least near their surfaces. If, by chance, those (due to radiation dose) metastable organic matter in the solid state will become warmed up by being injected into the interior of that solar system for the first time, then due to the exothermal reactions triggered, this quinoic matter will lose much of its excessive oxygen just as water (H_2O), and, by further decomposition, also as CO. At least two different processes can be responsible for this thermal effect to this early comet solid matter:

- By collisions of comets or pieces thereof in the cometary clouds or belts, thus converting kinetic into thermal energy;
- By being injected into the interior of that solar system for the first time, thus warmed up by the sun.

The specific internal energy of the (due to accumulated radiation, but frozen) metastable molecules certainly is sufficient to vaporize H_2O immediately (kinetically fast) as jets, lifting adjacent matter with them. The elimination of CO typically is a slower process, giving rise to extended, i.e. time-delayed, sources as frequently found in cometary comae. However, in contrast to that order of the kinetic time scales forming H_2O and CO, the vaporization of H_2O needs much more specific energy than that of CO; thus, the vaporization timescales are in reverse order. Moreover, even at elevated temperatures, H_2O freezing to water ice is a process being competitive to vaporization, and is most probable at lower temperatures.

Thus we do think a comet to contain only minor quantities of water ice *before* its first inner perihelion, as only collision processes can have produced it. However, *after* its first and, if periodic, its further perihelions much of the water formed will freeze to ice. Consequently, a “fresh” comet should differ very much from those “aged” by several near-sun perihelions. Astronomical observations of the activity of fresh comets seem to point into that direction.

It should be noted that the elimination of water from relevant sites (hydroquinones and alcohols) is a process relevant even at rather low temperatures, radiative activation energy provided. In contrary, elimination of CO is not, because it is maintained by destructing the molecular backbone structure. Thus CO is readily formed by thermal and radiative processes at grain surfaces as found in comae, also as extended sources.

By a quantitative stochiometric treatment of these hydrated polycyclic material, we can estimate that finally, i.e., after the processes discussed above, about 20% *per weight* of the total cometary *organic* matter is transformed to water ice and vapor. There may be inorganic (mineral) sources of water as found, e.g., in clathrates; however, inorganic chemistry is not discussed here. In this context it should be mentioned that hydroquinones easily form clathrates.

When losing much of oxygen *and* hydrogen by the elimination of water, it is just obvious that the organic cometary polymers remaining in the solid phase become more unsaturated and its relative nitrogen content is enlarged. Thus a rich nitrogen organic chemistry in cometary grains is a trivial consequence, as already found with p/Halley by Kissel and Krueger (1987). Nitriles and polymers of HCN are thus no surprise any more in cometary matter. Adenine is just one of the many pentamers of HCN. Aromatic rings containing two nitrogen atoms, like pyrimidine are formed with a fair probability in comets, too.

12.2 New *In Situ* Analysis of Cometary Dust at p/Wild-2

With the retrograde Comet p/Halley, the relative velocities to the spacecraft during encounter were very high (69 km/s with *Giotto*, and 78 km/s with VEGA). Thus dust impact mass spectrometry was not specific for the detection of molecules, only for atoms. Thus the elemental compositions could be determined very well, whereas the molecular information was poor at that time.

With the passage of the spacecraft *Stardust* near the prograde comet p/Wild-2 on January 2, 2004, molecular information was gained. In the case, due to the very low relative velocity of 6 km/s, only the outermost organic layers of the dust grains can be ionized during the impact. The instrument CIDA took impact mass spectra of cometary grains during this passage. For yet unknown reasons the number of well evaluable mass spectra from the about 30 impact events gained was extremely low (10 positive and 2 negative ion mass spectra). Nevertheless, some interesting results were found.

12.2.1 Corroboration of the Cometary Dust Prevalence of Nitrogen Chemistry

The two *cometary* negative ion mass spectra together were quite similar. Both were totally dissimilar to all the negative ion impact mass spectra we got from *interstellar* dust, as expected from a functioning instrument.

The dominant ion in both cometary negative spectra was CN^-. (e^- and H^- are trivially abundant.) This means that again nitrogen organic chemistry is prevalent. Also in sharp contrast to interstellar particles, the O^-. and the OH^- ion were of comparably little abundance. The meaning of this result is twofold. First, oxygen-organic chemistry plays a minor role in these particles. For instance, polyoxymethylene (POM) cannot be a major compound. Second, as such, and due to the fact that no water-solvated ions [namely $(H_2O)_n{\cdot}OH^-$, or $(H_2O)_n{\cdot}H^+$, with $n = 0, 1, 2$] were found at all, the grains cannot contain water ice as a major constituent.

At least in one of the negative spectra, a hint to the presence of some sulfur organic chemistry is given by the two isotope (although broadened) lines of SH^- (m/z = 33 and 35). Chlorine ions (m/z = 35 and 37) are within the target contamination limits. It is interesting to note that the cometary organic sulfur abundance is far above contamination level in this case – in contrast to interstellar grain chemistry, with which sulfur is within contamination level. Perhaps during the long-lasting and intimate coexistence of mineral cores and organic mantles in comets, some sulfur could be driven from minerals like troilite to the organic phase by radiative epithermal processes. Further more, S can act very much like O, forming similar products as CS or CS_2, as found in the coma gas phase. With solid phase mass spectrometry as with CIDA, the sulfur-organic analysis of molecules is difficult if S is found to be present, because S can be intermixed with 2O (e.g., thiophenol is isobaric to hydroquinone). Thus it is just good luck that S does not play a role at all in interstellar, and a minor role only in cometary organics.

12.2.2 Precursors of Amino Acids, Sugars, and Some Other Building Blocks in Cosmic Dust

As mentioned above (and already with p/Halley), the prevalent nitrogen chemistry lacks the company with oxygen in the same molecular structure. So it seems to be very important to note that no amino acids were found, although at least glycine and alanine would have been within the scope of the mass spectra. In contrary, together with the strong nitrile ion yield, there is an indication for the presence of aminonitrile. In liquid water this compound can be hydrolized to glycine. However, at cometary surfaces the pressure is too low to maintain the liquid state of water.

With interstellar dust-rich negative ion mass spectra were found, however, the class of amino acids could definitely be excluded to be present there, too. When comparing with laboratory simulations, for instance of Muñoz Caro et al. (2002), free amino acids were not found either. In this case, amino acids were produced from the irradiated ice analogues by strong hydrolysis, i.e., by boiling in $6n$-HCl. These conditions are related neither to interstellar nor to cometary chemistry in space. Only a few abiotic amino acids were found in a similar laboratory investigation by Bernstein et al. (2002).

When it comes to sugars, one should remember that these are structurally isomers of polyoxymethylene ("POM"). If present it would thus be difficult to discriminate them by impact mass spectrometry. However, as already mentioned, at least their abundance is low (if at all present). As a precursor of sugars polyines may well be present. Nevertheless, it has to be pointed out that homogeneous hydrolyzation to sugars is a very improbable process. Catalyzed heterogeneous processes at, e.g., mineral surfaces – may it be those of cometary dust grains itself, may it be Earth-borne particles – in a liquid aqueous site may, however, be possible.

The most important salt anions for origin of life are phosphates; also sulphates may have played an early role. As already found by Schulze and Kissel (1992) with Comet p/Halley's dust, there is no stoechiometric relationship between sulfur and oxygen or between phosphorous and oxygen. On the contrary, one is forced to the assumption that these elements are present in cometary dust mainly as sulphides and phosphides. This is again an indication that the cometary solid matter yet analyzed never had come into contact with liquid water. Especially phosphides would easily react with liquid water to phosphates, a main building block of life. (Some sulphides react under acidic conditions with liquid water.)

Pyrimidines and purines are very likely to be present in cometary and interstellar dust. This proposition is made not only due to direct experimental evidence, but even more due to homology arguments for most of the nucleobases regarding their radiation stability and processing of interstellar dust, i.e., in comets. In particular:

Adenine is the by far most important nucleobase, a derivative of purine (see the universality of cAMP, ADP, and ATP, the former as a messenger, the latter as an energy carrier). As being a pentamer (6-aminopurine) of the hydrocyanic acid, the latter being shown to be present in comets as early as 1910, its polymerization property under cometary thermochemical conditions is well known. Guanine (2-amino-6-oxopurine) seems to "remember" still interstellar matter due to its oxo-group. However, it cannot be excluded that it is produced later on the Earth.

Uracile (2,4-dioxopyrimidine) is the most interesting pyrimidine nucleobase, due to its quinoic structure. It may well be a pristine interstellar compound, as it is homologuous with some interstellar matter found by CIDA on board *Stardust*. This looks compatible with the fact that uridine is found in early RNA. Its methylated form, thymine, i.e., 5-methyl-2,4-dioxopyridine is a phyletically later form; thymidine is preferably found in DNA. Thus, uracile seems to "remember" the interstellar solid phase chemistry best of all nucleobases.

Cytosine (2-oxo-4-aminopyrimidine), being the most important pyrimidine nucleobase, somewhat resembles the guanine: Both are oxo-derivatives of the amino-NUC (NUC= pyrimidine, or purine). However, only aminopurine (adenine) is found in early nature (see above), whereas aminopyrimidine is not. As aminopyrimidine ($C_4N_3H_5$) lacks oxygen its direct origin from interstellar solid matter is improbable. On the other hand, it is not a polymer of hydrocyanic acid; thus, a cometary origin is not very probable as well.

Summarizing the nucleobases, it seems now very probable that the pristine ones are directly related to cosmic dust. Those related to interstellar dust, esp. uracile, show tautomery: The lactame (quinoic) form is tautomer to the lactime (quinol) form. We (see Krueger and Kissel, 2004) have postulated a similar tautomery between quinoic and aromatic moieties (see above) in the interstellar dust, as analyzed *in situ* by CIDA. However, we have to point out that there is a major difference between the uracile derivatives and the PQQ derivatives (discussed later on): The two oxo-moieties are in meta-position in the former case (at a single ring), whereas they are in ortho-position in the latter case (at an annealed structure with which no other possibility is given).

Sulfur seems to be implemented into nucleobases at a later phyletic stage. Thio-uridine is found in some t-RNA for apparently special functions. Although we found a hint for some sulfur-organic chemistry in cometary dust, it seems that it had not played role in space-borne prebiotics.

Let us make a general last statement with this chapter: The often-discussed assumption of “panspermia,” i.e., the origin of life directly from space, is not supported – at least with all the interstellar and cometary matter we have analyzed. Namely, it is obvious that most of the indispensable molecular building blocks of life on the Earth are definitely absent in that matter.

12.3 Combined Scenario of Origin of Life with Both Dust Types

12.3.1 Hydrolysis Mechanisms of Cometary Dust in Water

Based on our present knowledge about cometary dust the main building blocks of life are present there as chemical precursors. Only some nucleobases are most likely to be present as such already there. Combining evidence as found by *in situ* measurements at p/Halley (Kissel and Krueger, 1987) and p/Wild-2 (Kissel, Krueger, Silen, Clark, 2004) with spectroscopic investigations and laboratory simulations, mainly by Greenberg (1984), liquid water is needed to finally form the other building blocks from the precursors.

Free amino acids have never (with a few exceptions like 1-methyl-glycine) been found in cosmic dust at all. However, they are frequently found in meteoritic material on the Earth. It seems very probable that they are formed during and after atmospheric entry, as temperature and pressure within the meteorites at that time are at least sufficient to have liquid water and/or other polar and protic liquids therein. Under these circumstances hydrolysis is a probable process, the necessary reaction substrates provided. Amino acids can then be formed from amino nitriles, for instance. Moreover, they can be formed by inverse polycondensation, i.e., cracking of polymers by water addition, at least at low pH.

As already pointed out above, many of the main building blocks of life may be formed from cometary matter by hydrolysis. In these cases the mineral cores of the cometary subgrains may have played an important role: Various phosphates may have been produced from the mineral bulk phosphides. Sugars may have been produced by heterocatalytic hydrolysis at the mineral surfaces. Fatty acids are apparently produced (probably from nitriles); they are then ready to form micelles, as found by dispersion of powdered micro-meteorites (Maurette, personal communication, 1993).

12.3.2 Some Necessary Conditions for Systemic Chemical Self-Organization

The mere presence of the building blocks (at any celestial body as well as on the Earth) as known to be essential of today's life, even those of the earliest remnants of life we are aware of, is neither a necessary nor a sufficient condition for the origin of life.

In addition, Eschenmoser et al. (2000) have shown experimentally that nucleic acids can work by other chemistry than today: RNA can be formed with different nucleobases, even with hexoses instead of the pentose ribose, with pyrophosphates; it may translate into different amino acids. However, the effectivity (in a Darwinian sense: the "fitness", as defined by Eigen and Schuster (1971)) of the processes above is generally lower. Thus it is very probable that evolution on the Earth started on a purely chemical stage with different, though similar, building blocks.

Even more important, it is by far not sufficient, as especially Nicolis and Prigogine (1977) have pointed out. At least we will give here some important necessary conditions beyond pure chemistry. Nevertheless, it is unsure whether the set of all necessary conditions being mentioned together is a sufficient condition. It is important only that "conditiones sine qua non" are discussed here in the view how comets and other celestial objects could have provided those.

As further necessary conditions, we may state as follows.

1. Life is systemic. Thus just chemicals do not constitute life, but a physical system, like a proto-cell, is subject of evolution. Cometary grains are preformed systems that in liquid water do have the necessary in/out property due to the large dielectric constant of water (environment) and the low one inside. Thus polar substances are eager to form a dipole layer as a hull. These substances need not be fatty acids from the beginning; from the view of cosmic dust chemistry porphyrine-like structures were more probable.

2. Life is dissipative, or biologically speaking, metabolic. Thus, for self-organization free energy flow must be provided from the beginning onward. At an already-organized state this would not cause a problem, the energy provided either by chemical energy (nutrients) or by solar photons. However, if there were, by chance, all necessary chemicals already present, life could not start, because this would establish near thermodynamic equilibrium. Thus precursors that react exothermally to building blocks can give the initial energetic kick into this nonequilibrium stage.
3. Life is self-organization, thus chemical reactions must be in part highly nonlinear (third order in concentrations). The only way to establish this chemically is chirality with enantiomeric asymmetry. Enantiomeric excess needs not to be provided from the cosmic beginnings, but it can be evolved by a non-Darwinian process on the Earth (*tout-ou-rien*-process) due to Eigen and Winkler (1975). The "wrong" enantiomers can then be recycled by UV-racemisation (Krueger and Kissel, 2001).
4. Life can be established only by a special *diffusivity* of the chemicals involved. This can be seen by a careful inspection of the relevant reaction-diffusion equations (Nicolis and Prigogine, 1977; Krueger and Kissel, 1989, 2001). Catalysts must be nondiffusive; cometary grains as starters form a cage to provide this property (Greenberg and Krueger, 1996). By contrast, substrates and products must be diffusive, i.e., small molecules easily solvable in water.
5. The system size, or the diameter of the hull mentioned in (1), must be within certain limits, very much dependent, i.e., on the actual diffusion constants mentioned in (4); for proto-cells with simple chemical assumptions sizes about 3 μm come out to be optimal.

There are some more special necessary conditions. As these are beyond the scope here, we refer to the literature cited above.

12.3.3 The Question of Redox Catalysis Needed

With hydrolysis protons are transferred from one to another molecule. Due to Brönsted, the molecule ready to accept a proton is called a "base," and one to donate a proton is called an "acid." (We do not deal here with the Lewis acid-base concept). With proton exchange an energy transfer is takes place in any case.

However, electrons play a major role in anabolism as well as in katabolism. The abstraction of an electron is called "oxidation," its acception is called "reduction" of the molecule. Many important organic reactions, esp. polymerization processes like in RNA or peptide anabolism, are triggered by electrons, called "radicals." These processes in toto are thus called "redox"-processes: A catalyst may provide a free electron, the reaction starts, and at its end the electron is accepted again from the catalyst. The FeII/FeIII redox-system is one which is frequently used in technology and nature. Also other transition elements may act as such. It may act in homogeneous solutions; however, much more important in nature (in technology the Pt or Pd exhaust catalysers) is heterogeneous catalysis at phase boundaries (for instance, at clay surfaces) or at localised sites (e.g., the heme site with hemoglobin).

With cometary dust it seems clear since the work of Greenberg (1984), and was corroborated by our PUMA measurements (Kissel et al., 1986) that mineral nano-grains carrying a lot of Fe and Ni coated by organic matter and ices, constitute the cometary grains. The mineral surface-specific area of cometary matter may be as large as about 300 m^2/g. Thus, whence these grains are dispersed in liquid water, e.g., in the seas on Earth redox catalysis is easily available (Krueger and Kissel, 1989). One comet entering the atmosphere, after its explosion, may still seed about 10^{27} microsized intact grains, with the above necessary thermochemical conditions. Thus Greenberg (1996) asked: are 10^{27} particles, fulfilling the necessary conditions, enough (i.e. also sufficient, statistically) to start prebiotic evolution?

12.3.4 Possibilities and Limitations of Heterocatalysis by Mineral Surfaces

Mineral surfaces are often discussed as sites for self-organization toward life, even if the origin is thought to be purely terrestrial. The reason is twofold: First, several chemical reactions necessary do not work in homogeneous solutions, and however, do at such surfaces, e.g. at clays, or even at borax (sugar synthesis). Second, several catalysts are necessary, many of them being prebiotically present at mineral surfaces. The main type are redox-catalysts already necessary for primordial nucleotide synthesis. The mineral cores of cometary grains provide a lot of iron; thus, FeII/III-sites may act as electron acceptors and donors as well. In yet evolved life NAD^+ vs. NADH plays such a role, but these redox partners are (Nicotine-Amide-) Di-nucleotides that at the very beginning must have originated by the help of catalysis.

Also other catalytic processes were needed, e.g., the preference of the glycoside $3'$-$5'$- bonding vs. $2'$-$5'$ or even others. Zinc, present in cometary grains, may have been a surface catalyst in this case. Mercury (which has not been found in cometary matter) provides a different glycoside bonding.

Nevertheless, it is obvious that the first cells which remnants are found paleontologically did *not* carry mineral grains with them. Thus it seems probable that mineral catalysis had played an important role for prebiotic *chemical* evolution of reduplicating molecules and systemic compartimentation.

Another, yet unsolved, problem is the directed synthesis of several amino acids, and the bonding to peptides. Although some primitive amino acids could have originated from cometary dust by hydrolysis, several steps of synthesis cannot be performed in the directed manner by mineral surfaces, but obviously need organic enzymes. But what was the primordial origin of the enzymes?

12.3.5 Interstellar Dust and the "PQQ-Enigma" for Catalysis

Looking more carefully into the chemical structure of primordial coenzymes there is an astonishing "diversity in unity" (Duine, 1999). A huge "diversity" of, mostly nucleophilic, reactions very important for peptide as well as for RNA synthesis, already on an early bacterial level, are catalyzed by substances of astonishing "unity" in chemical structure, namely of quinoic type. For instance, flavines related to flavones are quinoic, riboflavine and a lot of quinoproteins and even quinohemoproteins (relation to early Fe?) seem to be very primordial.

The most interesting compound is pyrrolo–quinoline–quinone (PQQ) with which three different stable redox states are relevant: (1) the oxidised quinone state, PQQ, of that cofactor; (2) the free radical(!), intermediate semi-quinone, PQQH, state; (3) the reduced quinol (hydroquinone), $PQQH_2$, state being already completely aromatic. The high reactivity of PQQ with nucleophilic compounds (Oubrie, 2003) leads to adduct formation and later reactions with, e.g., water, cyanide, ammonia, hydrazines, alcohols, aldehydes, and ketones. Most of these compounds are found in cometary matter itself. Thus the presence of PQQ-related substances provided, synthesis of many prebiotics could even have been performed on the Earth with cometary matter in liquid water.

In this context, let us cite Duine (1999), p. 235: "... has this diversity (of functions) any physiological meaning or is it just due to evolutionary at random generation of catalysts which apparently have survived selection processes based on optimal functioning? It reflects our lack of knowledge on the details of catalysis..." This is the PQQ-enigma.

Let us try an answer just being, although well-founded by cosmochemical evidence, a speculation: At least two fundamental types of biotic chemicals obviously "remember" the organic phase of interstellar dust, namely, the primordial nucleobases and the quinoic, in part heterocyclic, poly-aromates, the most important of which being the PQQ-related cofactors. Similar, perhaps even more efficient, redox-behavior is known from other molecular types, too. Thus we postulate here that this "unity" in substance class as such is not a result of evolution on the Earth, but an early remembrance to the radiative most stable end products of interstellar dust chemistry. The high radiative stability makes even atmospheric entry (collisions with the upper atmosphere molecules, esp. H_2) possible without destruction. Thus these substances may also have seeded the early Earth and made the relevant catalysis possible. Nevertheless, it is obvious that further evolution had taken place within that class of substances during phylogenesis of two stems of life, as chemotaxonomy shows. Just archeae generally refrain from using PQQ cofactors primordially. Did the stem of archeae use sulfur-chemistry (from volcanic sources?) for catalysis, instead?

12.4 Conclusions and Further Goals

The chemical analysis of the organic phase main substance class of grains from a diffuse interstellar cloud sheds a new light on to cometary matter with respect to the origin of life. Comets are believed to be formed by accretion from dense interstellar clouds. Certainly, due to radiative processes with and entry of comets into the inner solar system, many chemical transformations had taken place. Thus it is a possibility to be discussed that cooperative processes of cometary and pristine interstellar matter may have started chemical, and finally biological, evolution on the Earth.

As a further goal, such processes should be investigated and simulated by laboratory measurements. The radiative formation of the quinone/quinol substances from PAHs, water (plus some nitrogen, e.g., as ammonia) is empirically well established. In a further step its catalytic properties with substrates believed to be present in cometary grains should be widely investigated.

References

Bernstein, M.P., Sandford, S.A., Allamandola, L.J., Gillette, J.S., Clemett, S.J., and Zare, R.N. (1999), UV irradiation of polycyclic aromatic hydrocarbons in ices: Production of alcohols, quinones, and ethers. *Science* **283**, 1135–1138.

Bernstein, M.P., Dworkin, J.P., Sandford, S.A., Cooper, G.W., and Allamandola, L.J. (2002), Racemic amino acids from the ultraviolet photolysis of interstellar ice analogues. *Nature* **416**, 401–403.

Duine, J.A. (1999), Review: The PQQ story. *Journal of Bioscience and Bioengineering*, **88**, No.3, 231–236.

Ehrenfreund, P. and Charnley, S.B. (2000), Organic molecules in the interstellar medium, comets and meteorites: A voyage from dark clouds to the early Earth. *Annual Review of Astronomy and Astrophysics*, **38**, 427–483.

Eigen, M. and Schuster, P. (1977/8), The Hypercycle. *Naturwissenschaften Part A:* **65**, 541–565; B: **66**, 7–41; C: **66**, 341–369.

Eigen, M. and Winkler, R. (1975), Das Spiel (The game). Piper, München.

Eschenmosher, A. and Krishnamurthy, R. (2000), Chemical etiology of nucleic acid structure. *Pure & Appl. Chem.*, **72**, No. 3, 343–345.

Greenberg, J.M. (1984), The structure and evolution of interstellar grains. *Scientific American*, **250**, 124–135.

Greenberg, J.M. and Krueger, F.R. (1996), Are 10^{27} enough? Evolution of life from cometary grains. *ISSOL Triannual Meeting*, Orleans/France

Kissel, J., Sagdeev, R.Z., Bertaux, J.L., Angorov, V.N., Audouze, J., Blamont, J.E., Büchler, K.V., von Hoerner, H., Inogamov, N.A., Khromov, V.N., Knabe, W., Krueger, F.R., Langevin, Y., Levasseur-Regourd, A.C., Managadze, G.G., Podkolzin, S.N., Shapiro, V.D., Tabaldyev, S.R., and Zubkov, B.V. (1986), Encounters with comet Halley – The first results. *Nature* **321**, 280–282.

Kissel, J. and Krueger, F.R. (1987), The organic component in dust from comet Halley as measured by the PUMA mass spectrometer on board VEGA-1. *Nature*, **326**, 755–760.

Kissel, J., Krueger, F.R., Silen, J., and Haerendel, G. (2001), On the substance class of interstellar grains as determined by CIDA onboard STARDUST. *Towards New Frontiers. Proc. of the COSPAR Int. Conference*, Warszaw (2000).

Kissel, J., Krueger, F.R. (2001), Time-of-flight mass spectrometric analysis of ion formation in hypervelocity impact of organic polymer microspheres: comparison with secondary ion mass spectrometry, ^{252}Cf mass spectrometry and laser mass spectrometry. *Rapid Communications in Mass Spectrometry*, **15**, 1713–1718.

Krueger, F.R., and Kissel, J. (2004), The Cometary and Interstellar Dust Analyzer at Comet 81P/Wild-2. *Science* (special edition), **304**, 1774–1776.

Krueger, F.R. and Kissel, J. (1989), Biogenesis by cometary grains – Thermodynamic aspects of self-organization. *Origins of Life and Evolution of the Biosphere*, **19**, 87–93.

Krueger, F.R. and Kissel, J. (2001), Chemical thermodynamics of systemic self-organization towards life by Nano-structured cosmic dust particles. *Proc. 1st Europ. Workshop Exo-/Astro-biology*, Frascati/Italy; ESA-SP, **496**, 43–48.

Krueger, F.R., Werther, W., Kissel, J., and Schmid, E.R. (2004), Assignment of quinone derivatives as the main compound class composing 'interstellar' grains based on both polarity ions detected by the Cometary and Interstellar Dust Analyser (CIDA) onboard the spacecraft STARDUST. *Rapid Communications in Mass Spectrometry*, **18**, 103–111.

Maurette, M. (1993), private communication.

Muñoz Caro, G.M., Meierhenrich, U.J., Schutte, W.A., Barbier, B., Arcones Segovia, H., Rosenbauer, H., Thiemann, W.H.-P., Brack, A., Greenberg, J.M. (2002), Amino acids from ultraviolet irradiation of ice analogues. *Nature*, **416**, 403–406.

Nicolis, G. and Prigogine, I. (1977), Self-Organization in Nonequilibrium Systems. Wiley-Interscience Publ.

Oubrie, A. (2003), Structure and mechanism of soluble glucose dehydrogenase and other PQQ-dependent enzymes. *Biochimica et Biophysica Acta*, **1647**, 143–151.

Schulze, H. and Kissel, J. (1992), Chemical heterogeneity and mineralogy of Halley's dust. *Meteoritics*, **27**, 286–287.

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