The Mineralogical Record

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the Mineralogical Record

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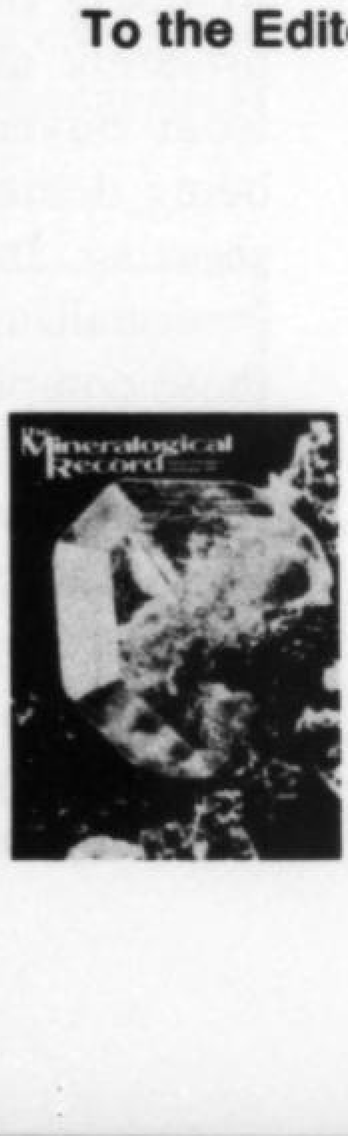
departments



WULFENITE. San Pedro Corralitos, Chihuahua, Mexico. An extraordinary transparent crystal measuring 1 1/2 cm across from this little known locality. Smithsonian Institution specimen.
Photo by Joel E. Arem © 1972.

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Editorial

Pre-Show Selling

As mineral shows become larger, more widely publicized and attended; the amount of money changing hands becomes very significant. Collectors have come to look forward to the major shows in anticipation of finding new specimens to buy. They know that the bigger shows tend to draw a large concentration of top mineral dealers. Because of this they expect to see a great variety of outstanding material from which to choose. Their eager anticipation on opening day may turn to bitter disappointment when they learn that much of the top material has been "creamed off" in a rash of pre-show private selling, representing one form of *tailgating.* This selling may actually occur at the tailgate of the dealer's truck but has become such an important activity that most of it takes place in hotel/motel rooms. To a lesser degree it also takes place on the show floor the day before the show opens. Dealers have been known to take in more receipts before the show than during the show. One dealer boasted on the night before a show that he already had sold enough to make the show a successful one for him even if he didn't sell anything during the show. Wise collectors, having time to arrive a day or two before the show, know they can make the rounds of the dealers' rooms and find a much more attractive offering. Those who wait for the show to officially open may be out of luck. Many dealers schedule special showings in their rooms for important customers before the show. The very finest specimens in their stock are there on display and the chances are excellent that these pieces will never get to the show floor.

It seems clear that this is not a happy development and, if allowed to continue, it will only lead to a lot of criticism of show sponsors, and a dimunition among collectors of their faith in the integrity of mineral dealers. Whether or not the practice can be controlled or even significantly discouraged remains to be seen. Certainly it is an important problem and should be faced by show sponsors. The original form of tailgating (selling from the tailgate near the show) has not been eliminated but it is kept at rather unimportant levels. People were quick to realize how unfair this activity is to dealers who have rented floor space. It seems to me that early selling is equally unfair to all but a small number of buyers.

At least one show sponsor devised a scheme for trying to bring this practice under control. The dealer's contract with the show specifies that pre-show selling is prohibited and that violators of the prohibition will not be allowed to return as dealers at future editions of that show. This approach should be quite effective since those usually involved have been dealers who covet their space at the show and would hate to lose it. Parking lot tailgating during the show is more difficult to control because the show officials can do little more than run the offenders off when caught. They haven't the leverage in this case that they have with dealers under contract.

Actually there are at least two faces to the pre-show selling problem. Retail dealers may feel it necessary to buy from wholesalers before the show while they have time to give some attention to it. Once the show begins they are often too busy to spend much time looking over the wholesaler's stock. One answer to this problem is to schedule the selling by wholesalers a day or two before the show opens, but under the control of show officials so that only retail dealers may do the buying, not individual collectors.

Quite obviously some dealers will object to being deprived of the opportunity to sell privately at shows. A louder cry may come from buyers who will strenuously object to being denied the special privilege of a private showing. In the interest of increasing the professionalism of mineral show management these complaints must be ignored. The enforcement of new rules banning pre-show selling will not work that great a hardship on anyone. The dealers and their special customers can still get together during the show. Imagine the heightened excitement at a show as all the big buyers queue up at the entrance so they may run to their favorite dealers as soon as the show opens and they can get through the gate. The anxiety over being beaten to a desired specimen may even produce a mini-state of panic buying overcompensating any losses suffered by the dealer from being denied the chance to sell early.

I have had little experience with shows in other hobbies (coins, antiques, etc.) but I am told that most do not permit pre-show selling. This being the case, should we not adopt a similar course of conduct?

JOHN S. WHITE, JR.

SPECIMEN MINERAL SHOW IN PASADENA

Of particular interest to mineral collectors is the show of the Mineralogical Society of Southern California on November 4 and 5 at Pasadena City College, 1570 East Colorado Boulevard, Pasadena, California. This Society, which was formed in 1931 (the oldest society west of the Mississippi) claims a uniqueness in their show which few societies can lay claim to. The show is entirely devoted to minerals. There will be over 100 exhibits featuring possibly the finest assemblage of private collections in the country. MSSC has among its members some of the most active and famous collectors in the western United States. Guest displays will include collections from many prominent collectors, as well as the major museums and universities in the area, including the Los Angeles County Museum of Natural History, California Institute of Technology and the University of California at Santa Barbara. Also featured will be four speakers prominent in the field of mineralogy who will conduct a symposium on minerals, mineral localities and mineral identification. Fifteen top mineral dealers in the country will offer specimens of interest to novice collectors through advanced collectors.

Of particular interest will be a display of tourmaline recently found at the Tourmaline Queen mine, Pala, California. This is probably the most important gem and mineral find in this country in the past decade. These magnificent specimens have created a wave of excitement among mineral collectors and many of the choice specimens can be viewed at this show. Other equally impressive displays will feature the collections of Dave Wilber, Ed Swoboda, as well as many exhibits of self-collected minerals and species collections. The Friends of Mineralogy will sponsor and coordinate educational exhibits. There will also be a meeting of the Friends of Mineralogy in conjunction with the show. This is one of the finest mineral shows in the nation and should not be missed.

FROM BELGIAN CONGO TO CONGO TO ZAIRE

The title suggests a travelogue but anyone could have remained in the same spot and made the excursion from the Belgian Congo to Zaire. What the title refers to is the succession of name changes for the central African country since 1948, culminating in Zaire. Not only has the name of the country been changed, but those of many cities and at least one province are now different. For mineral collectors it becomes more than a matter of political interest when a major mineral producing country undergoes a rash of name-changing. The problem of proper labelling of specimens is usually made more difficult, desirable consequences are rare.

When the Belgian Congo became the Congo there was still confusion because of the Congo Republic, a much smaller nation along its western border. The Congo has now become Zaire, which may not be easy to get accustomed to but at least there is now only one Congo.

Zaire is a country of considerable importance to the mineral collector. It has been, in recent years, the world's leading producer of industrial diamonds, uranium and cobalt, while ranking high in the production of gold and tin. Also mined are manganese, zinc, tantalum, tungsten, the platinum metals, and low grade coal. The uranium minerals of Shinkolobwe are among the finest and most unusual in the world. Because Shinkolobwe was already an African name it has been retained but the province in which it is found has been renamed Shaba (formerly Katanga), the Swahili word for copper.

These changes will probably be slow to gain acceptance and in the process there will be a great deal of confusion in the use of names involved, old and new.

THE COLLECTOR

by Richard A. Bideaux

Wulfenite, lead molybdate, is the most popular mineral in competitive exhibits, based on a survey I once made at a national show. Thus my personal preference for this species can be discounted as I choose it for the first of a series on collector's species.

Its appeal is based on sharp, brilliant crystals of good size, throughout a wide range of colors and habits. At most localities a single type of specimen predominates, but some mines have a wider variety, with every pocket differing in its production in some respect. With differences in associated minerals and matrix, most specimens have enough character that the mine and sometimes the pocket of occurrence can be identified at sight.

Specimens in all sizes are available, but individual localities rarely afford this range. Several hundred occurrences are recorded in the literature, and at least as many more are known. However, only a few localities world-wide have given up sufficient quantity that any collector can reasonably expect to acquire a specimen of quality.

In 1785, Franz Xavier Wulfen published a hand illustrated treatise on the lead ores of Bleiberg, Carinthia, Austria. For the recognizable drawings of crystals of "bleispath" (lead spar), wulfenite was named in his honor by Haidinger in 1841.

Bleiberg, thus considered the type locality, continues to provide occasional specimens to the present time. The number made available to collectors over the centuries must be enormous. Several years ago I heard of one collector in Bleiberg with over 1500 specimens of wulfenite from that locality alone. There is also a small public museum in Bleiberg having a fine display of very old specimens from this locality.

By recent standards, Bleiberg wulfenite is not especially attractive. Colors range from dull yellow to orange, usually color-banded perpendicular to the c-axis. Crystals are rarely half an inch, with an equant to tabular habit.

Perhaps the prettiest wulfenite from Europe is that from the Stephanie mine at Mies, Yugoslavia, with its lively orange color. These stepped pyramidal crystals, frequently showing marked hemimorphism, occur in groups up to cabinet size without matrix. (Hemimorphism is best seen when one side only of a wulfenite plate is built up to a pyramid, i.e., the ends of the c-axis are differently terminated.)

In 1955, Prof. Cornelius Hurlbut of Harvard studied similar crystal groups from the Helena mine, Schwartzenbach, Yugoslavia (*Amer. Miner., 40,* 857-860). In addition to pyramidal hemimorphism, these crystals sometimes have re-entrants about their girdles. These were proven to be twins, and the study suggests that all wulfenite crystals are similarly twinned, but with the re-entrants rarely developed. No twins other than this parallel-axis law are even suspected. Contact or penetration crystals, however symmetrically arranged, with the individuals at an angle to one another, are merely chance groupings.

The only other European locality represented by any quantity of specimens is Pribram, Czechoslovakia. These small gray pyramidal crystals sometimes have interesting mirror-like faces, apparently due to a surficial galena incrustation.

For many years the minor occurrences at Loudville, near Southhampton, Massachusetts, and the Wheatley mine near Phoenixville, Pennsylvania were the best recorded in the United States. These mines were lead producers during the Revolutionary War, and certainly both have an interesting assemblage of minerals. Their wulfenites are sparse in occurrence and micromount in size. Quartz, from which galena crystals have been naturally etched, provides the matrix for the yellow tabular crystals from Loudville. The Phoenixville occurrence is at its best when the gray to red pyramidal crystals are associated with pyromorphite.

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Fig. 1. **Bleiberg, Carinthia, Austria today.**

HANSEN MINERALS

1223 PORT ROYAL, ST. LOUIS, MISSOURI 63141

In lieu of quarterly lists we are planning full page specimen listings in future issues of the Mineralogical Record. Please contact us for specific requirements in minerals, reference material or cut gemstones. Please include a check with your order and postage consideration. Any specimen may be returned for cash or credit if you are not satisfied. Lists begin with Vol. 3, No. 1 (1972). See us at the following shows 1972: Detroit. 1973: Tucson; Cincinnati (Midwest Fed.), Oklahoma City (Rocky Mtn. Fed.). Hansen Minerals, Inc. Dr. Gary R. and Maurine Hansen. Ph. (314) 432-2882. (Showroom: 149 N. Meramec, Clayton, Missouri 63105, Ph. 314-726-2236).

amber barite on golden calcite!

meade county, south dakota

Extensive mining of six miles of concretion outcroppings in the Pierre shale formation by myself and Bill Roberts, Curator, South Dakota School of Mines and Technology Museum of Geology, has yielded the finest selction of this material found since its discovery in 1941. The disastrous spring flooding in western South Dakota eroded the outcropping to expose a quantity of concretions equal to 15-20 years of normal erosion. Classic single gem crystals, one of which is the largest and finest ever found; fine thumbnails, miniatures, cabinet specimens to several superb museum specimens will be held and offered for premiere showing at the:

GREATER DETROIT INTERNATIONAL MINERAL SHOW – OCTOBER – 13-15.

This fine mineral show will be the host for some of the finest mineral dealers in this country and we urge all collectors interested in fine mineral specimens to attend. Mr. and Mrs. Bill Roberts will be in our booth at the Show.

We have also completed several major exchanges with leading mineral museums and part of the available material is listed below and will be offered at the Detroit and Tucson Shows. No list is available on this composite lot of approximately 400 specimens. We sincerely hope to meet many new and old customers at Detroit and Tucson.

AZURITE, Chessy, Bisbee, Tsumeb.
STIBNITE, Japan, Romania.
BROCHANTITE, Tiger mine, Bisbee.
PYROMORPHITE, Germany, Cumberland.
APOPHYLLITE, Germany, Mexico.
TOPAZ, Germany, Brazil.
COPPER, Michigan, Arizona, Tsumeb.
MALACHITE, Bisbee, Tiger mine.
BLUE AQUAMARINE BERYL, Russia.
DATOLITE, Massachusetts.
TOURMALINE, Elba, Russia.
APATITE, Germany, Japan, Brazil.
RHODOCHROSITE, Germany, Hotazel.
CHALCOPYRITE, Japan, Pennsylvania.

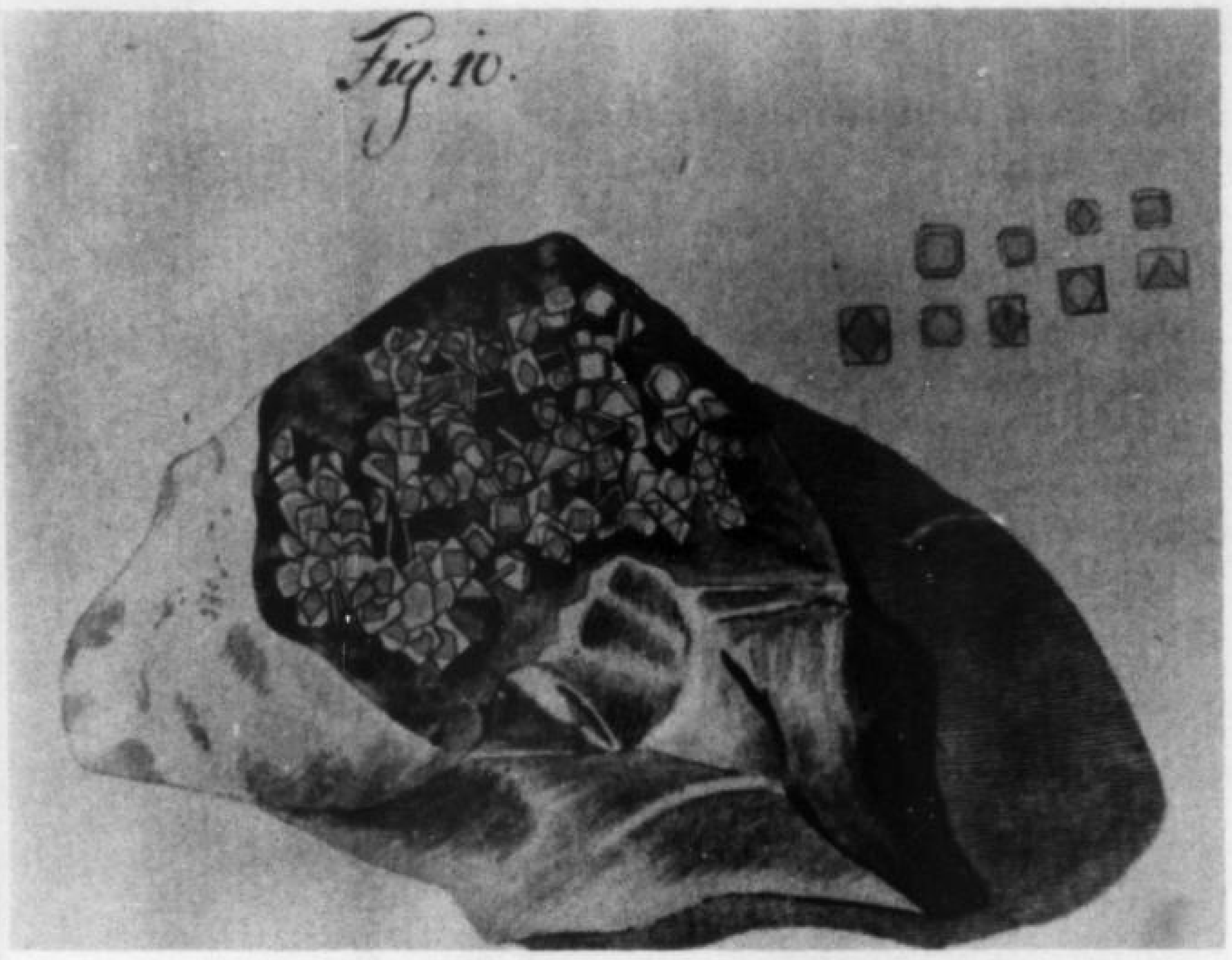

Fig. 2. **Plate from F. X. Wulfen's 1785 book.**

Fig. 3. **Wulfenite – Bleiberg Austria. Smithsonian Institution specimen. Photo by Joel E. Arem.**

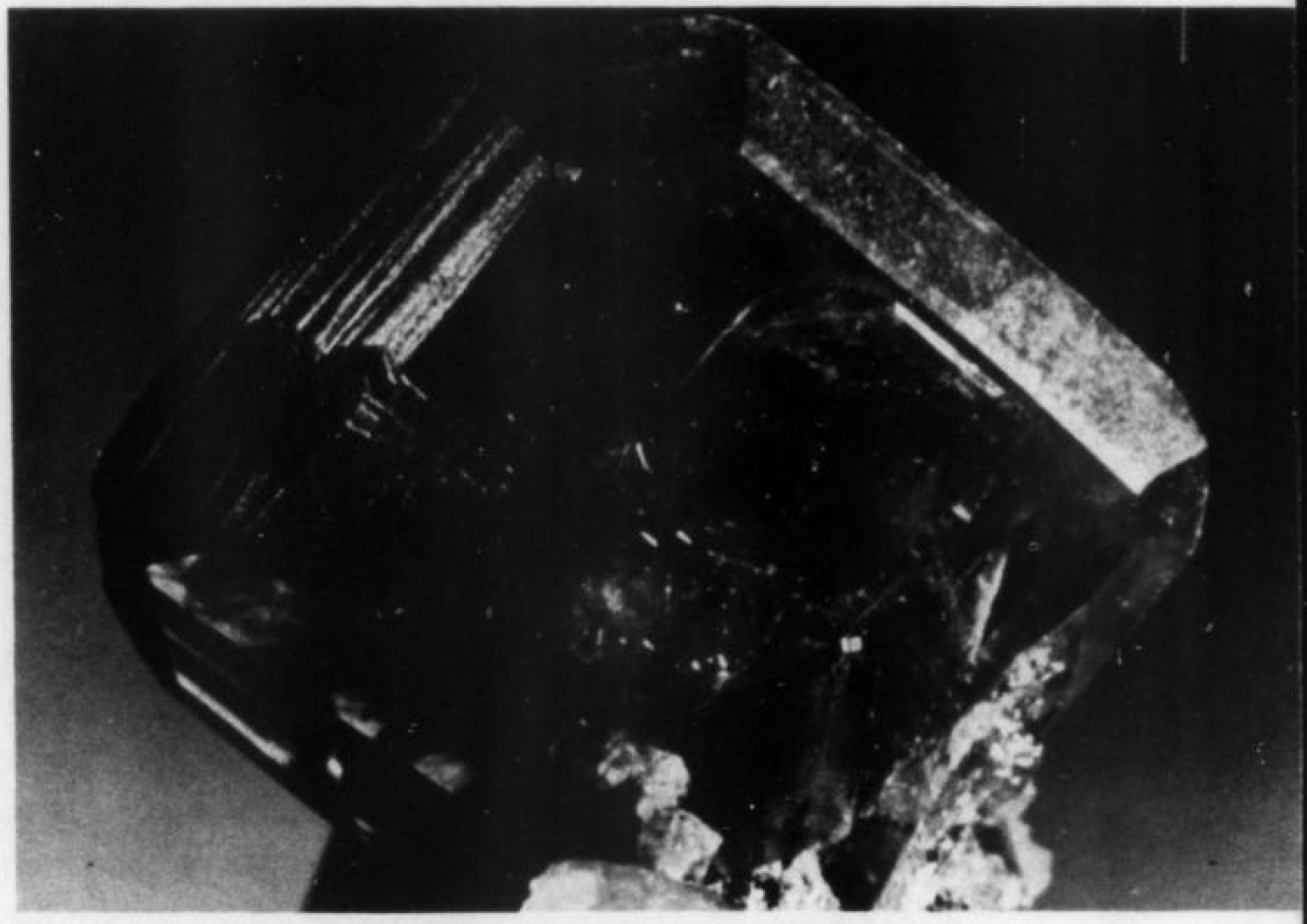

Fig. 4. **Wulfenite – Red Cloud mine, Arizona. Smithsonian Institution specimen. Photo by Joel E. Arem.**

The Collector, continued from page 148

J. R. Bartlett's "Personal Narratives 1850-1853" (the U.S. - Mexico boundary survey) tells of a mine newly discovered by Mr. Stevenson of El Paso. The Stevenson-Bennett mine in the Organ Mountains near Las Cruces, New Mexico was still providing numerous wulfenite specimens to the Foote Mineral Co. in the early 1900's. Caverns lined with wulfenite were found during mining operations; large plates of brown, opaque, diamond-shaped crystals to one inch are preserved in the American Museum in New York City and elsewhere. A large variety of types was found, including beautiful yellow transparent crystals. Although not operated for many years, small specimens can still be collected on the dumps and the interior workings.

In the 1870's the Trigo Mountains, Yuma County, Arizona occurrences were discovered. The list of mines in this district with wulfenite is long, but the Red Cloud is pre-eminent. The mineralogical world was then, and still is, enthralled by the spectacular deep orange-red color and size of the square to octagonal crystal plates from this mine. These crystals are usually isolated in cracks and small cavities; complete single crystals are relatively common, and groups on matrix are comparatively rare. Most crystals are at least 1/4 inch, and some have been found to somewhat over two inches.

This is a favorite haunt of California and Arizona collectors today; several times a year I hear of crystals to over one inch being successfully collected, but usually only after several trips to the mine have been made. Recent specimens tend to be a little paler in color, but this is offset by their sometimes perfect transparency.

The Red Cloud is the premier wulfenite locality in the world, and one of the most famous for any mineral. The 1970's would be an appropriate time to organize a centennial at the mine, and also to clean it up, as it is perfectly capable of these collecting experiences for another hundred years.

The Melissa mine, nearby the Red Cloud, produced a few specimens with identical color, but of characteristically pseudo-octahedral habit, also best seen in the American Museum's displays.

In the 1870's a gold prospect was located by Frank Shultz near Mammoth, Arizona. The upper workings of the Shultz gold mine, now the Mammoth-St. Anthony mine at Tiger, produced millions of pounds of wulfenite. These tabular orange crystals, exceptionally over two inches, were regularly distributed to collections around the world. Most pieces show wulfenite alone, perhaps with minor vanadinite, mimetite or descloizite; a few deep

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the state of the art

the electron microscopes and electron microprobe

by Wendell E. Wilson

Department of Geology and Geophysics, University of Minnesota • Minneapolis 55455

WHY READ THIS?

To the mineral collector, instruments like the electron microscope seem intuitively useful. Everyone with an inquisitive mind enjoys taking a "closer look" at nature and perhaps seeing things never seen before. The value of the microprobe may be less obvious. Consider that nearly half of the thirty new minerals reported in the *American Mineralogist* since 1968 have been analyzed using the microprobe. Clearly it would be of use to the collector to know, in GENERAL, how these instruments work and exactly what they can do. Few readers will be conducting their own analyses. However, armed with a little knowledge (and the help of a professional mineralogist with access to the equipment) collectors can help attack and solve problems that seemed hopeless before. Simply knowing that a mineralogical mystery can be solved is the one prerequisite to action. Furthermore, the work of others in the literature will become much clearer when their methods are understood. This article provides a generalized explanation of the theory and applications useful to mineralogists.

INTRODUCTION

Since around the turn of the century, four powerful tools for mineralogical analysis have evolved which utilize a focused beam of electrons. These instruments are: 1) the x-ray crystallographic analyzers (diffractometers and cameras) described in previous installments of this series (Arem, 1971), 2) the transmission electron microscope, 3) the electron microprobe, and 4) the scanning electron microscope. All of these machines are related in a sort of "family tree" which broke the surface in the late 1800's and has since blossomed into several generations of sophisticated research devices.

In the previous installments of this series on the state of the art in research mineralogy, Joel Arem pointed out that elements (such as the copper or iron targets in an x-ray tube) produce intense amounts of x-radiation of specific wavelengths when bombarded by electrons. This principle is used to produce a monochromatic beam of x-rays for x-ray crystallographic studies. It follows that if a person did not know the target element within a particular x-ray tube he could easily identify it by measuring the wavelength of radiation produced when the tube is turned on. Each element's characteristic radiation is its fingerprint and is unique to that element. This simple phenomenon is the basis of electron microprobe analysis.

The electron microprobe, or simply the microprobe as it is usually called, has become, in less than two decades, one of the most widely used tools available for specialized chemical analysis of minerals. The great strength of the microprobe is in the extremely small volumes of material required for analysis. Mineral phases as small as 0.001 mm (1 micron), or about a hundredth the size of the eye of a gnat, can be given a complete quantitative chemical analysis for all major elements without even destroying the sample. This is particularly valuable in the study of meteorites because grain sizes are often very small, and the limited amount recovered of most meteorites is very precious. Other applications include the identification of inclusions and intergrown phases, and the study of new minerals of which only minute amounts are available. For comparison, Tousimis and Marton (1969) have made the following estimation of the amount of material detectable by various analytical means:

wet-chemical analysis	10^{-9}grams
emission spectroscopy	10^{-12}grams
mass spectroscopy	10^{-13}grams
a human nose	10^{-13}grams
electron microprobe	10^{-16}grams
a dog's nose	10^{-18}grams (about 1000 large molecules)
a bee's "nose"	10^{-20}grams (about 10 large molecules)
limit (mass of lightest atom: Hydrogen)	10^{-24}grams

Nature's devices are still ahead of science, but we like to think that this is only temporary. Furthermore, the microprobe is extremely versatile in the forms which its data output can take, especially in qualitative rather than quantitative analyses.

The electron microscope, like the microprobe, uses a focused beam of electrons. Rather than observing x-rays produced, it is the reflected (scanning EM) or transmitted (transmission EM) electrons which are observed. The electron beam is reflected from or transmitted through the sample as light would be, and is collected and imaged on a TV screen or photographic plate. Because of the similarity between the electron microprobe and the scanning electron microscope each can often function as the other. Spectrometers can be attached to the scanning electron microscope, but the geometry of the instrument somewhat limits its versatility. The power of the electron microscope is illustrated by the fact that the human eye can distinguish features no smaller than about a tenth of a millimeter, and only as small as .0002 mm with the aid of a light microscope. Transmission electron microscopes have resolved features as small as .0000001 mm (1 angstrom)!

HISTORY

Magnified images formed by primitive electron techniques were produced by Ambrose Fleming in the late 1800's (Haine, 1961). Modern development began in 1926 when Busch published the first analysis of the "lens" effect of certain magnetic fields. The first transmission electron microscope was constructed by von Borries and Ruska around 1931, and by 1936 the state of the art had advanced to the point where resolution* was superior to that obtainable with light microscopes. By 1947, resolution down to 10 Å had been obtained (Fischer, 1954) and today the limit is down to about 1 Å.

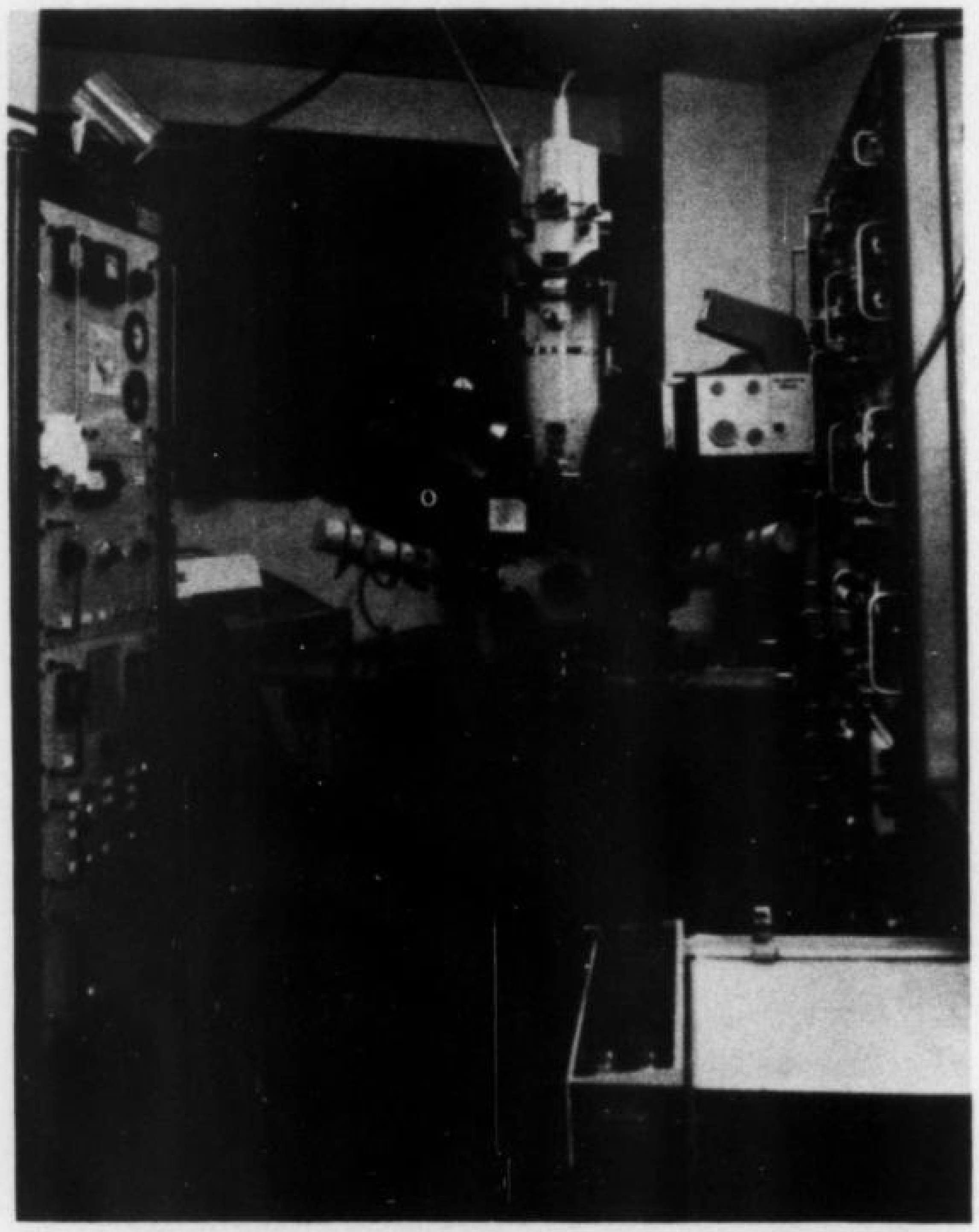

Fig. 1. **The Cameca electron microprobe in the Chemistry Department of Arizona State University. The large drums mounted on each side of the column house the spectrometers. Photo courtesy of Ed Holdsworth.**

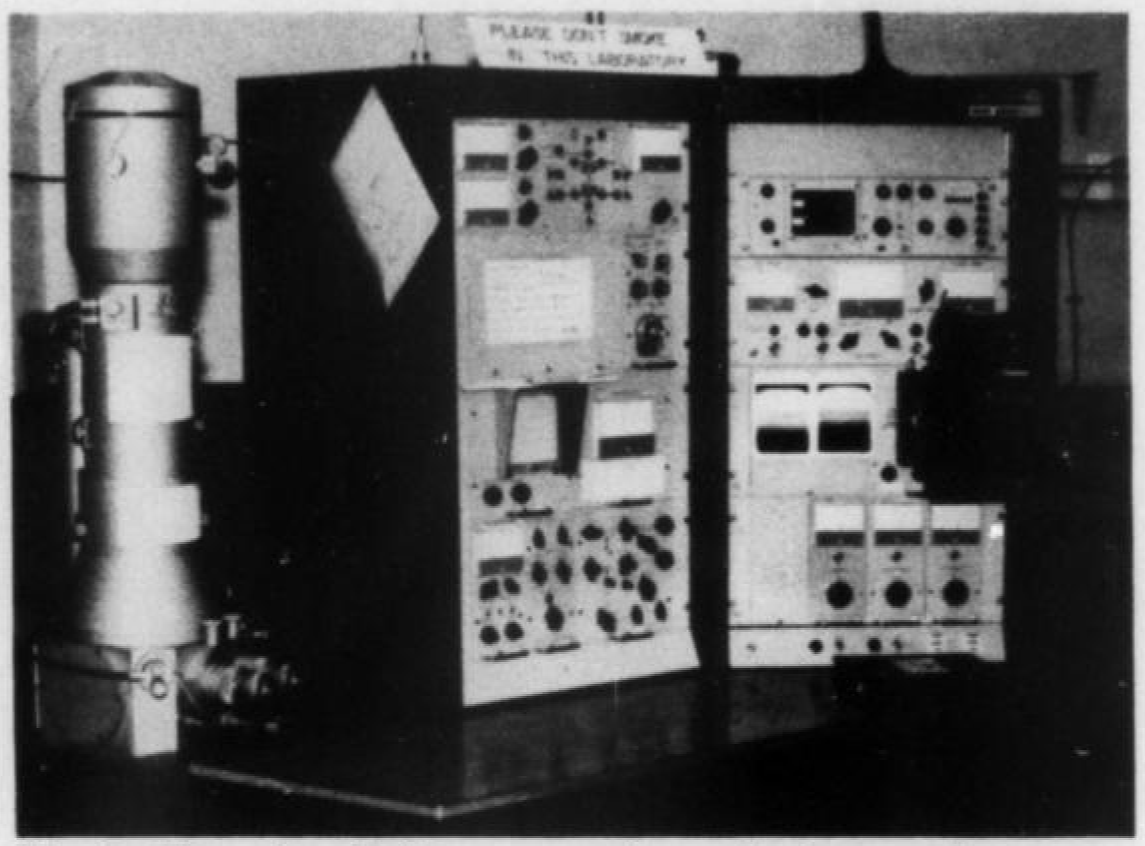

Fig. 2. **The Cambridge scanning electron microscope in the Space Science Center of the University of Minnesota.**

It was known even before 1920 that elements emit characteristic radiation (fluorescence) when bombarded by electrons of sufficient energy. It was also known that the amount of emitted radiation was proportional to the amount of the element present. The simple identification of elements by the radiation they emit (x-ray fluorescence spectroscopy) was developed in the 1920's. The technology which was developed for the x-ray fluorescence analyzer, transmission electron microscope, and extremely efficient vacuum (diffusion) pumps, made possible the marriage of these instruments into the electron microprobe.

In 1947 J. Hillier received a patent on just such a machine, which he called an electron probe microanalyzer. A focused beam of electrons was directed to a sample and the characteristic wavelengths of radiation were measured by a spectrometer. Hillier did not actively develop his invention, however, so the idea lay dormant until 1951 when Castaing, in a doctoral thesis, improved the instrument in many ways and discussed the precise relationship between x-ray intensity and composition of the sample. The basic concepts developed by Castaing have been used by all subsequent workers.

During the following years the number and variety of electron microprobes increased rapidly as more physicists and chemists became interested. In 1956 the first commercial microprobe was built and marketed by CAMECA in France. (A modern version of the CAMECA microprobe is shown in figure 1.) By 1961 there were at least a dozen companies manufacturing instruments. Electron microscopes have proliferated with similar speed since their introduction in the '30's.

THE INSTRUMENTS

A modern scanning electron microscope (SEM) is shown in figure 2. Using this machine, a fine beam of electrons

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*Resolution is usually described as the minimum distance between two objects at which they can still be distinguished as two separate objects.

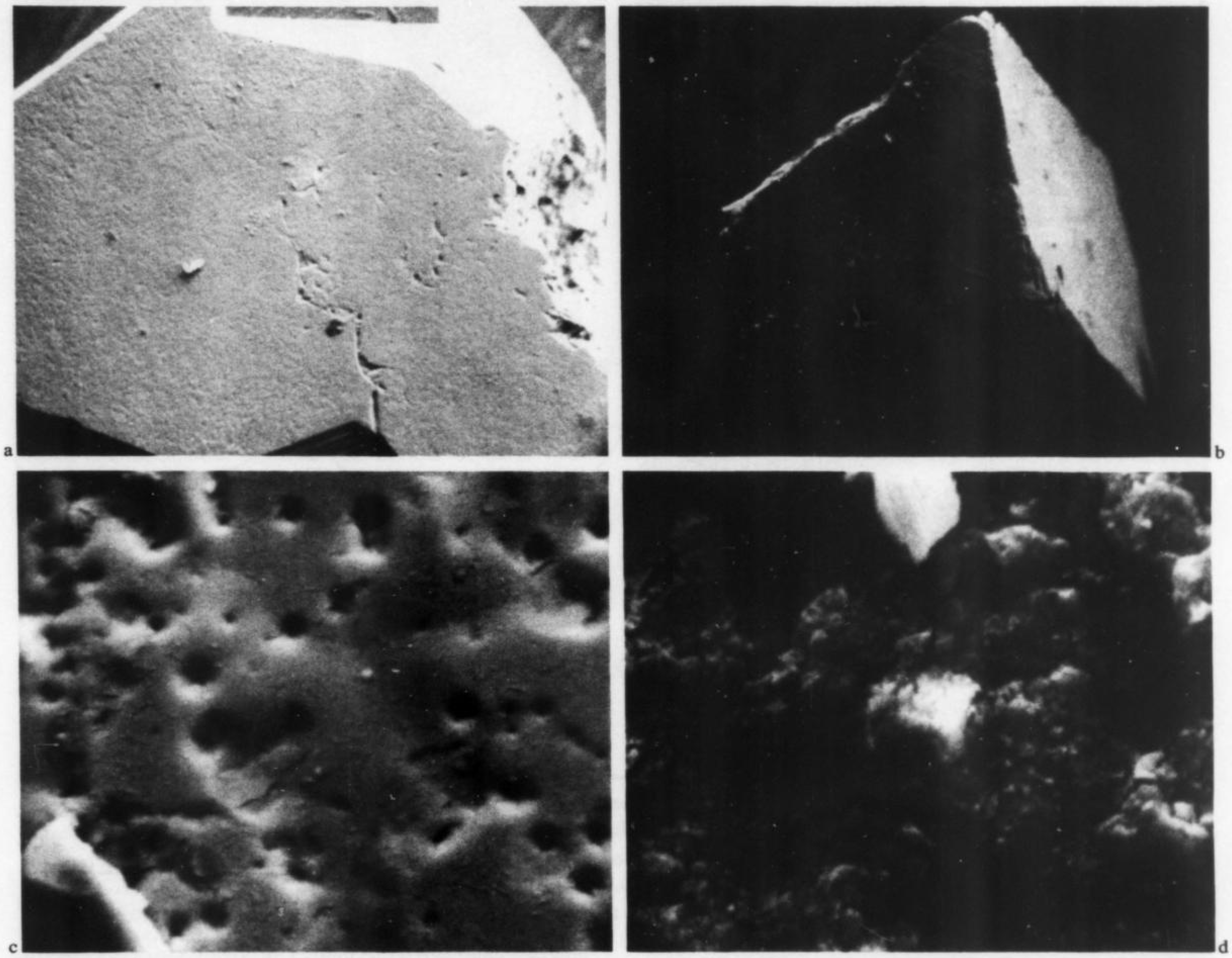


***Fig. 3.* Scanning electron micrographs of vanadinite and arsenopyrite. The (001) faces of vanadinite and arsenopyrite often appear frosty. This face is shown above in SEM photos of several magnifications: (a) vanadinite at 100X, (b) arsenopyrite at 50X, (c) vanadinite at 5000X, (d) arsenopyrite at 5000X. Frostiness on the vanadinite is seen to be due to tiny holes, possibly natural etch pits, whereas the arsenopyrite has a crusty surface due possibly to poor crystallization or a coating of impurities. The samples were coated with gold prior to analysis. The vanadinite is from the Apache mine, Gila County, Arizona, and the arsenopyrite is from Zacatecas, Mexico. Photos by the author and M. R. Coscio.**

is aimed at a sample surface, swept back and forth and up and down over a small area (a raster), and the electrons which bounce off are collected in a detector. A synchronized beam on a small television (cathode ray) tube is made to sweep the screen at the same time the electron beam is sweeping the sample. The intensity of reflected electrons measured by the detector is translated directly to brightness of the beam on the screen, and a picture appears (Fig. 3). Photos of such images were used in Richard Bideaux's article (1970) on "Mineral Rings and Cylinders". This "televised coverage" of tiny surface areas is limited in resolution only by the size of the focused electron beam. The electron beam has a very small conical angle relative to that of light used in light microscopes (Fig. 4). Consequently much higher magnifications accompanied by remarkable depth of field can be achieved with the electron microscope.

A second variety of the microscope is the transmission electron microscope (TEM)(Fig. 5). Images are produced simply by passing a focused beam of electrons THROUGH a sample and observing the shadow on a fluorescent screen beneath the sample. The image is enlarged to a visible size in the same way that an ordinary slide projector enlarges the tiny picture on the slide to an image several feet wide on the screen. Photos of opal structures in the *Mineralogical Record* article by Sanders and Darragh (1971) were made in this manner, as was figure 6 shown here.

The construction of the microprobe is very similar to that of the SEM. There are three main devices: the electron gun and electromagnetic lenses (as in the SEM), and the spectrometers. Figure 7 shows the arrangement of these devices. A small wire of tungsten is heated to a temperature at which electrons are emitted from its surface. The electrons are charged particles and are accelerated away by charged plates. Some of these electrons pass through a hole in the center of the plates and continue down as a beam. An electromagnet shaped like a ring can effect the diverging beam in the same way that a glass

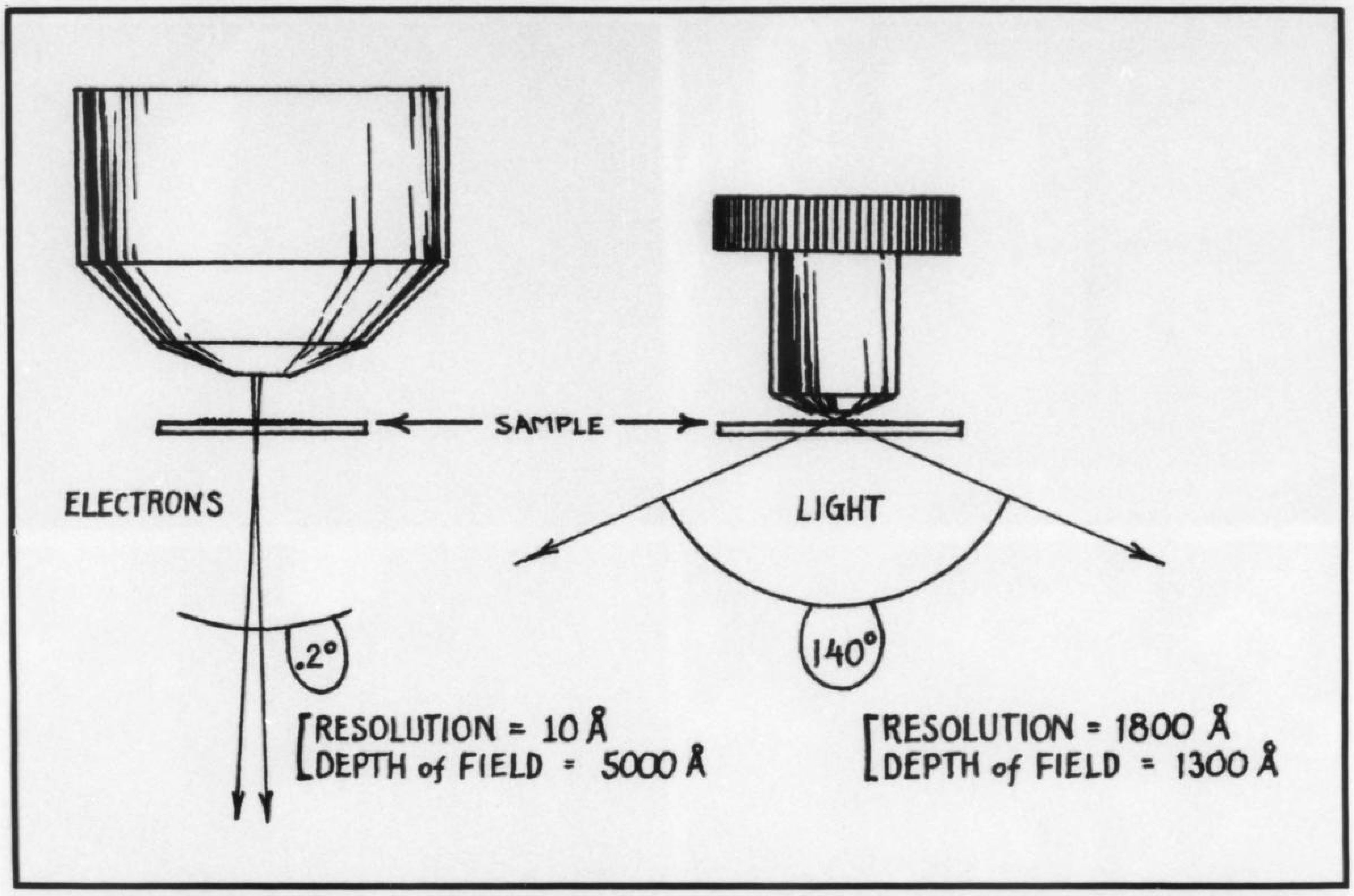


Fig. 4. **The relation between the conical angle of electron and light beams and the depth of field. The theoretical depth of field equals two times the maximum resolution divided by the tangent of half the conical angle. Obviously a smaller conical angle will increase the depth of field. Notice that in the example shown the depth of field of the electron microscope is 500 times as wide as the diameter of the smallest visible object. The ratio is closer to 1 : 1 for the light microscope. In practice the depth of field is often considerably less than the theoretical value for each type of microscope (Fischer, 1954).**

lens can bend and focus light. The advantage of the electromagnetic lens is that its focusing power can be adjusted merely by adjusting the current through it. This is analogous to being able to change the curvature of a glass lens at will. Two or three such electromagnetic lenses are used, and with them the electron beam can be focused to a small spot somewhat less than a micron in diameter. A sample to be analyzed is placed under this spot. The electrons strike atoms in the sample and x-rays are given off (for an explanation of the mechanism of this phenomenon see Arem, 1971). Electrons which are not absorbed bounce off the specimen surface and can be used to form an image as described above.

Some of the x-rays produced then enter the spectrometer. This device is simply an x-ray diffractometer in reverse. In previous papers in this series Dr. Arem explained the use of Bragg's equation

$$n\lambda = 2d \sin \theta$$

to determine *d,* the distance between layers of atoms in a crystal. All other factors are known: the wavelength

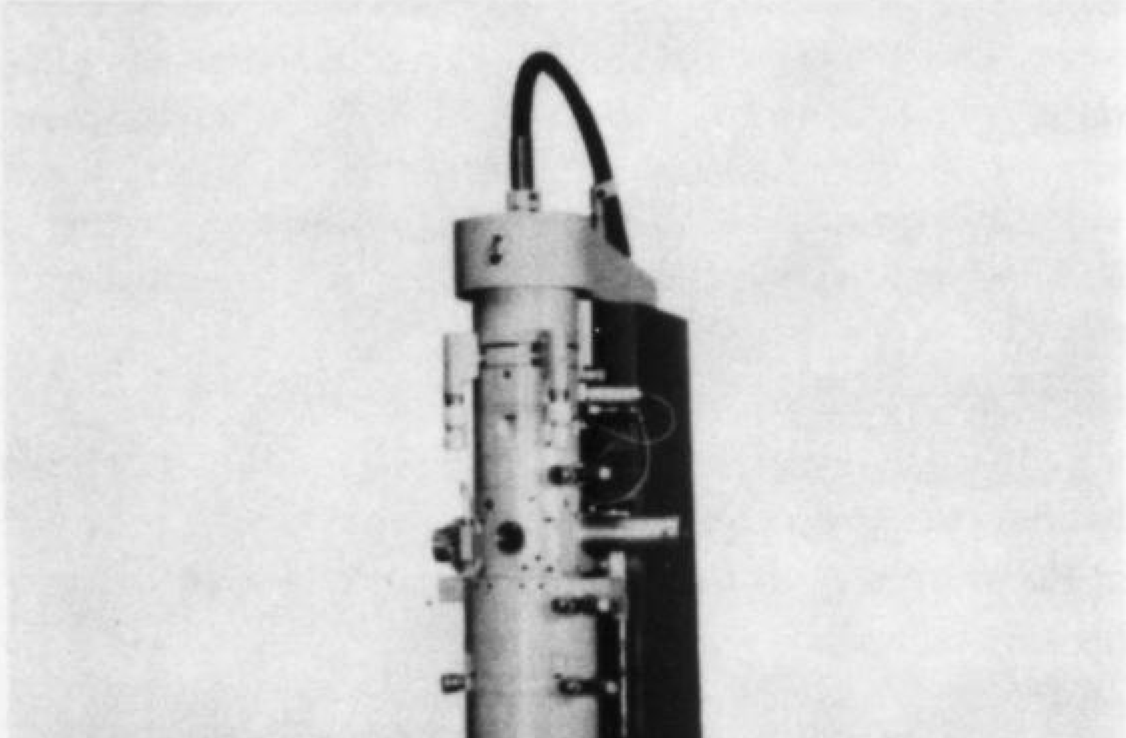


Fig. 5. **The JEOL JEM-100B transmission electron microscope. Samples are mounted in the center of the column rather than in the base, and images are projected on a fluorescent screen in the base near the eye-pieces. Photo courtesy of JEOL USA Inc.**

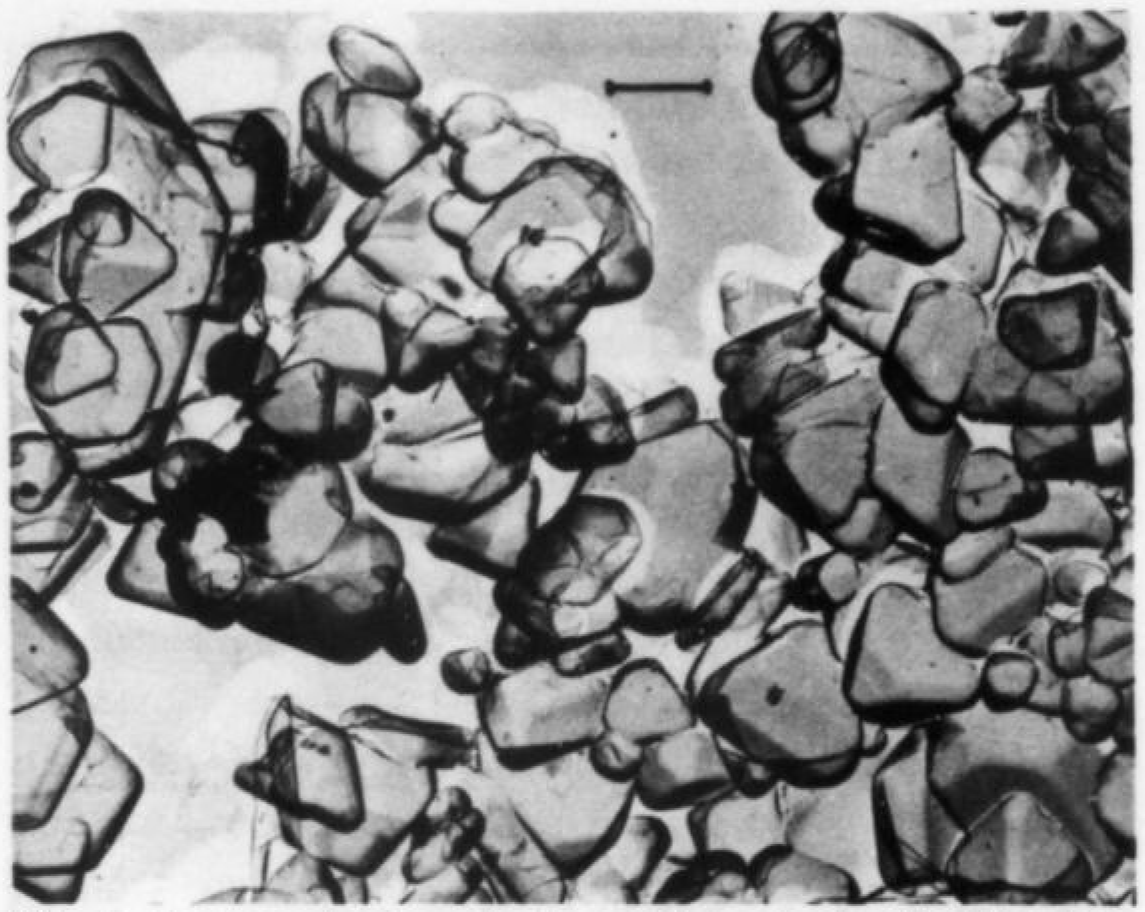


Fig. 6. **A transmission electron micrograph of silver bromide crystals (synthetic bromyrite to mineralogists) from the emulsion of a photographic plate. The "replica" technique was used for this picture because electrons are equally as destructive as light would be on the emulsion. The scale bar is 1 micron. Photo courtesy of 3M Company.**

(λ) of the x-rays, and the angle (θ) at which the x-rays strike the sample. In the spectrometer it is λ which is unknown, and so a crystal of precisely known *d* is used. The crystal and detector are set at a specific angle θ with respect to each other and the unknown. If the wavelength of x-rays striking the crystal at this angle satisfies the Bragg equation, diffraction occurs and the x-rays are passed on to the detector. If the x-rays are not of the proper wavelength to cause diffraction no x-rays will enter the detector. Each spectrometer, therefore, can be set to observe the x-rays emitted by only one element in the unknown at a time. Usually three or four spectrometers are built into a microprobe so that three or four elements can be analyzed simultaneously. The detector, or counter, in the spectrometer attempts to count every photon or particle of x-rays that enters it. By and large the counter does a good job, and only when the count approaches several hundred thousand photons per second does the device begin to miss counting a few percent of the x-rays. This can be corrected. Also present is a counter which collects reflected electrons so that SEM-type pictures can be made. Similarly, to convert an electron microscope into a microprobe it is necessary only to add spectrometers.

An alternative to the spectrometer is a device called a non-dispersive detector. Rather than measuring the wavelength of x-rays, the non-dispersive detector measures the energy contained in each photon of x-rays (energy and wavelength are inseparably related, their product being a constant). A measure of the energy is equally as diagnostic as the wavelength. The detector data may be displayed on a TV screen. Various energy peaks will appear which represent x-rays given off by specific elements. Element peaks may overlap somewhat, so resolution is lower than that obtainable with the Bragg-crystal spectrometers. The ease with which qualitative analyses can be conducted has nevertheless made the non-dispersive detector very popular.

There are a variety of supporting devices on every microprobe and microscope. An extremely high vacuum is necessary to allow electrons and x-rays to travel unhindered, and to keep the filament from oxidizing. For this reason efficient vacuum pumps (mechanical and diffusion) must be present. It is always useful to be able to see the sample while it is under the beam, and so a standard reflected-transmitted light microscope is usually built in. A TV tube is present for imaging, as well as several banks of impressive-looking electronics which are necessary for precise control of all the components. There is even a Polaroid camera which fits over the TV screen, making possible an instant, permanent record of the images. There are many other attachments and modifying devices available but detailed discussion of them is beyond the scope of this article and probably beyond the interest of the casual reader as well.

APPLICATIONS

Sample preparation. Usually samples for the microprobe are imbedded in plastic and polished to a flat, shiny surface. Petrographic thin sections are perfectly suited to such analysis as long as they do not have a coverglass. Samples for the microprobe and microscope must usually be coated with a thin layer (only a few atoms thick) of gold, aluminum or carbon. Samples for the TEM can be more difficult to prepare, because it is often required that no glass or glue be present on either side of the specimen. Powder samples for microprobe analysis can be glued to a slide, fused, or added to a glass medium of known compo-

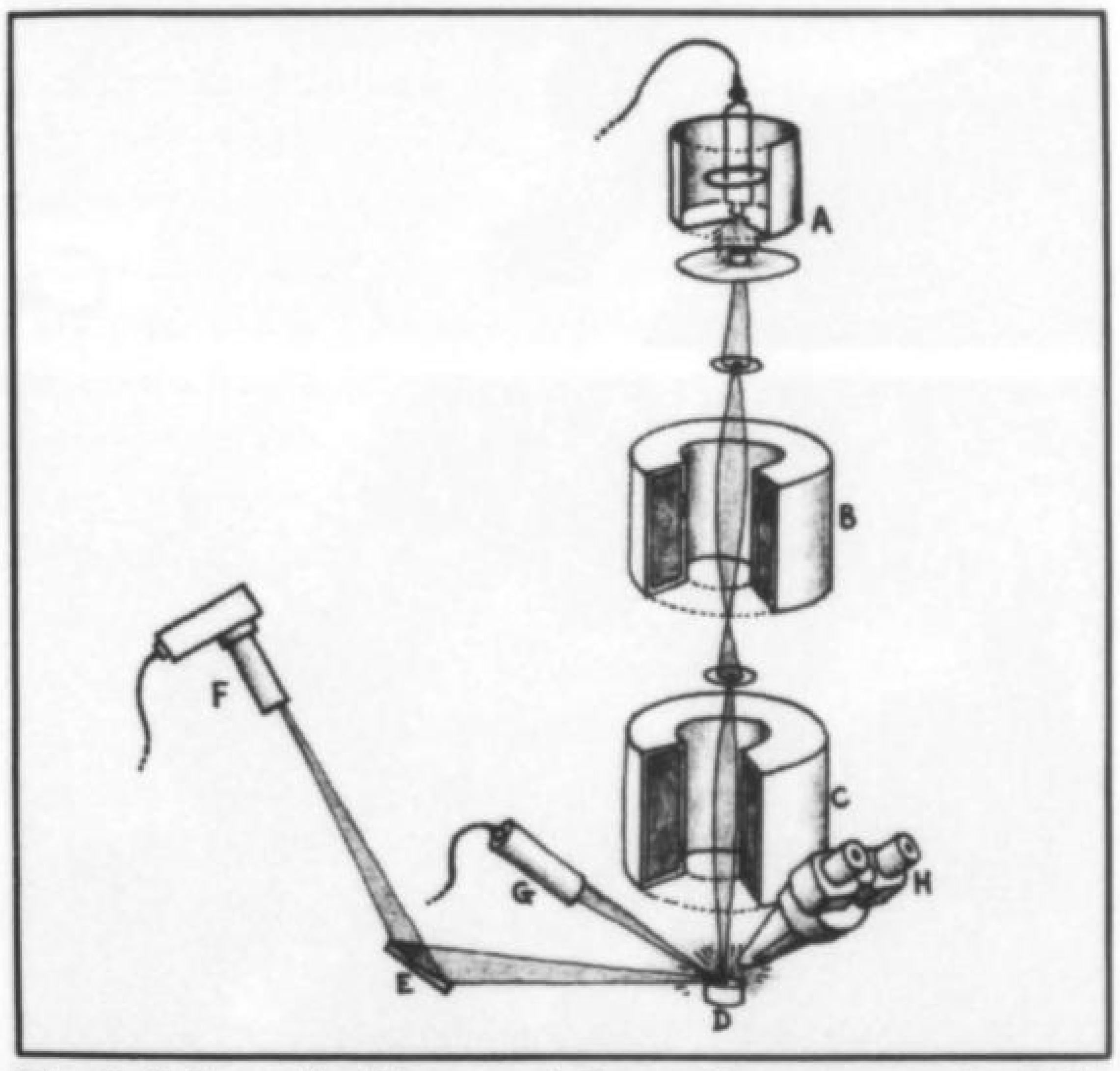
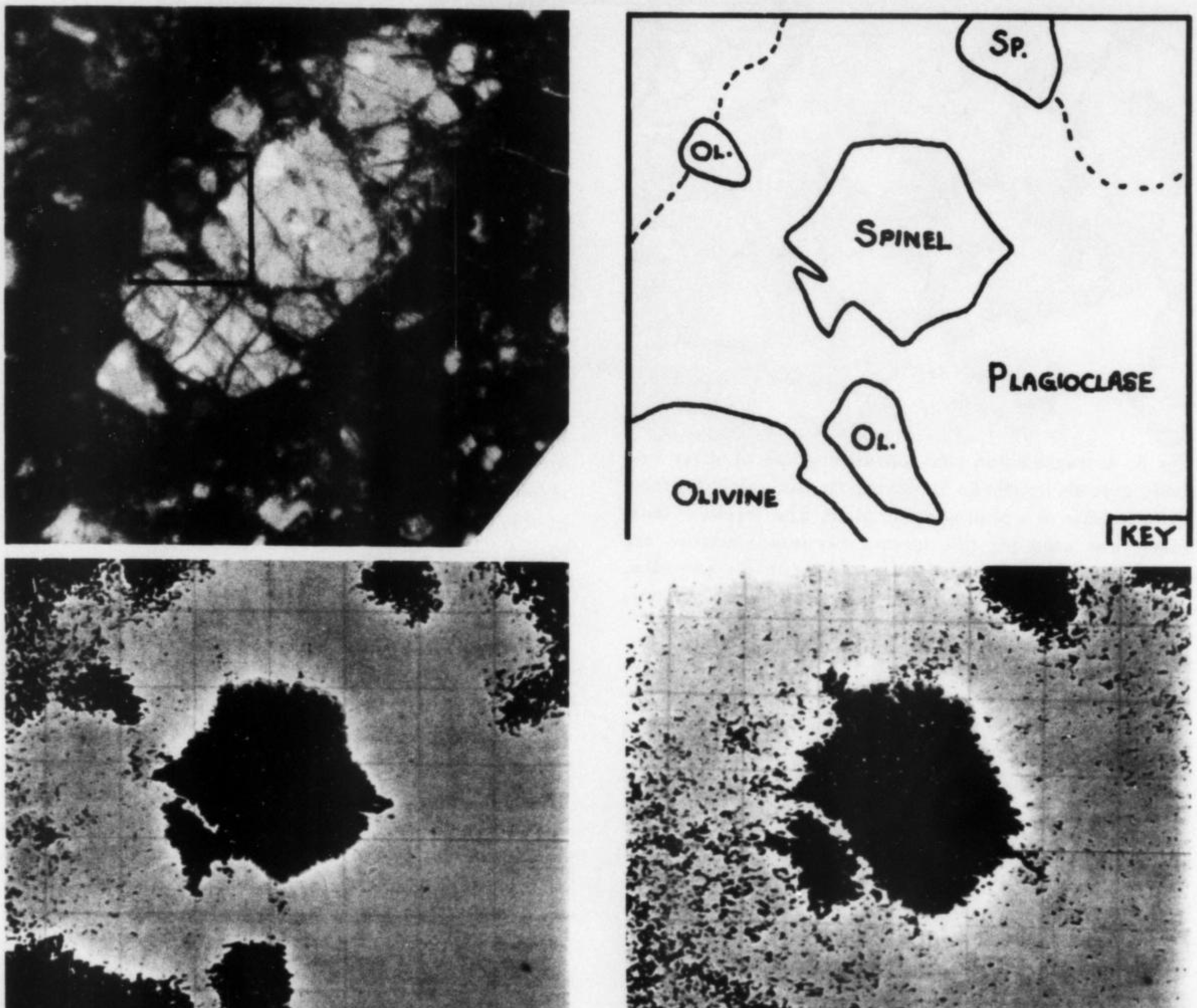


Fig. 7. **Schematic diagram of the main components of the electron microprobe-microscope. The electron source (filament) is at A, B is the condenser lens and C is the objective lens. Electron microscopes often employ a third lens (not shown) called the projector lens. The sample is at D, E is the spectrometer crystal, F is the x-ray detector, G is the electron detector and H is a light microscope for sample observation.**


SP.
OL.
SPINEL
PLAGIOCLASE
OL.
OLIVINE
KEY
Ca
Si
Fe
Cr

sition. The latter three methods allow a polished surface to be made on the sample. Samples for microscopic analysis which have extremely low relief can have their relief enhanced by "shadowing". This process consists of subliming a coating of atoms of some metal, "sprayed" on at a low angle to the specimen surface. When samples for TEM analysis are too thick a metal coating is sublimed onto the surface and then chemically floated off. The removed coating (replica) is placed on a grid and analyzed in place of the real sample. This technique was used to produce Figure 6.

Qualitative Analysis. Using the microprobe, a test to see if specific elements are present can quickly be made by setting the spectrometers for these elements and observing whether any radiation is counted. This is usually done using a stationary beam that rests on one spot on the mineral in question. The beam may also be made to scan a square area on the sample. If the spectrometer is set for iron, for instance, it will register every time the beam passes over an area containing iron. If the spectrometer signal is connected to a synchronized beam on the TV tube, an image of the sample will result in which all areas containing iron are light and all areas free of iron are black. In this way a "map" can be made of element concentrations in various mineral phases within the field of view on the sample. A Polaroid photo is taken of the TV picture for each element present in the sample, and when these photos are compared an approximate composition of each of the minerals can be seen. Figure 8 shows such a series of photos and the interpretation placed on them.

Electrons striking the sample are either reflected or absorbed and drained off as "specimen current". Some of the reflected electrons may be picked up by the detector; ALL of the absorbed electrons contribute to the specimen current. Elements of higher atomic number absorb fewer electrons. Because of this a TV "map" using specimen current instead of x-rays may be made which distinguishes areas of differing mean atomic number.

Sometimes it is useful to allow the beam to remain stationary and move the sample under it. A small motor can be attached to the sample holder which will move the sample at a slow, steady rate. If the signal from the spectrometers is sent to a strip-chart recorder the relative changes in the amounts of the elements present along a line across the sample can be graphically illustrated. This method is particularly useful when studying zoned minerals such as that scanned in figure 9.

A strip-chart analysis can also be performed by attaching the motor to the spectrometer and slowly altering the crystal angle while the beam spot remains stationary on the sample. This produces peaks on the chart corresponding to various elements in the unknown, and resolution is somewhat better than that obtainable with a non-dispersive detector. A scan can be made, using several spectrometers, which covers all possible elements, and relative compositions can be estimated from peak heights.

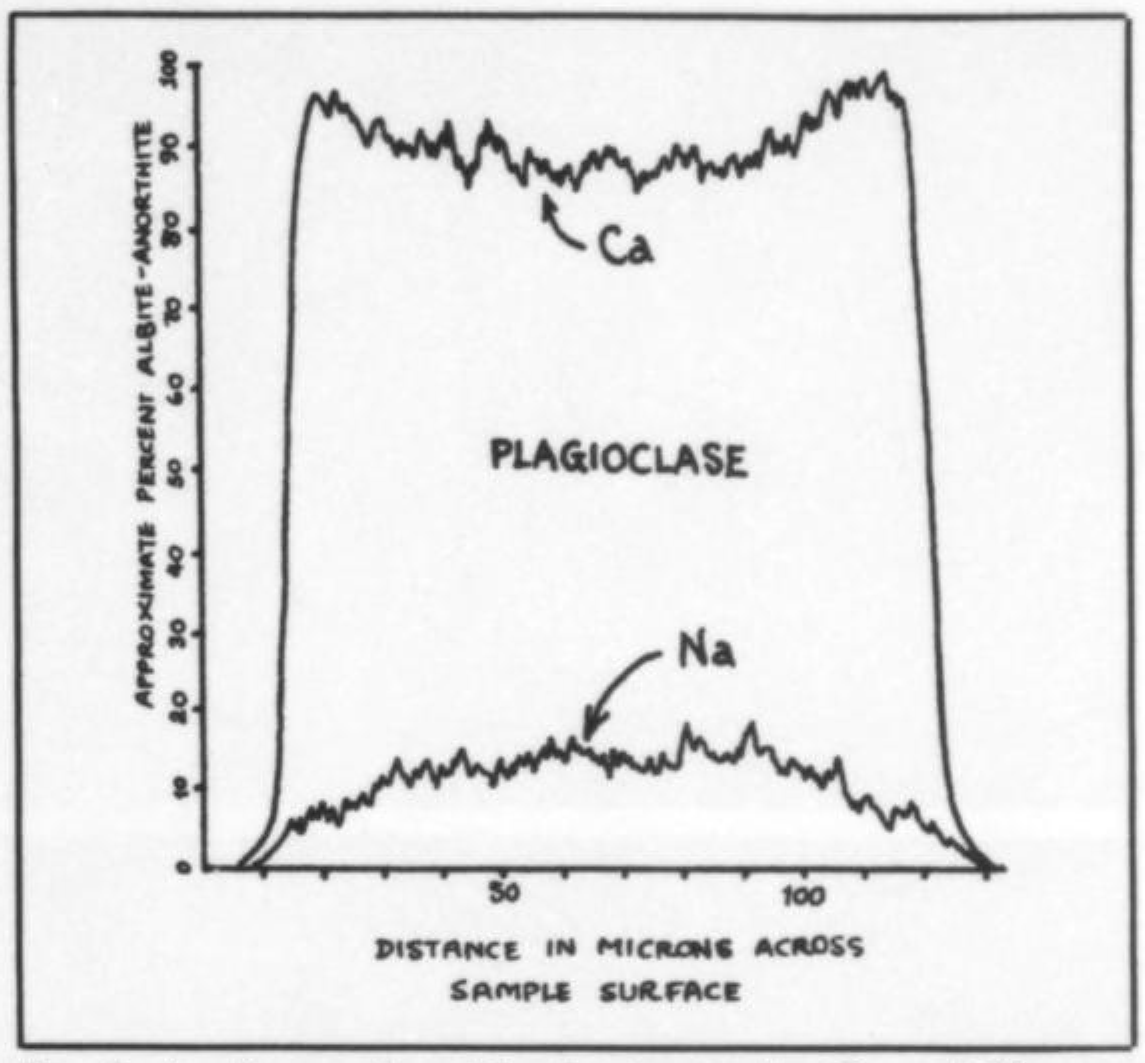


Fig. 9. **A microprobe strip-chart scan for Ca and Na content across a plagioclase grain from a meteorite. The scan revealed an unexpected zoning which is the reverse of common terrestial rocks. Normally plagioclase becomes more albite-rich as crystallization of a magma progresses, creating Na-rich outer zones rather than Ca-rich.**

Cathodoluminescence is a phenomenon whereby minerals visibly luminesce when struck by electrons ("cathode" rays). Many minerals in heterogenous polished sections can be quickly distinguished by the color or intensity of their cathodoluminescence. Apatite, for instance, glows light blue under the beam, barite glows green, calcite glows yellow or orange, and enstatite often appears red.

Crystallographic information can be obtained using a principle called "electron diffraction". An electron beam has a wavelength determined by its accelerating potential. Therefore the Bragg equation holds equally well for electrons as it does for x-rays. Minor differences exist but they can usually be made negligible. The wavelength is much smaller than that of x-rays, causing the diffraction lines to be much more closely spaced. However the efficiency of the electron beam is much greater, necessitating exposure times of only a few seconds rather than a few hours as with x-rays. Mineral standards are often used, and rings or spots on film are obtained (Fig. 10) similar to x-ray film images.

An alternative method of crystallographic analysis is the Kossel technique. The electron beam strikes the sample and the x-rays produced radiate away in all directions.

Fig. 8. **Element maps produced by the microprobe through imaging of x-rays given off by specific elements. The Sample is a section of rock 14319 of the Apollo 14 lunar samples, and contains a large, red spinel (pleonaste) crystal surrounded by calcium-plagioclase and olivine. Cr distribution serves to distinguish the spinel, Ca identifies the plagioclase, and the olivine contains Fe and Si but no Ca. The area scanned is about 250 microns square, the LARGEST area possible to scan with the Materials Analysis Corp. microprobe.**

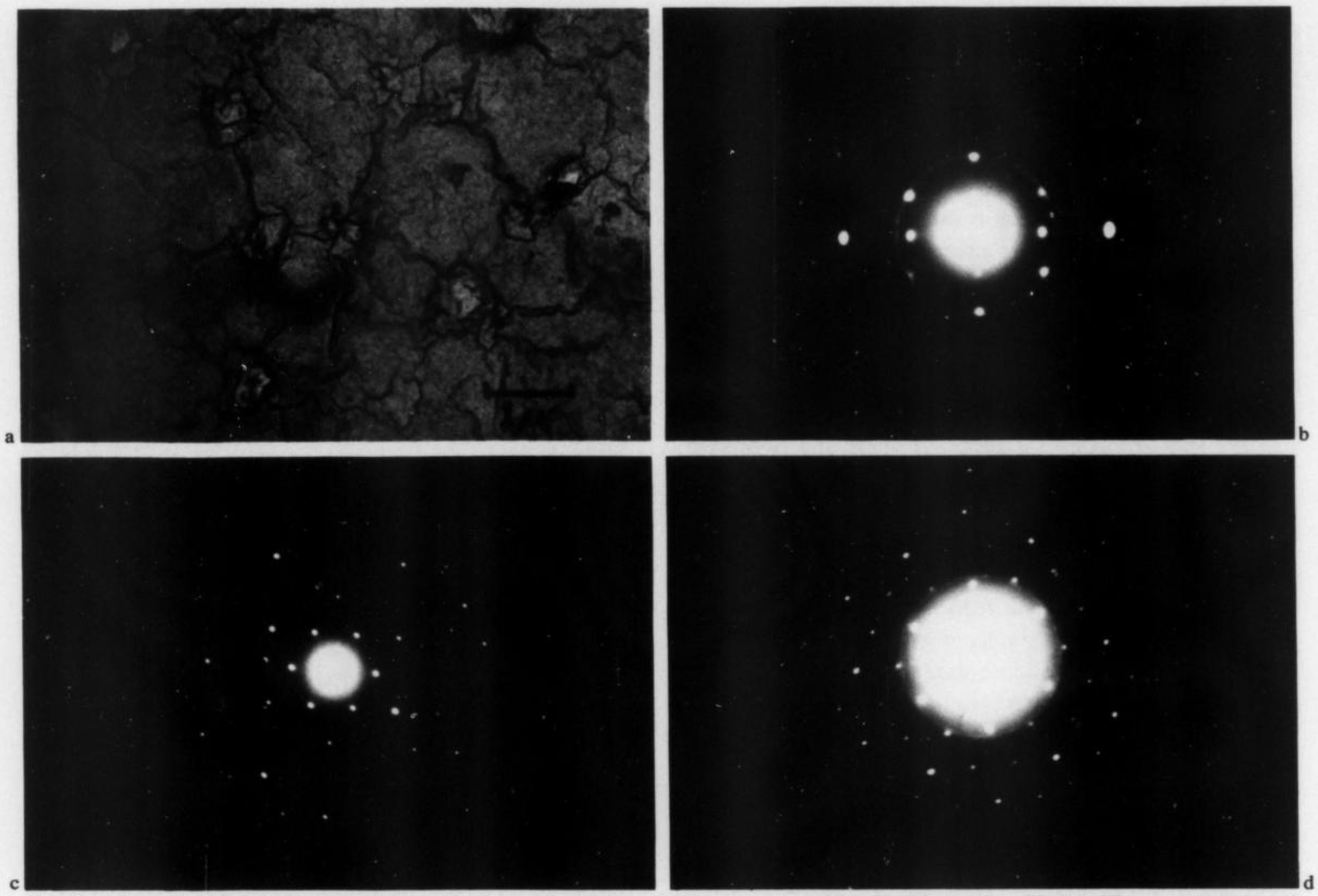


Fig. 10. **An example of the practical application of electron diffraction. Dr. Charles Meyer Jr., NASA Manned Spacecraft Center, conducted some experiments on the interesting subject of mineral crystallization in space near the fringes of stars. His synthesized material was too fine-grained to yield clear x-ray diffraction photos for mineral identification. (a) Transmission electron micrograph showing two unknown minerals called material A and material B. (b) Electron diffraction pattern of material B with Aluminum internal standard (the rings) (c) Material A. (d) Material A with Aluminum standard. The unit cell dimensions of material A were calculated relative to the standard, and material A was identified as enstatite. The cell of material B did not match with any known structure (Meyer, 1971).**

The x-rays which pass through the sample are diffracted and yield a number of diffraction cones. The cones do not all have the same axis as in the powder x-ray diffractometric method, and appear on film as INTERSECTING arcs (Kossel lines) of varying radii. When a particular radiation is desired a thin foil of an appropriate metal is placed in contact with the specimen and is instead struck by the electron beam. This variation amounts to placing the sample directly under the target plate in a standard x-ray tube whereas in the first variation the sample doubles as the target plate. The main difference between Kossel analysis and ordinary diffractometric analysis is that the former employs diverging, point-source x-rays whereas the latter employs, insofar as is possible, a collimated, parallel beam of x-rays. The Kossel technique can yield extremely accurate lattice spacing determinations as well as a measure of the perfection of the crystal (mosaic spread).

Surface features not resolvable with light microscopes can be seen with the SEM. However the most remarkable concept to come from electron microscopy is the imaging of crystal structures, with individual atoms and groups of atoms VISIBLE in their positions in a crystal (as in figures 11, 13 and 14). Magnification of over 9,000,000X has been obtained, but only the largest structures are directly resolvable at the present state of the art.

Quantitative Analysis. Qualitative analyses deal only in the determination of elements present and their approximate proportions in the unknown. In quantitative analysis, however, the interest is in determining the precise chemical composition of the unknown. In order to make such an analysis using the microprobe it is first necessary to have a standard or standards for comparison. The standards are minerals and pure elements, either natural or synthesized, which are extremely homogeneous and which have been subjected to careful wet-chemical analysis. An example is the olivine in the Marjalahti pallasite (a meteorite). Marjalahti olivine is homogeneous and its composition is very accurately known. Therefore it makes an ideal standard, and is used by many microprobe laboratories when analyzing minerals containing the elements in olivine. Ideally the standard should be as close in composition to the unknown as possible. Obviously a large number of standards are necessary in any well-equipped microprobe laboratory, but each standard is only a tiny chip, rarely

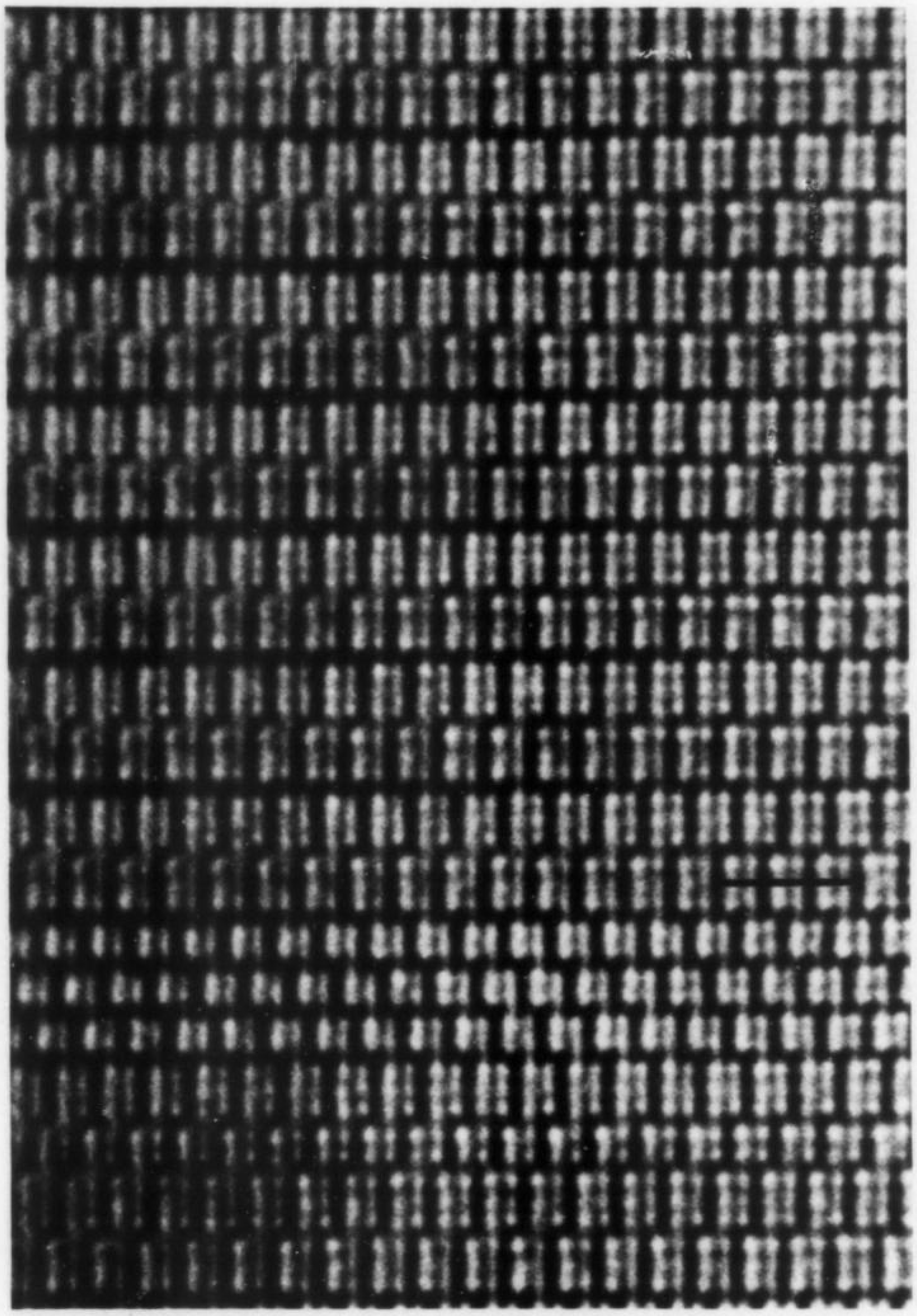


Fig. 11. **TEM photo made by Sumio Iijima, Arizona State University, of the crystal structure of the synthetic compound $Ti_2 Nb_{10}O_{29}$. The dark areas are the shadows of oxygen tetrahedra with Ti or Nb atoms at their centers. The octahedra overlap in the darker areas of the photo, as explained in Fig. 12. Stacking faults are clearly visible in the lower third of the photo, as compared with the normal layering series above. Scale bar is 30 Å, resolution is better than the diameter of the octahedra, about 3.5 Å. Instrument used is that shown in Fig. 5, the JEM-100B.**

larger than a millimeter or two, mounted in a holder two to ten millimeters in diameter. Dozens of standards can easily be stored in a matchbox. Figure 15 shows a small, one-inch block holding a large number of standards.

To run an analysis, the standards are mounted in the sample holder with the unknown. A vacuum is created in the sample chamber and the electron beam is turned on and focused. The standard for each element to be analyzed is placed under the beam and counts are accumulated on the spectrometers for a period normally ranging from 10 to 100 seconds. Then the unknown is placed under the beam and a series of readings are taken. After this the standards are again measured, and finally the spectrometers are purposely put out of adjustment for any element and a "background" measurement is obtained. Background counts are due to the "continuous spectrum" of the elements and to cosmic rays. The background reading is subtracted from the counts for each of the elements measured. During the analysis the readings from each spectrometer are automatically printed out by a teletype.

Unfortunately the proportion of x-rays counted for any given element does not necessarily equal the chemical proportion of that element in the unknown. If it did the analyst's job would be greatly simplified. The ratio of the intensities for a given element in the unknown and standard is always equal to some constant times the compositional ratio (the Beer-Lambert Law). A number of factors compose the constant. Some elements in the sample may absorb x-rays given off by other elements and convert that energy to x-rays of their OWN characteristic wavelength. There are also problems which involve the atomic number of the elements, the previously mentioned detector error (deadtime), and others.

The mathematics behind the correction factors is lengthy, to say the least, and relies heavily on complex and tedious successive approximations. Analyses of two-element compounds can usually be corrected by hand, but for minerals containing more than two or three elements the situation is nearly hopeless. Fortunately computers come to the rescue. In one or two minutes, usually less, a computer can reduce the data to an accurate chemical composition which would take months to calculate by hand. Some researchers of admirable patience, such as Goldstein and Comella (1969) and Bence and Albee (1968),

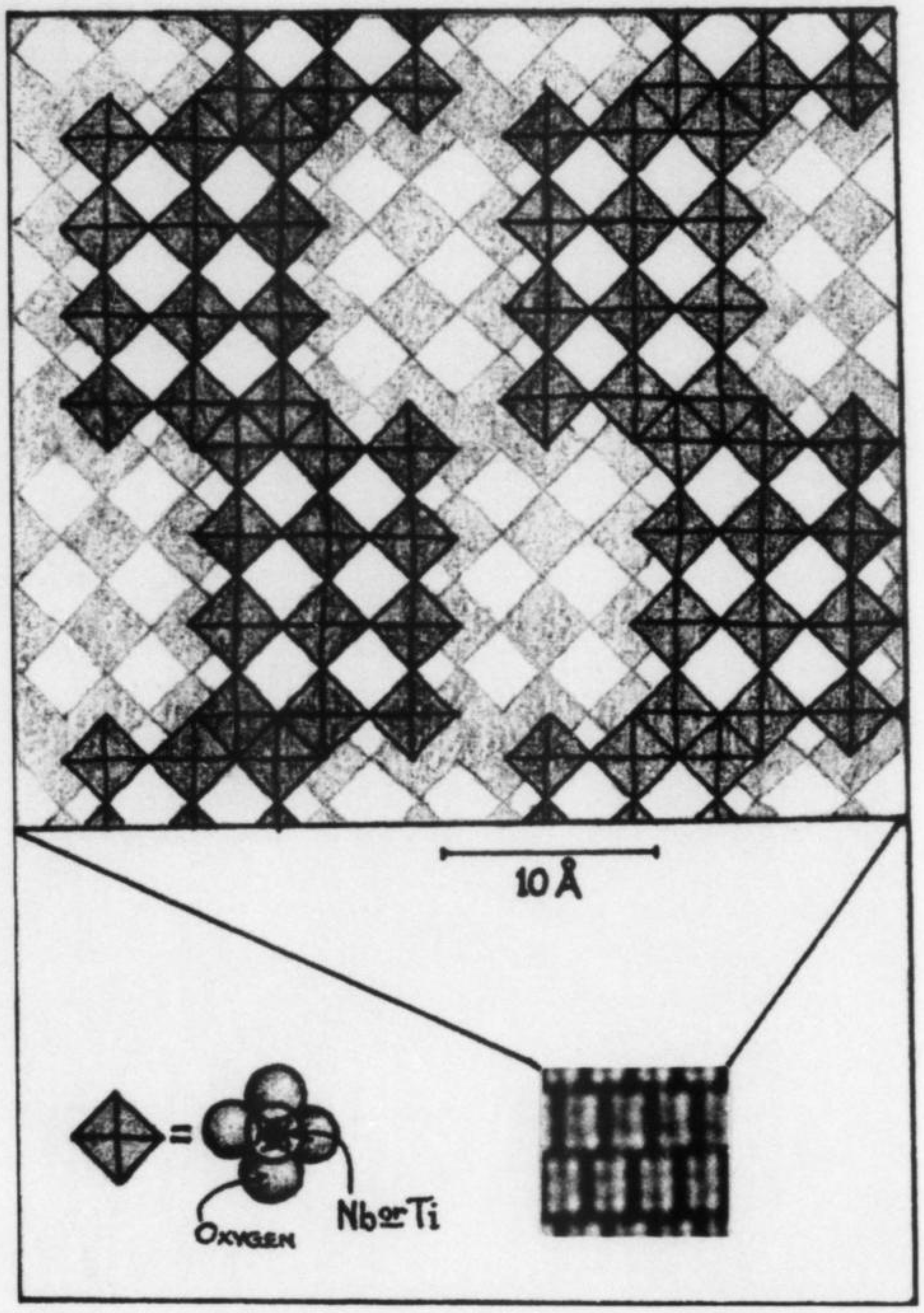


Fig. 12. **Explanation of the structure shown in Fig. 11. Off-set octahedral layers (top layer outlined in black, lower layer gray) overlap to give a shadow picture. Where individual octahedra overlap the image is darker.**

have done the work of writing out, bit by bit, the instructions which the computer must have to perform the calculations. The analyst's job includes converting his raw data to a form which the computer can understand, such as punched cards or punched tape. He must also tell the computer the composition of his standards, x-ray lines used (K or L), and other information. Figure 16 is an example of a typical raw-data print-out and results of the follow-up computer analysis.

Some laboratories have managed to eliminate even this last cumbersome step. Their teletype is connected by means of a telephone hook-up to a large computer wherein the program is on file. Within seconds after the teletype prints out the raw data (simultaneously relaying it to the computer) the computer has calculated the corrected composition and this is typed out. This is real luxury to anyone who has ever done it the long way.

For further information on theory and applications of the microprobe the reader is referred to Birks (1963) and Tousimis and Marton (1969). There are several good texts on electron microscopy, such as Haine (1961) and Fischer (1954). Particularly recommended is a recent article in *Scientific American* (January 1972) on the SEM by Everhart and Hayes.

SOURCES OF ERROR

Sources of uncertainty in quantitative microprobe analyses include variation in the electron beam power supply, physical positioning of the spectrometer crystals, sample preparation, reliability of standards, deadtime errors, electronic "drift" of the instruments, and the possibility of decomposition of the sample under the beam during the analysis. The variation in microprobe analyses of a particular sample by different people and/or laboratories is usually around 1 to 10 percent of the amount present. Microprobe SEM-type (back-scattered electron) images can be confusing because of the difference in reflectivity between compounds of differing mean atomic number.

LIMITATIONS

Hydrogen and lithium cannot, as yet, be analyzed using the microprobe, nor can such non-solids as helium and neon. The routine limit of detection is around a tenth of a percent for most elements, with an error limit commonly around two or three percent of the amount present.

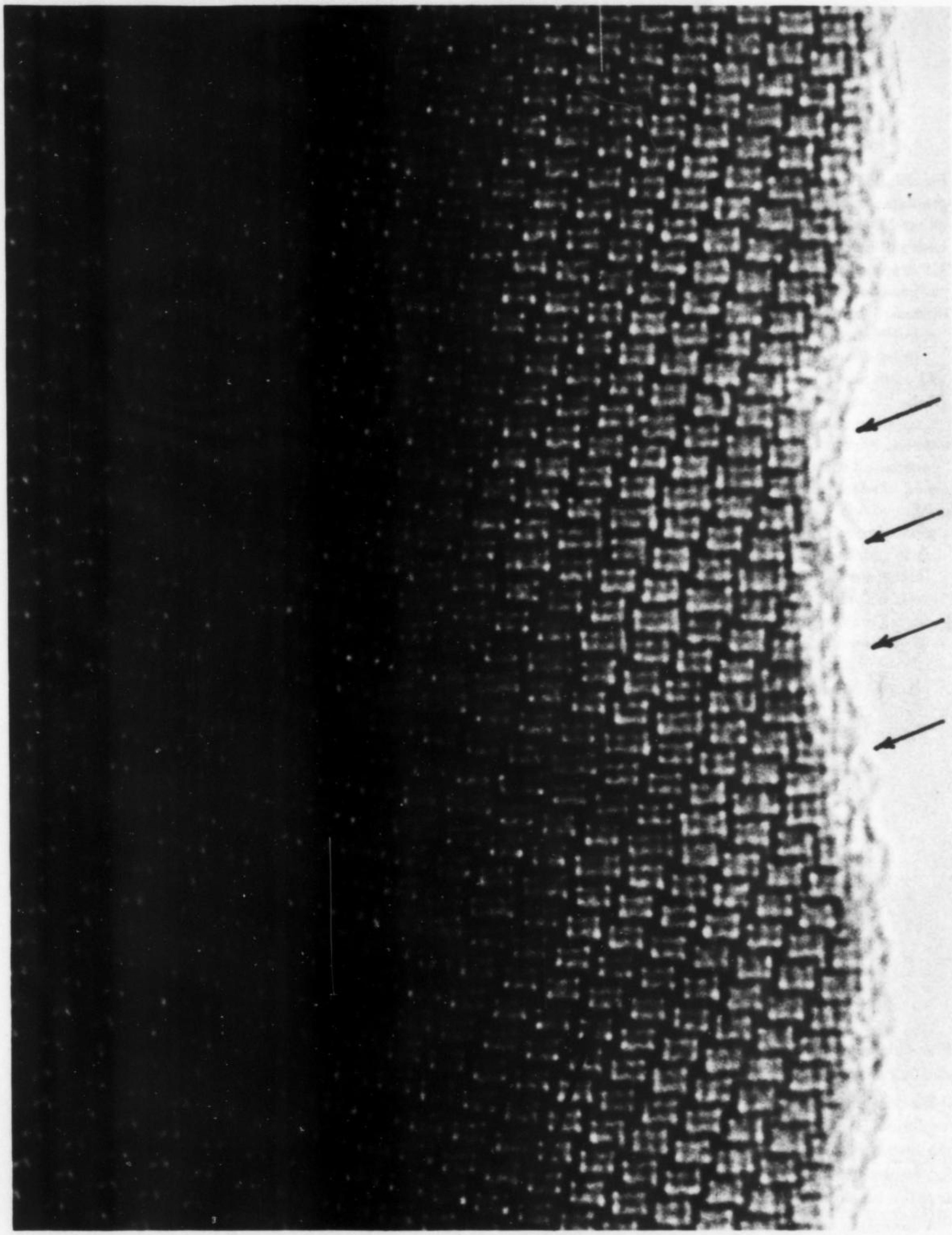


Fig. 13. **TEM crystal structure image of the synthetic compound $8Nb_2O_5 \bullet WO_3$ made by Sumio Iijima. The structure is composed of octahedra similar to that shown in Figs. 11 and 12. Dislocations are present in the direction of the four parallel arrows. If the reader finds these difficult to see, tip the page and look in the direction of the large arrow. The increasing darkness to the left is due to additional layers of atoms. Magnification is about 5,000,000 X.**

Fig. 14. TEM photo of graphite; magnification about 2,000,000 X. The layers of carbon atoms 3.4 Å apart are clearly visible. Photo by Sumio Iijima.

Trace elements, those present in amounts less than 0.1%, usually cannot be determined.

When using the microprobe as a SEM the maximum resolution is around 3000 Å, whereas a standard SEM can obtain resolution down to about 100 Å . The TEM can resolve atomic features as small as 1 Å, which is believed to be close to the theoretical limit.

A limitation which is imposed on researchers by the machines is cost. The CAMECA electron microprobe and accompanying equipment, for instance, costs about $130,000, and many electron microscopes cost around $100,000, compared to "only" $17-25,000 for an x-ray diffractometer. Individuals and companies not fortunate enough to own their own microprobe and microscope are usually charged anywhere from $20 to $80 per hour for their use.

A relatively new instrument called the ion microprobe mass analyzer (IMMA) uses a beam of ions instead of electrons, and a MASS spectrometer. Detection in the range of one part per hundred million and even one part per BILLION (about 10^{-18}grams) have been claimed; the price tag is nearly a quarter of a million dollars.

ACKNOWLEDGMENTS

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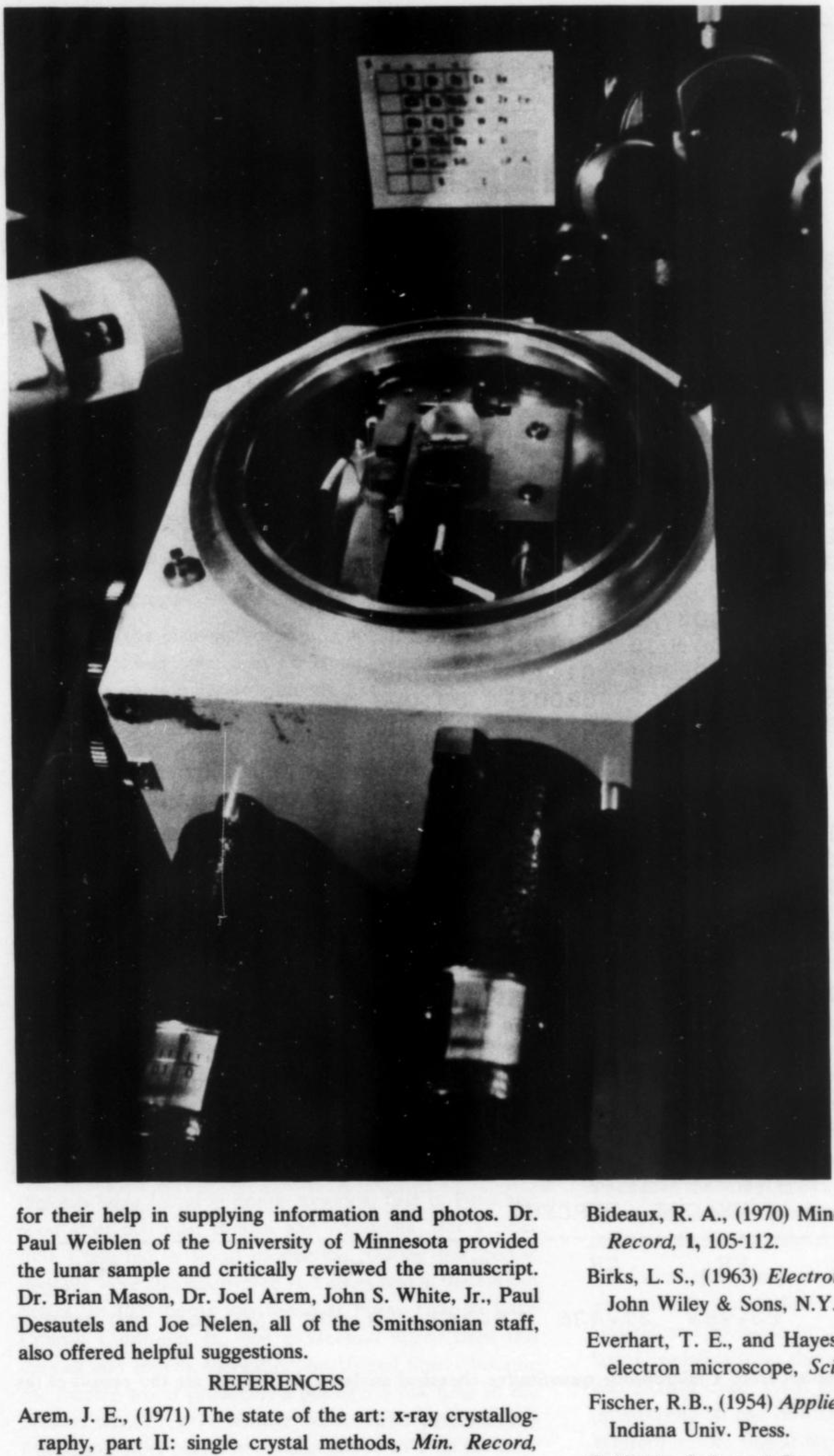

Fig. 15. The sample chamber for the Cameca electron microprobe. The small square block in the center (about one inch square) contains about thirty standards. Directly above the standard holder is a specimen mounted in a clear plastic disc. The light microscope attachment is visible at upper right. The sample chamber slides forward under the column and locks in place, as in Fig. 1. The cylindrical tubes hold controls for adjusting the position of the sample in the horizontal plane. The black dial at left is for vertical adjustment. Photo courtesy of Ed Holdsworth.

for their help in supplying information and photos. Dr. Paul Weiblen of the University of Minnesota provided the lunar sample and critically reviewed the manuscript. Dr. Brian Mason, Dr. Joel Arem, John S. White, Jr., Paul Desautels and Joe Nelen, all of the Smithsonian staff, also offered helpful suggestions.

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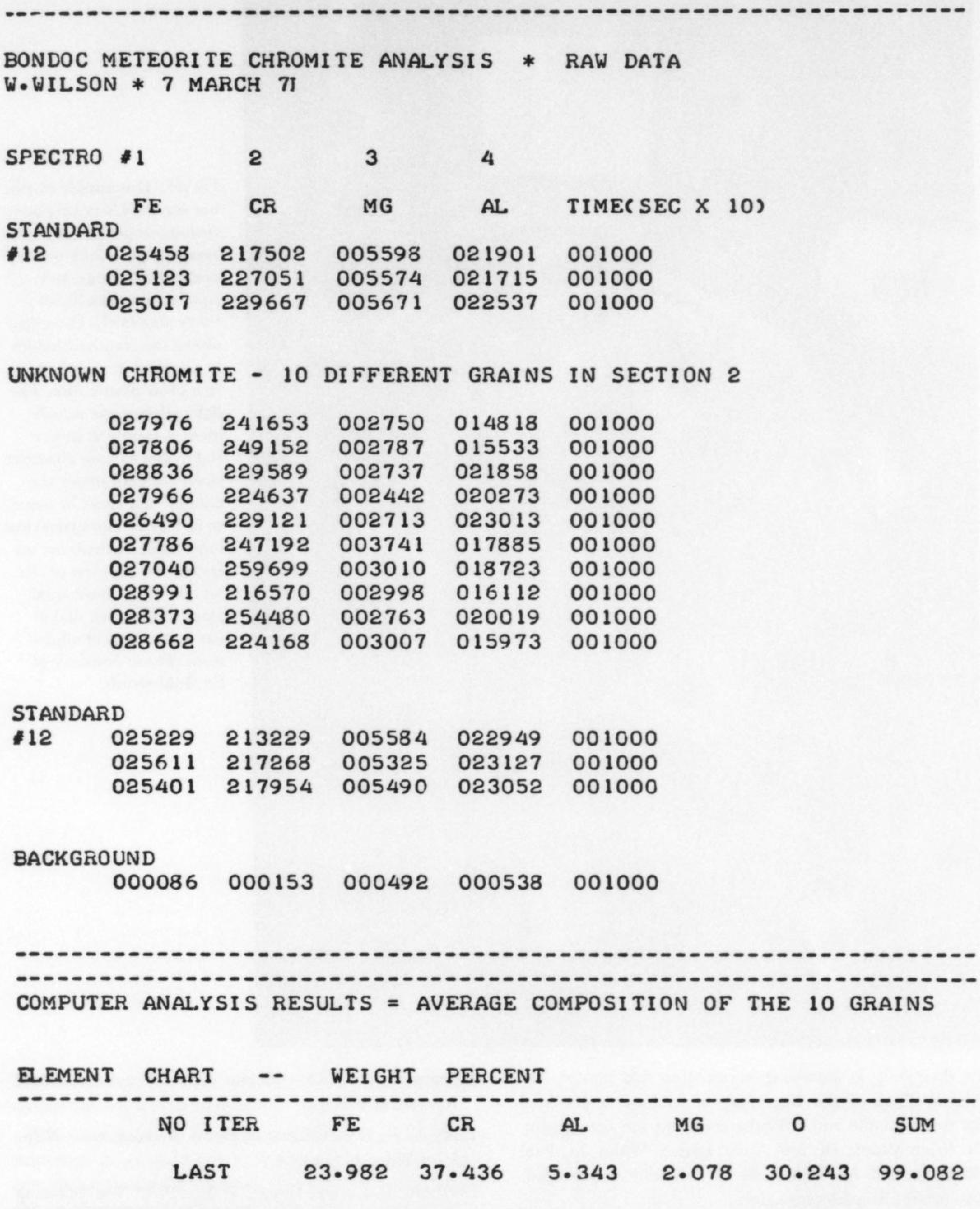

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BONDOC METEORITE CHROMITE ANALYSIS  *  RAW DATA
W.WILSON * 7 MARCH 71


SPECTRO #1       2       3       4

         FE      CR      MG      AL      TIME(SEC X 10)
STANDARD
#12      025458  217502  005598  021901  001000
         025123  227051  005574  021715  001000
         025017  229667  005671  022537  001000


UNKNOWN CHROMITE - 10 DIFFERENT GRAINS IN SECTION 2

         027976  241653  002750  014818  001000
         027806  249152  002787  015533  001000
         028836  229589  002737  021858  001000
         027966  224637  002442  020273  001000
         026490  229121  002713  023013  001000
         027786  247192  003741  017885  001000
         027040  259699  003010  018723  001000
         028991  216570  002998  016112  001000
         028373  254480  002763  020019  001000
         028662  224168  003007  015973  001000


STANDARD
#12      025229  213229  005584  022949  001000
         025611  217268  005325  023127  001000
         025401  217954  005490  023052  001000


BACKGROUND
         000086  000153  000492  000538  001000


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------------------------------------------------------------------
COMPUTER ANALYSIS RESULTS = AVERAGE COMPOSITION OF THE 10 GRAINS


ELEMENT  CHART   --   WEIGHT  PERCENT
------------------------------------------------------------------
           NO ITER     FE      CR      AL      MG      O       SUM

           LAST      23.982  37.436  5.343   2.078  30.243  99.082
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***Fig. 16.* A typical teletype print-out from a microprobe quantitative chemical analysis. At bottom are the results of the computer analysis of the data above.**

E. & F.N. Spon Ltd., London.

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Boron Minerals and Deposits

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PART I *USES, DISTRIBUTION AND ECONOMIC MINERALS OF BORON*

INTRODUCTION

Although the element boron was not discovered until 1808 when it was isolated by Sir Humphrey Davy, borax, one of the common borate minerals, has been known and used for thousands of years. The Babylonians probably welded their gold jewelry using a borax flux and the ancient Egyptians may have used it to preserve their mummies (U.S. Borax & Ch. Corp., 1967).

During the thirteenth century at the time of Marco Polo, the mineral was introduced into Europe and legend has it that it was Marco himself who first brought it from Asia to Venice. Borax found immediate use by the Venetian goldsmiths and for the next five hundred years the mineral, under the name of *tincal,* was a major article of commerce carried by westward moving caravans. This early borax came from Tibet which remained the only source until boric acid was found in steam vents (soffioni) of Italy. With this discovery, late in the eighteenth century, Italy became the chief producer of boron compounds (Connell, 1949).

Before the middle of the nineteenth century borate deposits were found in South America, first in Peru and soon after in Chile, Bolivia and Argentina. For a brief time Chile led in world production. During this period deposits were also discovered in Turkey and in the United States. In 1857 borax was found at Borax Lake in Lake County, California. In 1864 production began from this deposit and shortly thereafter the United States became the leading world producer, a position it has held to the present day. In 1871 borates were found at Columbus Marsh and other playas in Nevada and in 1873 on the floor of Death Valley, California. In 1882 rich beds of the then new mineral, colemanite, were discovered on the east wall of Death Valley and in the following years many other deposits of this mineral were located in California. Thus from the time of its discovery until 1927, colemanite was the chief source of boron compounds.

In 1925 in the Kramer district, Kern County, California, drilling located a large massive borate deposit composed mostly of borax and kernite. Until its discovery here, kernite was unknown. Underground exploitation of this deposit, begun in 1927 near the present town of Boron, forced practically all other borate mines in the United States to close. Later (1957) underground working gave way to open pit mining, and for the next decade over fifty per cent of the world production came from this pit. As great as is this deposit, it is now believed that it stands in second place, exceeded in both size and reserves by the Turkish deposit at Kirka.

Another great reserve of borax, also in California, is in the brines of Searles Lake. Searles Lake is for most of the year a dry lake with its surface covered by a firm, white crust of salt. It has long been known that the huge volume of brines beneath this crust contains from 1-1.2 weight per cent B_2O_3. However, it was not until the 1920's that a process was developed to extract the dissolved salts. Since then the brines of Searles Lake have been the source of not only substantial amounts of borax but also of many other products of economic importance.

Prior to 1930 the annual world consumption of borax amounted to only a few thousand tons. After that date an explosive increase in demand took place which was largely satisfied from the two California deposits, Boron and Searles Lake. Until recent years they produced approximately 90 per cent of the borax consumed by the Western world: Boron 60 per cent, Searles Lake 30 per cent. In 1968 the borax production of the United States was in excess of 1,000,000 tons.

Borates have been produced in Turkey since the end of the last century and, from the available production

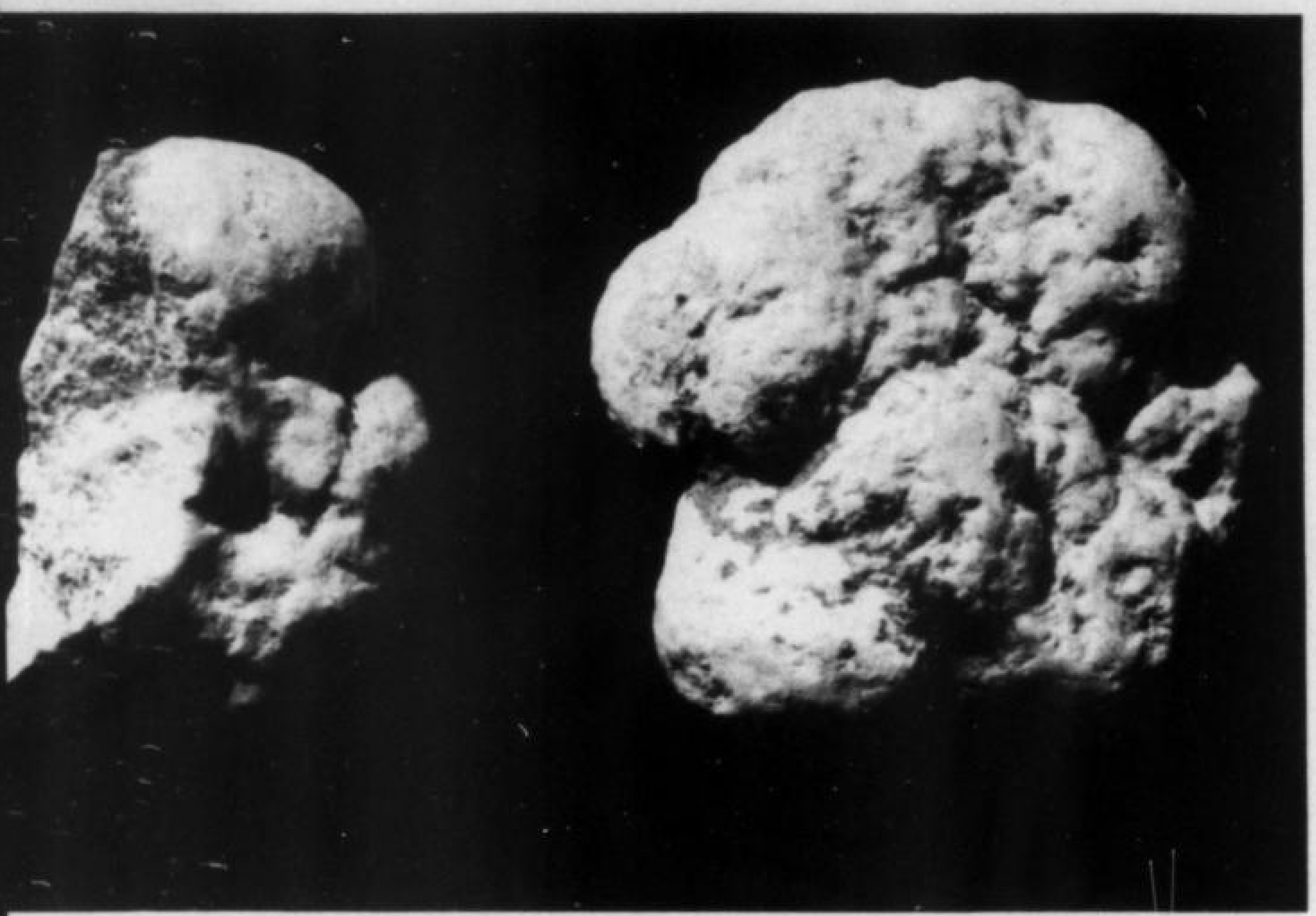

Fig. 1. **Typical "cotton balls" of ulexite composed of aggregates of fibrous crystals. When broken the fracture surface of the nodules shows a characteristic silky sheen.**

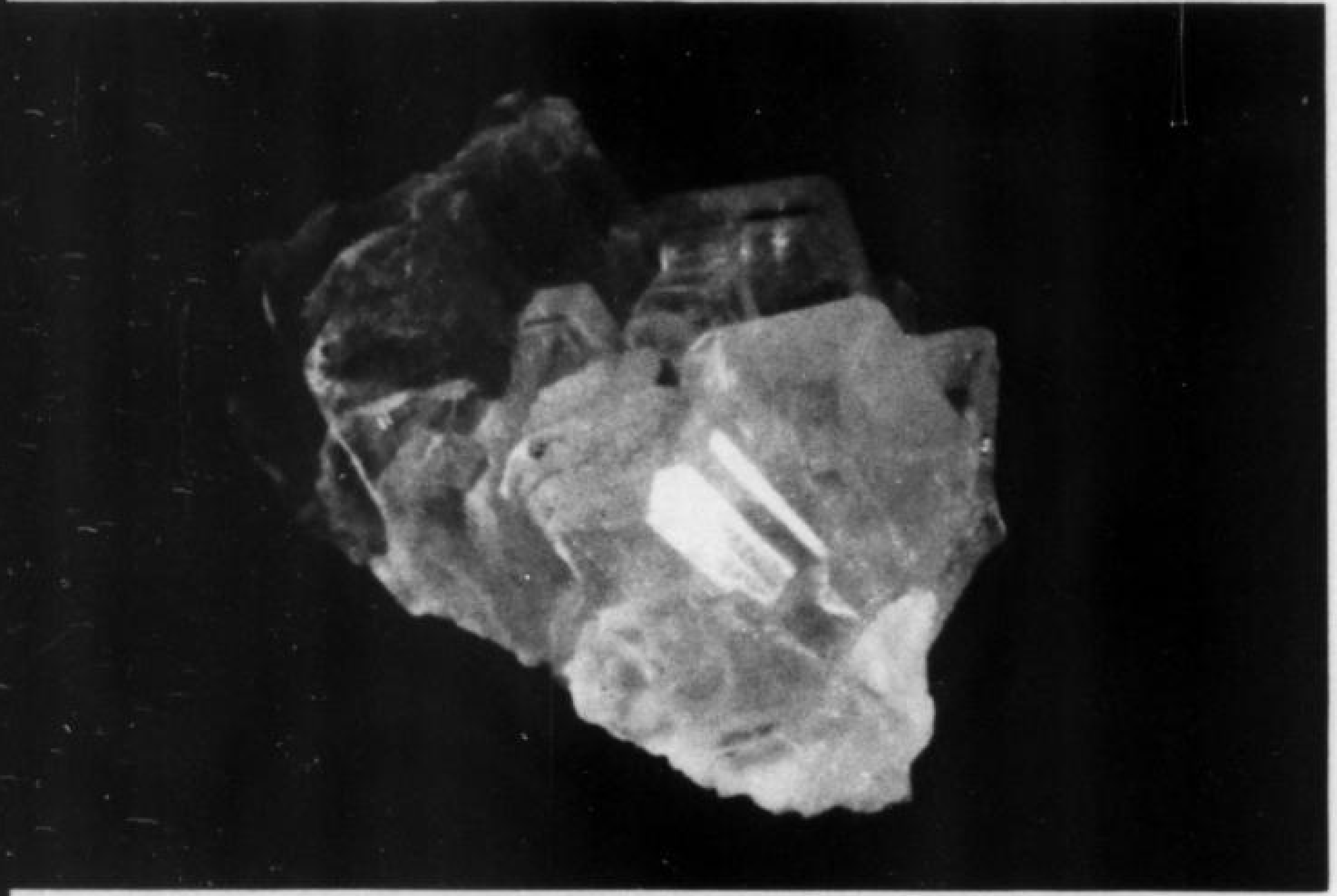

Fig. 2. **Inyoite, in well formed colorless crystals.**

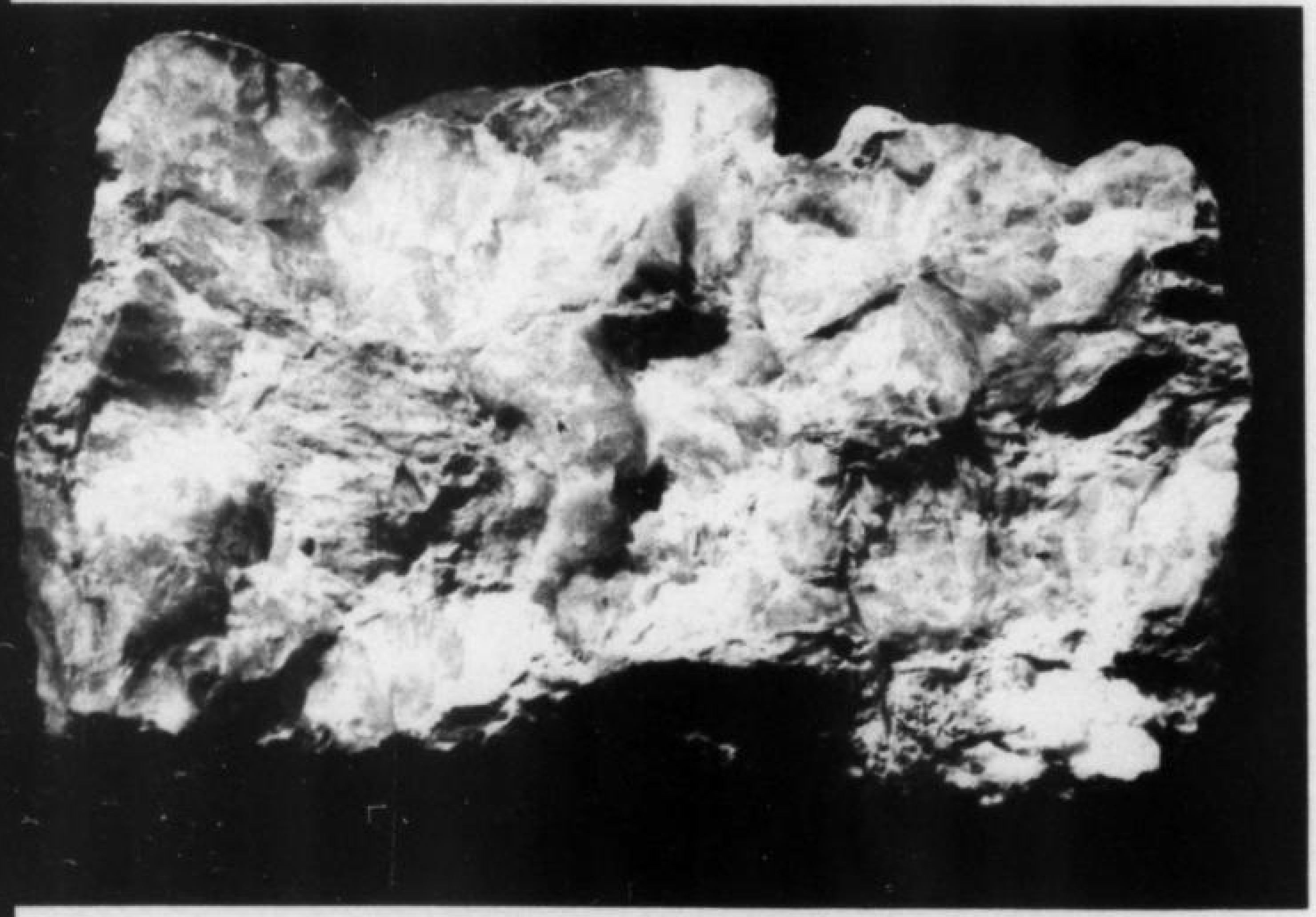

Fig. 3. **Colemanite in radial aggregates.**

figures, Turkey was for many years second only to the United States (Smith, 1960). Until 1954 all recorded production came from the Sultancayiri deposit in Balikesir Province. Since 1950 extensive exploration has resulted in the discovery of important new Turkish deposits. The most outstanding is a massive borax body "about 50 meters thick and of great lateral extent" (Dunn, 1966) located in the area of Kirka, with estimated reserves several times greater than those of Boron, California. Exploitation has been also very active; in 1969 Turkey produced 300,000 tons of calcium borate.

There is a small but steady production of borate in Germany as a by-product of the processing of the Permian saline series of Zechstein. However, because of the present level of consumption, it satisfies only a small part of the country's needs.

Until 1936 the Soviet Union depended on imported raw materials to provide its industry with boron compounds (Die Chemische Industrie,1940). But with the discovery in 1934 of the deposits of the Inder Region, east of the Ural River and just north of the Caspian Sea, it became selfsufficient. However, the meager information available regarding Russian boron deposits suggests that reserves are not large. Unusual minerals such as kotoite, szaibelyite and ludwigite that are mined require a more expensive and complicated mineral dressing process than is necessary for the hydrated borates. In Chile, for example, where there are available accumulations of the playa lake type, these minerals are not considered economic.

Successful exploration during the past one hundred years has resulted in a lowering of prices of boron compounds and a great increase in their consumption. The increase in production to keep pace with demand is shown by a few figures of the production of California, the dominant world producer. The year and approximate production in thousands of short tons are: 1890 less than 5; 1910, 20; 1930, 200; 1950 over 400; and 1968 over 1000.

This rapid increase in production indicates the extraordinary interest in borates, and indirectly their significance in modern technology. Laboratory research has pointed the way to new uses and field investigation has located large new reserves. During the past ten years three large deposits similar in type to Kramer have been found or explored: Tincalayu in Argentina, Kirka in Turkey (already mentioned) and Little Placer near Boron, U.S.A. The scanty information on these deposits suggests that their known and potential reserves are enormous (Industrial Minerals, 1970).

Even though borate reserves are more than adequate for the present and the immediate future, active prospecting and exploration is continuing, and some large consumers are seeking their own deposits.

USES

The principal commercial products are sodium tetraborates: borax, $Na_2B_4O_7 \cdot 10H_2O$ (decahydrate); $Na_2B_4O_7 \cdot$

$5H_2O$ (pentahydrate); and anhydrous $Na_2B_4O_7$. When the presence of the sodium ion or the alkalinity of borax is undesirable, boric acid, H_3BO_3, is used. Calcium borate also has direct application. These products find their greatest use in the glass industry, soap and cleansers, porcelain enamels and agriculture.

Borax and calcium borate are used in the manufacture of glass, particularly in glasses containing a high percentage of B_2O_3, called "borosilicates". The borate increases glass workability, strength and brilliance and gives it a high resistance to thermal shock. Laboratory and cooking glasswear, optical and weather resistant pieces such as traffic light lenses and sealed beam headlights are common objects made with borosilicate glass. Borates are also used in significant amounts in fiber-glass manufacture. This type of fiber is used widely as acoustic and thermal insulation, is woven in fireproof textiles or is combined with plastics in building and construction materials.

The use of borax in soap to hasten its cleansing action is well known. In the last few years the use of sodium perborate in this manner has greatly increased principally because of its mild alkalinity and strong bleaching action.

Borax and boric acid are also major ingredients of porcelain enamels for coating metal surfaces. These enamels provide a very hard, resistant and durable layer with attractive appearance to cover the surfaces of stoves, laundry equipment, refrigerators and appliances in general. Borax has unique properties as a fusing agent, providing low viscosity and great homogeneity to the enamels.

In agriculture borates are used in the preparation of fertilizers and herbicides as well as for washing solutions to control fungus in citrus fruits.

The list of other uses of boron compounds is long and includes the following: as corrosion inhibitors in antifreeze and hydraulic fluids, as abrasives, in cosmetics, pharmaceutical products, electrolitic condensers, food preservatives, insecticides, in the industries of leather tanning, textile, steel, in the manufacture of adhesives and starch, in the preparation of automobile fuels, in ceramics, refractories, metallurgy, metal working, anodyzing of aluminum, in the production of chemicals in general, nuclear shielding, and a host of others.

Boron has a very low atomic weight (10.82) and presents both metallic and non-metallic properties. Because of this dual nature it forms many unusual compounds with peculiar properties. Some very spectacular discoveries have been made, some of them are already available and others wait the possibility of their industrial production.

The manufacture of cubic boron nitride is a dramatic example. The successful synthesis of diamond in 1955 encouraged experimentation with boron nitride. It was argued that if under high temperature-high pressure conditions diamond can be made from graphite, perhaps under like conditions boron nitride, with structure similar to graphite, could be made to recrystallize with diamond-like structure and properties. This was accomplished at a pressure of about 85,000 atmospheres and a temperature of 1800° C. The cubic boron nitride known by the trade name *Borazon* is harder than diamond and has a greater thermal stability (Massey, 1964).

Another example of importance is the use of boron filaments in producing composite materials which, because of their exceptional properties, have great potential applications. The boron filaments have the stiffness and strength that indicate a capability of supporting more than five times the load supported by low carbon structural steel of comparable dimensions (Dunn, 1966). They have in addition the desirable qualities of lightness, resistance to stretching, thermal stability and chemical inertness. Several materials using such filaments have been

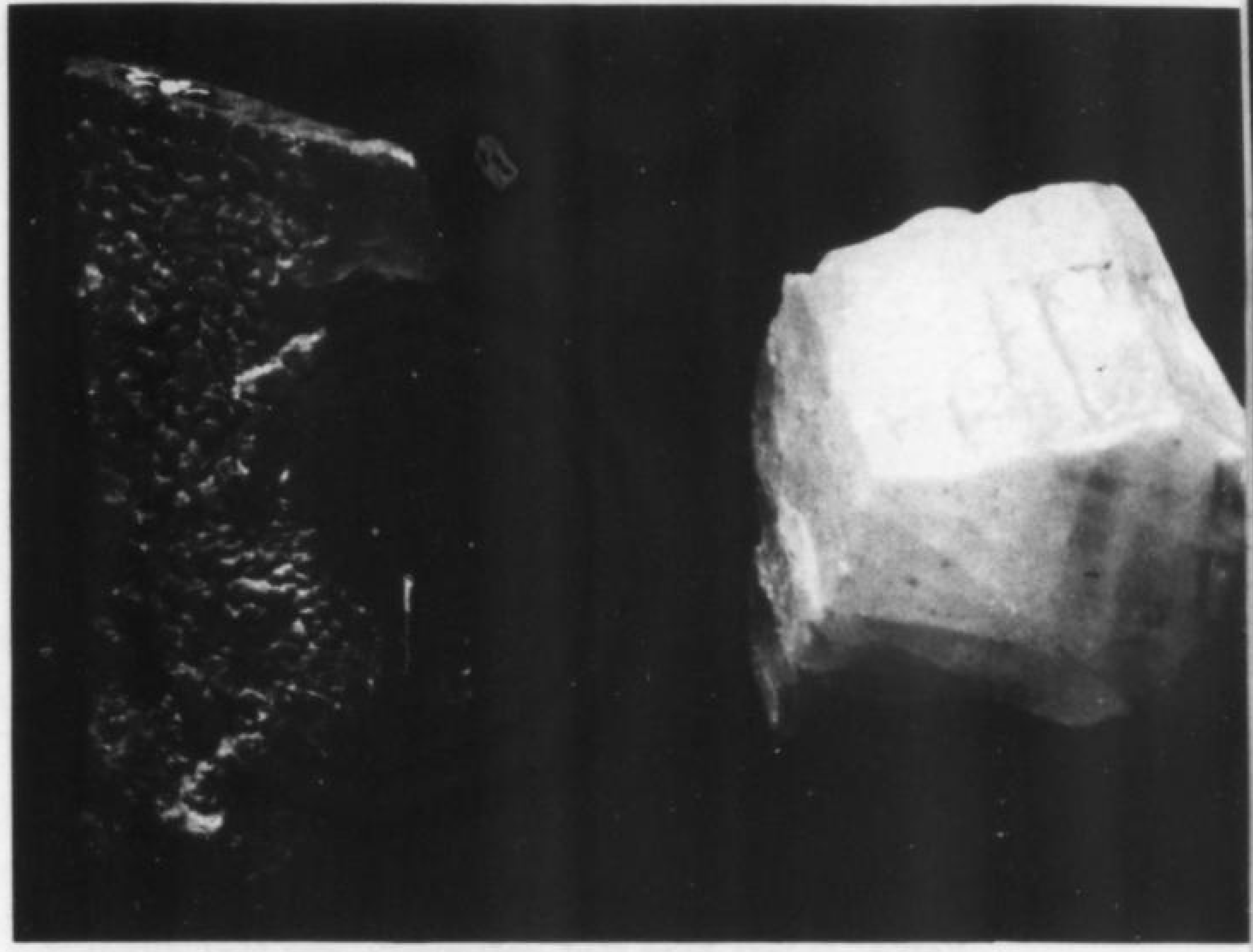

Fig. 4. **Kurnakovite crystals. The crystal at the left has been etched along cleavage cracks.**

Fig. 5. **Irregular nodule of hydroboracite composed of a fine-grained aggregate.**

Fig. 6. **The Ryan Borax works on the east wall of Death Valley. It was here that colemanite was first discovered in 1882.**

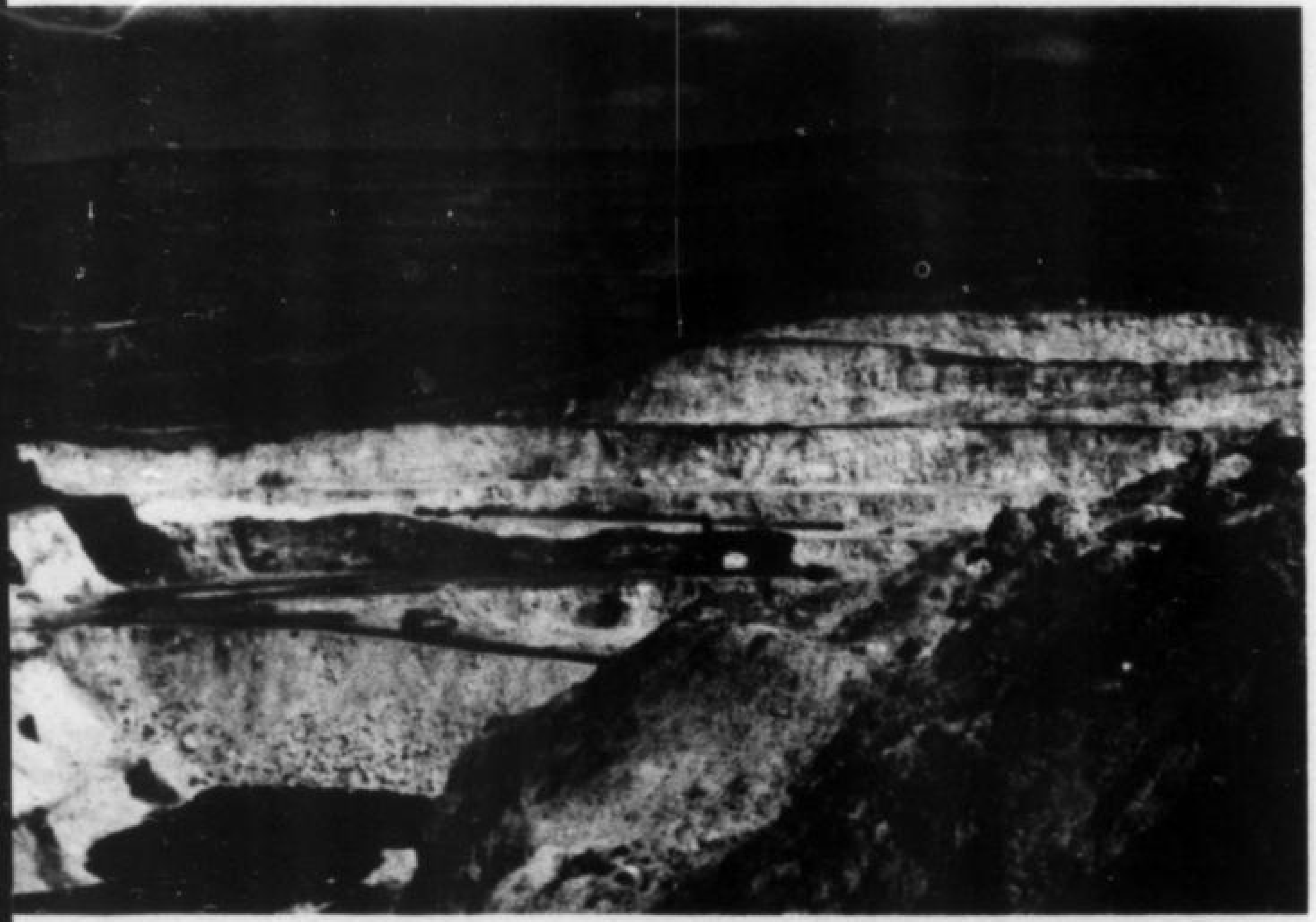

Fig. 7. **Mining of borate minerals in open cut, Boron, California.**

developed, and research is actively going forward on others.

These new discoveries and the rapid increase in the living standard of huge sectors of society the world over will create greater demands for boron compounds. Interest in boron minerals and deposits will grow accordingly.

RECENT PRODUCTION

In Table 1 are given the available figures of borate production in the western world from 1959-1968. Although the data are far from complete, they show the countries where production is significant and their relative importance in the market.

It should be called to the reader's attention that the figures given in the table are for crude ore. They are not given on the same B_2O_3 basis because of the different grades, mineralogical compositions or states of hydration.

WHERE IS THE BORON?

The boron content of the upper lithosphere has long been a matter of discussion and still remains unsettled.

The earliest work on this subject was by Goldschmidt and Peters (1932), who, from a study of 16 German granites obtained an average of 3 ppm of boron. New analyses and investigations on igneous rocks of other areas soon indicated that there are big regional differences in boron distribution. Lundegårdh (1946) found 30 ppm in igneous rocks from Sweden; Sahama (1945) determined 0.9 to 3 ppm for granites and 9 ppm for syenites from Lapland; Nockolds and Allen (1953) obtained 10 to 50 ppm in tonalites from southern California and Lyakhovich (1965) analysed tourmaline bearing granite which contains up to 310 ppm of boron. Relatively large differences were also found in basic and volcanic rocks (Vinogradov, 1960).

Because of these variations it is not easy to assume a representative value of the boron content in igneous rocks; Goldschmidt (1954, p. 283) recognized that his early estimate seems to be in general very low. Taylor (1965) suggested the figure is probably in the range 10-20 ppm and Fersman (1939, in Cherdyntsev, 1961) indicated a boron content of 50 ppm for the earth's crust.

The amounts of boron in sea water and marine sediment are better known and workers are in good agreement. The average content reported for sea water is 4.6 ppm of B; but there are horizontal and vertical variations ranging from 4.3 to 4.9 ppm (Igelsrud, Thompson and Zwicker, 1938; Culkin, 1965). Assuming the average value, there is a total of 6.5×10^{12} metric tons of boron in the hydrosphere.

The marine argillaceous sediments contain relatively large amounts of boron. Landergren (1945) found that there is a direct relationship between the boron in the sediments and the salinity of the water where they were deposited; he also suggested that the rate of sedimentation influenced inversely the boron content. The average values accepted by most authors are in the range of 110 to 120 ppm B (Goldschmidt, 1954, p. 286; Vinogradov, 1960).

Compared with argillaceous sediments, marine limestones and dolomites have low amounts of boron, from 2 to 10 ppm. Sandstones deposited in marine environments have a relatively low content derived from the ocean waters, but detrital tourmaline could increase it considerably. Tourmaline is a borosilicate, strongly resistant to chemical attack and mechanical action and may be a common clastic mineral in the sand fractions. In general the boron content of marine sandstones is somewhat higher (Sahama, 1945) than that of calcareous rocks.

As expected, marine evaporites have a relatively high boron content; and sedimentary marine iron ores are also rich in boron.

Continental clastic sediments are usually extremely low in boron. An exception is found in sediments deposited in arid regions within areas of volcanic activity where

Table 1

Production of crude borates*

Short Tons

Country	1959	1960	1961	1962	1963	1964	1965	1966	1967	1968
Argentina	9,900	5,097	7,656	20,777	27,120	18,049	51,181	39,586	20,124	28,858
Chile	6,345	3,218		4,203	6,573	7,306	5,073	4,125		
Italy	2,741	2,438	1,289		576	352				
Turkey	80,670	76,823	71,678	125,596	141,336	154,322	188,490	248,133		293,100
U.S.A.	619,946	640,591	602,591	646,613	700,183	776,279	807,000	866,000	955,000	1,026,000

*Production figures for Argentina from *Estradítica Minera de la Rep. Argentina* 1960—1965, 1966, 1967, 1968 Dirección Nacional Geología y minería, Argentina.

Other figures from *Minerals Yearbook* 1961—1968, U.S. Bureau of Mines, Washington, D.C.

soils may be also enriched in boron (Vinogradov, 1959). Terrestrial and fresh water clays contain very little boron, 5-10 ppm (Goldschmidt, 1954).

In general, the metamorphic rocks inherited the boron content of the parent rock. But during metamorphic processes, both regional and local, there was mobilization and recrystallization of boron compounds. For example, tourmaline is a common constituent of phyllites. In certain cases there is clear evidence of boron enrichment, in others a partial loss of the same element can be proved. Some authors suggest that the impoverishment is greater in rocks with higher degrees of metamorphism (Landergren, 1945).

Reviewing all the above mentioned figures, the most striking values of boron concentration are in the marine clays. It seems obvious that the sea water provided the boron, but what is not clear is how this element was concentrated in the seas. Goldschmidt (1937, 1954) computed the boron of the sea water and in the marine sediments and compared it with that of igneous rocks eroded during geological time. A spectacular deficiency resulted in the amount of boron contributed by the magmatic rocks.

Repeating these calculations using more recent values of boron content and units of one square centimeter, of the earth's surface, the following figures are obtained. Wickman (1954) estimated that 194 kilograms of igneous crust have been eroded per square centimeter of the earth's surface; and, assuming these rocks contained an average of 20 ppm boron (a conservative value), there are 3.9 grams of boron for each unit. He further calculated that from the 194 kilograms of weathered igneous rock there resulted 209 kilograms of sedimentary rocks. Of this amount 172 kg (82.3%) are shale, 17.3 kg (8.2%) are sandstone and 19.6 kg (9.4%) are limestone and dolomite. The increase in weight of the sedimentary derivatives over the igneous rocks is due largely to added CO_2 but with some additional water and oxygen. Assuming 120, 10 and 6 ppm of boron respectively for shales, sandstones and carbonate rocks, the result is 20.93 grams of boron for each square centimeter column. The estimated weight of water per square centimeter of earth's surface is 278.1 kg with a boron content of 0.5 grams. Adding both values gives a total of 21.4 grams of boron. This figure compared with 3.9 grams of boron in igneous rocks yields a ratio of approximately 5.5:1.

To justify this large imbalance Goldschmidt and Peters (1932) postulated that partition of the volatile boron compounds probably occurred at the beginning of the earth's history, and that they were important constituents of the primordial atmosphere. That a concentration of boron existed in the early atmosphere is no doubt true, but perhaps not to the extent that the above ratio indicates. But there is yet another means that must be discussed by which boron is contributed to the sea.

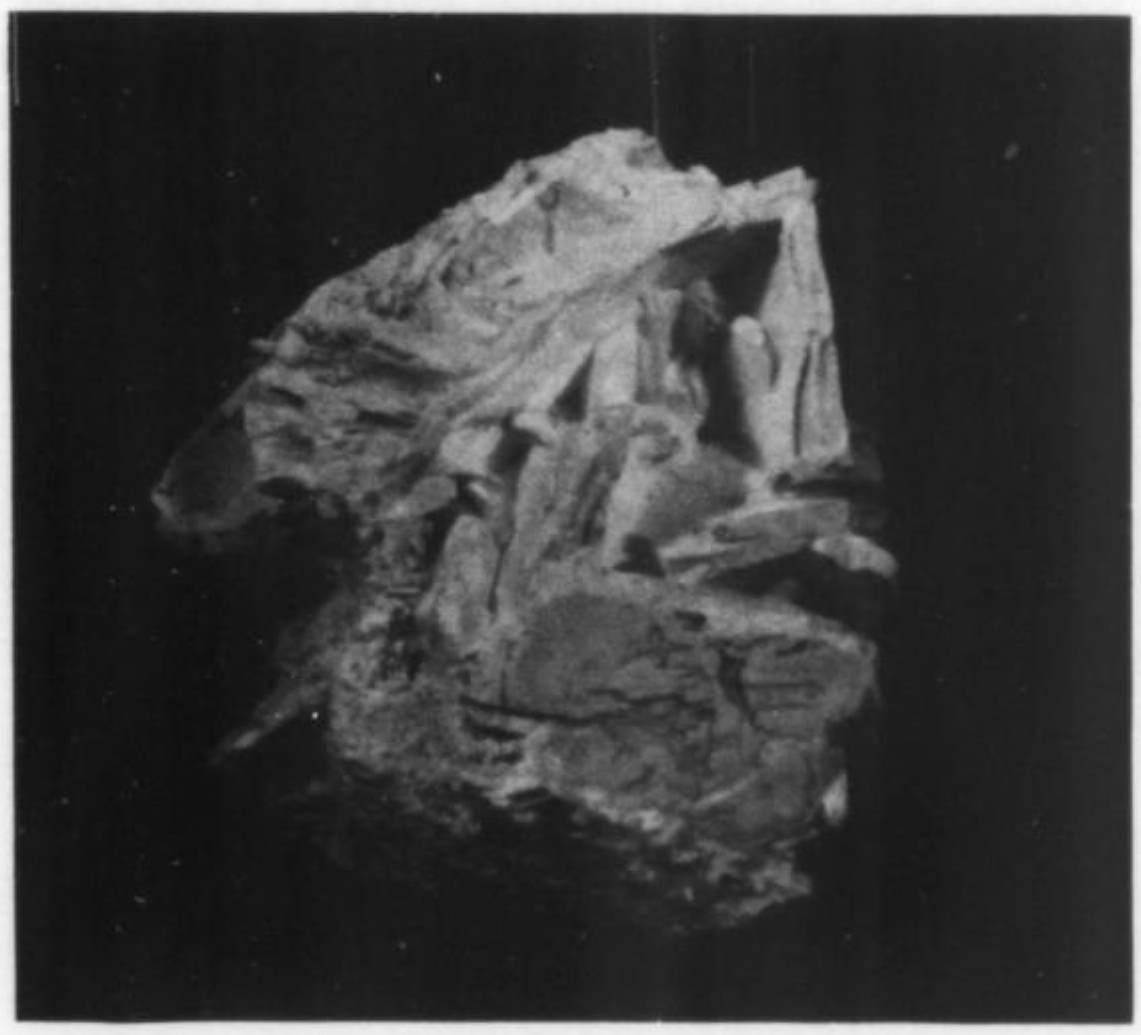

***Fig. 8.* Borax crystals. The crystals originally clear have altered to chalky-white tincalconite.**

Table 2
BORON MINERALS
Economic and Potentially Economic

Mineral	Formula	B_2O_3 content Wt %
Boric acid		
Sassolite	$B_2O_3.\ 3H_2O$	56.30
Hydrated borates		
Borax (= tincal)	$Na_2O.2B_2O_3.10H_2O$	36.51
Tincalconite (= mohavite)	$Na_2O.2B_2O_3.\ 5H_2O$	47.80
Kernite (= rasorite)	$Na_2O.2B_2O_3.\ 4H_2O$	51.02
Ulexite (= boronatrocalcite)	$Na_2O.2CaO.5B_2O_3.16H_2O$	42.95
Probertite (= kramerite)	$Na_2O.2CaO.5B_2O_3.10H_2Oq$	49.56
Tertschite	$4CaO.5B_2O_3.20H_2O$	37.32
Priceite (= pandermite)	$4CaO.5B_2O_3.\ 7H_2O$	49.84
Inyoite	$2CaO.3B_2O_3.13H_2O$	37.62
Colemanite	$2CaO.3B_2O_3.\ 5H_2O$	50.81
Hydroboracite	$CaO.MgO.3B_2O_3.\ 6H_2O$	50.53
Kurnakovite	$2MgO.3B_2O_3.15H_2O$	37.32
Szaibelyite (= ascharite) -	$2MgO.\ B_2O_3.\ H_2O$ -	41.38 -
Sussexite series	- $2MnO.\ B_2O_3.\ H_2O$	- 30.34
Anhydrous borates		
Ludwigite — paigeite series	$Mg_2Fe^{3+}BO_5$ - $Fe_2^{2+}Fe^{3+}BO_5$	17.83—13.48
Kotoite	$3MgO.B_2O_3$	36.54
Borates containing halogene		
Boracite	$Mg_3B_7O_{13}Cl$	62.15
Borosilicates		
Datolite	$CaB[SiO_4](OH)$	21.76
Axinite group	$(Ca,Mn,Fe^{2+})_3Al_2BO_3[Si_4O_{12}](OH)$	5.0-6.5 approx.
Tourmaline group	$Na(Mg,Fe,Mn,Si,Al)_3Al_6[Si_6O_8]$ $(BO_3)_3(OH,F)_4$	9-11 approx.

Boron has a small ionic radius (0.23Å for B^{3+}), too small for it to enter in large amount into the structure of the common rock-forming minerals. When it is thus accommodated, it is mostly in the tetrahedral position of silicon or aluminum in plagioclase feldspar. Boron is an essential element in tourmaline and small amounts of this mineral are present in some igneous rocks. It seems probable, however, that most of the boron in igneous magmas became concentrated in residual solutions that have formed contact metasomatic accumulations, pegmatitic bodies, hydrothermal deposits or reach the surface as hot springs.

The escape of boron from magmas extruded as lava on the earth's surface is easier and more complete than from plutonic rocks. Volatiles given off by volcanic rocks contain large amounts of boron which go directly into the atmosphere and shortly thereafter join the hydrosphere. If the total volume of volcanic rocks reaching the earth's surface during the Tertiary and Quaternary are considered, the boron added to the oceans via the atmosphere from volcanic eruptions during this time must have been truly great. If we extend our reasoning to include all volcanic processes, including submarine activities, that occurred during all geologic time, the amount of boron added to the seas, independently of erosion of the land surface, has been huge. "Huge" has only relative value for information is sketchy regarding the volumes of such gases and vapors and their boron content. However, we do get an indirect clue by analysing the waters of hot springs that issue as a posthumous volcanic effect.

For example, the Searles Lake deposit in California contains in its upper part (20-30 meters thick) an estimated 17 X 10^6 tons of B_2O_3 (approx. 1/3 is B). Quantitative studies based on C^{14} determinations (Smith, 1960), indicate that this tonnage resulted from an annual deposition by the Owens River of 700 tons of B_2O_3 during 25,000 years. The boron content of the river water, less than 1 ppm, was traced to thermal volcanic springs in Mono County containing as much as 11 ppm. There is boron in a lower part of the Searles Lake deposit (8-13 meters thick) that also required thousands of years to accumulate. This example gives an order of magnitude of the boron yielded from a single volcanic source in a geologically restricted period of time.

Table 3
Properties of Important
Boron Minerals

	Crystal System	Sp. G.	Hardness	Remarks
Sassolite	Tri.	1.48	1	micaceous scales
Borax	Mon.	1.71	2 — 2 1/2	3 cl. directions; prismatic crystals
Tincalconite	Hex.	1.88	1	Alt. of borax; white powder
Kernite	Mon.	1.91	2 1/2	2 cl. directions; colorless splinters
Ulexite	Tri.	1.96	2 1/2	3 cl. directions; "cotton balls"
Probertite	Mon.	2.14	3 1/2	2 cl. directions; needle-like crystals
Tertschite	Mon.(?)			fibrous, resembles ulexite
Priceite	Tri.(?)	2.42	3 — 3 1/2	fine-grained; white earthy
Inyoite	Mon.	1.88	2	good cleavage; colorless - white
Colemanite	Mon.	2.42	4 1/2	1 perfect cleavage; vitreous luster
Hydroboracite	Mon.	2.17	2	1 good cleavage: radiating crystals, colorless - white
Kurnakovite	Tri.	1.86	3	1 good cleavage; colorless - white
Szaibelyite Sussexite	Orth.	2.62 ↓ 3.30	3 — 3 1/2	fibers, silky luster; white-yellow
Ludwigite Paigeite	Orth.	3.6 ↓ 4.7	5	fibrous masses; black-green
Kotoite	Orth.	3.10	6 1/2	2 cl. directions colorless
Boracite	Iso.	2.95	7 — 7 1/2	Isolated crystals; colorless - green
Datolite	Mon.	2.9	5 — 5 1/2	Vitreous luster; colorless - green
Axinite	Tri.	3.30	6 1/2 — 7	1 cleavage; brown violet gray
Tourmaline	Hex.	3.0 - 3.2	7 — 7 1/2	No cleavage; commonly black

Another example of boron-bearing spring waters is given by Tagaya (1942). His studies of 404 hot springs of Japan showed they contained boron in the following amounts in ppm: 110 springs contained less than 3; 229 had more than 3 but less than 15; 26 had more than 15 but less than 30; and 39 contained 30 or more.

There are also springs very rich in boron, as Sulfur Bank Spring, California with 720 ppm; and the condensed steam from the Italian soffioni with a comparable amount (Clarke, 1924).

To stress further the importance of boron bearing hot springs associated with volcanic activity, it should be recalled that most of the present known commercial reserves were formed this way during the Cenozoic era. They include the giant Kramer district with reserves greater than 10^8 tons of borax. Furthermore, because of climatic conditions the waters from only a few of the many thousands of boraciferous springs of the world, that must have been active during that era, gave rise to borate deposits.

Because of the several ways, other than by erosion of igneous rock, that boron has reached the sea, it is believed that the sampling of the uppermost part of the lithosphere is not representative of the crust as a whole. Consequently, in the earlier mentioned ratio of 5.5:1 the quotient should be smaller. However, the difference is so great it seems unlikely that even with future evidence it will reach a value near one.

WHICH ARE THE VALUABLE BORON MINERALS?

In view of the steady interest in boron and its compounds, we present here a list of the important boron ore minerals, their chemical compositions and B_2O_3 content (Table 2). A general classification of the deposits is given later in Table 4. The inclusion of the borosilicates; tourmaline, axinite and datolite in Table 2 as potential ore minerals may seem arbitrary, for their B_2O_3 content is low and treatment necessary to extract it in commercial form would be expensive. But it must be understood that the definition of an ore mineral is basically economic and consequently relative. As mentioned earlier, a mineral that is an ore in one country may at the same time not be considered an ore in another country because of political and economic factors and constraints on international trade. For these same reasons, the classification of deposits in Table 4 includes all types of occurrences with present or of possible future economic significance.

A summary of the properties of the important boron minerals is given in Table 3 to facilitate recognition. But perhaps the most revealing proof of a borate is the time-honored test: dissolve the mineral in acid, mix the solution with alcohol and ignite it. A strong green color of the flame will indicate the presence of boron.

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(Part II will appear in next issue)

Fig. 1. **View of the Fairfax quarry showing the wall from which most of the specimens were mined during the 1967 "bonanza". Photo by Medici.**

MINERALS OF THE FAIRFAX QUARRY
CENTREVILLE, VIRGINIA

by John C. Medici
7272 Macbeth Drive, Dublin, Ohio 43017

The Fairfax quarry has been in operation for many years, mining Triassic basalt "trap-rock". For the mineral collector it has been, for the most part, an essentially barren quarry. Minerals have been sought here for more than 30 years, and the usual finds (if any) have been mediocre prehnite, apophyllite, stilbite, quartz and laumontite, typical minerals of the northern Virginia trap-rock. Trap-rock underlies much of the area between Centreville and Leesburg, in Fairfax and Loudoun Counties, respectively. The Fairfax quarry is probably the least interesting quarry in this area, both in quality and variety of material to be found, with the exception of the occurrence described below.

The exception is the well-known bonanza find in a fault zone in the quarry containing giant apophyllite crystals

Fig. 2. **The "doorway" in the quarry wall which gave access to the long prehnite tube on either side. Photo by Medici.**

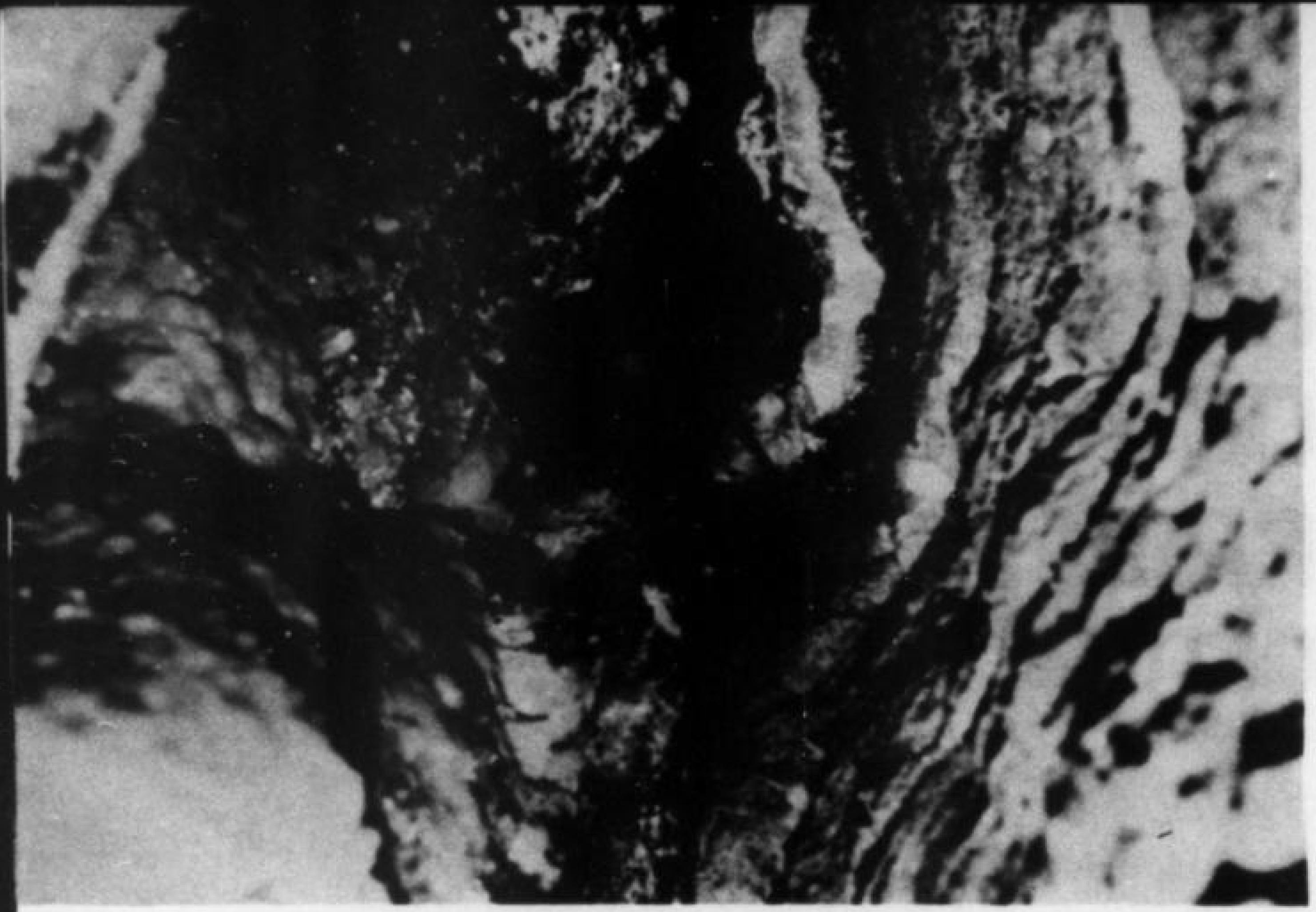


Fig. 3. **Looking into a portion of the prehnite and apophyllite lined watercourse. Photo by Medici.**

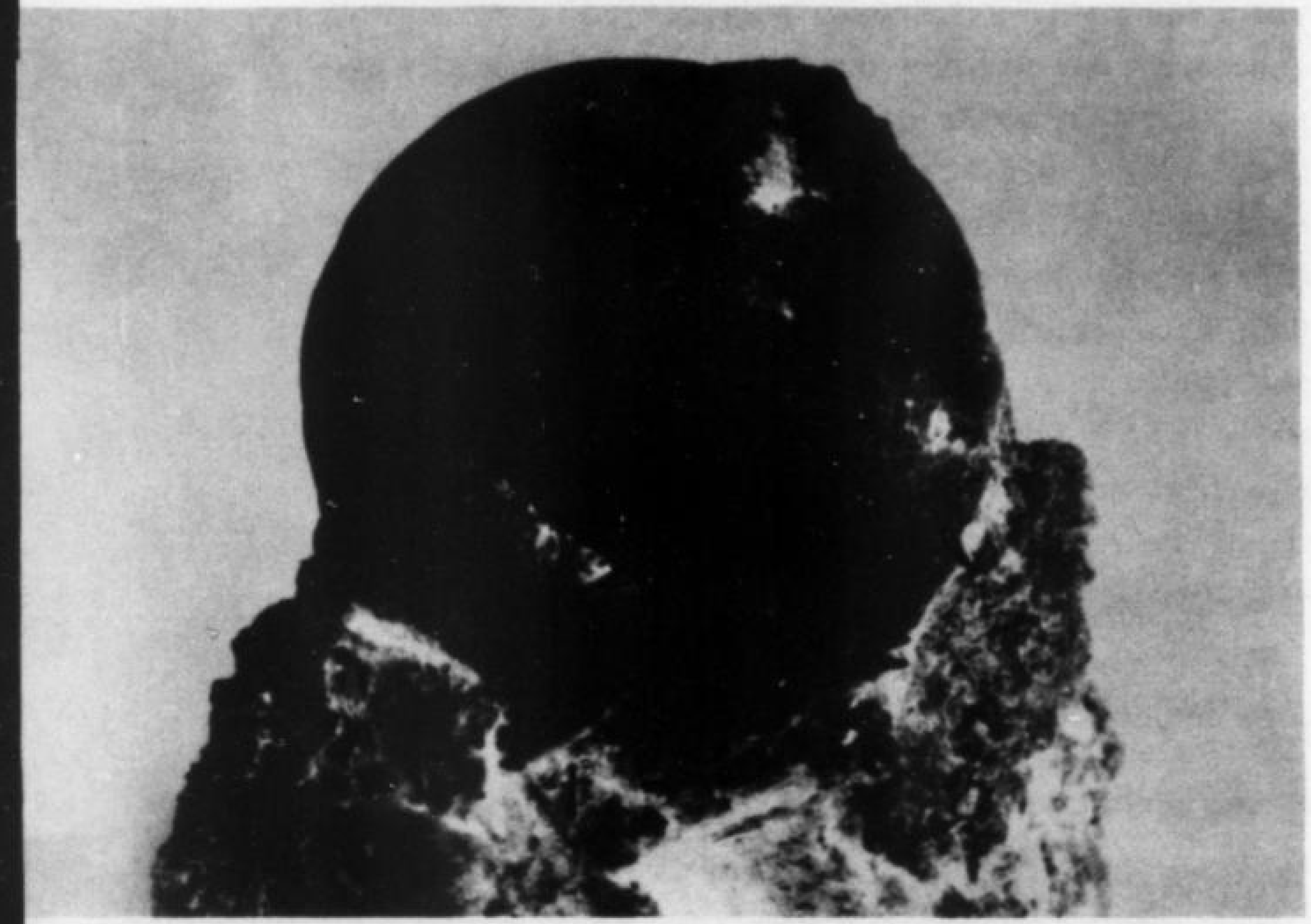


Fig. 4. **A prehnite ball attached to its byssolite and chlorite matrix. The ball is 1 inch in diameter. Note the ridge encircling the "equator" of the ball. Photo by Medici.**

Fig. 5. **Stalactitic prehnite from a cavity surrounded by byssolite and chlorite. Photo by Medici.**

on prehnite. This zone produced some of the finest mineral specimens of apophyllite known. Several are on display at the Smithsonian Institution, only 20 miles from the quarry.

Two tubes of prehnite (probably interconnected) have been found, one in 1953 and the other in 1967. The tubes represented watercourses through the fault. These watercourses provided an opening, in the otherwise dense rock, for the precipitation of crystals. Similar smaller fault-hydrothermal deposits occur throughout this area which probably contains more prehnite than any other area in the world, save the trap-rocks of northern New Jersey.

Since I did not become a mineral collector until 1964 I have no firsthand knowledge of the 1953 discovery. But I lived in nearby Baltimore, Maryland between 1965 and 1968 and heard stories of the find from several seasoned collectors in the Washington, D.C. area. The *Lapidary Journal* (April, 1968) article by Francis Trapp gives some history of Centreville mineral collecting. The 1953 find apparently yielded several times the number of specimens found in 1967. Between 1953 and 1967 remnants of the earlier find were occasionally unearthed. The largest apophyllites, however, were found in 1967. Of these, the largest crystal group (longest dimension 6 1/2 inches) was found by Isaac Richardson and now resides in the Smithsonian.

THE FIND

In early May, 1967, a blast was made in the northeastern corner of the Fairfax quarry. I visited the quarry the next weekend. Nothing showed up, although about 25 feet up the wall remnants of a partially mineralized, nearly horizontal, waterway could be seen extending for more than 100 feet along the wall. In June a heavy rain revealed that this mineralized area contained prehnite balls (exceeding 1 inch in diameter) blackened by actinolite (byssolite) and chlorite inclusions. The area was also filled with chlorite, byssolite, elongated quartz crystals (some skeletal), and chalcopyrite, over all of which I had walked just a month earlier! The rain was also responsible for allowing a "doorway" to be opened to the left (west) of this byssolite region. Across the top of this doorway, about 1 foot in, lay a prehnite tube which was nearly horizontal, extending about 20 feet to the right (east) and 15 feet to the left, parallel to the wall of the quarry. This tube varied from 6 inches to 2 feet wide, and from about one to 8 feet in height. To the extreme left it squeezed down to 6 inches in diameter and was filled with thaumasite. Apophyllite crystals, from micro (mostly cubic in shape) to over 4 inches (rosette-like aggregates of more tabular crystals) were scattered over the inside of the prehnite tube, quite a sight to behold! The small crystals were colorless and the larger mostly translucent milky.

The entire face of the wall was cracked by the blasting in this area and was very dangerous. The fault zone lay one to 4 feet behind this face, which rose to about 60 feet above the floor of the quarry. The rubble from the blast was some 20 feet high allowing easy access to the prehnite tube. The first person to find the area collected some of the prehnite and was then injured (fractured leg) when a quantity of debris fell on him from the wall. He left the quarry quickly to avoid having it closed to collecting by the insurance company, as often happens after such an accident. This was about two weeks before the 1967 National Gem and Mineral Show in Washington, D.C. The quarry was officially closed to collecting at this time due to fear that there would be an accident if people attending the show visited the area with inadequate caution and equipment. Due to my involvement with the show, I didn't get to visit the quarry until the end of the show. At this time, I removed several loose rocks at the top of the doorway to the prehnite tube and was bombarded by about 100 small specimens of apophyllite cubes on an intertwined quartz and chlorite matrix. These had come from an offshoot of the main prehnite tube. The apophyllites were quite uniform in size (~ 3/8 inch), and some of these made very fine thumbnails and miniatures.

The debris that people had been walking on to get to the pocket contained isolated prehnite "shells" surrounded by byssolite and chlorite. One of these contained a very fine prehnite stalactite, or 'finger". Several such fingers, one to 3 inches long, were found in the main tube but these were quite scarce. Unlike those from West Paterson and Prospect Park, New Jersey, they are not casts after anhydrite or glauberite, although some prehnite casts after anhydrite were found at the base of the prehnite tube.

All prehnite tube material was out of reach due to impasses in the tube, so equipment was made for specimen removal. Long electrical conduit tubing, with a bend at the end, was most effective for the side of the tube that was cracked by the blast, but a 6 foot chisel crowbar, 8 to 10 feet long sharpened metal bars, and chisels and hooks welded to pipe fittings were more effective on the solid side of the pocket away from the blast.

In all, about 60 people visited the site during the first two months after the opening of the prehnite tube; some to look, and many to collect. The serious collectors all worked on a buddy system due to the extreme dangers involved. My partners were usually Dave Siegert or Ken Boulier, both from the Baltimore area. Dave came up with most ideas as to equipment, and some of the tools were quite effective.

A week or so after the Mineral and Gem Show, I loosened a large piece of what I thought was thaumasite from the base of the prehnite tube to the left of the doorway. It was about 10 feet out of reach. In hooking it the material clanked like something harder than thaumasite. Care in removing this specimen proved very worthwhile for embedded in the thaumasite was a large apophyllite engulfing a small prehnite mound. The apophyllite is 4 1/2 inches on an edge and 6 inches maximum dimension. I have since removed the thaumasite to expose the entire crystal. It is free of damage due to the protective coating of thaumas-

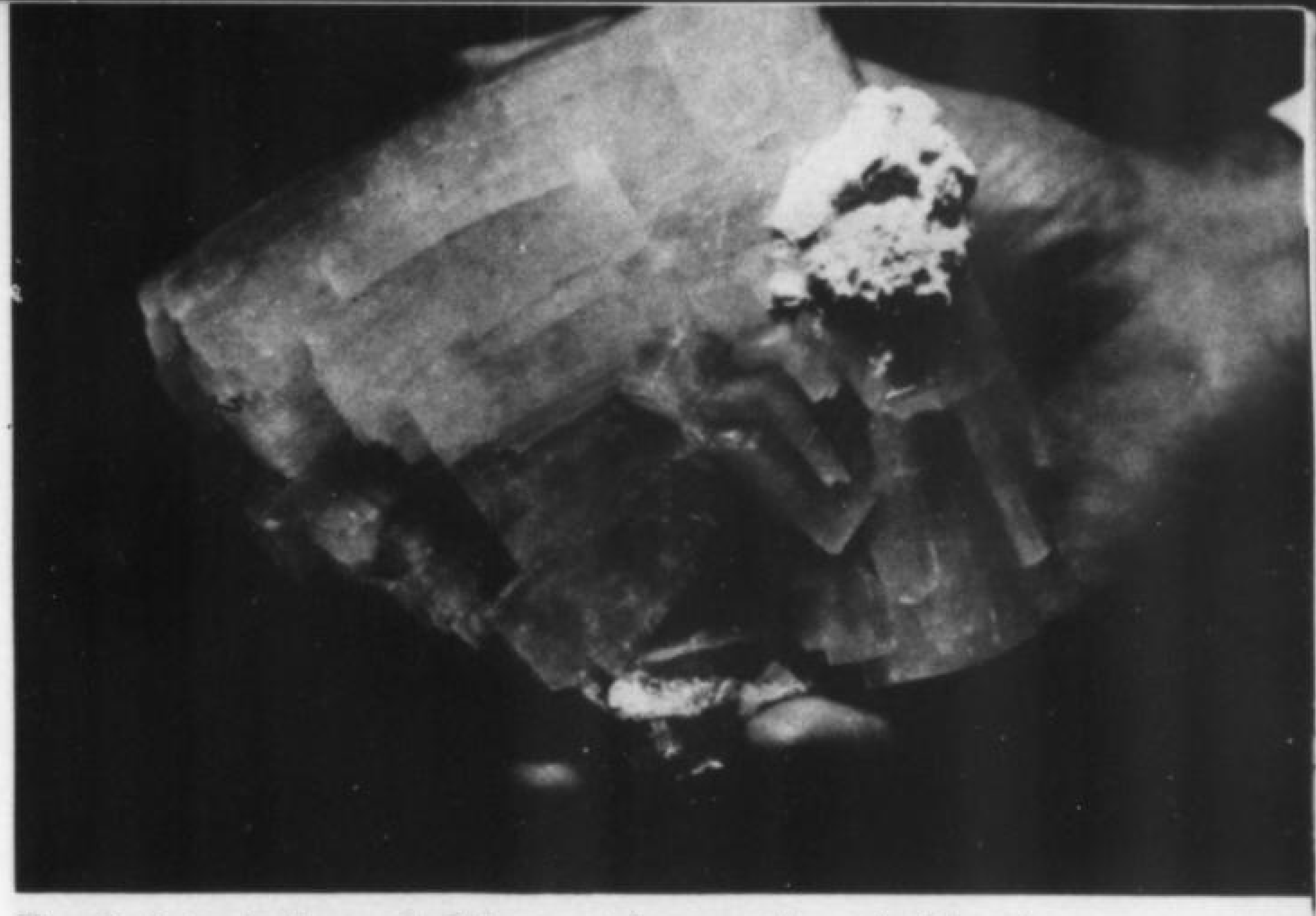


***Fig. 6.* A typical apophyllite crystal group from inside of the prehnite tube. This specimen was found embedded in thaumasite. Photo by Medici.**

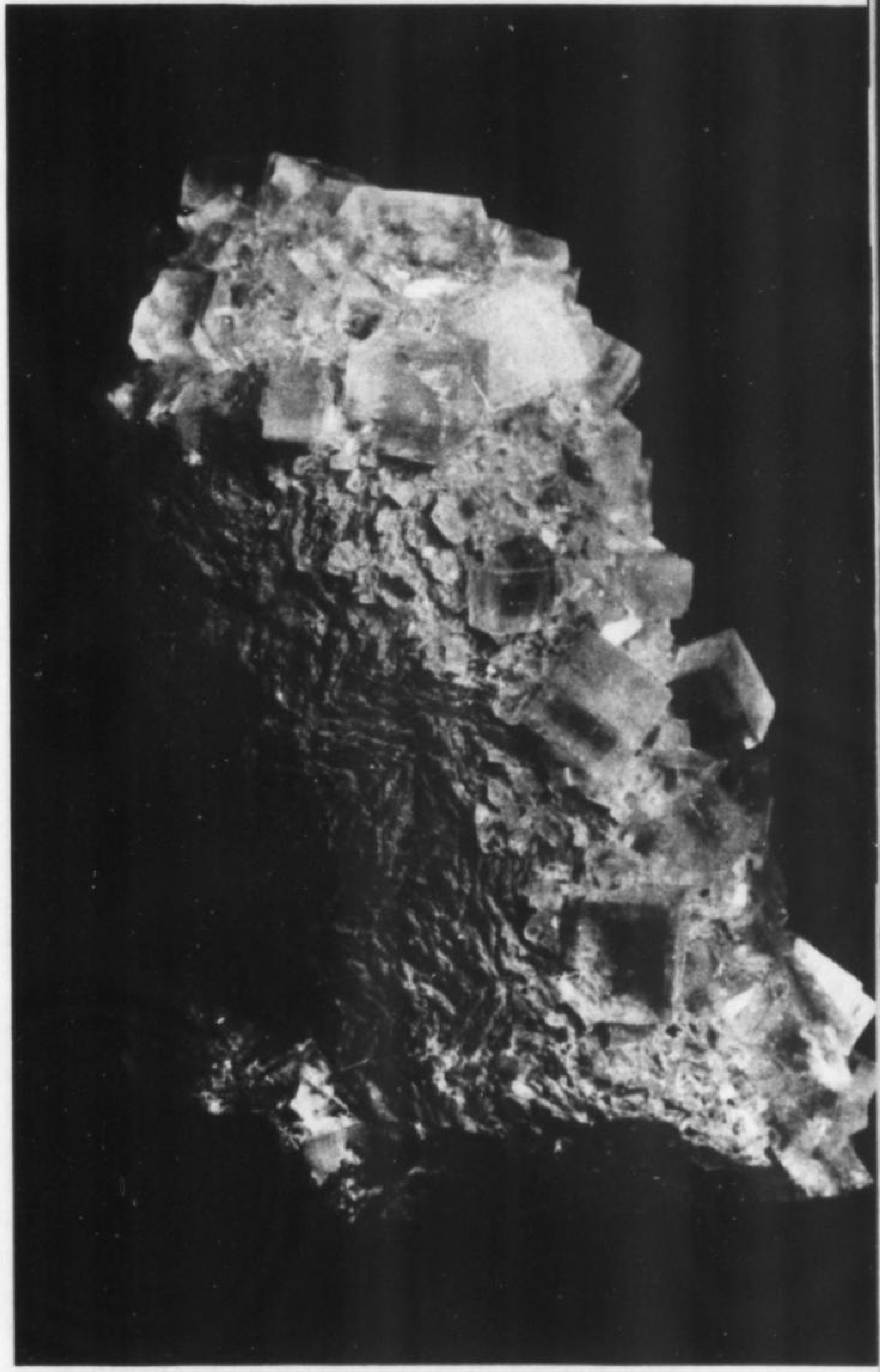


***Fig. 7.* Small (about 1/2 inch) apophyllite crystals attached to a prehnite "finger". Photo by Medici.**

***Fig. 8.* Massive thaumasite from inside of the prehnite tube. Photo by Medici.**

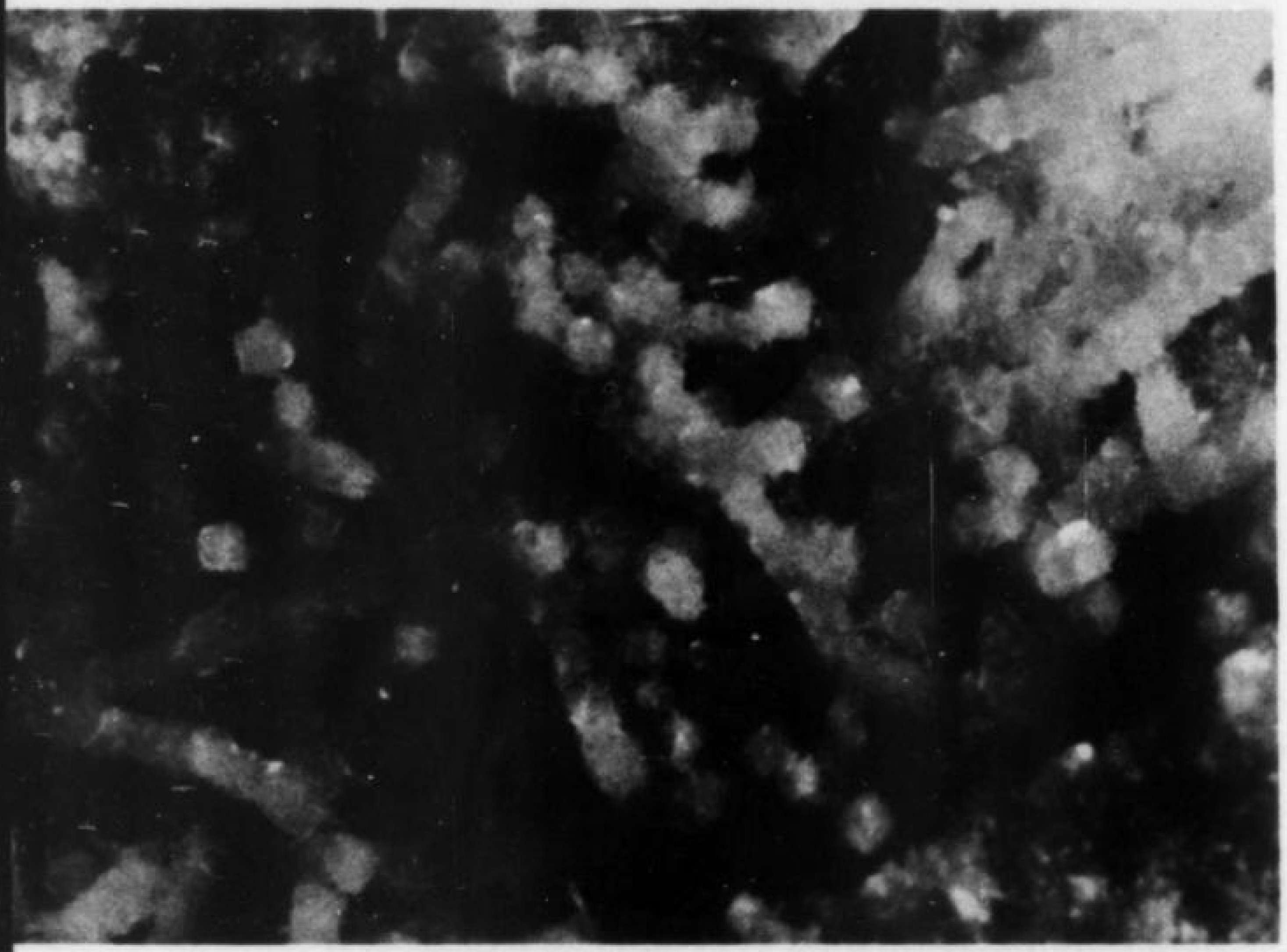


***Fig. 9.* Vermiform prehnite that formed on the outside of the massive prehnite tube lining. The elongate growths consist of stacked prehnite crystals. Photo by Charles Gilchrist.**

ite which nearly completely covered it. Nearly all of the large apophyllites (even the Smithsonian's largest) that came from this prehnite tube were damaged by caving of the roof and side material after the blast. My large apophyllite is probably the second largest from Centreville. Both it and the Smithsonian's are of the translucent rosette type. Most of the other large apophyllites found at Centreville were no more than 3 inches across.

By two weeks after the show, there were a number of collectors, including several families, present at the site. The superintendent, who had been observing the digging off and on during the previous weeks, asked everyone to leave when some of the children and unprepared adults (no hardhats, etc.) got too close to the dangerous overhang.

Not much digging went on for about a month. In the meantime a large portion of the cracked wall fell or was blasted down. My next visit to the quarry was in mid August and the whole doorway area had fallen, exposing a new opening to the west of the original doorway. About 30 feet further west the wall had also fallen, showing that the tube continued through this area and had originally branched out into the quarry. A small opening had previously been visible about 25 feet up the original quarry wall for some time, near the truck entrance to the quarry. I followed a small prehnite tube in this westernmost area for about 6 feet, and obtained one very nice apophyllite specimen. I left a large one at the end of the tube because it would have required another trip for extraction. However, the next time I visited the quarry that area had already been mined by another collector. I found two other collectors working in the biggest opening of the entire tube which continued for a total of about 60 feet. This opening was about 2 feet by 4 feet across and I had the pleasure of seeing the best apophyllite ever found at Centreville as it was collected by Isaac Richardson. This specimen is considered by many to be the best apophyllite specimen in existence. At one point the prehnite tube in this area divided into two tubes separated by byssolite with chlorite balls impaled on the byssolite hairs — quite spectacular specimens. Richardson had just recovered from an appendectomy, but he worked this 10 to 12 foot long area for nearly 5 days and accounted for many fine pieces of prehnite.

Meanwhile Siegert and I spent 10 hours removing overburden from the central opening and began working toward the other two collectors. In the two days that we worked the area we removed several of what are probably the most desirable specimens to come from Centreville, in terms of form and quality. This interval of Centreville collecting will probably be remembered by several of us as the most enjoyable and rewarding we've ever experienced. Lying in that tube of prehnite as we worked was like lying in a dream world, surrounded by sparkling crystals on a bright green background.

Thoughts of our well-being and that of our vehicles were at times secondary. The tube was tight, and one would find himself hammering a chisel in front of his face. One glance of the hammer against the wall of the tube and all you could do was wait for the glance back off your head. In one period of about four hours Ken Boulier, who had just had a gall bladder operation, helped me extract about 8 feet of the prehnite tube and lower it down to the floor of the quarry in a knapsack. I did most of the digging and Ken did the transporting to the car. When the car was loaded we thought one of us might have to walk home to save the springs and keep the tail of the car from dragging. Our headlights illuminated the tops of the telephone poles on the way home.

The prehnite tube was worked sporadically for about 5 months until November, 1967. At that time there were still several sheets of prehnite left in tight areas in the right side of the tube. Underneath the main tube, globs of prehnite and thaumasite, with epidote, magnetite, byssolite, chlorite, titanite, and bornite inclusions, were found. Some of this thaumasite was good enough for lapidary work. Ken Boulier and Anita Siegert have cut thaumasite and some very fine prehnite cabochons from Centreville material.

Considering the number of people working the area, and the danger, accidents were few. This was due mainly to great care taken by most. Ned Blandford broke a finger in a freak accident and Dave Siegert needed a few stitches in the head but in general we can consider ourselves lucky to have left this area without a serious injury. The collecting had required a great amount of rope climbing and work in tight places. In the Fall of 1967 several of us suffered from silicosis due to the large amount of byssolite dust present in the close quarters of the prehnite tube.

MINERALOGY

Mineralogically the base of the prehnite tube was the most interesting. The large apophyllites were nearly all at the base, inside the tube. However, the tube had cracked during its formation so apophyllite and prehnite were also produced on the outside of the tube. The prehnite at the base of the tube contained many tiny vugs and was more than 6 inches thick in places. The vugs were commonly lined with good prehnite crystals. In one vug stacked prehnite was found in a vermiform shape with water-clear apophyllite crystals hanging on byssolite hairs. Two unusual sulfosalts were found in the prehnite vugs. Wittichenite (Cu_3BiS_3) was seen frequently, and cuprobismutite ($CuBiS_2$) rarely. The latter was found as brittle hair-like crystals growing out of wittichenite crystals. One crystal of cuprobismutite formed a perfect bedspring-like coil. Wittichenite occurred in two distinctly different habits. It was found in irregularly shaped, rope-like growths having an etched-appearing dull gray surface and in stubby, lustrous, highly modified crystals. Other small metallic crystals of a copper color were determined, by x-ray, to be a mixture of wittichenite and bornite, though the bornite may have been present only as a coating.

Two distinctly different types of both apophyllite and prehnite are obvious. The difference can be attributed to their having formed either inside or outside of the prehnite tubes. Prehnite inside the tubes is inclusion-free and a beautiful bright green in color. That on the outside is dark green to nearly black due to inclusions of byssolite and chlorite. Much of it is intergrown with quartz crystals. The prehnite balls were found here and undoubtedly owe their origin to having been able to grow while nested in byssolite. Apophyllite inside the tubes is also inclusion-free and is usually seen in rosettes of tabular crystals. Apophyllite outside the tubes is cube shaped and is uniformly heavily included by byssolite and chlorite.

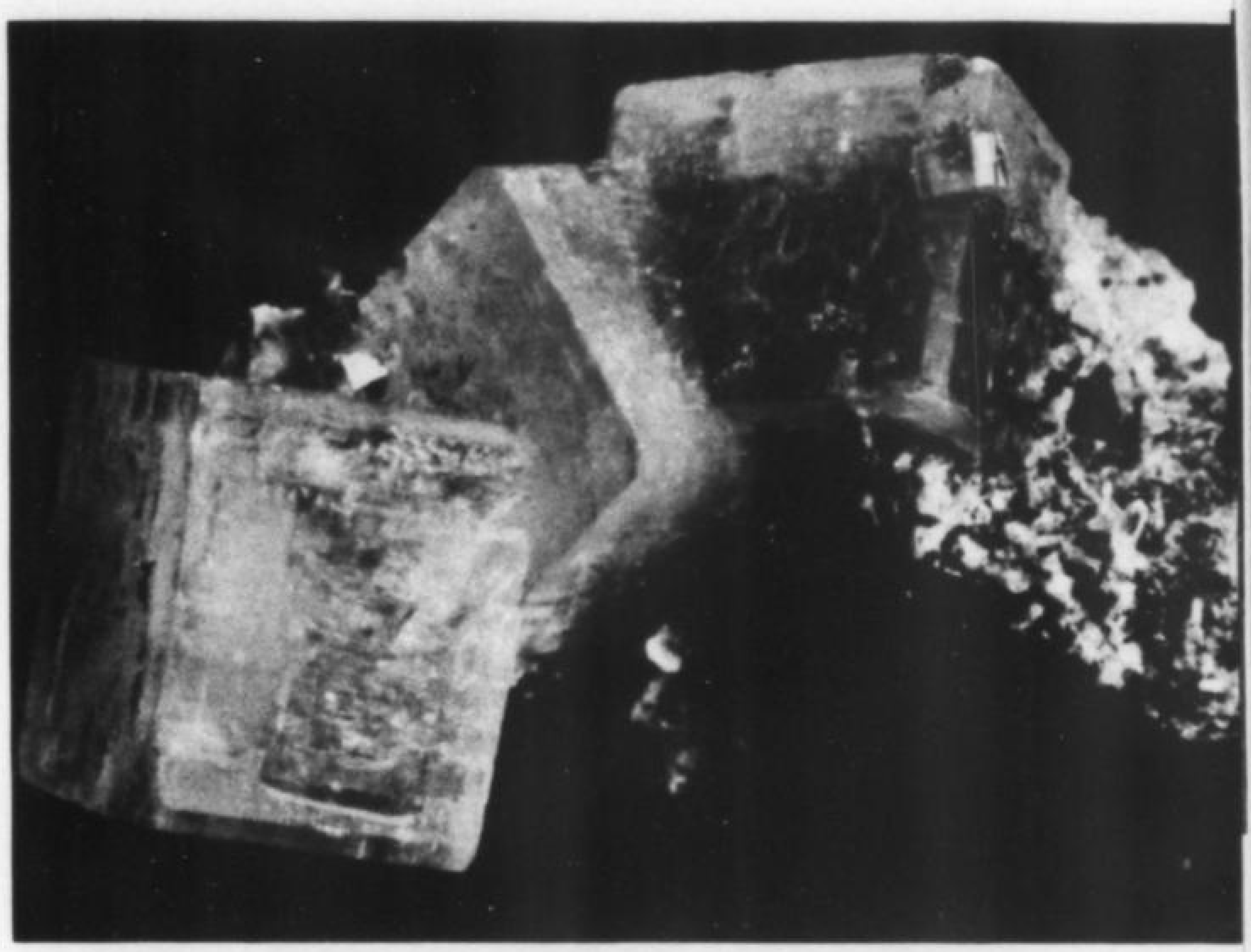


***Fig. 10.* Typical apophyllite pseudocubes from outside of the prehnite tube lining. Hundreds of these crystals were collected and all were approximately 1/2 inch on an edge. Photo by Medici.**

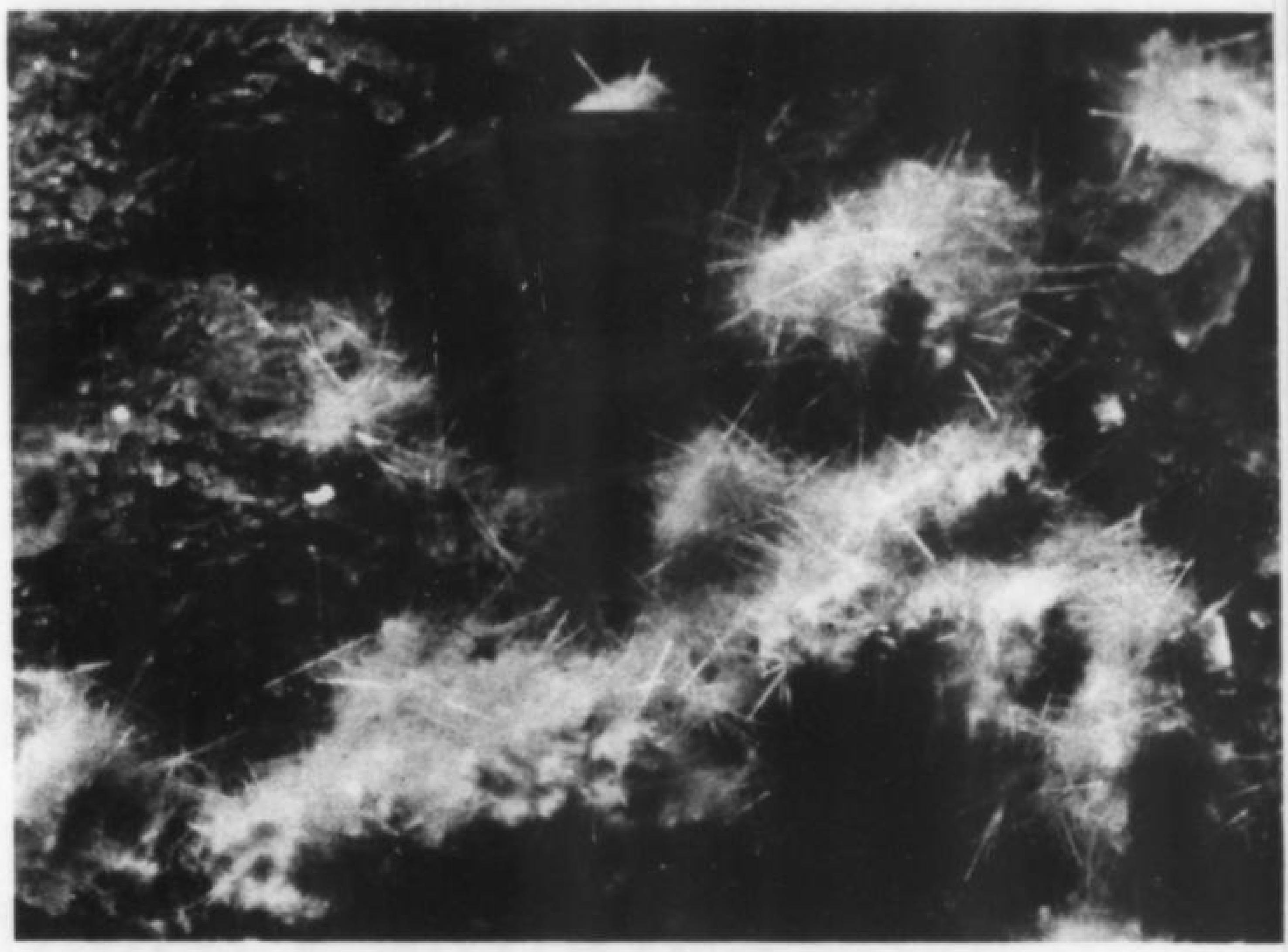


***Fig. 11.* Thaumasite and apophyllite on prehnite. Photo by Charles Gilchrist.**

The explanation for these differences seems simple. The material forming inside the tubes was separated from the wallrock so the parent solutions could not react with it. However, the solutions on the outside of the tubes did react with wallrock to form abundant byssolite and chlorite, much of which became incorporated in apophyllite and prehnite.

Large, crudely tetrahedral crystals of bornite were found embedded in prehnite, associated with byssolite, at the base of the tubes in contact with altered wallrock. These are considered by many collectors to be pseudomorphs after chalcopyrite, which is common in the quarry and is found in other parts of the fault zone. Some chalcopyr-

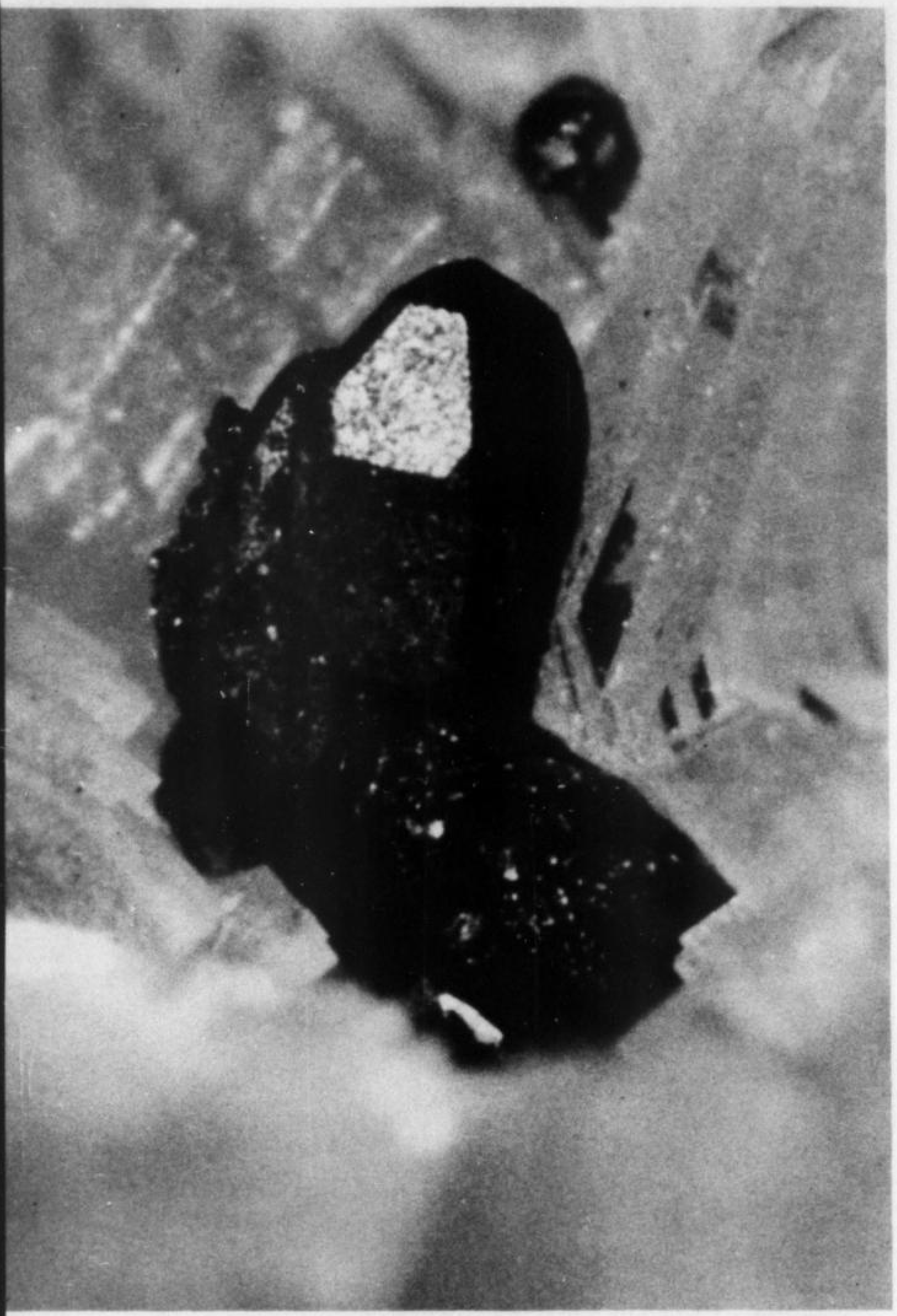


Fig. 12. **Wittichenite crystals on prehnite. The largest crystal is only 1 mm in length. Photo by Ben Kinkead.**

ite was found partly altered to bornite. The bornite "pseudomorphs" are large, some in excess of 3 inches and most about one inch across. These appear to have been among the very first minerals to form in the fault zone. The wallrock must have been covered with free-standing chalcopyrite crystals before any prehnite was precipitated. When prehnite began to form it buried the sulfide. It is impossible to know whether the conversion to bornite occurred before the prehnite crystallization or after it. A very small amount of chalcocite has been found in association with the bornite.

In addition to wittichenite-cuprobismutite, another pair of chemically similar and equally interesting minerals is found at Centreville. One of these, thaumasite, is abundant and the other, okenite, is rare. Thaumasite is an unusual mineral because it contains the sulfate, silicate, and carbonate anionic groups. It was very plentiful in the 1953 discovery. Large masses of solid, white, chalky-looking pieces were collected. It often completely buried the earlier formed minerals prehnite and apophyllite. In the later discovery it was found inside the prehnite tube in a few isolated sections. It occurred as white, radiating groups of crystals up to one cm across, and provided interesting specimens. The surfaces of solid thaumasite masses are covered with very delicate needlelike, colorless crystals. The only specimen on which okenite has been identified is a warty mass of prehnite with small colorless to pearly apophyllite crystals scattered over its surface. Small white specks (about one mm in diameter) of okenite are spread unevenly over this surface. These specks appear soft as velvet with tiny colorless "whiskers" sticking out slightly above the surface all around. Thaumasite, in colorless, acicular crystals up to one cm long, is scattered over all three minerals, okenite, apophyllite and prehnite. Much of the pale blue prehnite found at Centreville owes its color to a very thin film of either thaumasite or okenite on its surface. This film is usually white but often passes into blue. Its presence is a problem because it hides the attractive green prehnite and no satisfactory way is known of removing it.

Calcite at Centreville is usually in small crystals, orange in color. It is found in simple scalenohedra on prehnite and byssolite at the base of the tube and nested in thaumasite. More rarely it occurs as colorless, highly modified, equant crystals on prehnite.

Resinous brown to yellow wedges of titanite are restricted in occurrence to the open outer tube areas heavily forested with byssolite, quartz, chlorite and epidote. Included in the list below are some minerals found in the more massive trap-rock which are of little interest to collectors.

The absence of sodium would seem to account for the absence of such common trap-rock minerals as natrolite, heulandite, analcime, etc. Stilbite and laumontite have been identified in other areas of the quarry not associated with the fault zone minerals. The following list includes all minerals reported at Centreville; those in parentheses have not been verified.

Silicates

prehnite
apophyllite
laumontite
stilbite
actinolite-tremolite
"byssolite"
chlorite
titanite
epidote
quartz
thaumasite (also a
carbonate-sulfate)
okenite
diopside
babingtonite

Oxides
  magnetite
  hematite
  ilmenite
Native elements
  silver
Phosphates
  apatite
Carbonates
  calcite
Sulfides and Sulfosalts
  sphalerite
  bornite
  chalcopyrite
  chalcocite
  (wurtzite)
  wittichenite
  cuprobismutite
  (jamesonite)
  (greenockite)

FUTURE

The future of the Fairfax quarry looks bleak. The apophyllite- and prehnite-containing fault zone runs parallel to a highway at the front of the quarry, and the quarry will probably never be widened in such a way to expose more of this fault zone. Prehnite will be found at the quarry in small pockets occasionally, and will sometimes be associated with apophyllite, but the probability of another large prehnite concentration being exposed is unlikely.

Fig. 13. **White okenite attached to prehnite and apophyllite. Note that okenite densely covers the prism faces of apophyllite crystals but does not appear on the pinacoid faces. Photo by Joel E. Arem.**

Acknowledgements

The author is indebted to John S. White, Jr. for identifying many of the Centreville minerals and for editing of the manuscript. I am also grateful to Charles Gilchrist, Anita Siegert, and Ben Kinkead for many of the photographs.

What's New in Minerals?

Photos by Joel E. Arem

MORE ON BARYLITE

Since the last issue (Vol. III, no. 3) in which the extraordinary barylite crystal from a microcline (amazonite) pocket in Park County, Colorado was described, additional information has been supplied by the discoverer, Clarence Coil of Colorado Springs. He reports that the pocket "wasn't very large. It was confined in a four square foot area with a few stringers running down and pinching out at a two-foot depth. The pocket was level in a gully having a 30 degree slope." Mr. Coil let me examine some of the other specimens taken from the pocket—a most unusual suite of minerals for a pegmatite! The barylite is only part of the story.

Bearing on the occurrence of barylite (barium beryllium silicate) are the colorless crystals of barite found in the pocket by Mr. Coil. As can be seen in the photograph the barite is in perfectly normal looking tabular crystals, maximum size about 1 inch in length. One cannot escape the conclusion that barite was present in the rock that the pegmatite invaded. Some of the barite could have reacted with beryllium and silicon rich hydrothermal solutions to form barylite.

The discovery in the pocket of a 1 inch group of black cassiterite crystals (see photo) is not too surprising as cassiterite is a common pegmatite mineral. However the matrix of the cassiterite is an almost pure mass of dark purple fluorite crystals, a mineral not often encountered in pegmatites but one commonly associated with barite. If we may assume that the host rock contained barite then it follows that fluorite was probably also present and did not come from the pegmatite itself.

The remaining minerals gathered in the pocket include large (more than 1 inch on an edge) calcite rhombs, quartz (colorless druses, smoky, amethyst and chalcedony), clay, limonite(?), and amazonite.

The suite is rather remarkable, as stated earlier, and would have made a fine research subject for someone had he been able to collect the entire contents of the pocket along with some of the host rock. It would be interesting to learn if the latter is a barite and fluorite bearing sedimentary rock (limestone). The specimens shown in the accompanying photographs belong to Mr. Coil. I am deeply indebted to him for allowing me to examine them and have them photographed.

WULFENITE FROM MEXICO

All collectors must be familiar with the thick, caramel-colored wulfenites from Los Lamentos because they have come out of Mexico by the hundreds of thousands and are handled by every retail dealer in the world. The excellent orange tabular crystals in uncomplicated placements on white to light-grey calcite from the San Carlos mine, in Chihuahua, are also becoming widely known but these are not, and never have been, plentiful. Now there is a third major locality for wulfenite in Mexico—Cerro Prieto, 40 miles southeast of Hermosillo, Sonora (this according to George Bideaux, *Brewery Gulch Gazette,* May 1972).

***Fig. 1.* Cluster of colorless barite crystals. Clarence Coil specimen.**

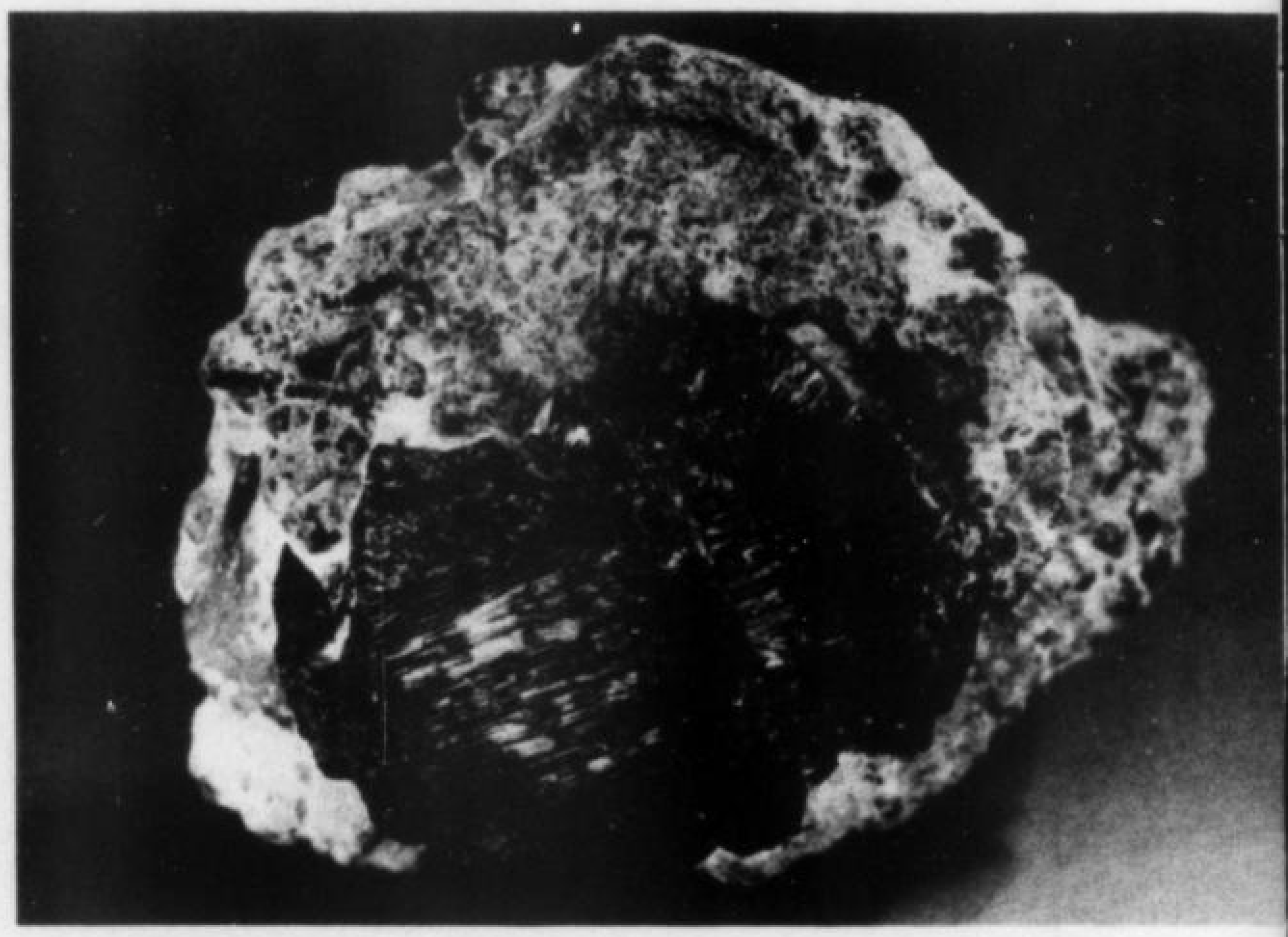


***Fig. 2.* Cassiterite crystals on mass of fluorite crystals. Clarence Coil specimen.**

Fig. 3. **Smoky quartz crystal 1 inch long coated by calcite and embedded in chalcedony. Clarence Coil specimen.**

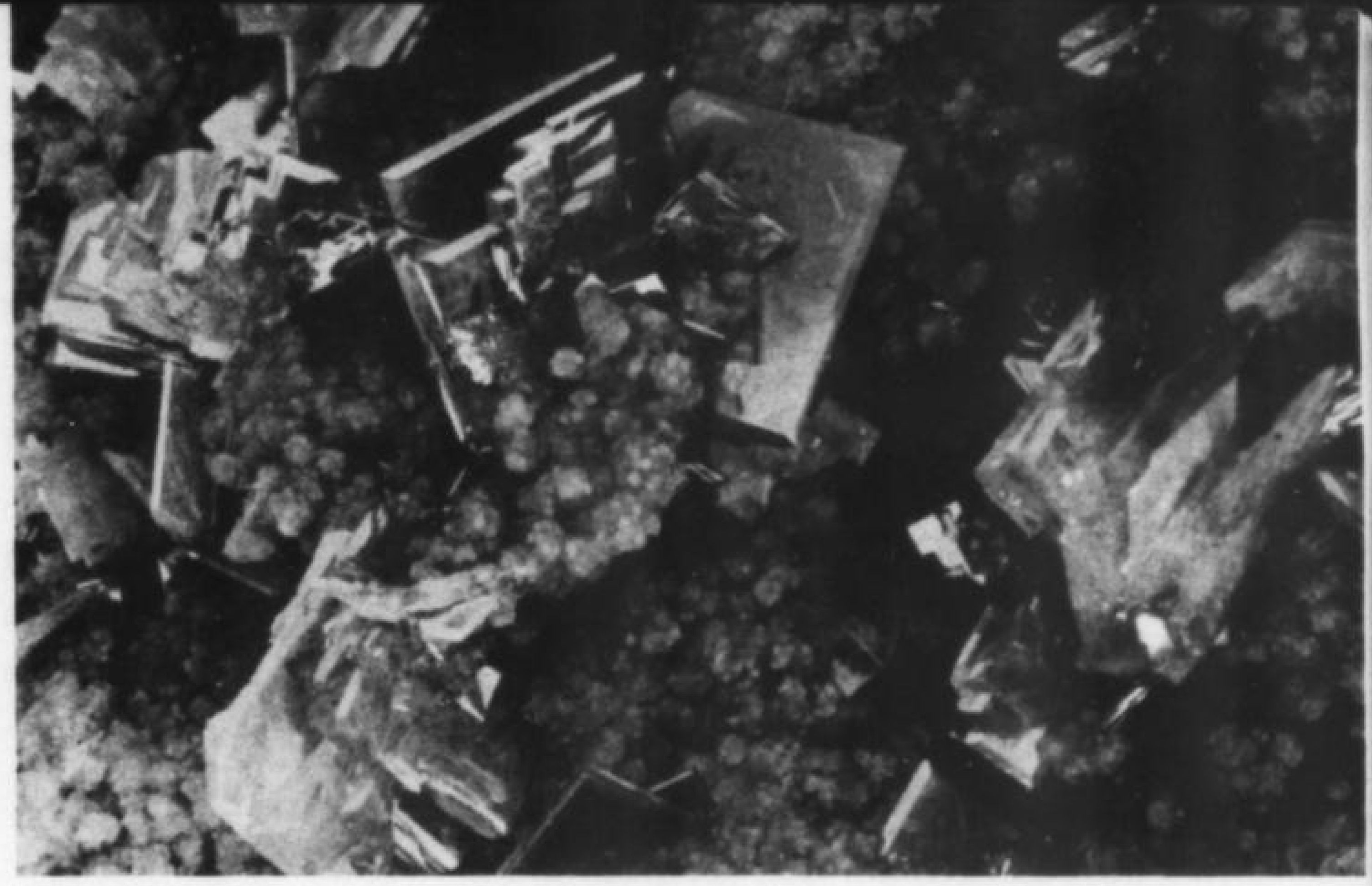


Fig. 5. **Wulfenite. Cerro Prieto, Sonora, Mexico. Smithsonian Institution specimen.**

Fig. 4. **Smoky quartz with amazonite. The quartz crystal is 1 1/2 inches long. Clarence Coil specimen.**

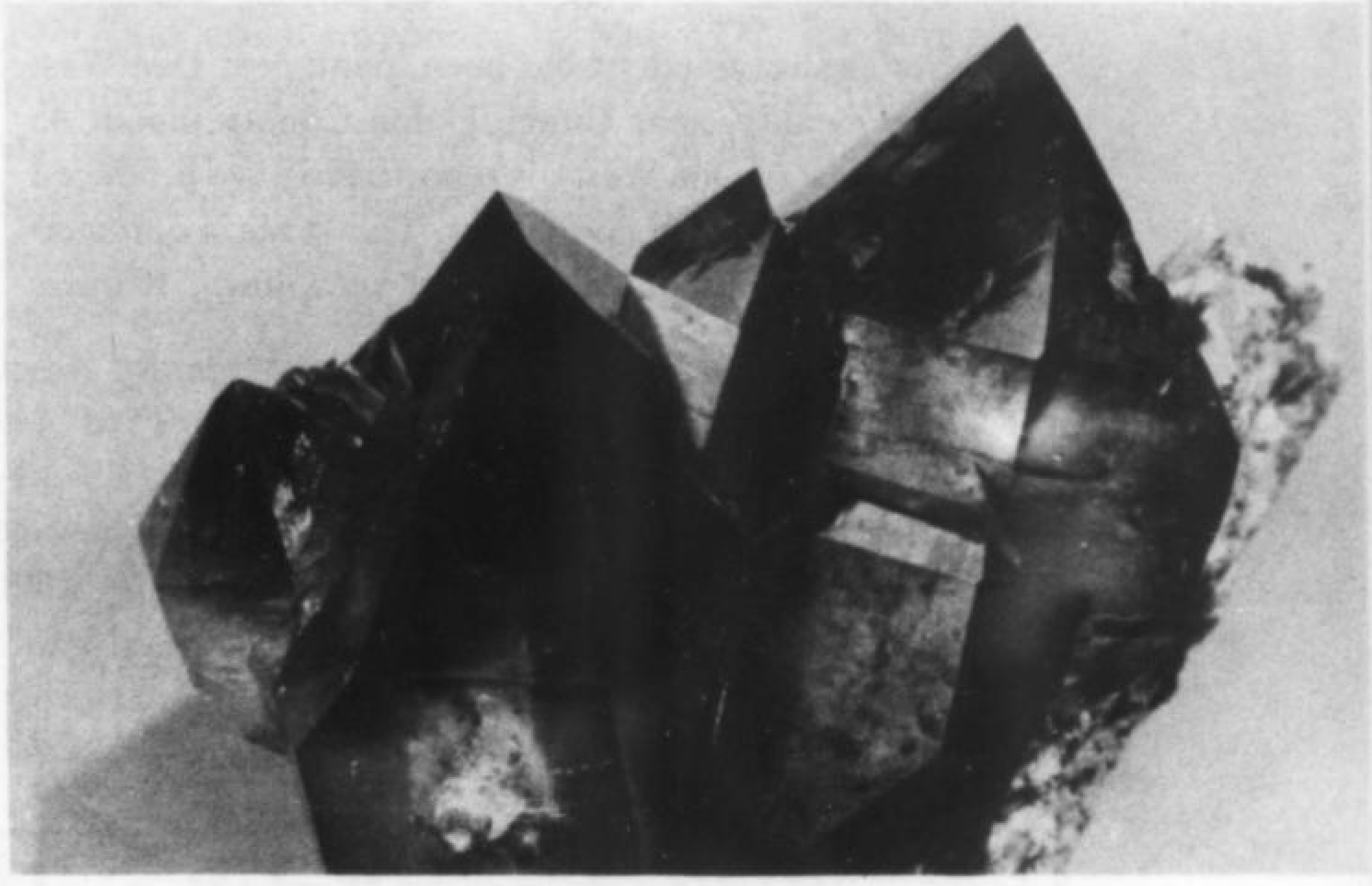


Fig. 6 **Amethyst. Due West, South Carolina. Smithsonian Institution specimen.**

The "new" wulfenite (actually, it has been coming out for about a year) is strikingly beautiful. It is quite reminiscent of Rowley mine (Arizona) wulfenite except that it is mustard yellow rather than orange. The specimens usually are busy, with crystals in groups of rather flat rosettes and random clusters perched on wart-like crusts of mimetite of the exact same color (see figure). The smaller and more isolated wulfenite crystals tend to be more square and transparent. The average crystal size and the dominant crystal size are about the same—one-half inch. The crystals rarely are larger but one specimen has been found consisting mostly of large single crystals three inches on one edge, the whole piece weighing 60 pounds!

It is said that the mine has produced a large number of specimens and that the potential exists for the recovery of many more. Rumor has it that the ownership and collecting rights are very much in dispute at the present time. Should these difficulties be resolved and the specimens carefully mined, we can look forward to seeing these fine wulfenite specimens on dealers' shelves for some time.

DUE WEST AMETHYST

Some of the best specimens of amethyst have come from the locality of Due West, in Abbeville County, South Carolina. The limited number of specimens produced have not been widely distributed and are not well-known among collectors. Two of the finest specimens (those figured here) are in the collections of the National Museum of Natural History (Smithsonian Institution). The simple clusters of large crystals are attached to a small piece of quartz matrix and each displays very well without additional support. The individual crystals are about three inches long and two inches wide. The amethyst color is deep but the crystals are not gemmy. In part they grade into a smoky shade of amethyst.

A recent check disclosed that the owner of the locality has just filled the pit with rock. The property is supposed to be tied up in litigation and the owner definitely does not want anyone to visit it.

Amethyst is found in many places along a semi-continuous, narrow belt that runs through Due West, extending northeastward into North Carolina and Virginia. In the opposite direction it reaches into Georgia and many very good, but paler, amethyst crystals have been collected there. At least a half dozen notable localities are in North Carolina alone, including the famed Lincoln, Alexander, and Iredell Counties.

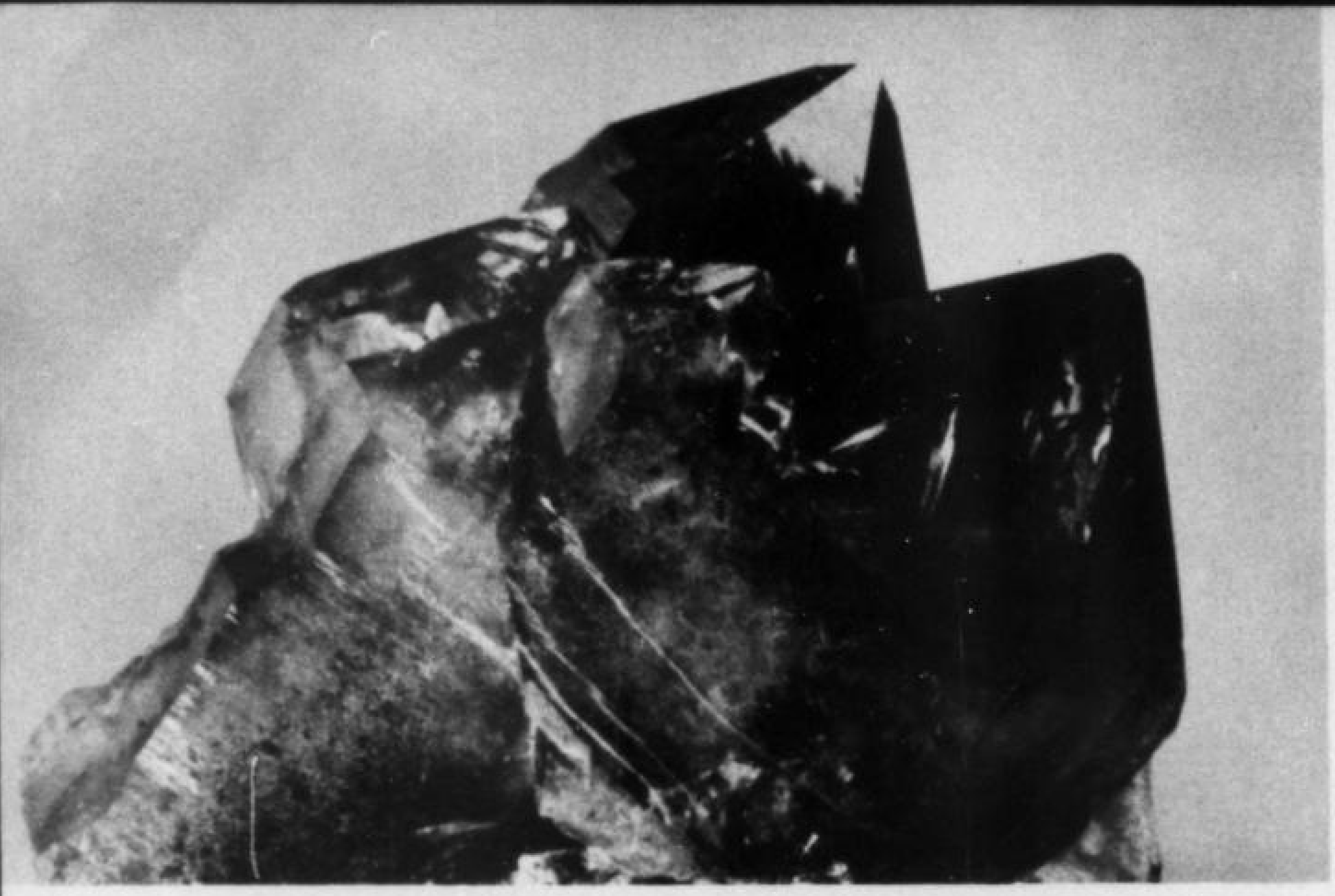


Fig. 7. **Amethyst. Due West, South Carolina. Smithsonian Institution specimen.**

Inferior quality amethyst has been found near Due West but a new locality, near Union, Union County (about 45 miles northeast of Due West), is reported to have produced some nice specimens of good color. This is not a commercial property and its potential is not yet known. It bears watching.

The Collector, continued from page 150

red crystals were found, beautifully associated with cerussite and dioptase.

A number of other pre-1900 mining operations in the western U.S. could have produced quantities of fine specimens, but few were saved. One of these occurrences, in the Lucin District, Box Elder County, Utah, was probably major, as badly broken but pure aggregates of crystals of large size but extreme thinness are in a few of the museums.

The Toughnut mine, Tombstone, and the Total Wreck mine, Empire Mountains, Arizona are also in this category. A very few old-time pieces from Tombstone with light yellow to orange tabular crystals to 3/4 inch on matrix, sometimes rosetted, show first rate potential was there. Only traces can be found underground in the fifteen miles of workings today.

There is a record of the Total Wreck having once shipped 5000 pounds of wulfenite concentrates in the 1920's, but I have seen only a single specimen collected in those days. This was as two complete one inch crystals of light brown color. In modern times, collectors' successes have been varied at this property, except for considerable mottramite incrusted and replaced groups.

The 79 mine near Hayden, Arizona also started operations prior to 1900, but wulfenite seems to have been saved as specimens only in the last twenty or so years. A 79 mine specimen, fairly recently collected, was the winner in the cabinet category of the all-wulfenite competition at the last Tucson show. This piece has a few orange, thin tabular transparent crystals approaching one inch on a matrix of sparkling mottramite. Other associations with rosasite or with smithsonite and aurichalcite are unusually attractive. The 79 mine is nominally closed to collectors at present.

The Rowley mine, near Theba, Arizona was apparently worked in the 1920's and 30's and then abandoned without the record of a single wulfenite specimen, yet the mineral must have been encountered from the grass roots. The first collectors on the property in the mid-1940's stumbled on a bonanza of specimens, and even now it is only necessary to move enough rock almost anywhere in the mine to be assured of some decent material. Tabular golden orange crystals to nearly one inch, water clear or with delicate phantoms, on white barite with a little mimetite or vanadinite are the majority of those found. Again, barricades have been erected by the mine owners recently against collectors.

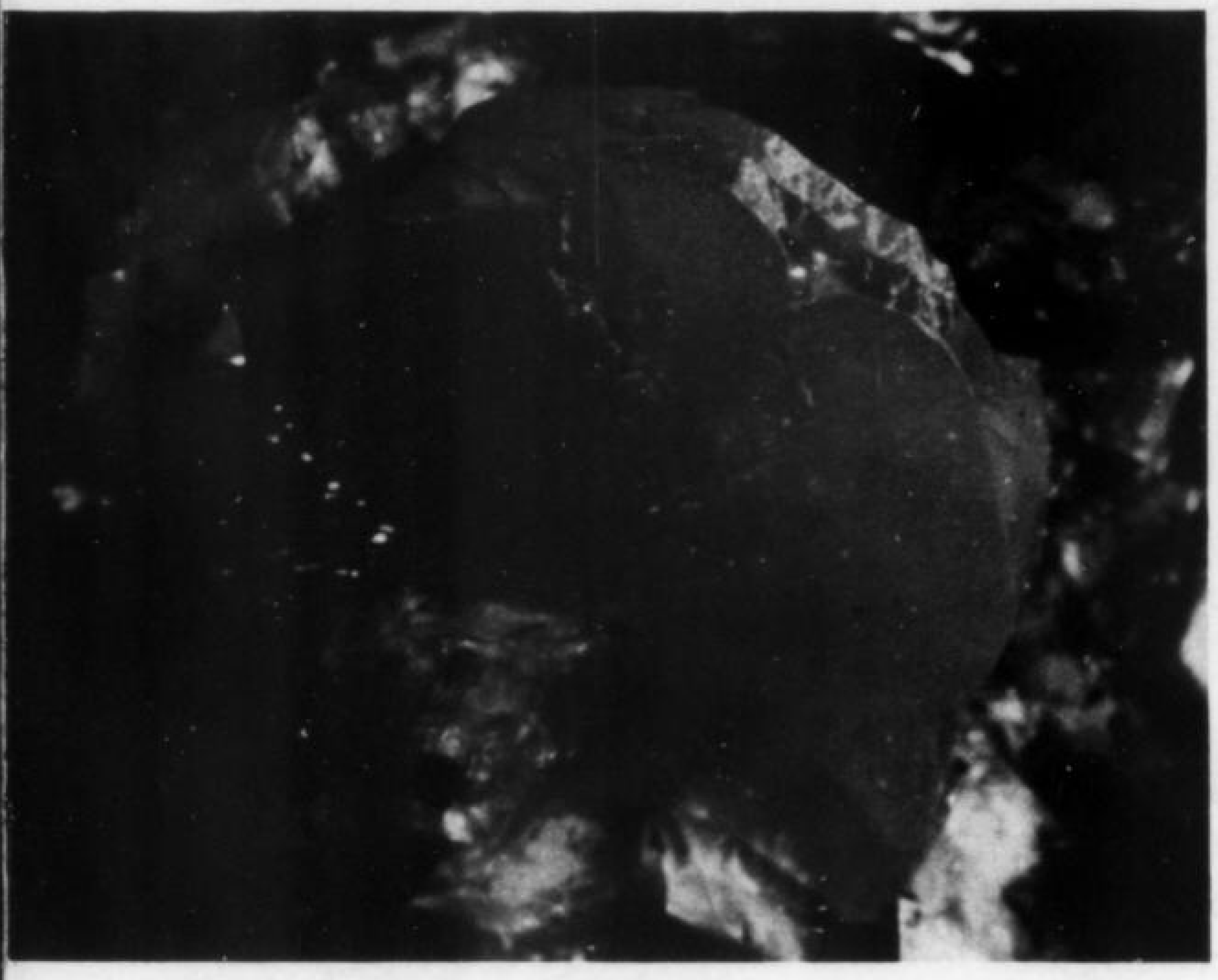


Fig. 5. **Wulfenite—Hilltop mine, Arizona. Smithsonian Institution specimen. Photo by Joel E. Arem.**

Fig. 6. **Wulfenite—Crna, N. Slovenia, Yugoslavia (formerly Schwarzenbach, Carinthia). Smithsonian Institution specimen. Photo by Joel E. Arem.**

The Old Yuma mine, near Tucson, Arizona, also was operated sporadically in the period from 1910-1940 with few of what must have been numerous wulfenite specimens saved. The wulfenites found here are very similar in appearance and color to those from Tiger, but are generally thicker and less transparent. Many loose singles and clusters with crystals averaging perhaps one inch, and rarely approaching three inches, have been found near the surface by a few hard working collectors during the past fifteen years.

The Hilltop mine, near Portal in the Chiricahua Mountains, Arizona, is a partial exception to having its best material destroyed during mining operations. The major pocket from this mine was worked for specimens alone in the late 1930's. The distinctive butter-yellow, opaque, rounded crystals up to nearly an inch, on limestone, are now to be found in collections around the world.

(to be continued)

Ed. note—The locality of Schwarzenbach has been properly moved from Austria to Yugoslavia in Bideaux's column but is is no longer in Carinthia and it is no longer known as "Schwarzenbach." The new name is Crna (or Crna pri Prevaljah) and since 1918 the region has been known as Northern Slovenia.

THE MINERAL SOCIETY OF MANITOBA

A new club, The Mineral Society of Manitoba, was formed in Winnipeg, Manitoba, Canada last September (1971) and was incorporated in May 1972. It's purpose: to further the study of Minerals and related Earth Sciences. Meetings are held the third Thursday of each month from September to May, inclusive, in room 211, Earth Science Building, University of Manitoba, with the June, July and August meetings being held outdoors at nearby collecting areas. Members bring their lunch or supper as the case may be. President is Mrs. Laurel Singleton and the Secretary is Mrs. Carol Smith. The mailing address is Manitoba Museum of Man and Nature, Natural History Division, 190 Rupert Avenue, Winnipeg, Manitoba R3B ON2, Canada.

Visitors are welcome.

Yedlin on Micromounting

In the past few months a number of people have queried as to the availability of Goldschmidt's *Atlas der Krystallformen,* a fabulous work of 18 volumes, 9 of which are line drawings of all crystal habits known to 1923, the year of publication. This set is an imperative addition to the library of a serious collector, be he interested in cabinet specimens, miniatures, thumbnails or micromounts, especially the latter, since so much of his identification is based on visual morphology.

Concurrent with the last inquiry, about June 20th, there arrived a catalog of books on geology and mineralogy—Reportorium No. 85, 1972—from Antiquariaat Junk, Postbox 5, Walderstraat 10, Lochem (Holland). Item 430 lists: "Goldschmidt, V., Atlas der Krystallformen, Heidelberg 1913-1923. 9 vols. (1 of description and 1 atlas to each.) pp 1869, with 1578 plates, wrs - 600 Dutch guilders. Still a few copies available." (Ed. note. Guilder value, 32 cents in June, 1972.)

Well, run, don't walk to the nearest air mail box. Or by cable—"Junk Lochem". Or by telephone—Lochem 05730-1725.

We got our set some years ago from another source, and if A.J. is sold out try Swets and Zeitlinger, 471 - 487 Keisergracht, Amsterdam, Holland. Price is about the same. In neither case should advance payment be made. You will be billed when you receive the set. Ours (and others purchased subsequently) was in mint condition, fine heavy paper, pages uncut, quarto size. Do it now!

Henry Barwood, Rt. 3, Box 144, Auburn, Alabama 36830, sends interesting data and comment. *I am sending four specimens of cacoxenite gathered recently, unspectacular but interesting, for this most abundant iron phosphate mineral is not reported from too many localities. Cacoxenite from Indian Mountain, Alabama is perhaps as good as any from recent finds, but it is available from other areas—hence my specimens to you. (NY's note. Fine material received. In addition to a specimen from the Indian Mountain locale, there were enclosed one each from Coosa County, Alabama, collected in 1970; from Rock Run Station, Alabama, 1971; and Cedartown, Georgia, March, 1972.)*

In the fall of 1969 two of us unearthed a large quantity of good micromount material at Indian Mountain. We found, in addition to strengite, beraunite and cacoxenite, fine rockbridgeite crystals, dark brown to black, exceptionally sharp and distinct. After much searching similar material was located on the dumps.

My gripe with some collectors is that they pay too much attention to silver pick specimens, old or otherwise. Where are the old time collectors we all read about who combed the mines and quarries for specimens? (Where indeed?) I've seen dealers hopping-up-and-down-happy that a mine was closed or worked out, and others, including mine foremen, who prevented collecting so that they could sell specimens. (Too true, but not universal. NY.)

We're glad to hear about finding Indian Mountain material on the dumps. Most of the finds, heretofore, came from two immense boulders, which provided practically all of the fine phosphate minerals presently to be found in collections. As to the selfish attitudes of some dealers and mine foremen, let's just say you cannot alter human nature, and the quest for a quick dollar is a powerful motivating force. You have to work around it.

Some details of the chemistry of cleaning copper are supplied by Professor Laurence W. Littau of Monmouth College in New Jersey. He takes us to task, somewhat, and explains the lye-rochelle salt solution workings. *It was with great interest and surprise that I read your statement in MINERALOGICAL RECORD covering the cleaning of copper with hydrochloric acid and the 'old time solution' of using a basic rochelle salt cleaner. Copper does not react with HCl. Any pits that may show up were portions of the specimen that were no longer metallic copper but had already reacted to form one or more of the many copper compounds. The beautiful blue color from the rochelle salt treatment (See M.R. Vol. 3 No. 2. March - April, 1972, page 85.) is a result of the formation of copper tartrate, which is soluble in basic (alkaline) solution.*

Under no circumstances ever clean copper with nitric acid. I have used HNO_3 *to remove a deposit of a lead compound from some clusters of quartz crystals. It worked, but this was done in a fume hood with a good exhaust fan to provide the needed ventilation.*

One small set of requests for information. Can you supply a list of the minerals found at Ft. Lee, New Jersey recently, and the suite from the Ecton mine in Pennsylvania?

Well, we can list from Ft. Lee (when part of Route 4 was constructed to connect with the George Washington bridge expansion across the Hudson River) the following

Fig. 1

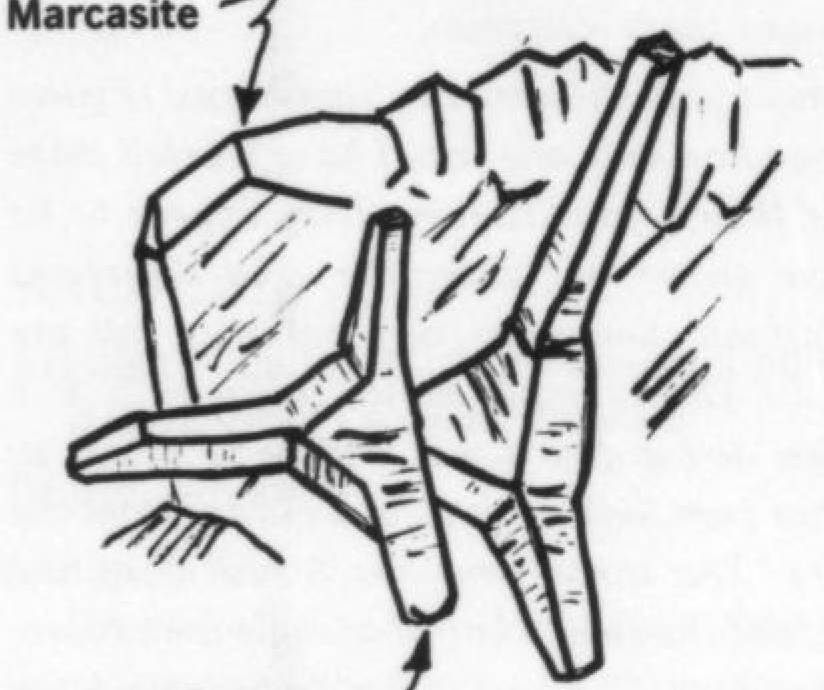


Fig. 3

Fig. 2

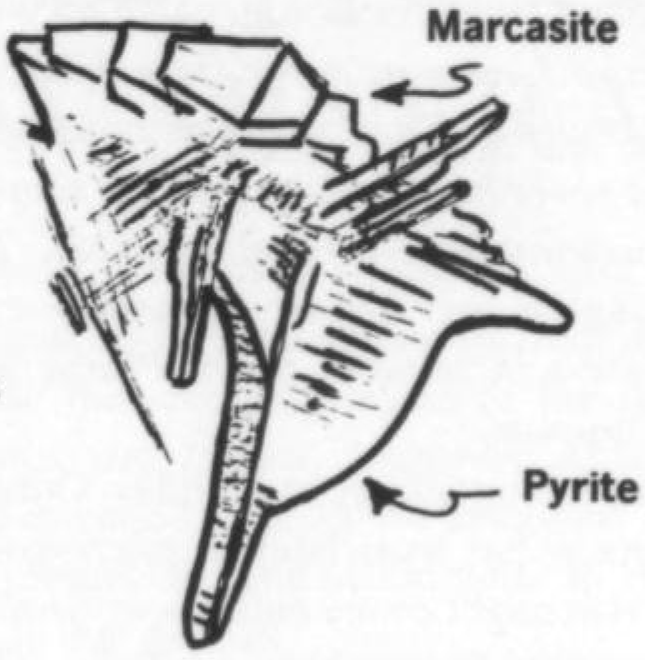


Fig. 6

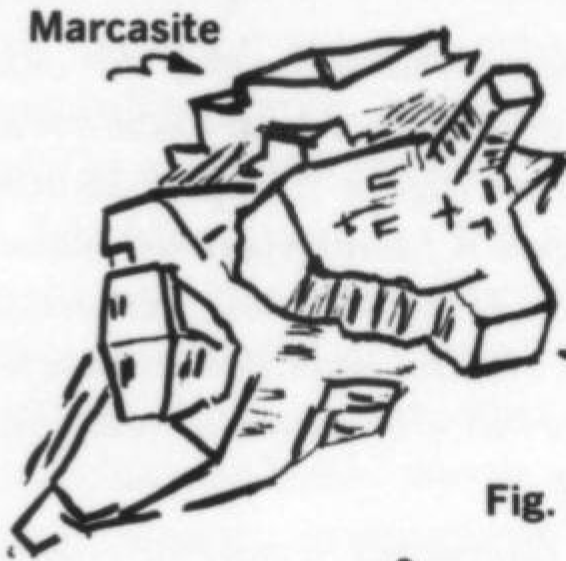


Fig. 11

Fig. 9

Fig. 7

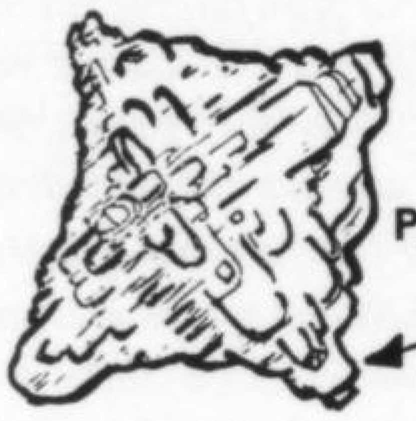


Fig. 4

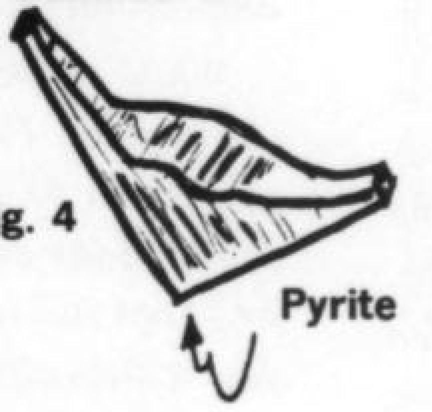


Fig. 5

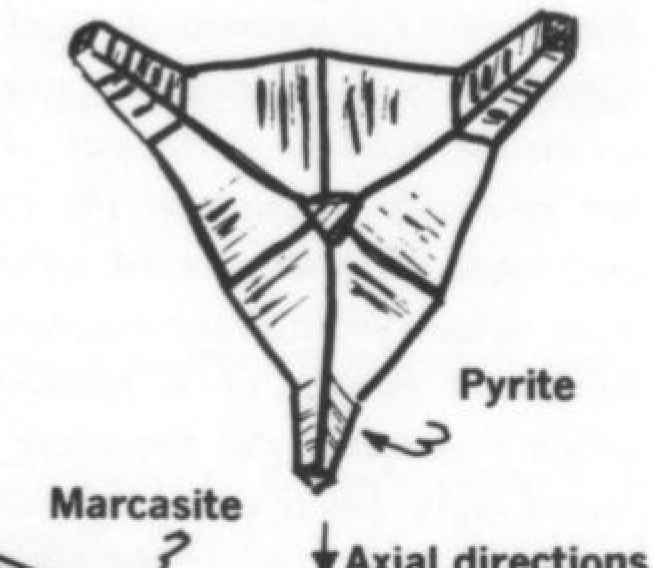


Fig. 8

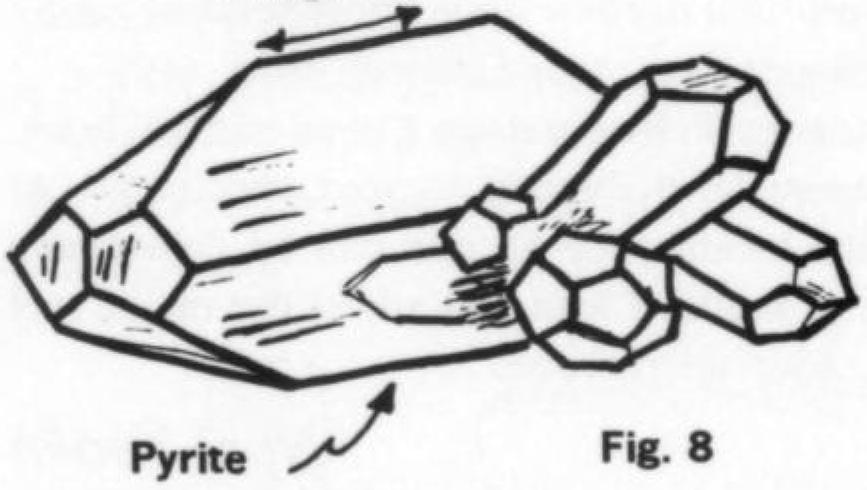


Fig. 10

species: Actinolite (byssolite), albite, analcime, andradite, apatite, apophyllite, datolite, epidote, hornblende, nepheline, pectolite, sphene, stilbite and zircon. Ken Hogan, 288 Schley Place, Teaneck, New Jersey 07666, who collected at the locality rather extensively, and who supplied the majority of our specimens, can probably list additional names. He is an advanced collector, and no doubt has material for swaps.

Ecton mine—that's something else. We know little of the mineralogy of this area. The late Mark Robinson of Pennsylvania did considerable collecting and research of the Ecton minerals. In December 1956 he sent us a specimen of devilline, $CaCu_4(SO_4)_2(OH)_6\cdot 3H_2O$. This was identified by Mary E. Mrose of the Geological Survey. It was at about that time that the mineral herrengrundite, from Czechoslovakia, was determined to be, in fact, devilline. Fleischer's *Glossary of Mineral Species, 1971,* lists devilline and makes no mention of herrengrundite. Ergo, change your labels, and move the specimens in your cabinet.

At all events, we'd like information. Send us your lists of minerals other than those above listed.

New Dealer in micromounts. W.D. Christianson, 127 Grove Street East, Barrie, Ontario, Canada. His catalog of micromount material contains 193 items, ranging from 25 cents to a dollar. The list is free for the asking, but as a matter of principle send a dime for postage. A small thing but considerate.

Now a quite serious critique. A knowledgeable visitor to the micromount meeting at Santa Monica, in a subsequent round table discussion, came up with this comment: *Never have I seen so many stereobinocular microscopes assembled in one place for immediate use. It was astounding! And never have I seen so many 'scopes needing cleaning, adjustment and general overhaul. This was likewise astounding! It was almost impossible clearly to discern objects through some of them. Please, add another item to your crusade.*

The limestone quarry at Dundas, Ontario, (near Hamilton) Canada has ever been a micromounter's haven. A present visit might prove entirely worthwhile. Gary Glenn, 8459 Parkway Drive, Niagara Falls, Ontario, sent the RECORD a report on curious pyrite-marcasite crystals from this locality. His letter and sketches of the minerals are here for your perusal. *For a number of years I have been collecting in a limestone quarry at Dundas. The site is the Canada Crushed Stone quarry, owned by Steetly Industries, Ltd, and others. It is very large and over the years has yielded good strontianite, celestite and sphalerite as well as some other sulphides and the usual mixtures of calcite, dolomite, fluorite and gypsum to be found on the Niagara Escarpment. A number of years ago I became interested in small sulphide veins which began to show up on the extreme north wall of the quarry. These veins ran vertically throughout the exposed height of the pit and, while badly weathered, afforded some good material. They ranged from about 4 inches to about a foot in width, consisting mainly of a pyrite-marcasite mineralization which penetrated the limestone to several inches. Associated were small areas of galena and sphalerite. The center of each vein, where open, was filled with calcite.*

A few of the pieces, after etching the calcite, yielded surfaces covered with well formed galenas, to 1/4 inch, with octahedral and dodecahedral modifications. This material was never really abundant.

The micro material offered the real surprises and kept us coming back throughout the following years. For a long time the material removed was never the same, although recently it has been mainly of the coxcomb marcasite type. The summer of 1970 produced both pyrite and marcasite in a seemingly endless variety of crystal forms. I have included sketches of some of them, but there were, in addition, many of the commoner habits as well as some transitional between these extremes.

Probably the most unusual were the 'stag horns' (figures 1. through 5.), found on only one trip. I have labeled these pyrite because of their crystallization. They appear to be cubes which have grown out along the axial directions in a dendritic fashion. Some are very complex; all are striated. (figure 3.) The example shown in figure 5. is a most unusual view and at first I was unable to orient it. It now appears that I am looking at a cube corner from the inside, as it were. The three arms reach out along the axes of the cube, and the small central triangle then represents an octahedral face. I wonder if the six broader faces are the pyritohedron.

A transitional phase between this form and the cube is represented by figure 6. Additionally I have found pyrite forming composite octahedrons (figure 7.), pyritohedrons elongated along one axis (figure 8.) and reticulated masses of hairlike pyrite (figure 9.). Along with this material is coxcomb marcasite (figure 10.) in beautiful irridescent hues. Unfortunately the marcasite is unstable, and soon disintegrates.

More recently we've been finding micro material consisting of masses of botryoidal sphalerite in amber to black, studded with bright silver-grey galena, showing (001) and (111) modifications, and marcasite blades, twinned cyclicly and forming discs of two or three 'knees' each.

While sulphide material is still available in this quarry (December 1971) the extreme variety of crystal forms evident in 1970 seems to have tapered off. I still consider it one of the most interesting localities in which to collect, and I am still surprised to come upon another variety that's just a little different than those I already have.

So now we admonish: Buy and use a good mineral book. Affix a permanent label directly to your specimens (At least include the locality, for all else can be determined from the mineral itself.). Clean and adjust the major tool of your trade, your microscope.

Neal Yedlin
129 Englewood Drive
New Haven, Connecticut 06515

MINERAL NOTES
NEW MINERALS

JULGOLDITE

Julgoldite, the $Fe^{+2}-Fe^{+3}$ dominant pumpellyite. A new mineral from Långban, Sweden.

Paul B. Moore

Lithos, 4, 93—99, 1971

Julgoldite, $(Ca,Mn)_2(Fe^{+2},Fe^{+3},Mg)(Fe^{+3},Al)_2(SiO_4)(OH)_2(H_2O)$, is the $Fe^{+2}-Fe^{+3}$ dominant member of the pumpellyite group occurring as a new fissure mineral from the "Amerika" stope, Långban, Sweden, associated with apophyllite, barite, hematite, magnetite, and two other species as yet unidentified.

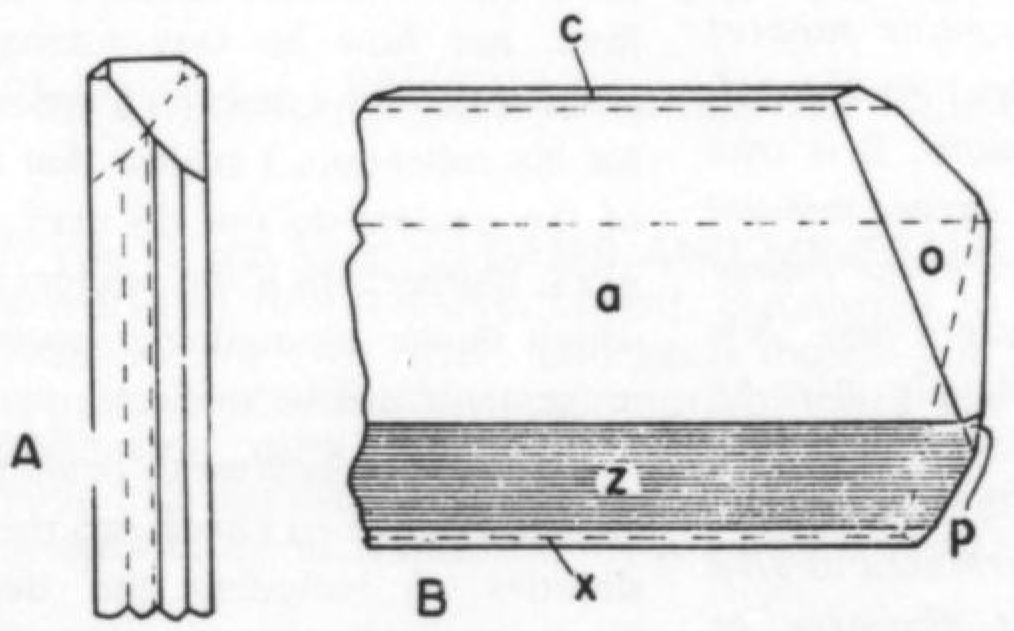
Julgoldite occurs as flat prismatic to bladed crystals up to 2 mm in greatest dimension, elongated parallel *b* and flattened parallel *a.* Crystals are usually twinned with *c* (001) as the twin plane. The color in hand specimens is a deep lustrous black, almost submetallic; small fragments are transparent greenish-olive with a bluish tinge. Hardness is 4 1/2. Specific gravity is 3.602. Cleavage is good, *a* {100}.

The new mineral is named for Professor Julian R. Goldsmith, University of Chicago.

Monoclinic — space group *A2/m*
$a =$ 8.92 Å $b =$ 6.09 $c =$ 19.37
$\beta = 97°30'$ Z = 4 S.G.(calc.) = 3.605
Biaxial (-) with $\alpha =$ 1.776, $\beta =$ 1.814, $\gamma =$ 1.836
2V large (50°-70°); anomalous interference colors. Optic plane is parallel to

b {010}. Strongly pleochroic with X pale brown, Y pale brownish-green, Z deep emerald-green.

Strongest x-ray lines: 2.950 (10), 3.84 (8), 4.80 (7), 2.568 (7), 2.778 (6).



Julgoldite. Långban, Sweden. A. Plan. B. Clinographic projection showing the forms *c* {001}, *a* {100}, *x* {$\bar{1}$02}, *z* {$\bar{1}$01}, *o* {111}, and *p* {$\bar{1}$11}.

TSUMCORITE

Tsumcorit [$PbZnFe(AsO_4)_2] \bullet H_2O$, ein neues mineral aus den oxidationszonen der Tsumeb-mine, Südwestafrika

B.H. Geier, K. Kautz, and G. Müller

Neues Jahrb. Mineral., Monatsh., 7, 305-309, 1971

Tsumcorite, a new hydrated arsenate of zinc, lead, and iron, was found in thin compact layers in the oxidation zones of the Tsumeb ore deposit, Southwest Africa. Paragenetically it is associated with Pb-Fe arsenates and sulfates which are present in limited amounts in the deep oxidation zones of this deposit.

The new mineral is translucent red-brown in color; the streak is yellow. Specific gravity is approximately 5.2. Hardness is 4.5. It is soluble in HCl.

Tsumcorite is named for the Tsumeb Corporation.

Monoclinic — space group *C2/m*
$a =$ 9.131 Å $b =$ 6.326 $c =$ 7.583
$\beta = 115.3°$ Z = 2
The optical character could not be determined; average refractive index $n \approx$ 1.90; 2V$\sim$90°. Pleochroic, from yellow to yellowish green.
Strongest x-ray lines: 3.244 (100), 4.663 (90), 2.863 (90), 2.742 (70), 3.021 (60).

INDIGIRITE

The new mineral indigirite, a hydrous magnesium aluminum carbonate.

L. N. Indolev, Yu. Ya. Zhdanov, K. I. Kashirtseva, V. S. Suknev, and K. I. Del'yanidi *Zapiski Vses. Mineralog. Obshch., 100,* 178—183, 1971

The new mineral indigirite, ideally $Mg_2Al_2(CO_3)_4(OH)_2 \bullet 15H_2O$, was found in the oxidation zone of the Sarylakh gold-antimony deposit in the basin of the upper part of the Indigirki River in northeastern Yakutia, associated with gypsum, amorphous iron oxide, quartz, hexahydrite, melanterite, limonite, gibbsite, and kaolinite.

Indigirite occurs as snow-white, rosette-like, radiating fibrous aggregates of very fine fibers, needles, or plates, up to 1 mm in length. Luster is silky to vitreous. Hardness is about 2. The plates and needles are flexible. Specific gravity is 1.6±0.1. The mineral is insoluble in water, alcohol, and ammonia; it is soluble with effervescence in acids or KOH.

Optically anisotropic with parallel extinction; elongation positive. Refractive indices: α 1.472, γ 1.502.

Electron microscope photographs show elongated tablets with irregular boundaries. The parameters of partially dehydrated crystals are $c =$ 6.23 Å (parallel elongation) and 3.16 Å (perpendicular to the elongation); these are close to *b* and *c* of artinite.

Strongest x-ray lines: 5.80 (10), 7.62 (9), 5.24 (9), 2.70 (9), 2.60 (9).

To the Editor

On labels

Dear Sir:

A comment in reference to labels: if I find very old, valuable labels, as I have found glued on some very old, 19th century specimens, and the specimens need washing, before doing so apply several coats of clear lacquer (nail polish variety) over the labels making sure that the edge is well sealed. Spread the lacquer a bit beyond the edge of the label. I avoid the sonic cleaner on such items, but they can then be immersed safely in soapy water and rinsed. It also prevents losing the inking, writing, etc., which sometimes occurs, even if the label stays on. I do not spray the lacquer for it cannot be controlled. I brush it on with a small brush. Again, nail polish bottles are perfect for that use as they come equipped with brushes.

Kay Robertson
Los Angeles, California

Smithsonian's surplus

Dear Sir:

I have a question about your editorial in the last issue (Vol. III, #1) of the *MR.* You state the following: "It is wrong for such a museum to allow its precious supply, perhaps all that has ever been found, to be doled out to species collectors." You are 100% right. I was under the impression that the Smithsonian was sort of owned by the "people of the United States", am I correct? I admit that a collection as huge as the Smithsonian's creates a lot of extra material that must be either sold or given away. How is this being done at this time? I notice that on the following page in the same issue a dealer from my own home town offers adamite, and he states that the specimens carry National Museum (Smithsonian) labels. How did he obtain these specimens? How could I or my club obtain specimens from the museum? You must admit the dealer is making a huge profit on the specimens that carry the museum labels. Perhaps the specimens are sold at auction in huge lots, that sure leaves the little guy out in the cold. Perhaps you can carry this letter in your next issue and see how others think. Thanks for your time and concern.

David O. Semsrott
Kirkwood, Missouri

The Smithsonian itself is not federal and technically is not "owned by the people of the United States." However, many Smithsonian activities are totally federally owned. The National Museum of Natural History, which contains the mineral collection, is one of these federal parts of the Institution and the building, staff and collections are supported in good part by federal funds. It is interesting that employees are often unsure whether their co-workers are under federal or private support because all internal activities overlap and are inter-coordinated so well.

Additions to the mineral and gem collection receive no taxpayer support at all. The money comes only through private funds or donations. It is true that large numbers of excess mineral specimens are generated in the course of operations but surprisingly few of these are the kind sought after by the present day breed of collector. Even when faced with this excess, the curators are not permitted to give away or sell any of it. However, as with all museums everywhere, exchanges are permitted. All the specimens you may see in collector or dealer hands with Smithsonian labels of one kind or another represent excess specimens exchanged for something of more importance to the collection. Since exchange programs are active there is no great accumulation of materials at the Smithsonian at any one time. Naturally, exchanges are not limited to dealers. Many collectors have successfully negotiated for specimens. The major requirement is that the specimen offered must be something needed and not easy to obtain by purchase. Also, the exchange value must be reasonable. Contrary to your statement I have known dealers to take severe losses on some of these specimens as well as making a huge profit on others. Both the dealers and the curators are familiar with the market and have a very good idea what the total value of a given lot of pieces should be. If you investigate you will find that most dealers operate on very slim profit margins. Ed.

Stimulating but frustrating

Dear Sir:

In reviewing my latest issue of *MR* (Vo. III, #2), particularly the "What's New in Minerals?" section, I found the description of the Tucson Show to be both very stimulating and extremely frustrating. First, for those of us who cannot attend this outstanding show, one finds the descriptions of the available material very rewarding and stimulating. Secondly, it becomes very frustrating for, with one exception, the reader has absolutely no way of knowing what dealers had a certain item, nor how he may attempt to obtain one of the described specimens for his collection. I realize that many of the dealers do not do mail order work, but perhaps if the readers know which dealer to contact, special arrangements can be made.

It may be of interest to dealers and collectors alike to check out the possibilities of including the dealer's name when his material is described in your column. With this type of information available, it may help increase the subscription rate.

May your success continue in providing a *Minerals Only* publication.

Ronald Sohn
Kettering, Ohio

We are in complete sympathy with your frustration but we feel we can follow your suggestion in only a limited way. In most instances the material described is handled by nearly every dealer advertising in our publication. The best way to get to know the dealers is to try to attend as many of the mineral shows as possible. You may establish contacts with many who will come to know your tastes in specimens and the things you are particularly eager to acquire. These dealers are just as anxious to find you as you are to locate them. Ed.

The 'in' group

Dear Sir:

I am a subscriber to *MR* and hope you are able to continue its publication. I am a professional chemist and an amateur mineralogist. For me the technical articles and such columns as Desautels and Yedlin are great. However, I would make one suggestion, if you want the support of the great mass of serious amateur mineralogists. That is that in many of the writings (including FM too) there is an air of righteousness and even snobbishness—it says to the reader "We are the "in' group; the professionals and the top collectors; if you didn't make the Tucson Show, you're not with it."

Please consider this if you want the support of the little people who may be the big shots of tomorrow.

Paul W. Morgan
West Chester, Pennsylvania

Your letter makes me feel that we have failed in one of our primary objectives, if what you say is true. We want very much to bring the amateur and professional together, not to promote cliques or special interests. I don't know how we can ignore the Tucson Show, however, as it is undeniably the best. We will be describing other shows too as we are able to attend them and if they warrant special attention. While many of the personalities you probably are including in your indictment may be guilty of taking satisfaction in their lofty stature among collectors, there is no move toward excluding anyone and, if such a move should ever develop, it would not be supported by this journal. Ed.

On "species collectors"

Dear Sir:

Your editorial in the January/February issue of "The Record" offered the following definition of the term "species collector":

> Species collectors are, in a sense, fanatical systematic collectors. The goal of most is acquiring a specimen of every known mineral no matter how minute or unattractive it may be.

The shortcomings of your "definition" are numerous to the critical reader and have prompted the following comments.

1. "The Record" has failed in what it set out to accomplish, namely, offer a clear, concise, and consistent definition of "species collector". Two-thirds of the editorial chastises "fanat-

ical systematic collectors" which, it is implied, is what is in fact meant by the term species collector. But in the last paragraph fanatical species collectors are contrasted with "reasonable species collectors" which- if The Record has a definition of "species collector" in mind—is clearly inconsistent. It would seem reasonable to suggest then that whatever a species collector is, it's definition must be sufficiently general to cover the cases of fanatical and reasonable species collectors alike (or any other case of species collector like, for instance, negligent species collectors). However, it is even more reasonable to suggest that The Record has not offered a discussion of the meaning of the term "species collector" but rather an exposition of a collecting attitude which characterizes a very limited set of collectors only.

2. The label "fanatical" often carries with it a negative connotation and, so, is a risky word choice. Fanaticism in its negative sense is simply the unreasoned use of enthusiasm which will many times result in a lack of respect for one's fellows as persons, and a consequent disregard for their rights as men. In this way we characterize collectors who badger curators or curators who badger collectors for their specimens. "Fanaticism" makes a remark about one's moral attitude; not his collecting attitude.

3. By using the word "fanatic", emotive overtones have been built into the definition which, as mentioned in the above paragraph, tend to be taken negatively. The Record has, thereby, moved from a value neutral characterization of the term "species collector" to an attitudinal assessment based on sketchy empirical evidence at best. The mistake would be of equal proportion if a complimentary connotation had been built into the definition.

4. Mention of the goal that motivates species collecting is somewhat naive and hardly constitutes an argument against species collecting. From the practical impossibility of obtaining every possible mineral species the editorial then is at a loss to describe what that goal of the species collector should be:

> What is not so easy to understand is what motivates the species collector to continue once he has discovered how difficult or impossible certain species are to obtain.

This profession of dismay seems rather odd when earlier some rather good reasons and goals encouraging species collecting had been given:

> On the surface this may seem a worthwhile and reasonable endeavor. Certainly its educational value is potentially great.

And later in the essay:

> Building a "limited" species collection can be very educational and the practice should be encouraged.

It seems quite plausible to characterize this as the goal of any—as you put it—reasonable species collector who himself is probably in fact not such a rare species as is made out. At best, the editorial discourages on the very limited class of fanatical species collecting which is a reasonable aim. But it is unfair to extend this recommendation to species collecting in general.

5. The capacities of species collectors have been seriously underestimated:

> Further, a large percent of rare species are in no way interesting to look upon.

Obviously, many rare minerals have no aesthetic worth; but, when correctly catalogued, they do take on a scientific significance which the species collector like most other ordinary men is perfectly capable of appreciating.

* * *

Some interesting peripheral points can be raised from the closing remarks of the editorial:

1. The editorial revealed a rather presumptious stance towards the average collector at large:

> The famed Roebling, Canfield, and Bosch Collection, now integrated into the Smithsonian Collections, were built by reasonable species collectors. These collections became important additions of valuable research and reference specimens. There are numerous modern collections of a similar nature that may end up in museums where the probability of preservation is much greater. These collectors are not competing with the museums but are utilizing their energy and resources to gather specimens that will ultimately supplement those of the museums.

The latent conclusion that a critical reader will inevitably draw from such remarks is that any collector who does not "use his energy and resources to gather specimens that will ultimately supplement those of the museums" is in competition with the museums. My collection was not consciously planned to supplement that of a museum. It was planned initially as an educational and aesthetic supplement to allow *me* to more fully appreciate the complex world of minerals.

2. One should be just as wary of donating his collection to a museum as well as inconveniencing some mineralogically apathetic relative. The label "museum" does not have built into its meaning "higher probability of competent preservation." Museums are administered by people and are, consequently, not perfect. Indeed, museums have been known to have been staffed by incompetent curators or staff, or, in some extreme cases, no curator at all! Rather, donation of collections should involve considerations of *the hands that they reach.*

3. The Record also seems to have forgotten that it was through the hands of generous public-minded, non-fanatical species collectors that the nucleus of many museum collections was formed. It is remembered later that the Roebling species collection formed the nucleus of the Smithsonian collection. It seems that most successful museums rely heavily on the collecting establishment at large. Gratitude and not resentment towards collectors builds great museum collections.

* * *

It has been said that it is much easier to comment negatively than to construct positively; to this end I am compelled to offer an alternative analysis. The following alternate definition of species collector is offered:

> One who compiles two or more independently defined objects agreed upon publically as being discreet mineral species, i.e., not varieties, may be taken as a mineral species collector.

More loosely, a species collector is one who collects mineral species. Importantly, this definition is not confused with any built-in evaluative terminology which deserves an independent study.

Several distinctions help locate the province of a mineral collector with respect to evaluating his collecting attitude. Those who collect a given class of objects merely for the sake of their collection and without regard for their preservation may said to be accumulators. The accumulator can be distinguished from the assembler who does care about the intrinsic worth of an object and will take appropriate measures to preserve it. What results is an assemblage which is one step above an accumulation (my mother's rock garden). But an assemblage is not yet in any interesting sense a collection. A man who puts together a collection will exhibit some care in organizing and labeling his objects while an assemblage will count only as a disjointed array of unlabeled and unclassified objects. A set of minerals without labels is a mineral assemblage; not a mineral collection. What distinguishes the assembler from the collector is the fact that the collector will demonstrate a spontaneous desire to learn about or understand the objects he collects. It is in this regard that The Record distinguished mineral collectors from "rockhounds" in the reply to the Marcus letter in the Nov./Dec. issue.

In conclusion I can now propose a description of an ideal or proper mineral collecting attitude: *In the collection of minerals, the ideal or proper mineral collector will in fact strive for the following: the accumulation and preservation of minerals and the maximization of aesthetic appreciation and scientific understanding of minerals.* This perfect ideal prescribes a pattern of conduct for which we as ordinary men should strive.

Stanley B. Keith
Tucson, Arizona

On Wisconsin Marcasite

Dear Sir:

A recent issue of the *MR* (Vol. II, p. 247) featured some marcasite "stalactites" from the Blackstone mine, near Shullsburg, Wisconsin... Those in the habits pictured are probably restricted to the Upper Mississippi Valley zinc-lead district, but I have seen them in mines in northwest Illinois, southwest Wisconsin, and eastern Iowa. They are described and pictured in U.S. Geol. Survey Prof. Paper 309, Heyl et al, 1959, pp. 87-88. They are not formed like ordinary stalactites. The ones with the holes (tubes) grow upward in large vugs, or upward and sideward. Stalagmite-like forms may project from the roof of the vug, *but they* have no central tubes. Most tubes are capillary in diameter, a few are 2.5 cm across. Sphalerite forms with central tubes partly filled with skeletal galena also are found growing upward. Forms without tubes grow downward. Rectilinear box-like attenuated galena crystals also grow in the vugs and have central tubes. They are rare. Some are in the Field Museum in Chicago. They and many of the other types came from the Marsden Black Jack and Bautsch mines south of Galena, Illinois. Most of the ones I've seen recently in Wisconsin were in the Eagle Picher Calumet mine south of Shullsburg. So if they have central tubes they grew upward! They are not supergene sulfides, as the habits and the paragenesis they show are identical with those of the main ores.

Allen V. Heyl
Evergreen, Colorado

A sour note

Dear Sir:

Andrew Cowper Lawson, erstwhile Professor of *Geology* at the University of California, was many things to many people, but a mineralogist he surely was not! In fact, his one effort with respect to description of a new mineral species (iddingsite) went awry because of his inability to distinguish between a single phase and a mixture.

Under the circumstances it seems somewhat incongruous that his portrait should be included in Pemberton's article, "New minerals from California," as though he (Lawson) were a mineralogist.

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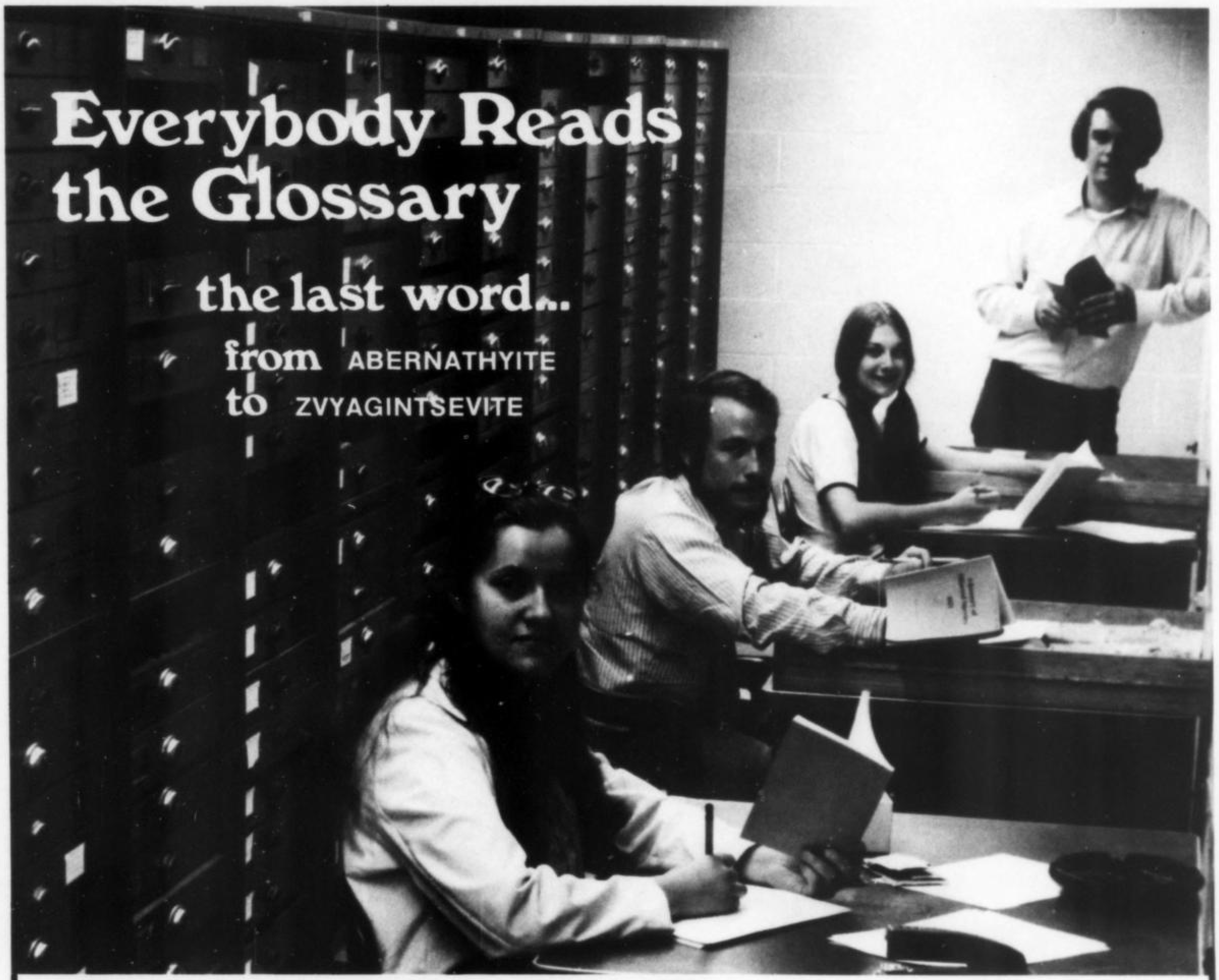
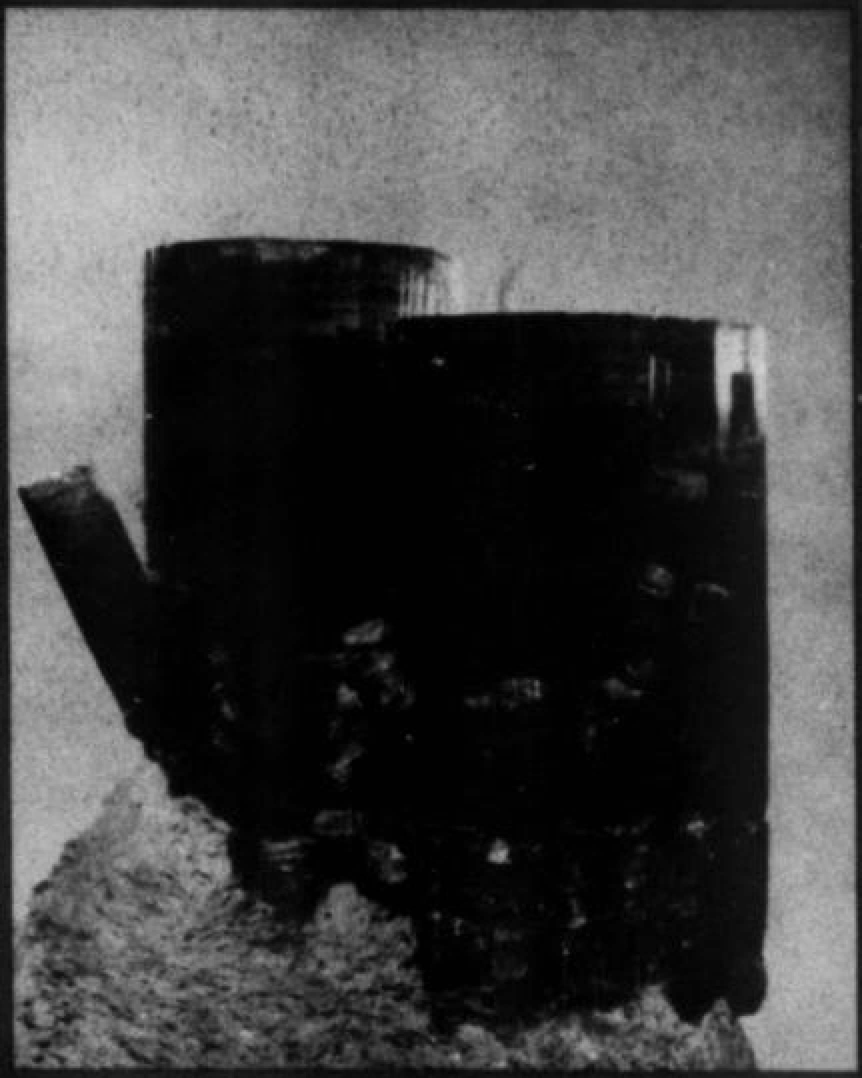

Everybody Reads the Glossary
the last word...
from ABERNATHYITE
to ZVYAGINTSEVITE

2.



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