- Burton RS (1983). Protein polymorphisms and genetic differentiation of marine invertebrate populations. *Marine Biology Letters* 4: 193–206.
- Hedgecock D (1994) Does variance in reproductive success limit effective population sizes of marine organisms? In: Beaumont AR (ed.) *Genetics and Evolution of Aquatic Organisms*, pp. 122–134. London: Chapman and Hall.
- Hedgecock D, Tracey ML and Nelson K (1982). Genetics. In: Abele LG (ed.) *Biology of the Crustacea* pp 284–403. New York: Academic Press.
- Hedrick PW (2000). *Genetics of Populations*, 2nd edn. Sudbury, MA: Jones and Bartlett.

- Knowlton N (1993). Sibling species in the sea. Annual Review of Ecology and Systematics 24: 189–216.
- Nelson K and Hedgecock D (1980). Enzyme polymorphism and adaptive strategy in the decapod crustacea. *The American Naturalist* 116: 238–280.
- Utter F and Ryman N (1993) Genetic markers and mixed stock fisheries. *Fisheries* 18: 11–21.
- Whitlock MC and McCauley DE (1999). Indirect measures of gene flow and migration: $F_{ST} \neq 1/(4Nm + 1)$. Heredity 82: 117–125.

PORE WATER CHEMISTRY

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Introduction

As marine sediments are deposited, they trap sea water in the pore space between grains. This pore water (sometimes called interstitial water) may represent more than 90% of the volume of the bulk sediment in fine-grained deposits near the sediment-water interface. The volume fraction of the bulk sediment that is water is called the porosity. Porosity usually decreases rapidly with increasing depth through the uppermost sediments, with the profile depending on lithology and accumulation rate. Ultimately, porosity may decrease to only 5-20% as the sediment becomes lithified. As sediments are compacted during burial, the pore fluid is squeezed upward, traveling through fractures, burrows, or perhaps the sediment pore space itself.

As sediment is buried, its composition may be modified by chemical reactions, a process called chemical diagenesis. Pore water provides a medium that permits a solute to migrate from a site where it is produced to another site where it may be removed. For example, in organic-rich sediments, pyrite (FeS₂) is a common end product of diagenesis. While the intermediate steps in pyrite formation are not fully understood, they involve sulfate reduction to sulfide at sites where reactive organic matter is found, and reduction of insoluble ferric oxides to form soluble ferrous iron at sites of iron-bearing minerals. Iron sulfides have very low solubility, and their deposition is usually localized at one of the two sites. If sulfide is released faster than ferrous iron, the sulfide diffuses from its site of production on an organic-rich particle to the mineral containing iron, where it forms insoluble iron sulfides. This can produce pyrite overgrowths on iron-bearing minerals. Alternatively, if the iron is more readily released, it diffuses to form iron sulfides near the sites of organic particles such as shells or localized pockets of organic substrate.

Because diagenesis may alter only a small fraction of the solid phases, its impact may be difficult to detect from studies of solid phases alone. Pore water chemistry is much more sensitive to such changes. For example, in a sediment of 80% porosity, dissolution of 0.1 weight percent CaCO₃ from the solid phase (near the detection limit measurable in solid phases) would make a change of 6 mmol kg^{-1} in the concentration of dissolved calcium. This change in pore water would be easily detectable because it results in a concentration 60% greater than that in the starting sea water. Of course, this calculation assumes that the pore water acts as a closed system, which is generally not the case as noted below. However, this example illustrates that pore water chemistry is more sensitive than solid phase chemistry to diagenesis.

Studies of pore waters have become a standard tool for understanding the biogeochemical processes that influence sediments, and considerable efforts have been invested during the past several decades to develop techniques to collect samples, evaluate whether vertical profiles exhibit artifacts introduced during collection and handling, and develop approaches to model the observed profiles and obtain quantitative estimates of reaction kinetics and stoichiometry. Usually, modeling approaches assume steady-state behavior, but when timedependent constraints can be established, nonsteady-state approaches can be applied.

Reasons to Study Pore Water Composition

The study of pore waters can reveal many processes that are important in regulating the biogeochemical cycles of the ocean and in evaluating the impact of diagenesis on the sedimentary record recorded in solid phases. Some applications of pore water studies are given below.

Calculation of Mineral Stability

Thermodynamic calculations can be carried out to determine which solid phases should be dissolving, precipitating, or in equilibrium with the pore fluid chemistry. While these calculations do not guarantee the presence of minerals that are at or above saturation, or the absence of minerals that are undersaturated, they are a very useful indicator of whether it may be worthwhile to search for minerals that could be present in only trace abundance.

Identification of Sites of Reaction and Reaction Stoichiometry

Maxima in pore water profiles indicate localized inputs, and minima define sinks for solutes. However, defining the transition between source and sink regions requires location of inflection points in the pore water profile. If the pore water profile is in steady-state, material balance calculations can be carried out for solutes if the transport mechanisms are known. This usually involves fitting a reactiontransport model that defines the depth dependence of the net reaction-kinetics. Transport processes are discussed below, and may include molecular diffusion, advection, and macrofaunal irrigation. The impact of reactions occurring at depths beyond the range of sampling may also be evident in pore water profiles.

Interpretation of the Sedimentary Record

Are changes in solid phase profiles with depth due to diagenetic reactions during burial, or due to temporal variations in the composition or rain rate of solid phase inputs? Pore water profiles provide a way to evaluate the contemporary rates of reactions (assuming they are in steady-state) and predict the effect of diagenetic reactions on solid phase profiles. Solid phase changes that exceed the diagenetic effects derived from modeling pore water profiles must reflect nonsteady-state behavior in the input of solid phases to the sediment column.

Estimation of Benthic Exchange Rates

Sediments are a sink or source for many solutes in the water column. Thus, they can play an important role in regulating the composition of the overlying waters. This approach provides information that can be compared to direct measurements of benthic fluxes (*see* Bottom Landers).

Recovery of Deep Pore Water that may be Fossil Water

The trapping of pore fluids as sediments are buried may potentially preserve fluid from a time when ocean composition differed from the present, such as the last glacial period when salinity should have been greater than at present and the isotopic composition of water should have been heavier. However, pore water is an open system, and diffusion facilitates the re-equilibration between fossil pore water and bottom waters. Consequently, relict signals may be difficult to detect, even in the absence of any influence of diagenetic reactions.

Sampling Techniques

Initial studies of pore waters utilized retrieval of cores, sectioning them into intervals, and centrifugation to separate pore waters from the associated solids. This approach works well for many solutes in sediments with high porosity, as long as appropriate precautions are taken to minimize artifacts (changes in composition attributable to recovering and processing samples). During sample processing, it is often critical to regulate temperature and eliminate contact between reducing sediments and oxygen, depending on the solute of interest. For studies related to near-surface diagenesis, it is essential to obtain cores that have undisturbed interfaces and with bottom water still in contact with the sediment. To extract water from low porosity sediments, or minimize contact with gas phases, squeezing techniques have been developed. Several kinds of squeezing devices have been utilized, but all rely on compressing sediments while permitting water to escape through a filtration assembly.

To avoid artifacts associated with retrieving cores from the deep sea, devices have been developed to carry out filtration *in situ*. These devices avoid the pressure- and temperature-dependent perturbations associated with core retrieval, but have their own logistical difficulties in deployment to minimize leakage and obtain accurate sampling resolution. One strategy drives a probe called a harpoon into sediments; openings at various distances along the harpoon shaft permit water to be drawn through filters into sample reservoirs. Another device collects cores, seals the bottom, and squeezes water by driving a piston and filter pack down onto the core; sequential aliquots of water are collected and assumed to represent water from progressively deeper intervals. Other strategies have relied on inserting probes that contain water that may communicate with pore water through a dialysis membrane. These devices, named 'peepers', require several days to equilibrate with pore waters and must be initially filled with a solution that will not significantly contaminate the surrounding sediment with exotic solutes.

Several of the artifacts noted above may be avoided through the use of *in situ* electrodes that can be inserted directly into sediment and measure activities of various solutes. Systems to measure oxygen and pH are often used. Very recently, new electrodes to measure pCO_2 , sulfide, iron, and manganese have been developed. By using microelectrodes, gradients over short distances can be resolved.

Finally, some tools have been developed to retrieve pressurized cores and extract pore fluids onboard ships at *in situ* pressures (*see* **Deep Sea Drilling Methodology**). These tools are particularly important where high quantities of methane are found, either dissolved in pore fluid or as a gas hydrate.

Limitations of Pore Water Studies

Observation of the Net Process

Some solutes may be involved in more than one reaction. This limits the ability to uniquely define reaction stoichiometry.

Required Assumptions

Pore water profiles are usually assumed to be steady-state. If boundary conditions vary, pore waters respond, but there is a temporal lag in response that increases with depth. The profile should exhibit concentrations that are roughly averaged over this response time. A second problem may be the existence of unidentified transport processes, such as macrofaunal irrigation (see below). A third problem is that patchiness of organisms on the seafloor may lead to localized effects, such as caches of freshly deposited organic matter in burrows. It is not always possible to collect and process sufficient cores to evaluate the spatial heterogeneity introduced by these effects, that may occur on horizontal scales of centimeters to meters. In the Equatorial Pacific, for example, benthic fluxes of oxygen calculated from pore water profiles collected with replicate cores at the same site have been shown to vary by 30%, and inferences based on a single core have an inherent uncertainty.

Sampling Resolution

Gradients may exist over very short vertical or horizontal distances that cannot be easily resolved during sampling. In organic-rich slope sediments, for example, microelectrode measurements show that the thickness of oxygenated sediments may be only 1–2 mm. Furthermore, if micro-environments are present within burrows or inside shells, this can lead to localized sites of reaction, but the pore water measurement of sectioned cores defines an average for the zone sampled. Most studies are designed to evaluate vertical gradients, as it is usually difficult to evaluate any horizontal gradients, if they are present.

Sampling Artifacts

These may be created by changes in temperature, pressure, exposure to oxygen (or perhaps any gas phase), activities of stressed organisms, or deterioration of samples between collection and storage (see **Table 1**). Some of these changes appear to be reversible, while others are not. Some changes involve the direct reaction of the solute in question, while others are indirect due to the co-precipitation or adsorption of one solute with the solid formed by the direct reaction of another.

Diagenetic Reactions and Biogeochemical Zonation

The seafloor receives a rain of sediment that is a mixture of biogenic debris and detrital materials. Some of these components are rather reactive and undergo diagenesis at very shallow depth. Of paramount importance are reactions related to the oxidation of reduced carbon in organic material to form carbon dioxide. The details of organic carbon diagenesis are not well understood, and a detailed discussion of relevant reactions is beyond the scope of this article. However, organic carbon diagenesis involves microbial catalysis of reactions that result in decreasing the free energy of the system through the transfer of electrons from the organic material to terminal electron acceptors. Dissolved organic carbon is produced, and some escapes from sediments into the overlying water, but most of these reactions result in production of carbon dioxide, which reacts with water to form carbonic acid. A consistent pattern has been observed in the distribution of the principal terminal electron acceptors with increasing distance from an oxic water column. Oxygen, nitrate, manganese dioxide, ferric oxides, sulfate, and finally carbon dioxide serve as the principal electron acceptors. Some representative reactions are illustrated in Table 2.

Table 1 Known artifacts in pore water studies

- 1. Changes in temperature. Consistently observed for boron, potassium, and silicon; sometimes observed for acid, calcium, and magnesium.
- **2. Changes in pressure.** Precipitation of carbonate during retrieval of cores from deep water is consistently observed in carbonate-rich sediments. As a consequence, phosphate and uranium are often lost.
- **3. Exposure to oxygen.** Consistently observed for ferrous iron. As a consequence, phosphate, silicon, and perhaps other metals are affected by precipitating ferric oxyhydroxides.
- 4. Gas exchange. Exposure to a gas phase permits any gas dissolved in the sample to partition among the available phases present. In sediments under pressure, high concentrations of dissolved gases (e.g. methane,) can accumulate and form bubbles when retrieved to the surface. Also, some containers are permeable to certain types of gases.
- **5. Stressed organisms.** Some animals may excrete large amounts of ammonia when they are stressed. Stress can occur due to temperature and pressure changes as cores are retrieved, or due to physical disturbance. Some bacteria may contain vacuoles rich in nitrate; these vacuoles may break when samples are centrifuged.
- 6. Deterioration during sample storage. Filtering samples can screen out most bacteria, but may not inhibit reactions that might occur inorganically. For example, oxygen will eventually diffuse into plastic sample bottles and oxidize ferrous iron. Precipitation of ferric iron can be inhibited by acidification of the sample.

Table 2 Biogeochemical zonation and proton balance

(A) Principal reactions involving electrons and protons Oxygen reduction zone $O_2 + C_{org} + H_2O = HCO_3^- + H^+$ $NH_3)_{org} + 2O_2 = H^+ + NO_3^- + H_2O$ $2Mn^{2^+} + O_2 + 2H_2O = 2MnO_2 + 4H^+$	
Nitrate, manganese reduction zone	
$2NO_3^- + 2.5C_{org} + 1.5H_2O = 2.5HCO_3^- + N_2 + 0.5H^+$	
$5Fe^{2^+} + NO_3^- + 12H_2O = 5Fe(OH)_3 + 0.5N_2 + 9H^+$	
$2MnO_2 + C_{org} + 3H^+ = HCO_3^- + H_2O + 2Mn^{2+}$	
$NH_3)$ org + $H^+ = NH_4^+$ (also occurs in deeper zones)	
Sulfate, iron reduction zone	
$4Fe(OH)_{3} + C_{org} + 7H^{+} = HCO_{3}^{-} + 4Fe^{2+} + 9H_{2}O(Fe > S)$	
$SO4^{-2} + 2C_{org} + 2H_2O = HS^- + 2HCO_3^- + H^+(S > Fe)$	
	20-
$250_4^2 + Fe(OH)_3 + 3.750_{org} + 0.25H_2O + 0.25H^2 = FeS_2 + 3.75H_3$	
with resilicate source. $2SO^{2-} + (Fo^{3+}) + Ma^{2+} + 2.75C + 2.25H O - FoS + (Ma^{2+}H^{+})$	
$250_4 + (1e)_{clay} + Mg + 5.750_{org} + 5.251_20 = 1e0_2 + (Mg + 1)_{clay}$ Methane production zone	$f_{clay} + 5.751100_3 + 1.7511$
$2CH_{\circ}O + H_{\circ}O = CH_{\circ} + HCO_{\circ}^{-} + H^{+}$ (fermentation)	
$(HCO_{2}^{-} + H^{+} + 4H_{2})_{ava} = CH_{4} + 3H_{2}O_{2}(CO_{2}^{-} reduction)$	
Carbonate dissolution (primarily in oxygen reduction zone)	
$CaCO_{3} + H^{+} = Ca^{2+} + HCO_{3}^{-}$	
(B) Net production of protons from organic matter diagenesis	
Electron acceptor	Protons per mole C_{ox} (ignoring NH ₃)
Oxygen	1.0
Nitrate	0.2
Manganese	-3.0
Iron	- 7.0
Sulfate (iron-free)	0.5
(ferric oxide)	- 0.07
(Fe-Mg exchange)	0.47

This sequence of reactions has led to the concept of biogeochemical zonation, with each zone named for the solute that serves as the principal electron acceptor or that is the principal product (Figure 1). The sequence of zones is determined by the chemical free energy yields released by possible reactants. The thickness of each zone is dependent on the rate of reaction consuming the electron acceptor, the rate



Figure 1 Biogeochemical zonation. The rain of organic carbon to the seafloor and its burial provide a substrate for metabolic activity, as microbial communities transfer electrons from the organic carbon to terminal electron acceptors. This results in the conversion of organic carbon into carbon dioxide, and may be accompanied by the conversion of oxidized forms of nitrogen, sulfur, and metals (MeO) into reduced forms: molecular nitrogen that escapes and metal sulfides that are buried. Sediments can be divided into zones, characterized by the principal acceptor that is present, or by the key product (in the case of methane). In some cases, distinct zones may be observed where manganese and iron are the principal acceptors, but these often overlap with the nitrate and sulfate zones. This schematic does not include the details of transport, but acceptors migrate downward from overlying waters, or are produced in an upper zone and diffuse downward. The drawing is not to scale. The relative thickness of each zone varies, depending on input of reactive organic material and the availability of different acceptors, and the deeper zones do not form where the rain of labile organic materials is too low. The oxygen reduction zone may be only a few millimeters thick in margin sediments, tens of centimeters thick under open-ocean equatorial sediments, and many meters thick in open-ocean sediments that underlie oligotrophic waters. The geometry of each zone may be convoluted due to the presence of macrofaunal burrows or other heterogeneities.



Figure 2 Schematic illustration of iron cycling to maintain a diagenetic front at a constant depth near the sediment-water interface, as explained in the text. Only the recycled component of iron is shown.

of a reactant's transport through sediments, and the concentration of the acceptor in bottom waters or in solid phases. Zones may overlap, and tracer studies have shown that they need not be mutually exclusive. The existence of the deeper zones depends on the availability of sufficient reactive organic matter.

Boundaries between zones are often interesting sites, and may provide environments where specialized bacteria thrive. As soluble reduced reaction products form at depth, they may diffuse upward into the overlying zone, where they are oxidized. One example is illustrated in Figure 2. In iron-rich systems, ferrous iron produced at depth diffuses upward, until it encounters nitrate or oxygen diffusing downward. At this horizon, ferrous iron is oxidized to ferric iron that precipitates as an oxyhydroxide, often leaving a visible thin red band in the sediments that marks the ferrous/ferric transition. Continued accumulation of new sediments transports the ferric oxyhydroxide downward relative to the sediment–water interface, beyond the penetration depth of oxidants, where the ferric iron is again reduced to ferrous iron; the ferrous iron

diffuses upward again and is re-oxidized. Studies of pore water have confirmed this redox shuttle system, which maintains a horizon of sediments rich in ferric iron at a consistent depth relative to the sediment-water interface. Manganese can undergo a similar cycle to produce a manganese-rich horizon. In sulfur-rich sediments that are overlain by oxygenated bottom waters, the upward diffusion of sulfide through pore waters brings it into contact with dissolved oxygen. This provides a unique environment that may be exploited by the sulfuroxidizing bacteria Beggiatoa, an organism that utilizes the energy released by sulfide oxidation and forms bacterial mats (see Marine Mats) frequently found where low oxygen bottom waters may exclude predators.

Diagenetic Modeling

Substantial advances have been made in the development of mathematical models to quantify the effects of the diagenetic processes that influence pore water profiles. Important processes include those mentioned below, but a full discussion of appropriate formulations to describe these processes is beyond the scope of this article (see the Further Reading section for the mathematical development).

Chemical Reactions

Some solids dissolve and others precipitate. Many reactions are driven by redox processes associated with the oxidation of organic matter, largely catalyzed by microbial activities as they extract metabolic energy. Some of these are illustrated in Table 2. These redox reactions can also result in the production or consumption of acid, depending on the suite of reactants available. The addition of acid should be buffered by the dissolution of carbonate solids, if they are present, and removal of acid may promote precipitation of carbonates. For example, as shown in Table 2B, utilization of oxygen as a terminal electron acceptor is quite effective in producing acid, and should favor the dissolution of any carbonate minerals in the oxygenated zone. If manganese or iron serves as the terminal electron acceptor, acid is consumed, and carbonate may precipitate from the pore waters. If sulfate serves as the terminal electron acceptor, and no iron oxides are available to permit iron sulfides to precipitate, pore waters are acidified and may dissolve carbonates. A similar behavior occurs if iron can be leached from silicates and exchanged for dissolved magnesium. However, if iron oxyhydroxides are present, they dissolve and favor carbonate precipitation. This example illustrates the importance of iron availability in helping regulate the pH of marine pore waters. The behavior of nitrogen (oxidized to nitric acid if oxygen is present, and consuming a proton if it is released as ammonia in the absence of oxygen) also contributes to pH buffering. Many other solid phases respond to these pH changes, changes that are largely influenced by the oxidation of organic matter and the behavior of carbonate and iron-bearing minerals.

Another interesting effect is the co-precipitation of some trace constituents with phases created by cycles of a more abundant substance. For example, as ferrous iron diffuses upward, other trace metals or phosphate may co-precipitate with the oxyhydroxides when oxygen or nitrate is encountered. These constituents may re-dissolve as the ferric oxyhydroxides are buried more deeply.

Reversible Adsorption and Desorption

Pore waters are in intimate contact with solid surfaces, and may exchange solutes reversibly on short timescales. Consequently, a change in pore water concentration is accompanied by an additional change in the adsorbed inventory. If a solute is strongly adsorbed, its transport will be dominated by movement of the particulate phase, rather than by migration through the dissolved phase. The ionic speciation of the solute is often critical in determining the degree of adsorption. Adsorption and desorption equilibria are temperature dependent, and are responsible for some of the artifacts noted earlier.

Diffusion

The random motion of solutes in pore waters results in a net transport from regions of high concentration to regions of low concentration, as described by Fick's laws for diffusion. This is the principal mechanism for transport over short distance scales, and the rate of diffusion depends on the solute in question, the porosity of the sediment, the temperature, and to some extent on the ensemble of other ions present and their concentration gradients. This last effect results from the speciation of the ion and cross-coupling among ion gradients that produces electrical potentials. A rough estimate of the relationship between length- and time-scales for which diffusion is effective can be obtained from using Fick's Second Law to evaluate the time for a diffusive front to migrate from a perturbation introduced in a one-dimensional system. The time is given by the relationship $t = x^2/(2D)$, where t is the

time for response at a distance x from the perturbation in a sediment with a diffusivity of D. In deep-sea sediments, many solutes have diffusivities in the range of $5 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$, so the diffusive front migrates approximately 1 cm in 1 day, but requires 30 years to migrate 1 m and 0.3 million years to migrate 100 m.

Advection

It is most convenient to define pore water spatial coordinates relative to the sediment-water interface. If sediments are accumulating and contain some water, pore waters must be moving relative to this interface. In addition, flow may be driven by strong heating at depth, or other externally imposed forcing. These directed flows are considered advection and may be an important transport mechanism. The relative importance of advection in transporting a solute can be evaluated by considering the dimensionless Peclet number, D/UL, where D represents the diffusivity through sediments, U is the flow velocity, and L is the length scale over which transport must be accomplished. If this number is much larger than one, advection can be ignored, and transport is dominated by diffusion.

Irrigation

In coastal and slope sediments, organisms create burrows that act as conduits through which bottom waters may move (see Macrobenthos). Flow through a burrow may be driven by active pumping by the organism, or by hydrodynamic effects created by the flow of bottom waters past the burrow orifice. Thus, the presence of burrows creates a complex geometry for the effective shape of the sediment-water interface and for the biogeochemical zonation that should parallel the burrow walls. Burrows may provide a pathway for communication between deep sediment and overlying water that does not depend on vertical diffusion. Because communication depends only on transport through the dissolved phase, it is called irrigation. This transport is distinct from bioturbation, a process that may also be important, but it is slower and involves the physical mixing of both solids and water by organismal activities. Accurately quantifying the effect of irrigation has posed a significant modeling challenge, and for convenience it is usually introduced into equations as a parameter called non-local transport. Irrigation effects are commonly observed in estuarine, shelf, and slope locations overlain by oxygenated bottom water. The importance of irrigation in promoting benthic exchange depends on the density of burrows, the depth to which they penetrate, how frequently they are flushed, and the length scale over which diagenetic reactions for the solute of interest take place. Effect of irrigation on pore water profiles have not been detected in sediments overlain by bottom waters low in oxygen, due to the exclusion of macrofauna, or in deep-sea settings where macrofauna are less abundant than in margin settings. Irrigation effects are greatest in the upper 10 cm, but pore water profiles in some deep basins of the California Borderland indicate observable effects to nearly 2 m.

Boundary Conditions

Pore water profiles are dependent on boundary conditions. An upper boundary condition is imposed by the solute concentration in the overlying water, although complications exist if the solute is very reactive. Above the sediment-water interface is a diffusive sublayer that may be several hundred micrometers thick in the deep sea, and thinner in more energetic environments (see Turbulence in the Benthic Boundary Layer). A significant concentration gradient may exist through this zone if the scale length characterizing the solute profile in the sediment is small enough to approach this distance. It can be more difficult to identify a lower boundary condition. Sometimes the solute will approach a constant value if its reactions cease at depth. In other cases, the solute may reach a constant value dictated by solubility constraints or by its disappearance.

Interpretation of Pore Water Profiles

Some examples of pore water profiles are illustrated in Figure 3, drawn schematically to illustrate the range of behavior that may be observed when different factors are important. Several assumptions have been made in drawing these profiles. One is that they represent steady-state, relative to the sediment-water interface. A second is that the diffusivity is not depth-dependent. A third is that any reactions go to zero at infinite depth. A fourth is that advection has been ignored. The shape of a profile is a clue to interpret what factors are important and their depth dependence, but the shape may not have a unique interpretation, particularly if these assumptions are not valid. It is also important to remember that concentration gradients of solutes adjust until transport is equal to the net reactions occurring. If a solute is involved in competing reactions, such as dissolution of one phase and precipitation of a less soluble phase, the net reaction could be zero and no concentration gradient would be created.



Figure 3 Schematic pore water profiles for various combinations of reaction and transport that conceptually illustrate observations made in field studies. Depth scales vary widely for these examples. (A) Reaction at a discrete horizon, with diffusive transport from the site of reaction to the overlying water. An example of this is the profile of chloride in sediments of the Mediterranean Sea created by dissolution of deeply buried (several hundred meters) salt deposits. Another example of this style of profile includes observations in ODP pore waters that reveal interactions of basaltic basement rocks where they contact pore waters in the overlying sediment, removing magnesium and releasing calcium. (B) Coupled reaction-diffusion profiles. In this example, organic carbon is oxidized to carbon dioxide (TCO₂) utilizing oxygen as the electron acceptor. The reaction is assumed to occur only above the dashed line, and the curvature defines whether the solute is consumed (O_2) or produced (TCO_2) . (C) Coupled nitrification and denitrification. In this example, it is assumed that any ammonia released by degradation of organic matter is completely oxidized to nitrate (nitrification) if it enters the oxic zone (including ammonia diffusing from below). The nitrate produced diffuses downward and is converted to N_2 in the nitrate reduction zone (denitrification). Inflection points in the curves define the horizon separating these zones. Because of the competing production of nitrate in the oxic zone and removal in the nitrate reduction zone, sediments may be a net source or net sink for nitrate in the overlying water column, depending on the relative availabilities of reactive organic matter and oxygen. In this example, the competing reactions balance so there is no nitrate gradient at the sediment-water interface. Open-ocean sediments are relatively efficient at recycling their fixed nitrogen during diagenesis, while denitrification in margin sediments may lose 30-70% of the fixed nitrogen that rains to the seafloor in those locations. (D) Reaction, diffusion, and irrigation. In this example, TCO₂ is produced throughout the sediment column, but the rate decreases with increasing depth (dotted line). Reaction products are transported by diffusion and irrigation in the upper zone, and by diffusion only in the lower zone. If sampling defines the average concentration at each depth, the nonlocal irrigation effect provides an apparent sink for TCO₂.

See also

Authigenic Deposits. Benthic Boundary Layer Effects. Bottom Landers. Calcium Carbonates. Deep Sea Drilling Methodology. Macrobenthos. Marine Mats. Methane Hydrates. Ocean Margin Sediments. Sedimentary Record, Reconstruction of Productivity from the. Turbulence in the Benthic Boundary Layer.

Further Reading

- Aller RC (1988) Benthic fauna and biogeochemical processes in marine sediments: The role of burrow structure. In: Blackburn TH and Sorensen J. (eds) *Nitrogen Cycling in Coastal Marine Environments*, pp. 301–338, New York: John Wiley.
- Berner RA (1974) Kinetic models for early diagenesis of nitrogen, sulfur, phosphorus, and silicon. In: Goldberg ED (ed.) *The Sea*, vol. 5, pp. 427–450. New York: John Wiley.
- Berner RA (1980) Early Diagenesis. Princeton: Princeton Press.
- Boudreau BP (1997) Diagenetic Models and Their Implementation, Berlin: Springer-Verlag,.
- Boudreau BP and Jorgensen BB (2000) The Benthic Boundary Layer: Transport Processes and Biogeochemistry New York: Oxford University Press.
- Boudreau BP (2000) The mathematics of early diagenesis: from worms to waves. *Reviews of Geophysics* 38: 389-416.
- Burdige DJ (1993) The biogeochemistry of manganese and iron reduction in marine sediments *Earth Science Reviews* 35: 249–284.

- Fanning KA and Manheim, FT (eds) (1982) *The Dynamic Environment of the Ocean Floor*. Lexington, MA: DC Heath and Co.
- Froelich PN, Klinkhammer GP and Bender ML, *et al.* (1979) Early oxidation of organic matter in pelagic sediments of the eastern equatorial Atlantic: Suboxic diagenesis. *Geochimica Cosmochimica Acta* 43: 1075–1090.
- Lerman A (1977) Migrational processes and chemical reactions in interstitial waters. In: Goldberg E, McCave I, O'Brien J and Steele J (eds), *The Sea*, vol. 6, pp. 695–738. New York: John Wiley.
- Li Y-H and Gregory S (1974) Diffusion of ions in sea water and deep-sea sediments. *Geochimica Cosmochimica Acta* 38: 703–714.
- Luther GW III, Reimers CE, Nuzzio DB, and Lovalvo D (1999) In situ deployment of voltammetric, potentiometric, and amperometric microelectrodes from a ROV to determine dissolved O2, Mn, Fe, S(-2), and pH in porewaters. *Environmental Science and Technology* 33: 4352–4356.
- Manheim FT and Sayles FL (1974) Composition and origin of interstitial waters of marine sediments, based on deep sea drill cores. In: Goldberg ED (ed.) *The Sea*, vol. 5, pp. 527–568. New York: John Wiley.
- Nealson KH (1997) Sediment bacteria: Who's there, what are they doing and what's new? Annual Reviews of Earth and Planetary Science 25: 403-434.
- Van Der Weijden C (1992) Early diagenesis and marine pore water. In: Wolf KH and Chilingarian GV (eds) *Diagenesis III, Developments in Sedimentology* pp. 13-134. New York: Elsevier.

PORPOISES

See MARINE MAMMAL OVERVIEW

PORTS

See SHIPPING AND PORTS

PORTUGAL CURRENT

See CANARY AND PORTUGAL CURRENTS