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THE MINERALOGICAL RECORD

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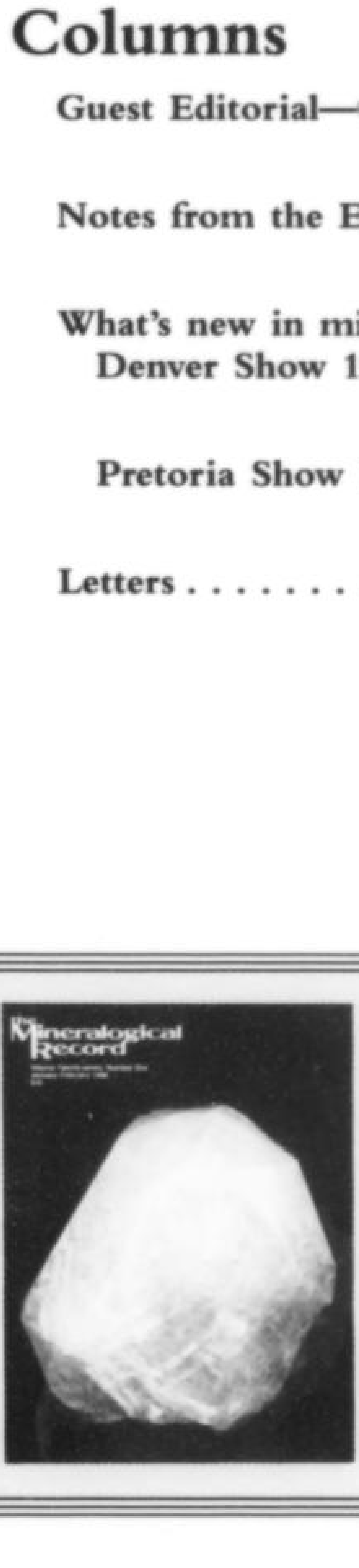
Articles

Columns



COVER: CALCITE crystal, 19.5 cm, fluorescing red-orange under shortwave ultraviolet light; from Dal'negorsk, Russia. See page 9 for a photograph of the same specimen under normal light. Van Scriver/Pliaskov Minerals; photo by Jeff Scovil.

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Guest Editorial

GIVING GIFTS LIGHTS LIVES!

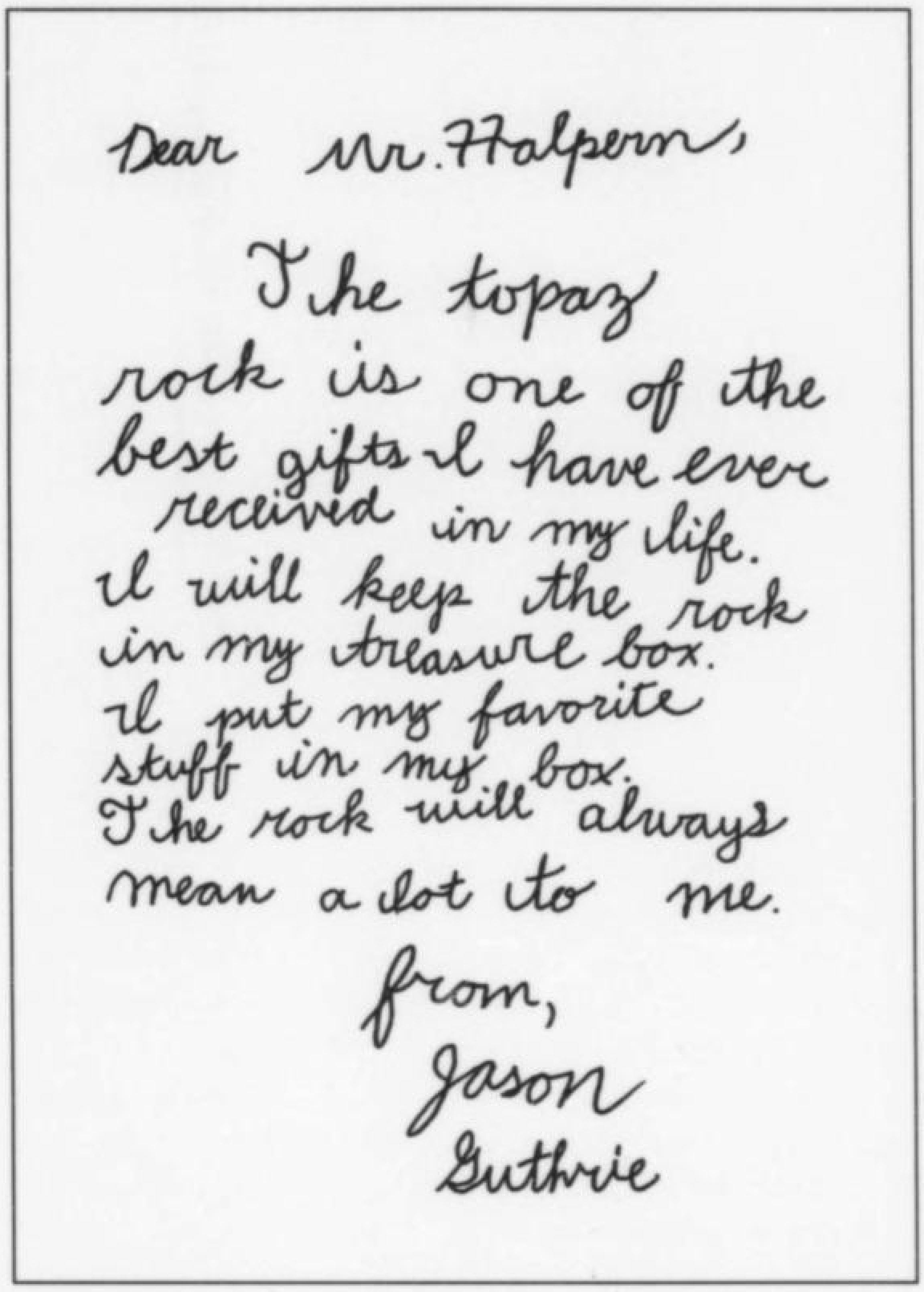
The lure of crystals possesses primordial power. Even to the individual totally untutored in geology, mineralogy or crystallography, the sight of a mineral crystal with its elegant beauty and distinctive geometry can arouse a reaction of awe. Observers are often astonished when informed that the special form of the crystal under view is not the result of human contrivance but rather is an effect produced entirely by nature's forces, a product of the natural interaction of particular subterranean elements, temperatures and pressures. When the crystal's surprisingly regular geometric shape is accompanied by a visually appealing color, the mesmerizing effect is enhanced. A phenomenon of the earth is revealed.

Many collectors were first introduced to the captivating world of crystals by viewing the collection of a friend. All collectors are growing older; but new people are constantly being born, many of whom *could* find great enjoyment in minerals if made aware of them. As collectors, each of us has a splendid opportunity to broaden the minds of the young by introducing them to that facet of creation which has entranced and sustained us: the world of crystals.

Collectors: I invite you to acquire and set aside in a place easily accessible to you a group of crystallized mineral specimens for the express purpose of tendering them as gifts. Whether you collect in the field or with "the silver pick," choose a number of inexpensive but well-crystallized specimens of such attractive, yet relatively hardy minerals as amethyst, smoky or colorless quartz, and pyrite. When refining your collection by removing early acquisitions for which you have subsequently acquired superior replacements, transfer some of the "starters" to the give-away box. Then invite children to see your crystals. Give specimens to those young visitors who evidence a positive reaction to the minerals in your collection.

Our editor (who also makes a habit of gifting young people with specimens) has told me of the approach to giving followed by a lady he knew, the late Trudy Hauser of Cincinnati. She gave minerals to young visitors but she always charged them ten cents for each specimen, believing they would value it more if it had cost them at least a few cents of their own money. I myself always give a specimen in a protective box and with an accompanying label which states the mineral's name and locality. I include the labels of any prior owners as well as my own.

Many mineral dealers do something similar at mineral shows when troops of school children are bussed in, or when a child shows some interest in their stock. They may simply present a small specimen for free, or they may take the trouble to prepare and lay out beginning-level specimens at token prices of ten to twenty-five cents. The child goes home with something fascinating.



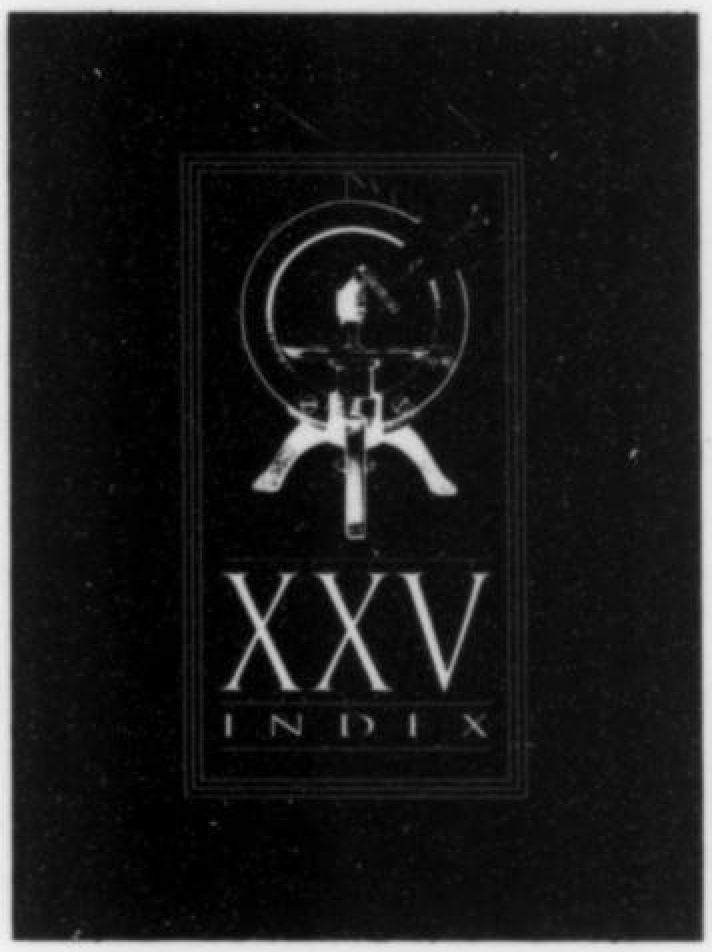
Dear Mr. Halpern,

The topaz
rock is one of the
best gifts I have ever
received in my life.
I will keep the rock
in my treasure box.
I put my favorite
stuff in my box.
The rock will always
mean a lot to me.
from,
Jason
Guthrie

In giving, one enjoys the satisfaction which stems from opening a child's awareness to an exciting world. By so doing, you may well broaden youthful lives. At the same time, you will enrich your own spirit with the glow which comes from sharing. Give a crystal. Instill a passion. Spark a life!

Jack Halpern
45 Forest Side Avenue
San Francisco, California 94127

notes from the EDITOR



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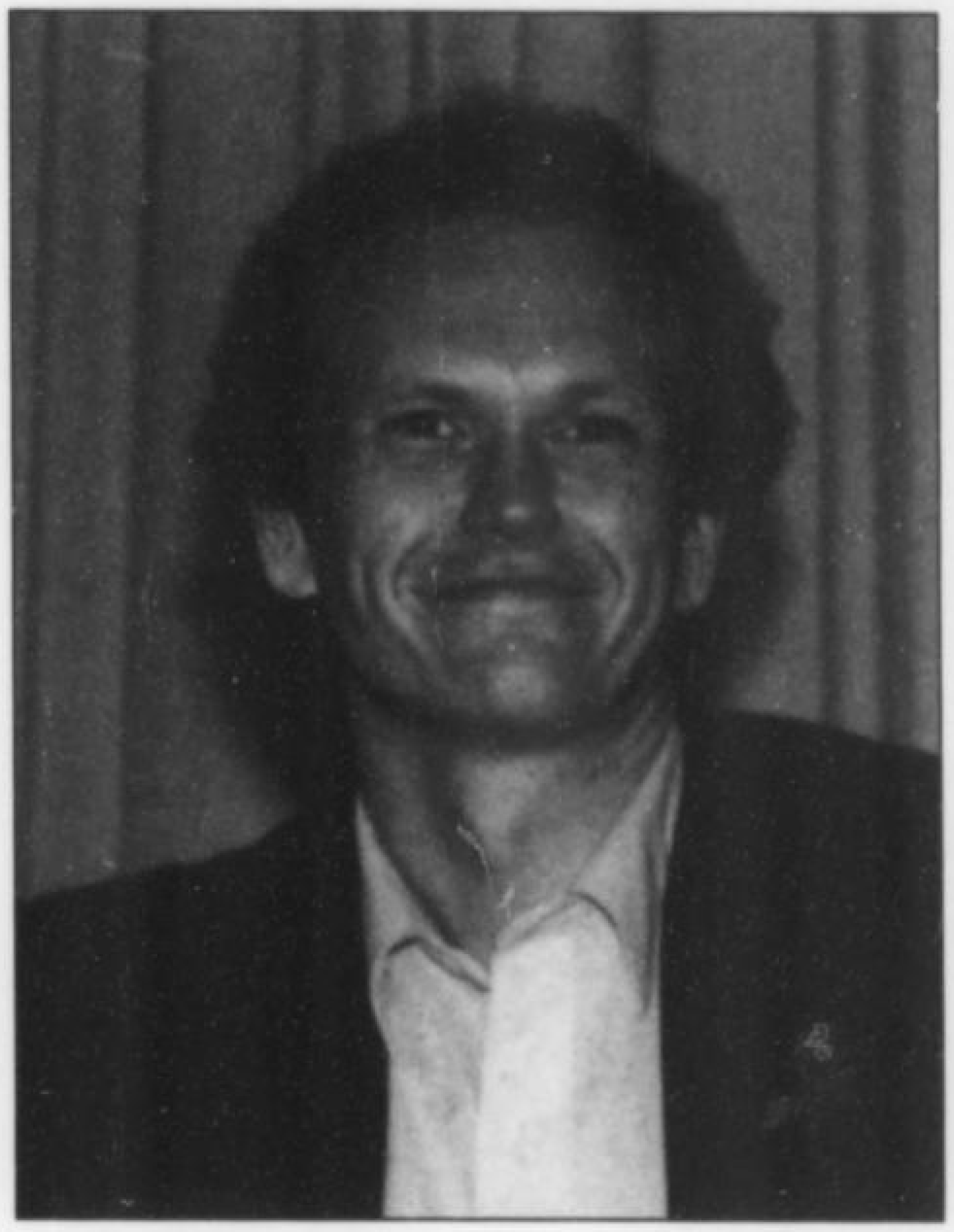
A tremendous amount of time and hard work has gone into the preparation if this index, and we are very proud of it. Even those readers who do *not* possess full sets of back issues will find it extremely useful, not only in accessing the issues they do own but it determining which other back issues they will want to acquire. Authors will be able to find a full bibliographic citation for any article without having to look it up in the magazine. And collectors with special interests (e.g. Pseudomorphs, epitaxy, quartz, or Arizona localities, to mention just four) will find complete listings of every sustantive reference to their specialty that has ever appeared in the *Mineralogical Record*. We strongly feel that no serious reader should be without this reference work.

Copies can be ordered directly from the Circulation Manager for $35 plus $3 postage and packing. Credit card orders may be faxed 24 hours a day to 520-544-0815.

NOTICE

Died, Ronald E. Bentley, 46, in Windsor, Connecticut. Ron was well-known in the mineral world as a collector, dealer, curator, consultant, writer, historian, lecturer, show promoter, and special friend of the *Mineralogical Record*.

Born in Philadelphia, he began a lifelong interest in minerals around 1962 through the encouragement of his family, the local mineral club, and the Easthampton mineral dealers Alvin and Marjorie Schortmann. He soon found himself spending weekends and summers visiting the Schortmanns and working with Alvin in the mineral shop, sorting, pricing and arranging specimens. When the Schortmanns went on vacation, Ron tended the shop and was paid in specimens.



Ronald E. Bentley
(1948–1995)

In 1971 Ron graduated with a degree in Business Administration" from the Lowell Technical Institute in Lowell, Massachusetts; the Schortmanns decided it was time for them to retire, and they offered their business to Ron. A purchase arrangement was arrived at, and later that summer the Schortmanns' stock was trucked to Windsor, Connecticut, where it reopened as Bentley's Minerals. At the same time that Bentley's Minerals was getting off the ground, Ron took a job working for Ray-tech Industries (manufacturers of ultraviolet lights and lapidary equipment) for a couple of years to help support his mineral business. In time he took on a partner, Jim Logan, and together they operated the business until moving to Tucson in 1980.

Ron developed a strong interest in the historical side of mineral collecting in 1972, when he was given a stack of 80 issues of *The Mineral Collector* magazine dating from 1894 to 1909. His friendship with the prominent Brooklyn mineral collector and micromounter, Neal Yedlin, also helped to foster his enthusiasm for things historical. This interest manifested itself first in his important collection of old mineral specimen labels, begun in 1972, which ultimately grew into one of the two or three best label collections in the world (it is today preserved in the Mineralogical Record Library). He also became quite knowledgeable in the field of antiquarian mineralogical literature, and, along with his father, Earl, developed an interesting collection of antique miners' lamps and mining memorabilia. In 1977 he was invited to share his enthusiasm through a new column in the *Mineralogical Record* entitled "The Historical Record." It ran for seven years, and was a popular feature.

Ron donated his time and energies to the *Mineralogical Record* in other important ways too. In 1978 he began helping with the annual fund-raising auction during the Tucson Show, putting in time every year until the auction ceased in 1989.

In Tucson Ron indulged his interest in minerals mainly as a hobby while obtaining his real estate license. But in 1981 he took a new job that utilized his long experience in minerals: he was hired as curator and mineral-secretary for Texas oilman Perkins Sams, who was in the process of rapidly building what he hoped would become the world's finest private collection of minerals. Working with his old friend, former Smithsonian curator Paul Desautels (who had been retained as consultant and buying agent), Ron spent several interesting years traveling the world in the service of high-finance mineral collecting.

The Sams collection was sold to the Houston Museum of Natural Science in 1985, and Ron accompanied it for a time, continuing in his role as curator. But the position soon came to an end, and Ron left Texas to set up his own consulting business back home in Connecticut. It was at this time, in 1987, that Ron joined the Board of Directors of the Mineralogical Record, a position he continued to hold until his death. During his years on the Board he was instrumental in obtaining important donations, helped to arrange for the magazine's special full-color supplement on the Carnegie Museum of Natural History, and played a leading role in Board actions which have helped preserve the future of the magazine.

Ron's major contribution to the content of the *Mineralogical Record,* in addition to his columns, was a series of articles written with Pete Dunn and Wendell Wilson on mineral fakes, frauds, mislabeling and trimming in 1981–1986. He also assembled a warm tribute to his late friend Neal Yedlin, published in 1979.

After his return to Connecticut Ron consulted privately for a number of clients regarding collections, appraisals and curating, and he found time to branch out into yet another area of the mineral world: show promoting. Ron founded the show in Springfield, Massachusetts, in 1988, which has since been taken over by Marty Zinn, and continues successfully as the annual East Coast Gem and Mineral Show.

In addition to his mineralogical pursuits Ron was an avid horticulturist specializing in the raising of orchids, a knowledgeable collector of fossils and seashells, and a devoted fan of science fiction. A passion for all of natural history characterized his life; and his college training (he started out in Electrical Engineering) provided for a more technical understanding of science which he never ceased to find useful.

During the years of his long illness Ron always maintained his contact with the Mineralogical Record and fulfilled his duties as a Director, serving as President from 1989 to 1991. He will be fondly remembered as a kind, intelligent and supportive friend who generously shared his passion for minerals in a way that enriched all around him.

Ron Bentley is survived by his mother, Dorothy S. Bentley, his brother Carl R. Bentley, and also a nephew, two aunts and two uncles.

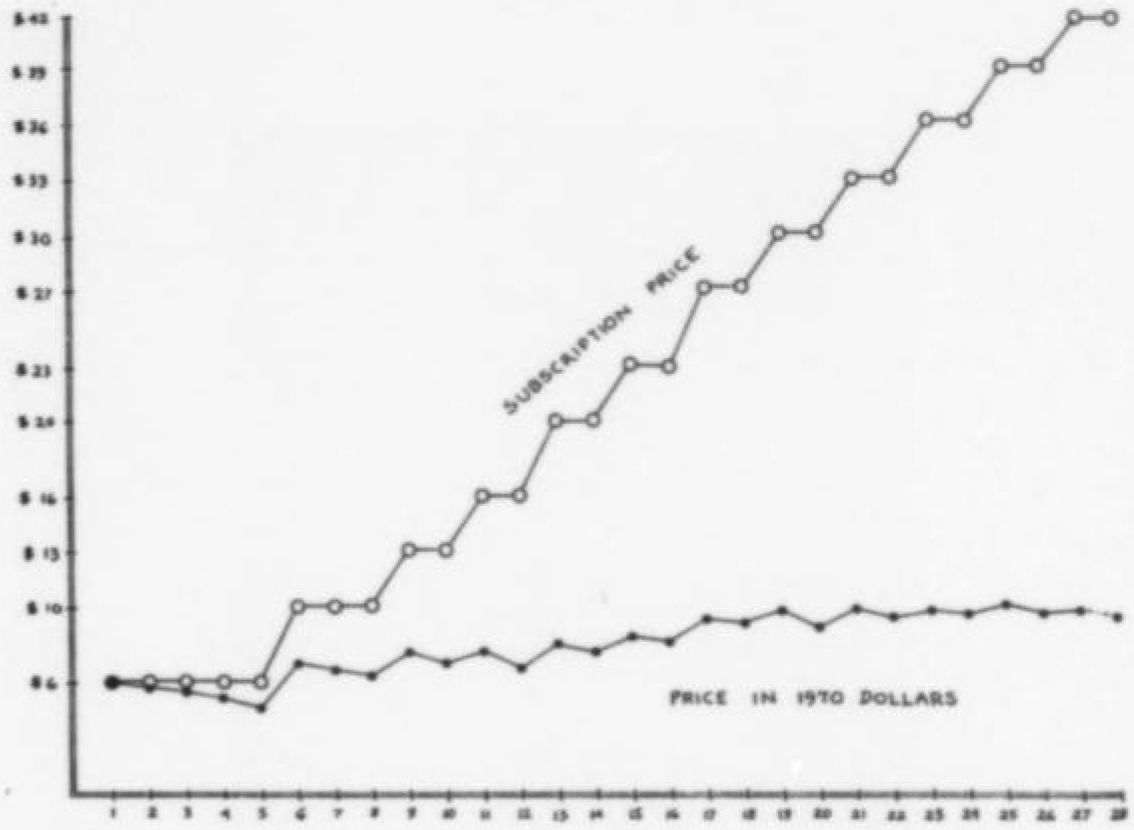


Figure 1. **Annual subscription price and equivalent in constant-value 1970 dollars, 1970–1996 (data courtesy of the Bureau of Labor Statistics, Washington).**

SUBSCRIPTION PRICE

Part of the aggravation associated with getting older is that you can remember when everything was so much *cheaper.* Back in 1970 you could mail a first-class letter in the U.S. for 6¢, and a subscription to that bright new magazine, the *Mineralogical Record,* cost only $6 (four black & white issues totalling 178 pages). Today a stamp is 32¢, and the price of a domestic subscription is now going up to $42 (six full-color issues totalling nearly 600 pages in 1995).

Why does the price have to go up again? Because, sad to say, everything we utilize in the production of the magazine is continually becoming more expensive. Fortunately the average rate of inflation has been low in recent years. To cover the two-year period since our last increase will require a rise of only $1.50/year (3.8%/year). This is a little more than the average U.S. inflation rate because of particular factors such as the cost of magazine paper (up 17% and still rising fast).

To put the price of the *Mineralogical Record* in perspective it is always useful to look at the complete history of the subscription price relative to the average rate of inflation. Figure 1 shows that, although the price has gone from $6 to $42 in 26 years, the actual price in constant-value 1970 dollars is still down around $10. This real increase of $6 to $10 has paid for the tremendous increase in size and color over those years, an improvement which everyone has welcomed.

But why, some subscribers ask, can some other popular magazines such as *National Geographic* or *Scientific American* or even *Lapidary Journal* offer a 1996 subscription at significantly lower prices than we do? The answer has simply to do with economies of scale. Color separations, for example, which are film negatives used in color printing, cost a fixed amount regardless of how many copies of the magazine are printed. Consequently if the number of subscribers were to double, the cost to each one for color separations would be cut in half. The same is true of typesetting. And even in the case of printing, the cost per issue goes down significantly as the press run goes up.

Our problem as mineral collectors is that only about 6,000 of us are of a mind to subscribe to a high-quality specialty magazine such as the *Mineralogical Record*. If our interest was in a more populous field or hobby where 15,000 or 20,000 or 50,000 enthusiasts were disposed toward subscribing to a fine specialty publication, the price would be significantly less. But that is not the case; minerals are our love, and there are only so many of us with this particular passion and a mind enquiring enough to want to read about it. So we're stuck having to pay more for the limited-run publications we like. But, speaking on behalf of the authors, photographers and editorial staff of the *Mineralogical Record,* we will be working as hard as we can to produce the best-looking and most informative and authoritative magazine possible with the money you give us. We hope that all of our readers around the world will consider their money well spent and their pleasure well worth it.

MSA AT TUCSON

The Mineralogical Society of America (MSA), a cosponsor of the Tucson Mineralogical Symposium, will have a booth on the main floor of the Tucson Gem and Mineral Show this year. People are invited to stop in at the booth to learn more about the MSA, its interests and publications, or just to chat about minerals.

On Thursday of the show (Feb. 8) curators from important museums including the Smithsonian Institution, Harvard Mineralogical Museum, Natural History Museum of Los Angeles County, American Museum of Natural History, and others will be on hand in the booth to meet and talk with interested show-goers. (A schedule of the hours during which specific curators will be present will appear in the show program available at the door.)

AREA CODE PROBLEMS

The telephone company recently changed our area code from 602 to 520. Unfortunately, some callers have been unable to reach us using 520; apparently not all telephone systems, especially in Europe, are programmed to recognize the new code. Due to many complaints from businesses here in southern Arizona, the telephone company has extended the "transition period" through the end of 1996; during this time, the old area code of 602 will *also* be in service. So, if your call does not go through using 520, try it again using 602.

Mineralogical Record

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Since 1990 the Mineralogical Record has been producing hand-made limited-edition reprints of some of the rarest and most sought-after antiquarian color-plate mineral books. Each edition has sold out quickly and become a collector's item in its own right. These beautiful and interesting works make fascinating and useful additions to any library. People on our mailing list receive **advance notice** of each new edition by mail. A place on our list is yours for the asking . . .

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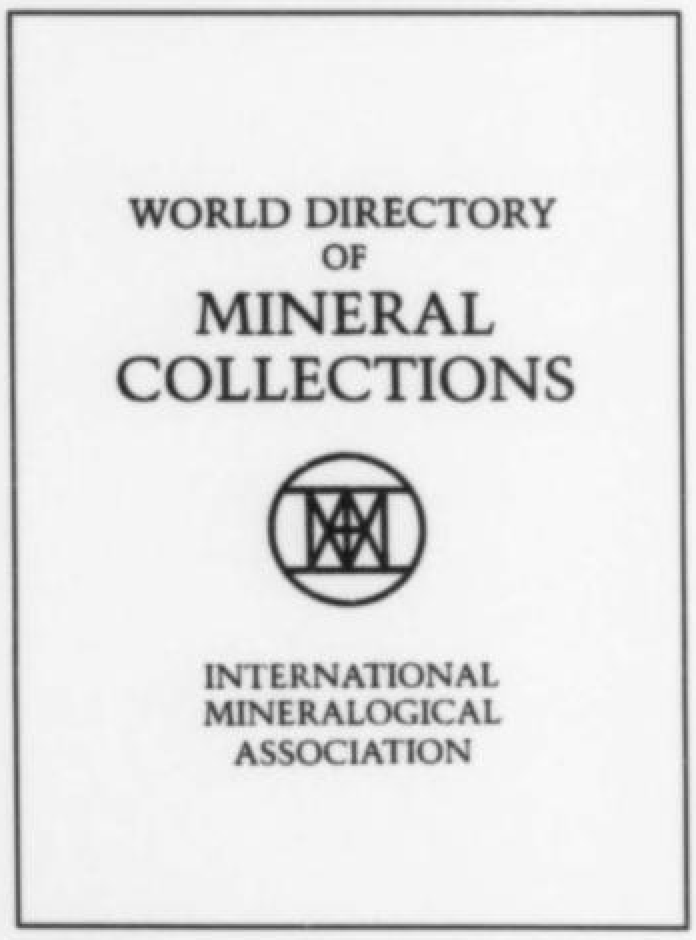

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LUMINESCENCE IN MINERALS

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Luminescence is not only a source of beauty and interest in minerals, but is also of great scientific and economic importance. Most familiar to the student of mineralogy is the colorful luminescence of some minerals under ultraviolet light, known as photoluminescence or fluorescence. The causes of these colors are similar for all types of luminescence. A basic understanding of luminescence phenomena can give insight into a mineral's formation and the details of its structure and chemistry.

INTRODUCTION

Luminescence is the non-thermal emission of visible light by a substance. The emission of visible light by minerals in response to irradiation by ultraviolet light is a prime example. The principal mechanism for most types of luminescence is essentially the same, that is, the interaction of incident energy with electrons in a solid. One of the great scientific discoveries of this century is that the electron energy levels within an atom can have only discrete, specific values; that is, they are *quantized*. Because these energy levels have discrete values, the energy differences between levels are also quantized, and this provides the basis for explaining the mechanisms of luminescence in minerals.

There are numerous varieties of luminescence. Those produced by exposure to incident energy or radiation sources are distinguished by the type of incident radiation. Table 1 gives a list of different types of luminescence and the associated source of excitation. Of the types of luminescence listed, two have had the greatest use by mineral enthusiasts and professional mineralogists. These are photoluminescence and cathodoluminescence. The primary reason for their popularity is the relative ease of producing ultraviolet light (for fluorescence) and an electron beam (for cathodoluminescence). Because of their popularity, this paper will constrain its discussion to these two types of luminescence.

There are many comprehensive references in the literature listing minerals that luminesce (e.g., Robbins, 1994; Henkel, 1989). We will not attempt to supplement these here; however, we will consider a few "classic" localities for luminescent minerals which provide insight into some interesting geochemistry.

***Table 1.* Different types of luminescence.**

Name	*Excitation Source*
Photoluminescence	Ultraviolet radiation
Cathodoluminescence	Electrons
Ionoluminescence	Ions
Roentgenoluminescence	X-rays
Chemiluminescence	Chemical reactions
Bioluminescence	Chemical reactions in living organisms
Triboluminescence	Several mechanisms including the breaking of bonds (not well understood)
Phosphorescence	Time-delayed emission due to low probability transitions (not excitation source specific)
Thermoluminescence	Time-delayed emission due to release of trapped electrons as a result of thermal energy input

LUMINESCENCE MECHANISMS

In order to discuss luminescence mechanisms, we first need to state a few definitions. Luminescence in minerals involves electronic processes occurring in certain atoms or combinations of atoms in a mineral structure. Most of what happens in a luminescent system can be described without resorting to complicated terminology, diagrams or equations. We can easily think about three basic processes: (1) absorption of external energy or radiation (i.e. ultraviolet light), (2) transfer of energy, and (3) emission of visible light. The processes of luminescence are diagrammed in Figure 1. Absorption of incident energy can cause an electron (possibly more than one) to be raised into a higher energy state. This electron will ordinarily be in its lowest energy state (or *ground* state) prior to absorption. It is said to be in an *excited* state after absorption. An electron may have many excited states, each one higher in energy than the next. However, we need to consider only one excited state here. The common way to show this absorption process is with cartoons like those in Figure 1. The electron can be thought of as "leaping" into a higher energy position within its atom, and the atom itself can then be thought of as existing in an "excited" state.

Just as the electron can become excited by absorption of incident radiation, it can return to its ground state by the emission of energy. The energy levels that the electron takes

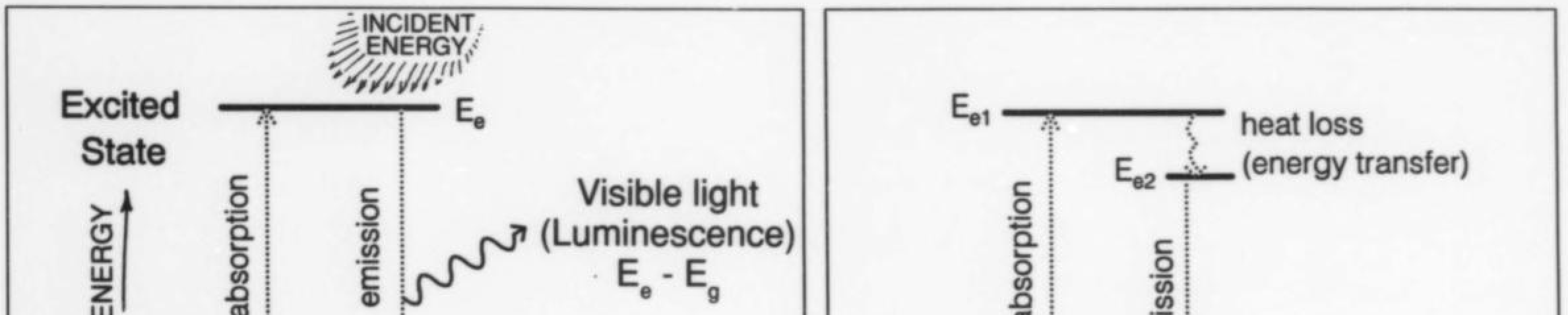

***Figure 1.* Schematics of energy levels in atoms and the transitions which result in luminescence.**

***Figure 2.* Calcite crystal, 19.5 cm, from Dal'negorsk, Russia. Left: normal light. Right: under shortwave ultraviolet light. Van Scriver/Pliaskov Minerals; Jeff Scovil photos.**

are quantized; the energy emitted will be equal to the difference in energy between the excited and ground states. The emitted radiation can be described by both its energy and its wavelength, and the two are inversely proportional. If the absorption and emission were equal and opposite to one another, then the energy (hence the wavelength) of the emitted radiation would be the same as that absorbed (Fig. 1a). For example, if the incident radiation was light in the ultraviolet range then light in the ultraviolet range would be emitted when the electron returned to its ground state, and our eyes would not see it.

However, the luminescence process is usually more complex. More commonly, there is one or more intervening steps between absorption and emission, which involve a transfer of energy. Figure 1b illustrates such a process. Absorption causes an electron in the ground state, E_g, to jump to an excited state, E_{e1}. Rather than relaxation directly back to the ground state the electron can move to another excited state, E_{e2}, of lower energy. This transition, however, does not result in emission of light, rather it transfers energy directly to the crystal by increasing atomic vibrations which we call heat. As the excited electron then returns to the ground state from the E_{e2} excited state, emission may occur. Because the difference in energy between the second excited state and the ground state (E_{e2}-E_g in Fig. 1b) is smaller than the difference between the first excited state and the ground state (E_{e1}-E_g), the light emitted in this process will have a longer wavelength than the absorbed energy. For example, if the incident energy is light in the ultraviolet range, emission may be in the visible part of the spectrum, hence we see it as luminescence. This difference in energy and wavelength between the absorbed and emitted radiation is necessitated by the physical law of conservation of energy. If no energy transfer occurs, *the emitted energy must be equal to the absorbed energy.* This fact is known as *Stoke's law,* and if there is an energy difference between the absorbed and emitted light then the shift in energy is known as *Stoke's shift.*

Atoms in which the energy levels are appropriately separated so as to emit energy in the visible region of the spectrum are known as *activators.* The processes that we have been describing make up the simple luminescence mechanism of a mineral with an activator atom in its structure. Most often the activator is present in a mineral in very small concentrations; however, in some cases the activator can be a major constituent. It is within or near this type of atom that the absorption, energy transfer and emission processes occur. As was mentioned above, a given atom may have multiple excited states to which electrons can move. It turns out, however, that not every excitation (absorption) or relaxation transition is possible for a given atom. Certain transitions in an atom may be forbidden. Also, different allowed transitions may have different probabilities of occurring. Further consideration of activators will be presented in the next section.

We can now make a bold leap into a more involved mechanism, but one that is very important in many luminescent minerals. Here we will look at the interaction between two atoms in the luminescence process. In Figure 1c the energy levels have been split into two parts, representing the levels in two atoms. In the first atom an electron absorbs energy and is moved to an excited state within that atom. The energy of the excited electron in the first atom can be transferred to the second atom, causing excitation of its electron. In this case no excitation by external radiation in the second atom is necessary. In the second atom an excited electron drops into its ground state with the emission of visible light. This process can occur between the same kind of atoms, or it can occur between different kinds of atoms. In the latter case the emitting atom is called an activator, and the absorbing atom is called a *sensitizer* or *co-activator.* The transfer of energy can be directly from the excited sensitizer to the activator, as pictured in Figure 1c, or the sensitizer may actually go through emission whereby the emitted radiation is then absorbed by the activator. This more complex mechanism is important because the probability of the electron absorbing radiation and leaping into the excited state can be very small in certain activator atoms. The probability can be so small, in fact, that luminescence emission would never be seen from these atoms regardless of the intensity of the radiation applied to the mineral. However, if a sensitizer atom is nearby, and this atom can strongly absorb the incident radiation (i.e., the probability of absorption is very high), then emission from the activator can occur following the transfer of energy from the first atom to the second.

One further luminescence mechanism is important for us to consider. This is illustrated in Figure 1d. In this diagram we show a small energy transfer process that can occur near the excited state. Sometimes an electron in the excited state may be able to move around from atom to atom within the mineral's structure. If it can do this, it may eventually become stuck on a particular type of neighbor atom or perhaps some defect in the mineral structure (a vacancy or an atom in the wrong position). The electron gives up some of its energy when this happens, hence there is a drop in its energy state. The electron cannot return to its original ground state from this new position. That transition is forbidden and the electron is said to be *trapped*. It must wait until enough vibrational energy from the mineral's structure (i.e, atom-atom vibrations) knocks it back up into the higher-energy excited state, and then it can drop down into the ground state and emit visible light. The time-delayed release of the electron from the trapped state is the basic mechanism for what is usually called *phosphorescence,* i.e., a long decay of the luminescence after the incident source has been removed. The same mechanism also produces what we call *thermoluminescence,* the emission of light when trapped electrons are moved back up to their original excited state by an external heat source.

It is important to sort out some of the terminology at this point. Fluorescence, in the strict sense, involves only transfers between ground and excited states, often with some energy transfer as heat to produce a Stoke's shift. The process is quite fast, much faster than the naked eye can detect, and stops almost instantaneously when the radiation source is removed. Fluorescence processes can be slowed if the probability of emission is small. This can result in luminescence with a very brief, barely detectable, decay in emission after removal of the source. Phosphorescence, in the strict sense, involves an intermediate excited state, from which emission, created by an electron dropping into the ground state, has a very low probability. It is not like trapping-related emission decay, because the emission is from this second excited state and not from the original excited state. Phosphorescence can have a very long decay, e.g. many seconds or even minutes. This sort of mechanism is seen in organic chemical compounds and is often of a different wavelength or color compared to the fluorescence. Finally there is thermoluminescence, which is emission produced when the excited electrons are bumped out of their traps by an externally applied heat source. Absorption may have occurred at any time prior to trapping, possibly years before. Or the electrons may have been boosted into their excited states by the action of natural radioactivity. In any case, the emission is related to the application of external heat or the heat always present in the mineral due to atom-atom vibrations. It is this latter mode of thermoluminescence that is often called "phosphorescence" for minerals at room temperature, though it is not literally correct. George Blasse, one of the current experts in luminescence theory, has suggested the term "afterglow" for emission from trapped electrons without the application of heat (Blasse and Grabmaier, 1994).

Luminescence due to the presence of an activator element is by far the most common and important. However, there is a second type of "center" that can induce luminescence. The presence of certain types of defects in the structure of a crystal can also cause luminescence. Defect centers are quite difficult to characterize, and in many cases we simply do not understand their role in luminescence. One type of defect that is fairly well understood, however, is known as a Frenkel defect, or simply an F-center (Walker, 1985). In halite, NaCl, displacement of a Cl^- ion will leave a vacancy in the structure where the Cl should reside. This can occur as an accident during crystal growth or it can be caused by bombardment by very energetic radiation. As a mechanism of charge balance, an electron can become trapped in this vacancy. Just as in an atom, there exist different energy states for this electron in the vacancy trap. Transitions can then occur between energy states, and if transitions emit light in the visible, we see luminescence. F-centers are known to occur in a number of minerals, in particular the alkali halides.

PHOTOLUMINESCENCE (FLUORESCENCE)

By far the most easily accessible type of luminescence and hence the most popular amongst mineral enthusiasts is photoluminescence, widely referred to as fluorescence. As previously mentioned, the main cause of photoluminescence is the presence of activating elements in the mineral, so further discussion of these activators is warranted. The concentration of such activators may be quite small (in the parts per million) or they may be a major constituent of the mineral.

Activators

From the previous discussion we learned that the electronic structure, that is the difference between energy levels, of an atom governs its ability to serve as an activator of luminescence. In this section we will consider some of the more important activator elements and how they work in luminescent minerals. The most common activator is probably manganese in the divalent state (Mn^{2+}). In this oxidation state, it often replaces Ca^{2+} in carbonates, phosphates and silicates, but it can also be found in sulfides and many other kinds of minerals. Divalent manganese, particularly when present in calcite, has a very small probability of absorption of ultraviolet light. Hence, calcite with Mn^{2+} and with no other activators or sensitizers will not be visibly luminescent. However, much calcite from Franklin, New Jersey, is strongly luminescent when exposed to shortwave ultraviolet light, with the emission known to be from Mn^{2+} in its structure. The reason for this strong luminescence is the presence of a sensitizer, divalent lead (Pb^{2+}), which also replaces calcium in the structure. The lead atoms strongly absorb in the ultraviolet. There is then energy transfer to the Mn^{2+} atoms, which readily boosts their electrons into an excited state. Fluorescence is relatively slow from Mn^{2+} in calcite, due to the low probability of emission (just as low as for absorption). If Mn^{2+} were not present in Franklin calcite, what would happen? Probably we would see emission from the Pb^{2+} directly, with a different emission color. However, there is enough Mn^{2+} present in Franklin calcite that this situation never occurs.

Other sensitizers in calcite can create strong emission from Mn^{2+} in response to longwave ultraviolet, most notably rare earth elements (REE). In this case the luminescence emission from the calcite can appear different due to the summed emission from the Mn^{2+} and from the REE themselves. In silicate minerals there is another way to get around the problem of the small absorption probability for Mn^{2+}. In silicates the silicate groups themselves can absorb ultraviolet and transfer this energy into Mn^{2+} (or other activators). Hence, the silicate framework of the mineral acts as a sensitizer. Thus, willemite from Franklin and other localities has very strong luminescence from Mn^{2+} relatively independent of the lead concentration. Other silicates can behave similarly.

Mn^{2+} is not only a common activator, but a versatile one. It can produce luminescence in any color of the visible spectrum. A complete discussion of how this is achieved is well beyond the scope of this article, but suffice it here to say that the type of atoms surrounding the Mn^{2+} and their positions in the mineral's structure largely determine the color of emission. The most common emission colors for Mn^{2+} are from yellow through a deep red.

In addition to acting as sensitizers, the REE can also be very strong activators. These also substitute for Ca in many minerals (Mariano, 1989; Mariano and Ring, 1975). Of particular interest is REE activation in phosphates like apatite. The fifteen REE (La to Lu) are geochemically very similar and are therefore almost always found together in nature. Several REE ions such as Ce^{3+}, Eu^{2+}, Eu^{3+}, Sm^{3+} and Dy^{3+} can act simultaneously as activators with the resulting luminescence color being a combination of them all. For example, the different luminescent colors of the apatite in Figure 10 are due to different proportions of Sm^{3+}, Eu^{3+} and Mn^{2+} (John Hanchar, personal communication). Luminescence in REE-doped phosphates can be extremely intense and has been used extensively in the phosphor industry.

Another important activator is trivalent iron (Fe^{3+}). This ion produces the deep red luminescence common in feldspars and is probably responsible for the deep red emission of many scapolites, eucryptite, and other silicates. Interestingly, trivalent as well as divalent iron can "quench" the fluorescence activity in other activator ions, such as Mn^{2+}. This is because trivalent iron has extremely strong (high probability) absorption in the ultraviolet and blue part of the spectrum, which effectively takes away the excitation energy from other activators.

Chromium in the trivalent state is another important activator, responsible for the fluorescence of rubies, spinels, and several silicate minerals. It is probably a more common activator than generally assumed. Activators in minerals can take a variety of forms. We have been discussing single impurity atoms above, but activators may also be a major constituent in the structure. For example, rhodochrosite has mainly Mn^{2+}, and the luminescence is a beautiful shade of red. Some activators are not actually contained in a mineral structure in the strict sense, but are present as inclusions of a second mineral or fluid phase. This is generally the way in which uranium (actually uranyl, UO_2^{2+}) activates many non-uranium minerals. Inclusions of a hydrocarbon can produce luminescence in fluorite. The brown color and wonderful fluorescence and phosphorescence of fluorite from Clay Center, Ohio, is due to hydrocarbon inclusions. Still other "activators" are actually groups of associated atoms. These include tungstate, vanadate, titanate, molybdate, zirconate and others. Scheelite, with tungstate groups or WO_4^{-2} units, is the prime example of this type of activator. The tungsten atom alone will not activate luminescence, but requires the tetrahedral group of oxygen atoms about it to form a luminescent system. All of the above mentioned activators are metal cations; however, certain anions and anion groups are known to cause luminescence. A prime example of this is S^{2-}. Activators can interact with each other and with sensitizers to produce quite complex luminescent processes in minerals.

Generation of Ultraviolet Light

Ultraviolet light can be generated in a variety of ways, but the form most used by mineral collectors is the "low pressure" mercury discharge lamp. This is a simple fluorescent-type lamp with filaments on each end to volatilize the mercury inside into vapor. It then uses a high voltage to produce a conduction path through the mercury vapor. The vapor atoms are thus excited by the high voltage, and lose this excess energy by emitting light. One can think of this as the gaseous state analog of the basic fluorescence mechanism in an activator. The mercury atoms can emit several wavelengths of light depending on the state to which they have been excited. If there is a higher pressure in the mercury lamp the mercury atoms can collide more often and lose their energy to heat (or velocity) of the other atoms. At high enough pressures this occurs fast enough to limit the excitation that occurs from the high voltage, and the lamp produces mainly lower energy, i.e. longwave, ultraviolet and visible light. Hence shortwave ultraviolet lamps use lower gas pressures. Because the absorption processes in mercury atoms are quantized, the emitted light from these states can have only certain energies. This, in turn, means that ultraviolet light from a lamp consists of only certain wavelengths of ultraviolet (and visible) light. Popular longwave ultraviolet lamps usually use an ultraviolet-emitting phosphor inside the lamp envelope. This phosphor absorbs shorter-wave ultraviolet light and converts it into a longer ultraviolet wavelength, effectively boosting the longwave ultraviolet output of the lamp. The phosphor is effectively fluorescing in the ultraviolet.

All ultraviolet lamps also produce visible light. This must be carefully removed or the lamp cannot be used to view fluorescence effectively. The usual method is with glass filters of special compositions that selectively pass ultraviolet light, but absorb visible light. As most collectors know, these filters do not work perfectly, and all pass some purple or red light. The filters also deteriorate with use, as do the lamp tubes themselves.

Other sources of ultraviolet light are the sun; hydrogen and other types of discharge lamps; special laser systems; and "hot" sources. The last type consist of so-called "black body" emitters whose incandescence merely extends into the ultraviolet. Because of the ultraviolet component in sunlight, the color of many minerals in sunlight is in part produced and enhanced by fluorescence. Common examples include autunite and some fluorite, especially the purple/green specimens from Durham, England, which fluoresce blue.

CATHODOLUMINESCENCE

In cathodoluminescence the excitation source is a beam of accelerated electrons, rather than ultraviolet light. Because of the added complexity and expense associated with electron sources it has not found as much favor among mineral collectors; however, it has found wide use by mineralogists and petrologists (Remond, 1977; Marshall, 1988; Barker and Kopp, 1991).

As with ultraviolet light, a beam of electrons can be created by several different mechanisms. The two most widely used are the cathode ray tube attachments for petrographic microscopes and electron microprobes. The electron microprobe is a sophisticated and expensive piece of equipment. Because of cost, ease of use, and versatility, cathodoluminescence microscope attachments are used more often. These attachments use a cold cathode electron gun which must be operated in a vacuum. The accelerating energy and the electron current can both be varied.

For the most part, the mechanisms and activators for photoluminescence are the same for cathodoluminescence. There are, however, slight differences in the details between the two, and cathodoluminescence has a few unique qualities which are very desirable. The depth of activation from the electron beam is much less than from ultraviolet light. This allows for better spatial resolution and yields greater detail in fine-scale luminescence patterns. Also, the luminescence intensity, or yield, is generally higher in cathodoluminescence than in photoluminescence due to the higher density of excitation energy in the sample. Finally, the intensity and energy of the source can be easily varied, which allows more versatile experimentation.

LUMINESCENCE ZONING IN MINERALS

Now that we have looked at the mechanisms of luminescence, let's turn our attention to the kinds of information that luminescence can reveal about a mineral. We will first consider luminescence zoning. The most obvious variations

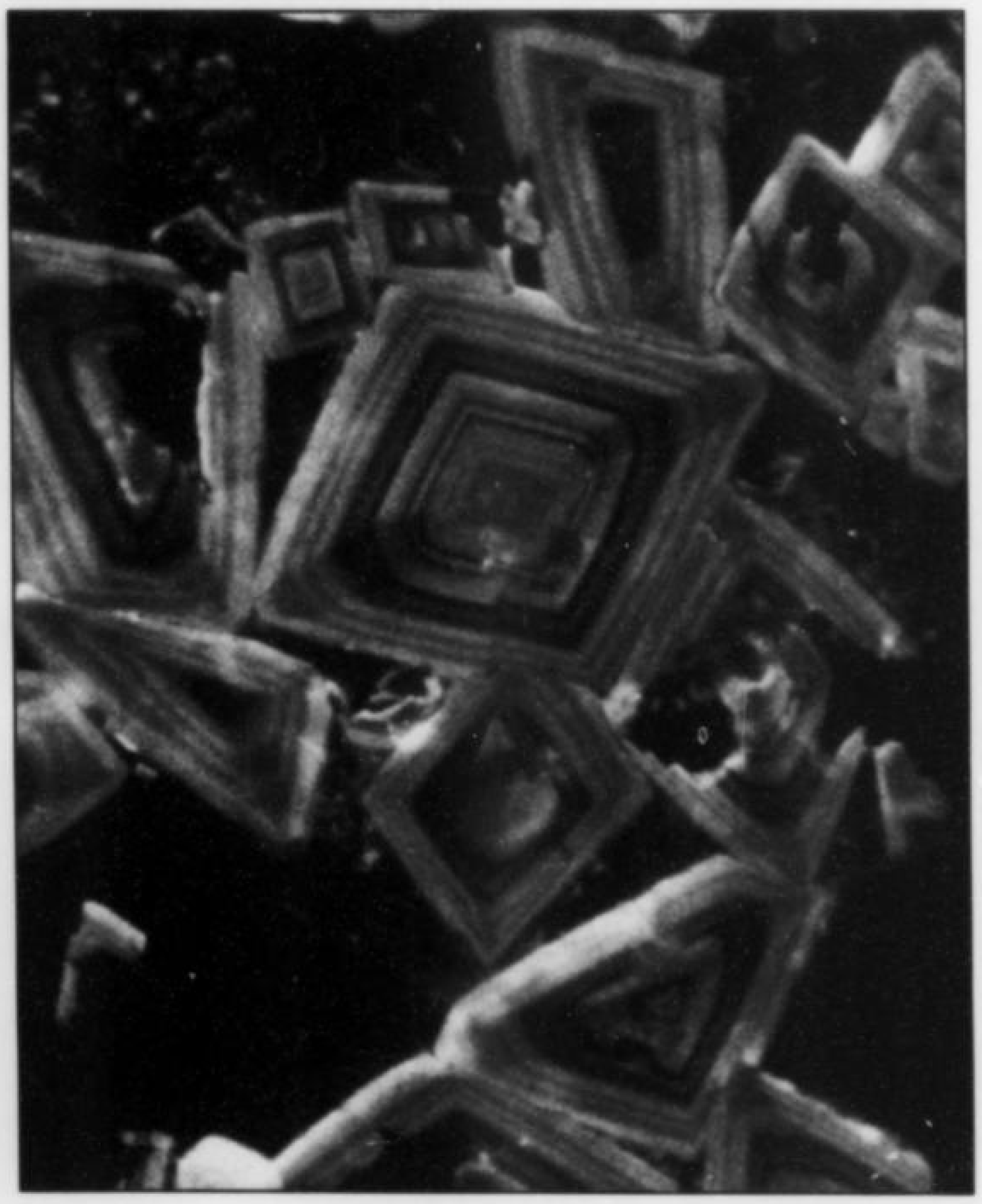

Figure 3. **Cathodoluminescent image of concentric and sectoral zoning in dolomite, Burlington Formation, Mississippi. From Reeder and Prosky (1986).**

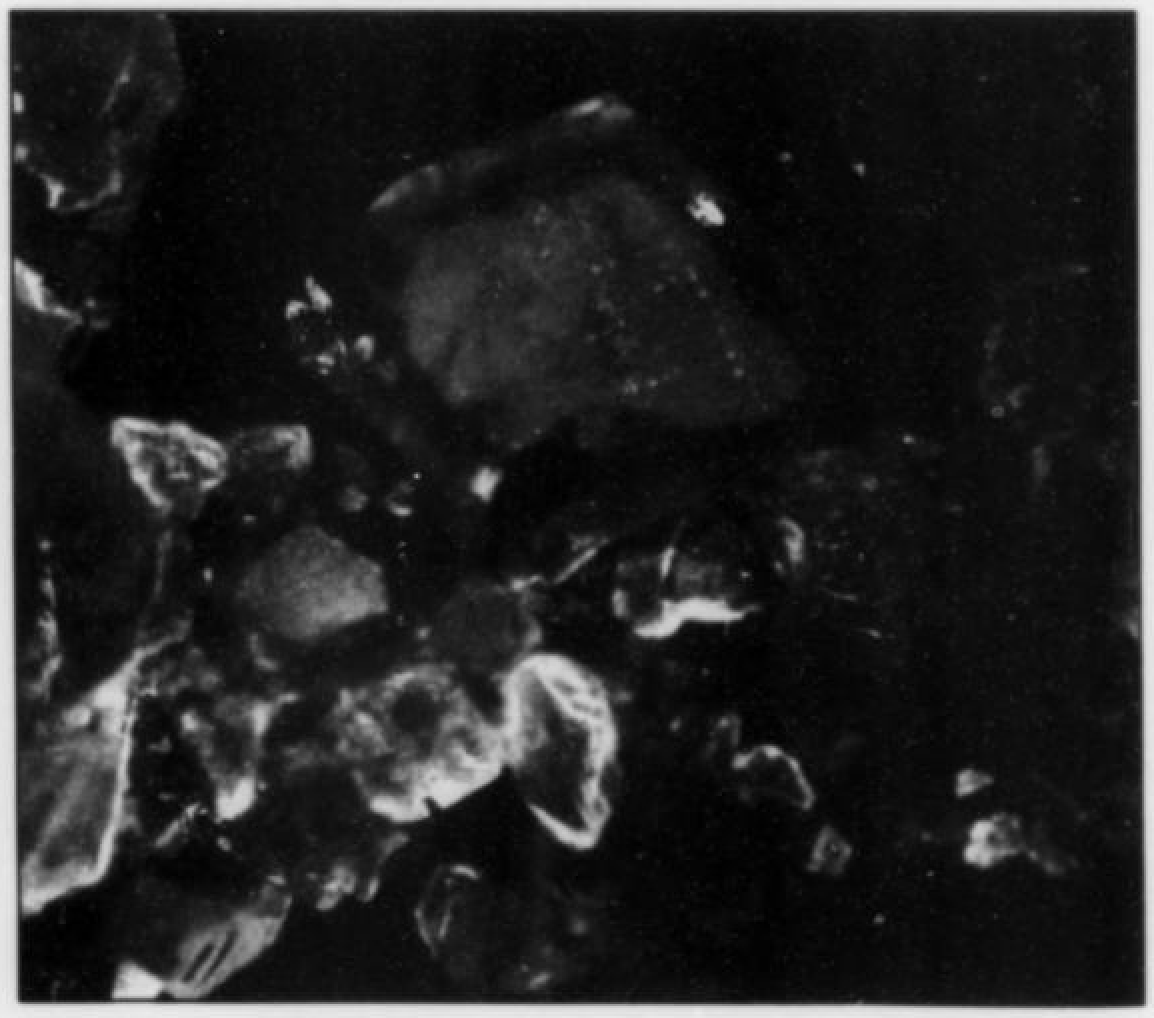

Figure 4. **Scheelite crystals to 2 mm, from the Camp Bird mine, Ouray County, Colorado. The outer zone fluoresces blue but the molybdian cores fluoresce yellow. Peter Modreski photo.**

***Figure 5.* Willemite (green) and calcite (red) fluorescing in place underground at the Sterling Hill mine, 500 level, 1200 stope. The view is about 30 cm across, and was shot using shortwave ultraviolet light. Photo by Peter Modreski.**

in luminescence can be seen between different minerals in a rock that luminesce differently. Magnificent examples of such intercrystalline luminescence are observed in the many mineral associations found in the ores and host rocks of the Franklin-Sterling Hill, New Jersey, deposits (Fig. 5). Luminescence differences between different minerals are used extensively for distinguishing minerals that may look similar in visible light. They can also be of great help when trying to pick out very small crystals in a rock, or prospecting for a particular mineral like scheelite. For the purposes of this paper we will refer to zoning as spacial differences within individual crystals, in other words intracrystalline zoning.

Zoning in minerals is a spatial difference in a particular property or characteristic such as composition, color, symmetry or luminescence. Luminescence zoning is not only beautiful but can provide a wealth of information about such aspects as the morphologic history of a crystal, changes in the environment during crystal growth, growth mechanism, and differences in the atomic structure at the crystal's surface. Because the most common cause of luminescence is the presence of some activating element, luminescence zoning most often reflects compositional differences between different portions of a single crystal. There are several different types of zoning which occur during crystal growth and each can provide unique information. The different zoning patterns that will be discussed can be distinguished by their spatial relationships within single crystals. Although discussed here in terms of luminescence, they can also pertain to zoning of any other property or characteristic of the mineral, but are usually related to compositional differences.

Zoning can occur on many scales and in many different spatial relationships. Zoning may also occur within a mineral by diffusion which may alter the original zoning patterns that formed during crystal growth. Diffusion-induced compositional zoning has been studied extensively in metamorphic garnets (see Spear, 1993 and references therein) as well as other minerals. Of greater variety and potentially more illuminating are zoning patterns generated during crystal growth.

Concentric Zoning

The most familiar type of luminescence zoning observed in minerals is concentric zoning. If growth occurs on all crystal faces more or less evenly, then different intervals of growth will produce concentric layers from the center of the crystal outward. Concentric zoning is seen as compositional differences between these layers of the crystal. The width of the concentric zones may be narrow and the number may be large, as in the dolomite shown in Figure 3. Or they may be wide and as few as two in number (Fig. 4). The boundary between zones may be sharp or it may be diffuse with a smooth gradation throughout the crystal. If sharp, the boundary of different luminescent layers is parallel to the growth surface that existed at the time of growth of those

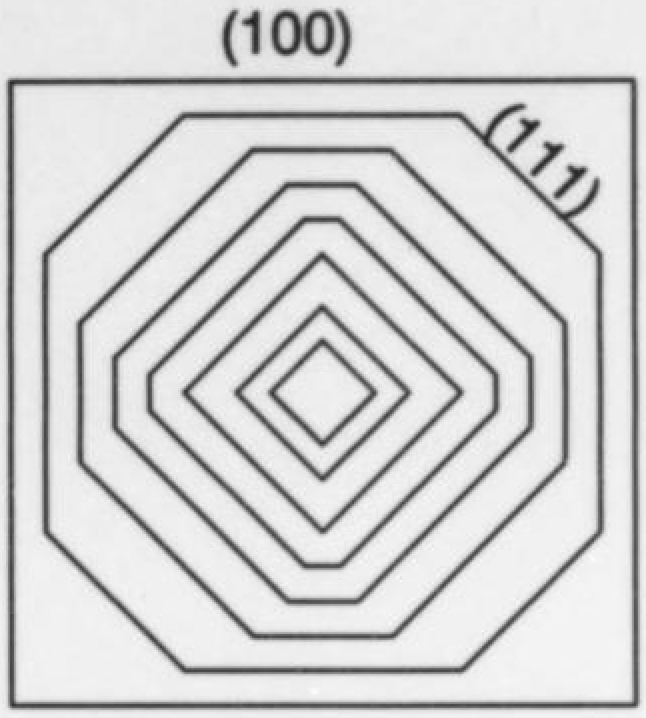

Figure 6. **Schematic cross-section of a cubic crystal showing concentric zoning and changes in morphology during growth.**

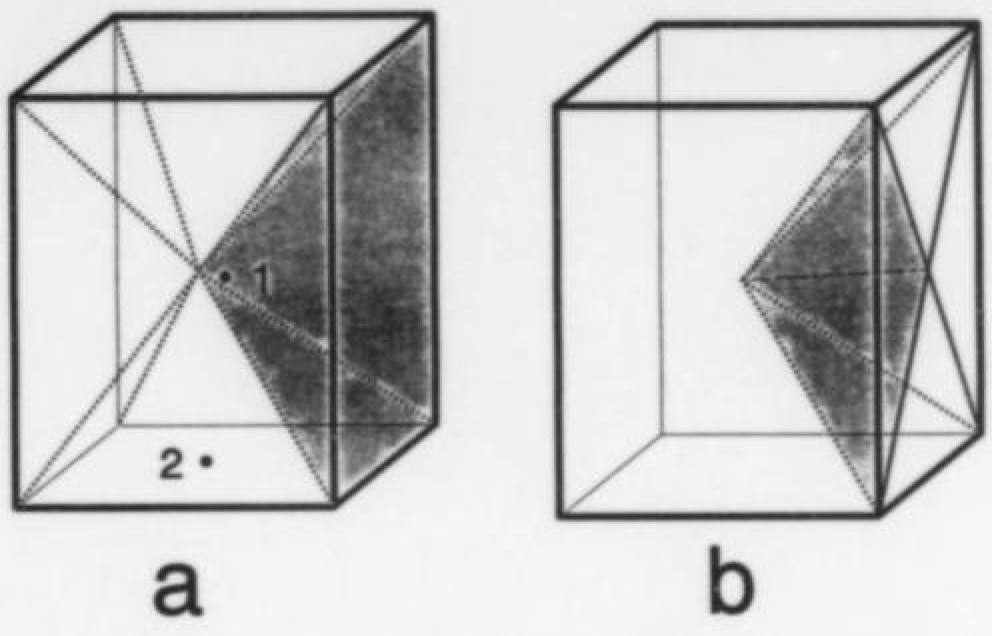

Figure 7. **(a) Schematic of a tetragonal crystal with one of the prism sectors shaded. (b) The same crystal with a growth hillock on the prism face and one of the subsectors shaded. See text for details.**

layers. Changes in the orientation of a given concentric zone delineate regions of the crystal that grew under different crystal faces. Individual concentric zones presumably formed during a specific time interval; consequently they allow for the determination of time-equivalent or coeval portions of different regions of the crystal. This can be thought of as analogous to a stratigraphic sequence. Because concentric zones form parallel to growth surfaces, concentric zoning reflects the morphologic history of a crystal. This is illustrated in Figure 6; concentric zoning shows that the crystal was initially bound by octahedral {111} faces. As the crystal grew outward the cube {100} faces started to form and eventually dominated the crystal morphology. Concentric zoning reflects temporal changes in the environment while a crystal is growing (Spear, 1993). For example, as a crystal is growing outward from a nucleus, changes in the solution or melt composition may be reflected in the composition of the crystal. If the identity or concentration of a luminescence activator fluctuates with time, then concentric bands which grew during different periods will show these differences in their luminescence. Such compositional differences within a crystal can also be induced by changes in growth rate as well as temporal variations in solution properties such as pH, temperature, oxygen fugacity, etc.

Sectoral Zoning

Two genetically similar types of luminescence zoning that do not reflect temporal changes but rather lend information about growth mechanisms and differences (anisotropies) at the crystal surface are sectoral and intrasectoral zoning. A sector is a region of a crystal that has formed by incorporation of atoms or growth units on a given crystal face. Figure 7a shows an idealized tetragonal crystal that is bounded by two forms, the prism {100} and the pinacoid {001}. Outlined by dotted lines are the sectors associated with each face, and one of the {100} sectors is shaded. One can imagine that as this crystal grew from a nucleus at its center, the shaded volume was formed as material was added onto the corresponding prism face. The entire volume of our crystal is then made up of four prism sectors and two pinacoid sectors. Compositional differences between portions of symmetrically different sectors that grew at the same time are known as sectoral zoning. Such compositional differences may lead to differences in luminescence. A magnificent example of sector zoning is found in the gypsum crystals from the Chain Lakes, Alberta, Canada (Fig. 11). The requirement for differences between coeval portions of the different sectors is quite important. If we were to compare the luminescence between points 1 and 2 of the crystal in Figure 7a we would be comparing portions of the different sectors that grew at different times. The portion of the {100} sector at point 1 grew long before 2 in the (001} sector. Because 1 and 2 are not coeval, we could not rule out the possibility of compositional differences between them being due to temporal changes in the environment (i.e. concentric zoning). The presence of concentric zones, however, lets us determine what regions of different sectors grew at the same time. Assuming a uniform growth environment, at least in the immediate vicinity of the crystal, the presence of sector zoning tells us that the corresponding faces were somehow different. It has been proposed that the difference causing the differential incorporation of the activating elements is either in the atomic structure of the different faces or the rate at which they grew (Hollister, 1970; Nakamura, 1973; Dowty, 1976).

Unlike concentric zoning the interface between regions of different luminescence for sector zoning is not parallel to the crystal faces; rather it coincides with the boundary between two different sectors (the growth sector boundary). Growth sector boundaries are most easily determined by changes in the orientation of concentric zones, if present.

Intrasectoral Zoning

One of the most common mechanisms of growth is the spiral mechanism, particularly in mineral growth from aqueous solutions. The potential for spiral growth occurs when a screw dislocation in the crystal intersects a crystal face. The displacement of the surface around the dislocation creates a step on the face where the dislocation emerges (Fig. 8). For energy reasons (Burton *et al.*, 1951; Sunagawa, 1984),

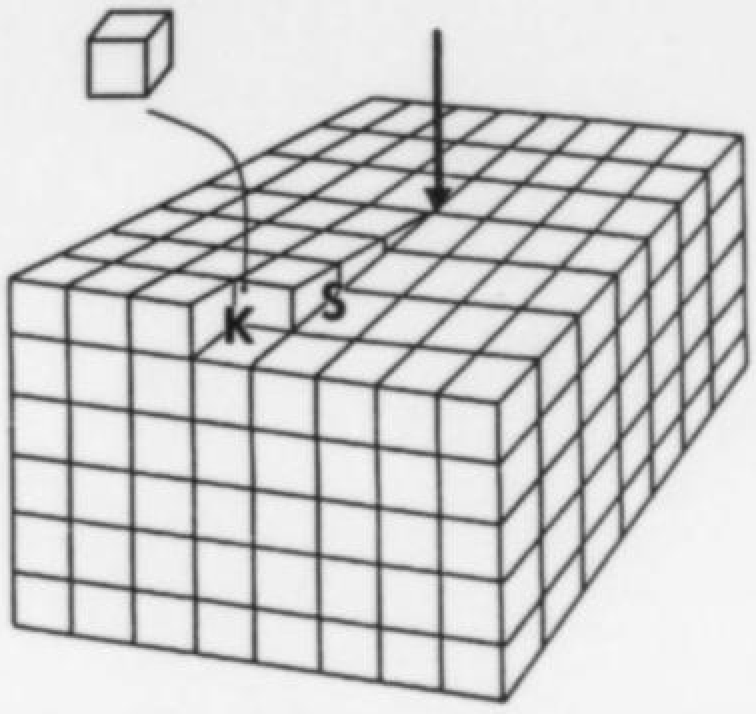

Figure 8. Schematic of a screw dislocation intersecting a crystal face (indicated by arrow) and creating a step. S marks a step site and K marks a kink site.

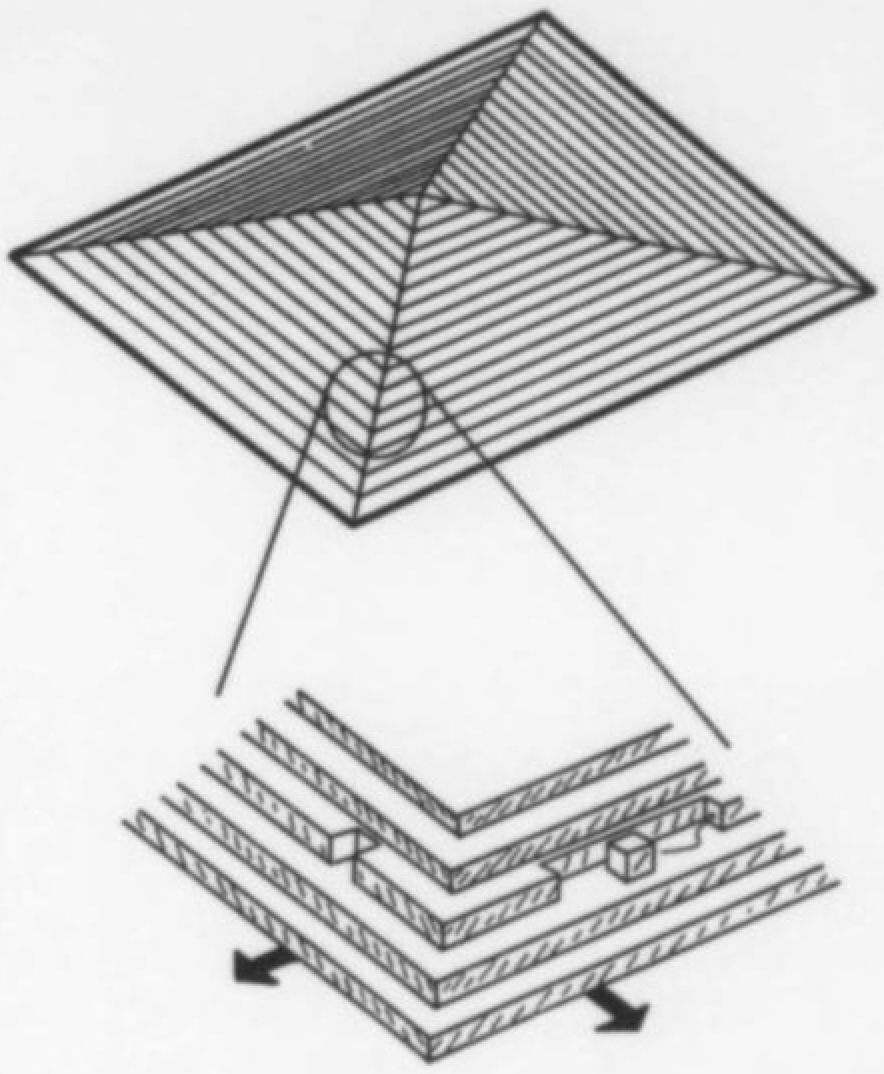

Figure 9. Schematic of a polygonized growth hillock with four vicinal faces. The lower portion of the figure shows a blow-up of steps on the vicinal faces and the presence of protosites.

incorporation of atoms or growth units on the crystal face takes place preferentially along steps, and more specifically at kink sites within a step (Fig 8). A kink site or a "protosite" can be thought of as the surface representation of a bulk crystallographic site. For example, in the halite structure there is a regular crystallographic site where Na atoms reside. This site has six Cl atoms around it in an octahedral arrangement. Where the structure is truncated by a crystal face this site is not fully surrounded by six Cl atoms, and before incorporation of a Na atom, or a substituting atom, we call it a protosite.

As material is added at the step it grows laterally. Because the step terminates at the dislocation, the step will spiral around its origin during growth, hence the name spiral growth. One common manifestation of spiral growth is the formation of growth hillocks on the crystal face. If conditions are right, growth hillocks will develop as polygonized features with straight steps and definite angles between steps of different orientation (Fig. 9). Polygonized growth hillocks exhibit vicinal faces which are very shallow surfaces that vary only slightly in angle from the crystal face. Each vicinal face is comprised of growth steps of like orientation that propagate in the same direction during growth (Fig. 9). Analogous to a sector, portions of a crystal that have grown by incorporation of atoms or growth units onto a specific vicinal face are known as subsectors (Fig. 7b). In Figure 7b the prism face grew by the spiral mechanism as indicated by the presence of a four sided growth hillock. The dashed line from the center of the crystal to the apex of the hillock represents a screw dislocation. One of the subsectors associated with a vicinal face of the hillock is shaded. Similar to sectoral zoning, compositional differences between coeval portions of symmetrically different subsectors is known as intrasectoral zoning. Again, these compositional differences often lead to differences in luminescence. Figure 10 shows intrasectoral zoning of the prism $\{10\bar{1}0\}$ of apatite (Rakovan and Reeder, 1994).

The presence of intrasectoral zoning tells us several things. First, the face associated with the sector that is zoned grew by the spiral mechanism. Also steps of different orientation, making up different vicinal faces, segregated the elements which are causing the luminescence differences between subsectors. Paquette and Reeder (1990) proposed that it is the specific structure of growth steps on vicinal faces that lead to differential incorporation of activators that cause luminescence.

We have seen that luminescence in minerals has many applications in petrologic studies. Luminescence differences between minerals can be used for quick recognition and identification of certain minerals. One can also quickly get a feel for the distribution of a mineral in a rock sample. Luminescence zoning within single crystals can tell us many details about its formation. Finally, with knowledge of activation in other samples it is possible to make an educated guess as to the activator(s) in a sample based on the color of luminescence. However, to unequivocally determine the ions causing luminescence, luminescence spectroscopy is necessary.

LUMINESCENCE SPECTROSCOPY

Spectroscopic methods can be used to determine the presence and identity of ionic impurities that cause luminescence. They can also reveal the valence state of particular ions, their coordination in the structure, the presence of ions in different, non-equivalent sites in the structure, local site symmetry, and other details about the local structure of the mineral (Waychunas, 1988; Fritsch and Waychunas, 1994). There are three types of measurements that fall under the category of luminescence spectroscopy; these are absorption, emission, and excitation spectroscopy.

Absorption spectroscopy measures the amount of light

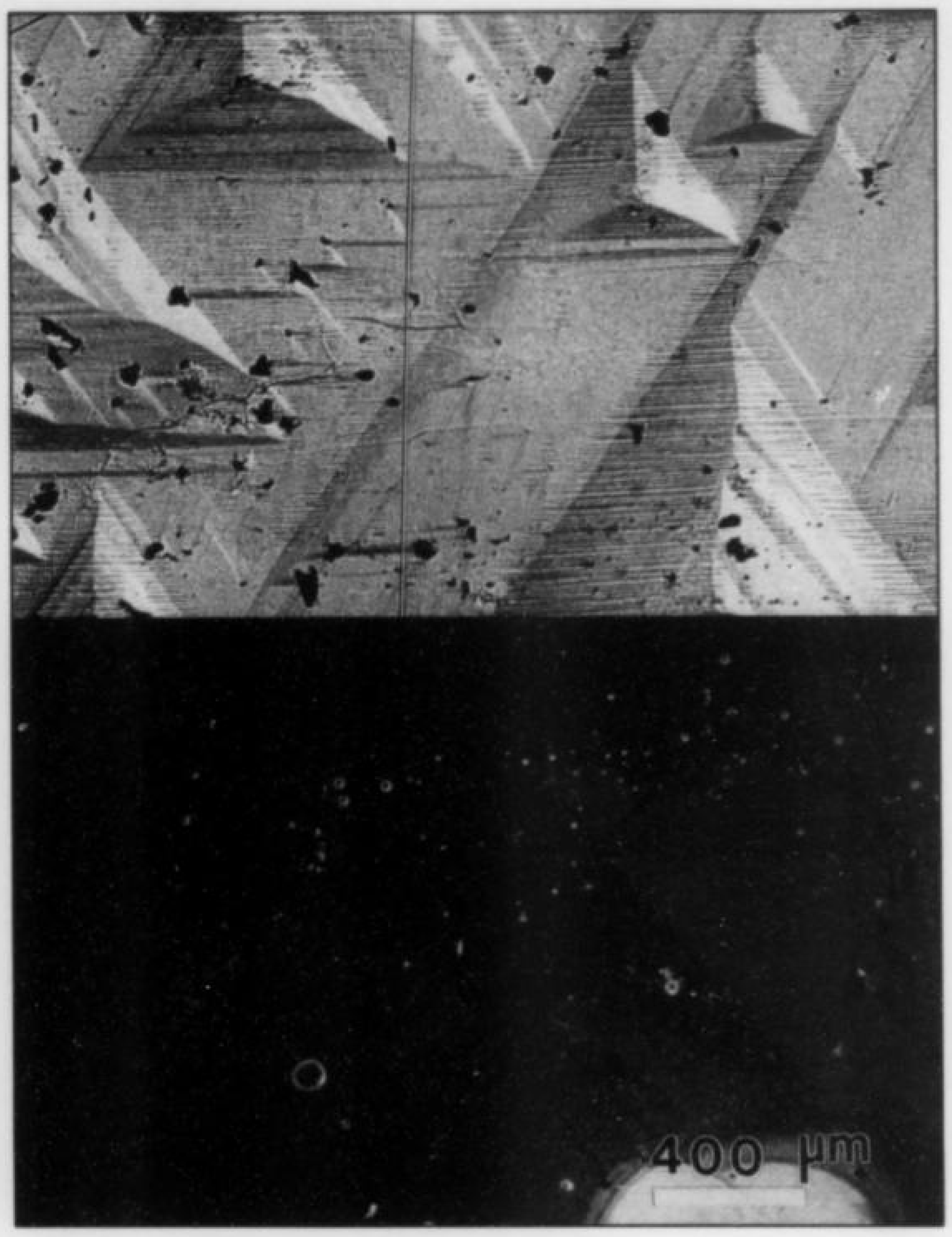

***Figure 10.* Intrasectoral zoning in apatite: (a) Reflected-light image of trigonal growth hillocks on the {10$\bar{1}$0} face of apatite, Golconda mine, Minas Gerais, Brazil. (b) Cathodoluminescence image of a different region of the same crystal face. Differences in luminescence correspond to symmetrically different vicinal faces of growth hillocks in (a). Photograph by John Rakovan.**

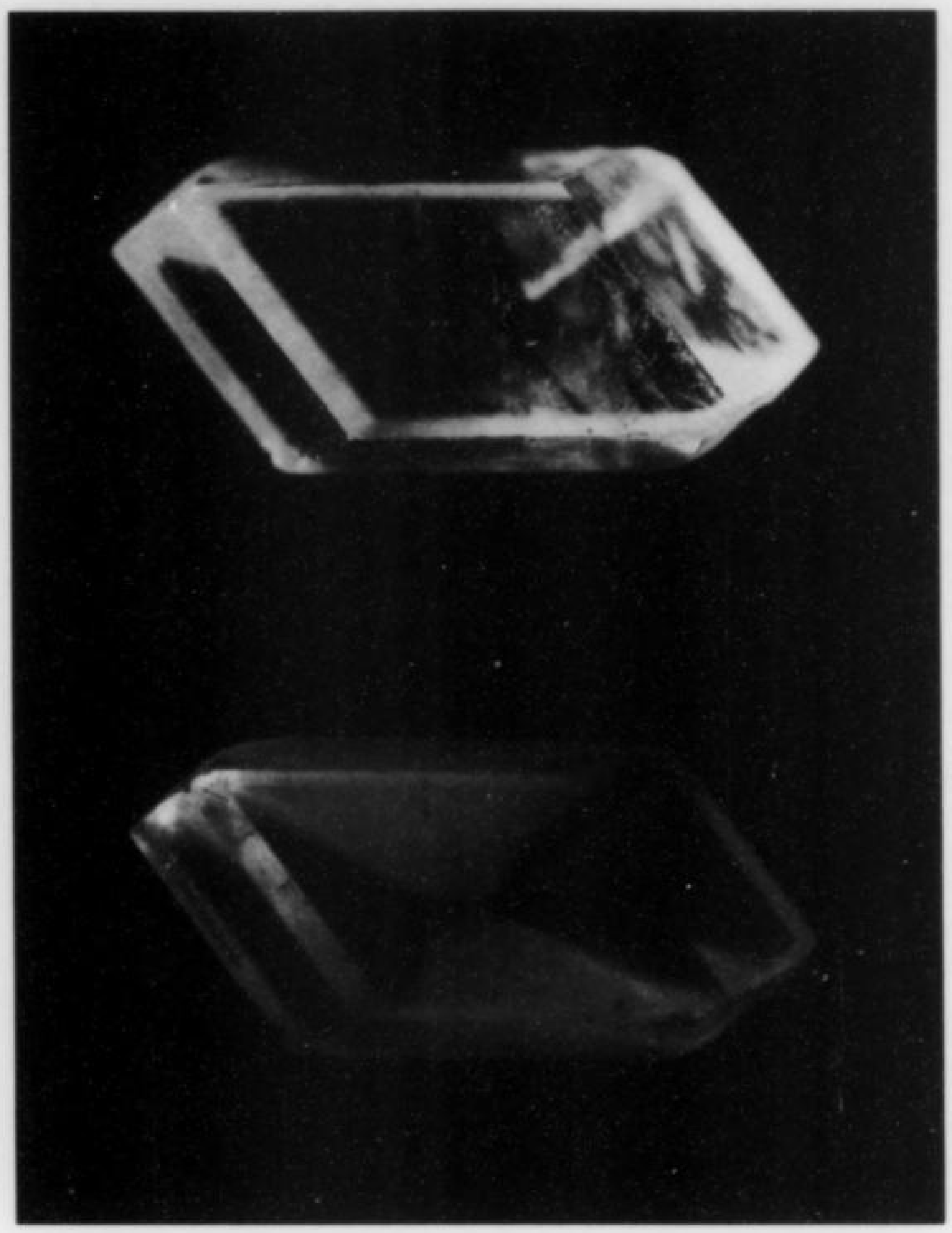

***Figure 11.* Gypsum, Chain Lakes, Alberta, Canada. (a) Plain light image, (b) photoluminescence image showing sector zoning. Luminescent sectors are under the {120} faces. Photograph by John Rakovan.**

absorbed and/or transmitted by a sample as the wavelength of the incident radiation is varied by use of a tunable monochromater. The intensity of the transmitted light can then be plotted for every wavelength. Such a plot will show which wavelengths are transmitted and which are absorbed by the sample.

Excitation spectroscopy is similar, but rather than measuring the intensity of the transmitted radiation, the intensity of the emitted light at the wavelength of the luminescence is measured. Often times there will be several wavelengths of light being emitted, and a full spectrum must be collected for each emission. Two monochromaters are required to collect an excitation spectrum, one to scan the wavelength of the source radiation, and one set at the emission wavelength to be measured. The excitation spectrum will show the wavelengths of radiation that produce luminescence when they strike the sample. These must obviously be absorbed by the sample to create luminescence, so information can be obtained by comparison of the excitation and absorption spectra. If the two spectra are very similar, then the ion(s) that are emitting must be the same ones that are absorbing. Comparison of the absorption spectra with standards containing known luminescence activators can then allow the identification of the activator in the sample. If the two spectra are different, however, there can be two possible reasons. First, the mineral may have several types of ions that absorb but only one is the source of emission. Second, the absorbing ion may be different than the emitting ion as is the case of sensitizer-activator pairs. In optimal cases, both the activator and the sensitizer can be determined.

The reverse of excitation spectroscopy is emission spectroscopy. The monochromater of the source radiation is fixed at a given wavelength (e.g., "longwave" ultraviolet, and the radiation emitted by the sample is scanned. This results in a spectrum of emitted luminescence which can indicate the identity of activators and sensitizers.

CLASSIC LOCALITIES

There are a few locations in the world that are considered to be classics because of their production of numerous and varied mineral specimens having interesting and spectacular luminescence. As we have seen, the potential for most luminescence in minerals is controlled by their chemistry. Activator elements are necessary, and may be augmented by possible sensitizers. Also necessary is the absence or low level of elements like iron which can quench luminescence. Because of these requirements, the classic localities are geochemically very interesting and oftentimes not only produce minerals with unusual luminescence, but exhibit an

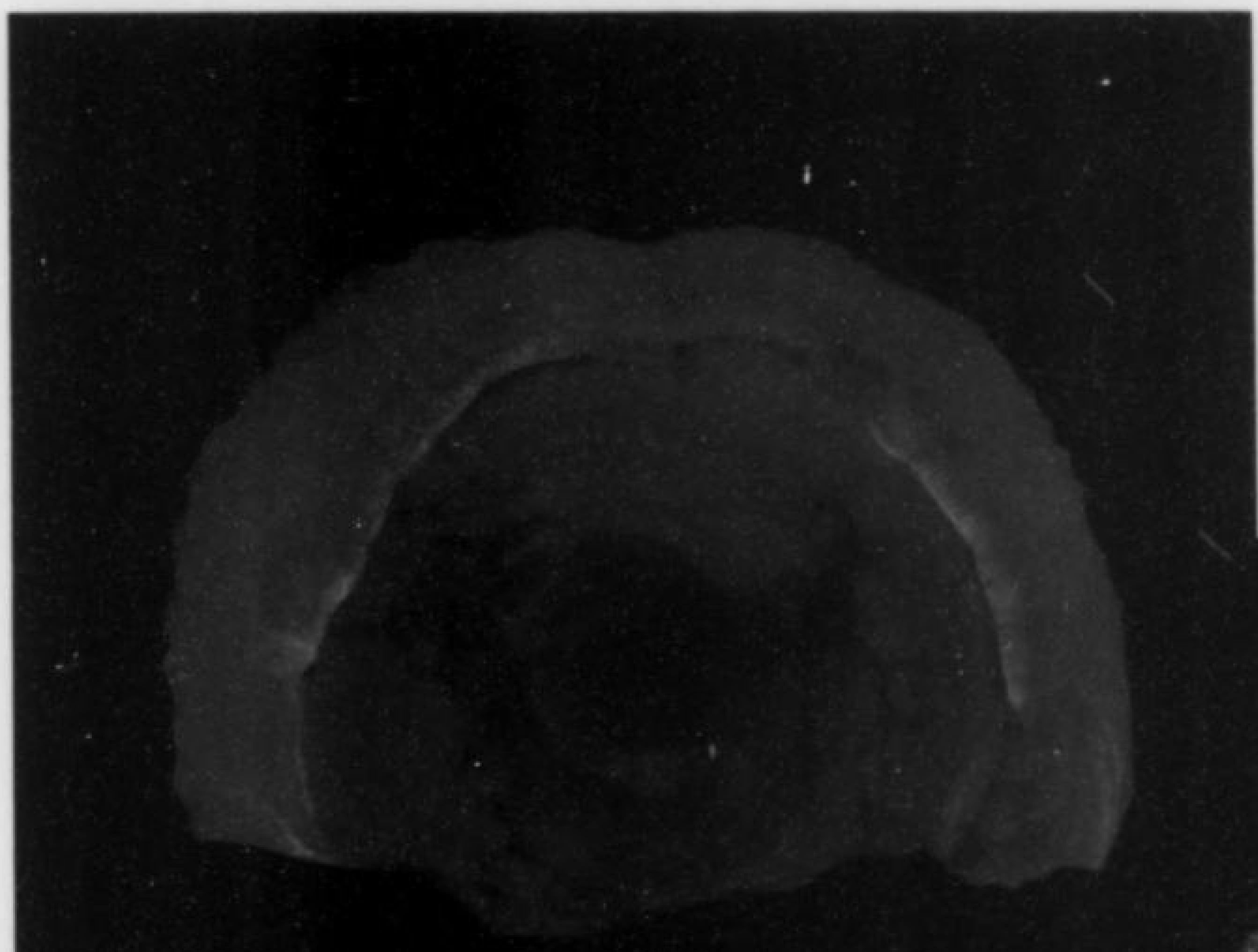

Figure 12. Quartz (chalcedony), 5 cm, from Apache Creek, Catron County, New Mexico. Photo (under shortwave ultraviolet light) by Peter Modreski.

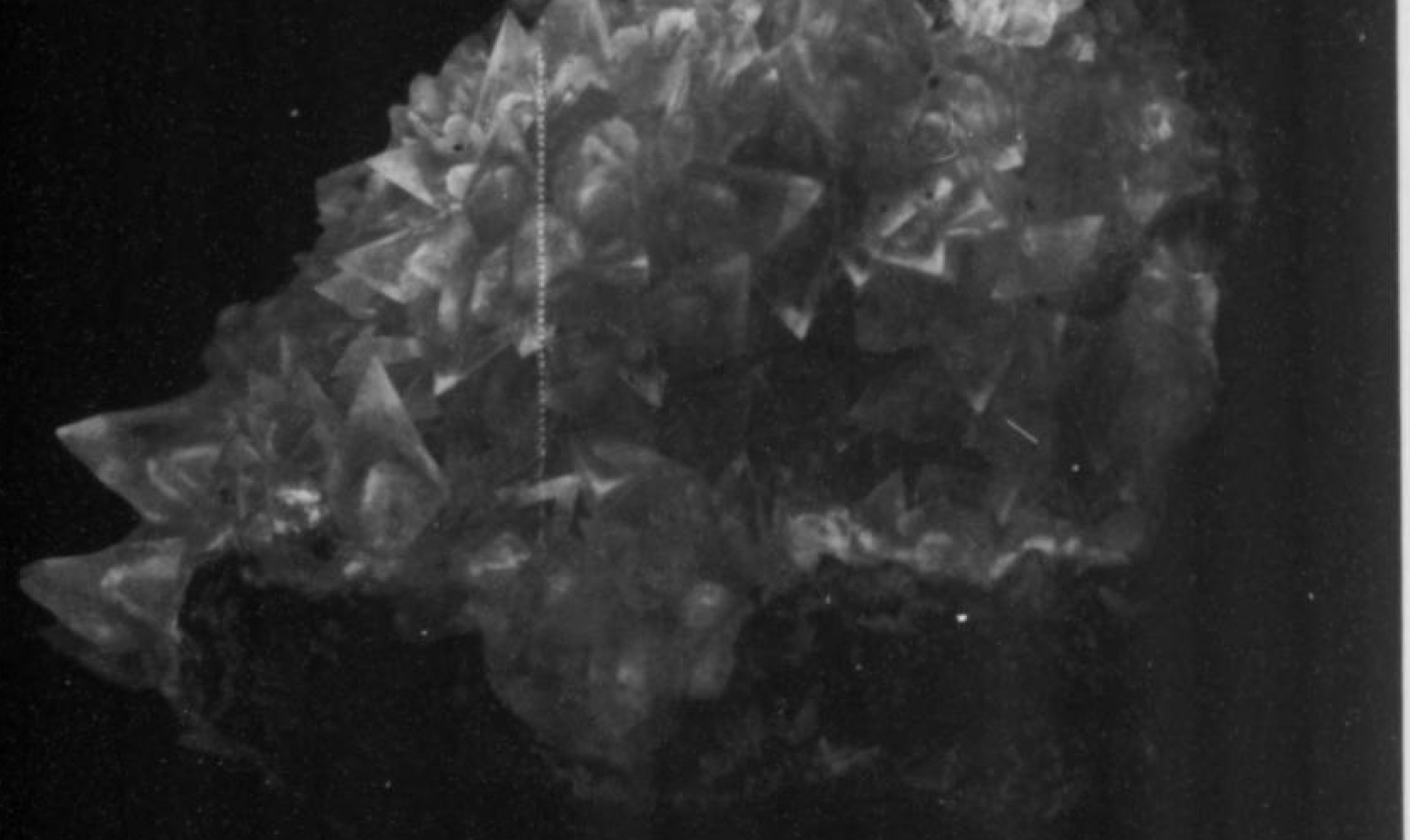

Figure 13. Calcite crystal group, 4.5 cm, from the Waldo mine, Socorro County, New Mexico. Photo (under shortwave ultraviolet light) by Peter Modreski.

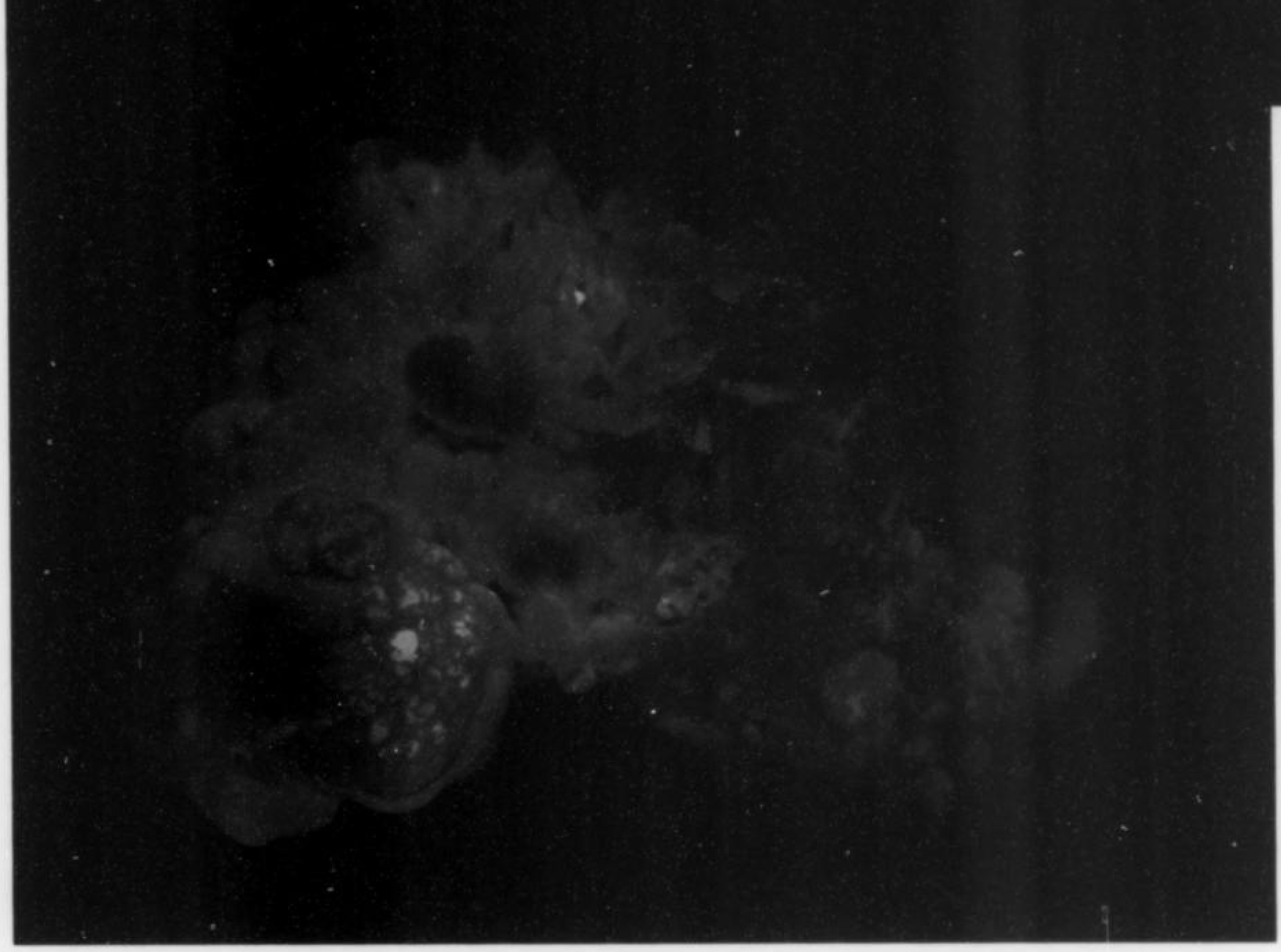

Figure 14. Calcite with intergrown, fluorescent green opal, 7 cm, from the Kelly mine, Socorro County, New Mexico. Photo (under shortwave ultraviolet light) by Peter Modreski.

unusual suite of minerals. All classic luminescent-mineral localities have a number of aspects in common. They usually have a fairly low concentration of quenching ions in their minerals, and they usually have a variety of available activators. In addition, they usually have a large variety of mineral structures that can contain the activators.

The pre-eminent locality is Franklin, New Jersey. Here the availability of divalent lead and manganese and the relative paucity of iron, copper and nickel in the luminescent minerals allow for strong luminescence in many mineral species. Interestingly, there is plenty of iron as well as other quenching elements around; however, they are partitioned so strongly into minerals like franklinite that they do not interfere with the luminescence of species like calcite. Franklin is unusual in the number and variety of silicates and other minerals found there, and in the number of luminescing species. The geochemistry of the deposit is unusual enough that many species common at Franklin are rare or not found elsewhere in the world. The trademark mineral association of Franklin is spectacularly green-fluorescing willemite embedded in a bright red-orange fluorescing calcite (Fig. 5). However, several dozen other fluorescent minerals are found here, many of them with magnificent luminescence, and occurring together in combinations of unusual beauty and diversity.

A locality similar in some ways to Franklin is Långban, Sweden. Here divalent lead and manganese are the chief activators, but the overall compositional range is more restricted than at Franklin. The common calcite from Långban luminesces a spectacular deep red color. Many other minerals common to Franklin are also found at Långban.

Mont Saint-Hilaire in Québec, Canada, is another remarkable locality. Differing from Franklin and Långban, Mont Saint-Hilaire is not a mining operation for metal ores, but for road fill and general construction rock. Most of the rock quarried is an alkali syenite complex with a great many unusual minerals, and rather low iron content. Many species found at Mont Saint-Hilaire occur nowhere else in the world, and for many other species the most spectacular finds in the world are from this locality. Luminescence is activated by divalent manganese, uranyl, the S^{2-} ion, trivalent iron, rare earths and probably other activators.

A relatively new locality that few, if any, of us have seen in person is in the general region of Tajikistan in the central Pamir mountains (Dara-i-Pioz). From this region comes a remarkable combination of luminescent minerals found only rarely at other places in the world. Especially dramatic is the combination of pink-fluorescing agrellite with blue-fluorescing baratovite, but some 20 other luminescing minerals are also known from this region. As with other deposits in Russia, notably on the Kola peninsula, the rocks are of the high-alkali pegmatite and syenite types, resulting in a large number of unusual silicates.

FURTHER SOURCES OF INFORMATION

In the short space of an article it would be impossible to discuss fully every aspect of luminescence. There exists an enormous body of literature on the subject from the fields of mineralogy, physics, chemistry and materials science. For more detailed works on the physics behind luminescence phenomena in minerals the reader is referred to Blasse and Grabmaier (1994), Walker (1985), Marfunin (1979) and Leverenz (1968).

Also, for those who wish to share their interest in luminescent minerals, there is the Fluorescent Mineral Society (FMS). The FMS is an organization which promotes the collecting and displaying of fluorescent minerals, and fosters investigative work into activation mechanisms, development of color standards for descriptions of emission color, and other of interest to the fluorescent mineral enthusiast.

ACKNOWLEDGMENTS

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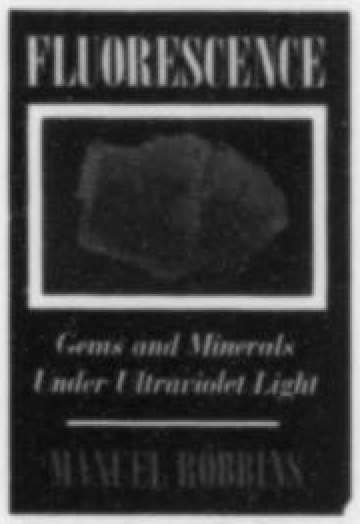

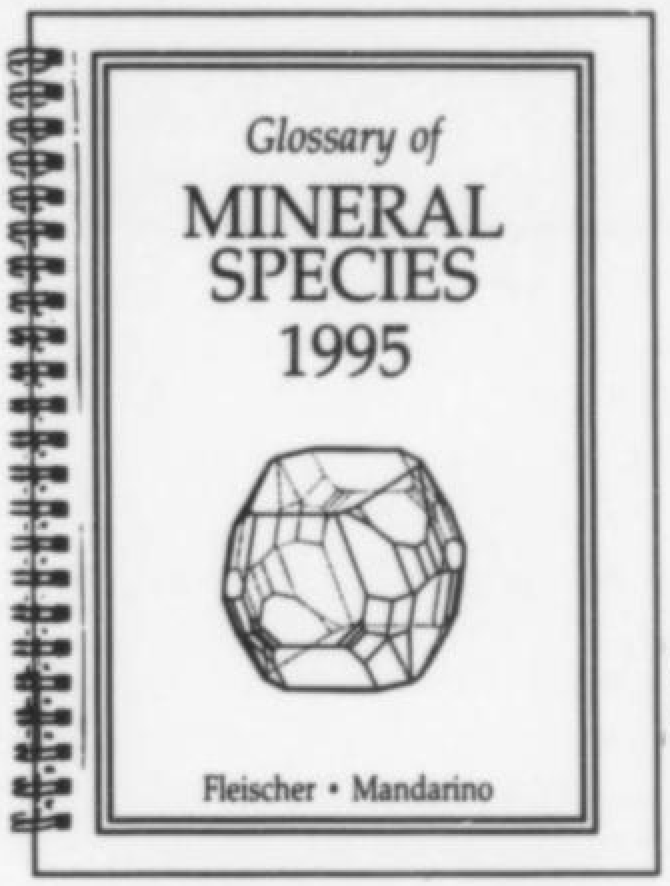

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TUCSON MINERALOGICAL SYMPOSIUM

FLUORESCENCE AND LUMINESCENCE IN MINERALS

INTRODUCTION

Fluorescence is one of the most striking physical properties of minerals. It is a tool in mineral identification, an indicator of chemistry and internal structure, and a distinctive component of the aesthetic appeal of minerals. Many collectors acquire their first interest in minerals through exposure to the magical beauty of fluorescence.

This symposium, in conformance with the objectives of the Friends of Mineralogy, combines papers on descriptive and locality-oriented topics, with research reports from scientists studying the properties and activators of fluorescent minerals. Several papers deal with the field of cathodoluminescence, familiar to petrologists but not well-known by most mineral collectors; and several describe the applications of modern instrumentation, including visible and ultraviolet lasers, to the excitation and measurement of luminescence. A unique feature of the symposium will be the demonstration of mineral fluorescence excited by a 193-nm excimer laser, brought to Tucson specially for this purpose by Dr. W. R. L. Clements of MPB Technologies, Inc., Dorval, Quebec.

Calcite, the theme mineral of the 1996 Tucson Gem and Mineral Show, is also one of the most notable fluorescent minerals. Though much calcite is not fluorescent, the mineral does provide some of the world's most outstanding fluorescent specimens. These include well-crystallized, red- to pink-fluorescent manganoan calcites from many localities worldwide (Ouray, Colorado, Dal'negorsk, Russia, and Charcas and Santa Eulalia, Mexico, are just a few noteworthy examples). As well, there is the fiery red-orange fluorescence of calcite from Franklin and Sterling Hill, New Jersey, and calcite from sedimentary and hydrothermal occurrences which can fluoresce in a remarkable variety of yellow, green, white, blue, violet and pink colors, the interpretation of which tests the limits of our understanding of activators and luminescence mechanisms. Several papers in this symposium address aspects of the luminescence of calcite.

FLUORESCENT MINERAL SOCIETY

Visitors to the 1996 Tucson Show are invited to view the special exhibits of fluorescent minerals sponsored by the Fluorescent Mineral Society. Within a special darkened exhibit area, a display of some 70 cases of outstanding fluorescent specimens from worldwide localities and from both public and private collections has been assembled for this year's show.

P.J.M.

17TH ANNUAL TUCSON MINERALOGICAL SYMPOSIUM

Saturday, February 10, 1996
Sponsored by Friends of Mineralogy,
Mineralogical Society of America, Tucson Gem and
Mineral Society, and Fluorescent Mineral Society

10:00 a.m.	Introductory remarks *Peter J. Modreski and Glenn A. Waychunas,* co-chairmen
10:10	Luminescence zoning in minerals: a phenomenon of beauty and illuminator *John Rakovan* and Richard J. Reader*
10:30	Fluorescent mineral—some answers, questions, and enigmas *Peter J. Modreski*
10:50	Single color and multicolor fluorescence in calcite *Manuel Robbins*
11:10	Luminescence mechanisms and activators in Terlingua-type calcite, and in benitoite and related silicate minerals *Glenn A. Waychunas*
11:30	The influence of heating on the luminescence of calcite *Roger A. Mason*
11:50–12:00	Discussion
12:00–1:00	Lunch break
1:00 p.m.	Uranium-activated fluorescence in minerals of the Franklin-Sterling Hill area, Sussex County, New Jersey *Richard Bostwick*
1:20	Fluorescent minerals of the Karnes uranium district, south Texas *Alan J. Cherepon*
1:40	The fluorescent characteristics of coal; a petrological, chemical, and technical perspective *Stephen L. Bend*
2:00	Cathodoluminescence in the study of rocks and minerals *Henry L. Barwood*
2:20–2:30	Discussion
2:30	Activators for cathodoluminescence in minerals *Anthony N. Mariano*
2:50	Cathodoluminescence of charoite and associated minerals *Barbara Dutrow* and Darrell J. Henry*
3:10	Illuminating gems with visible monochromatic lasers: what can it do for the gemologist? *Brigitte Wopenka, John J. Freeman, and Jill D. Pasteris**
3:30	A combined microscope/fluorescence spectrometer system for mineralogical and gemological applications *Jan Kihle* and John R. Gilchrist*
3:50–4:00	Discussion
4:00	Demonstration of mineral fluorescence excited by a 193-nm ArF excimer laser *Wallace R. L. Clemens*

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*speaker

ABSTRACTS

Luminescence Zoning in Minerals: A Phenomenon of Beauty and Illumination

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In many instances luminescence in a single crystal is not homogenous. Rather, luminescence may show well-defined spatial variations in both intensity and color. Such luminescence zoning is not only beautiful but can lend a wealth of information about the morphologic history of a crystal, changes in the environment during growth, mechanism, and structural differences at the crystal surface. In minerals, luminescence zoning most often reflects differences in the distribution of major, minor or trace elements that act as activators or quenchers. Compositional heterogeneities are typically created during crystal growth, however, post-growth processes such as diffusion can significantly alter original zoning patterns. Here we constrain our discussion to growth zoning only.

An important feature in the interpretation of zoning patterns is the spatial relationship between regions of different luminescence and the growth surface (i.e., the crystal faces). Among the several types of luminescence zoning found in minerals, the most widely recognized is concentric zoning. Here, luminescence varies in concentric bands from the center of the crystal outward, and the boundary between regions of different luminescence parallels the crystal face responsible for the bands' growth. Concentric zoning generally reflects temporal changes in the environment during crystal growth. Changes in the identity and size of crystal faces during growth may be reflected in concentric zoning patterns; hence they can record the morphologic history of a crystal. For some minerals, habit variation has been used to indicate changes in fluid composition.

Two other types of zoning commonly found in minerals are sectoral zoning and intrasectoral zoning. The compositional differences expressed in these types of zoning are not associated with temporal variations in the environment; rather they are due to differences in surface structure between different crystal forms during growth. The volume of the crystal under a given face (i.e., that has formed by growth of that face) is known as a sector. Sectoral zoning is a compositional difference between portions of symmetrically different sectors that grew at the same time; it is often seen as luminescence differences between sectors [i.e., the (100) and (110) sectors in calcite]. Sectoral zoning indicates that the crystal forms associated with the different sectors have different affinities for incorporation of the activating elements during growth.

Intrasectoral zoning is a compositional difference between time equivalent regions within a given sector. The formation of such compositionally distinct subsectors is dependent on the mechanism of growth and is known only for the spiral growth mechanism. Intrasectoral zoning is often seen as luminescence differences between different subsectors. The boundary between subsectors is oblique to the crystal face and cuts across parallel segments of concentric bands when present. As with sectoral zoning, intrasectoral zoning reflects differing affinities at the crystal surface for incorporation of luminescence-activating elements. However, for intrasectoral zoning the differences are on a single face and not between different faces as in sectoral zoning. It has been suggested that the structure of symmetrically different growth steps on a face is the cause for this differential incorporation.

All of these types of zoning can produce spectacular and interesting luminescence patterns and can reveal many secrets of a crystal's formation. Some of the most studied examples of luminescence zoning are found in calcite. Mn^{2+} is the most common activator of luminescence in calcite, although other elements may also play a role. The complex multiple zoning patterns in calcite facilitate the use of luminescence for the interpretation of growth history.

Fluorescent Minerals—Some Answers, Questions and Enigmas

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The nature of fluorescence in many minerals today is well-understood, and has been for a long time. In contrast, for many other minerals—some rare, but some quite common—we have only tentative hints toward understanding the causes and mechanisms of their luminescence.

In cases of simple activators in well-characterized minerals, the situation is clear and is explainable in terms of crystal field theory or molecular orbital theory: Mn^{2+} in calcite, halite, willemite, wollastonite, apatite and others; Cr^{3+} in ruby and spinel; Fe^{3+} in feldspars; Eu^{2+} in fluorite; other REE (Rare Earth Elements, especially Sm^{3+} and Dy^{3+}) in apatite, zircon and various silicates; S_2^- in minerals of the sodalite and scapolite groups; WO_4^{2-} in scheelite; and UO_2^{2+} in uranyl minerals. Of those minerals in which fluorescence is not yet well-understood, for some it is because the basic investigations into trace element content, spectroscopy and the synthesis of doped analogs have yet to be performed. Others have eluded understanding because complex mixtures of activators are present, or because the physical principles which control the luminescence (defect sites, trapped electrons, and semiconductor minerals which must be interpreted in terms of band theory) are more complex, and require sophisticated techniques and equally sophisticated understanding to interpret. Most mineralogists are not crystal physicists, and most of the latter have insufficient motivation to apply their talents and methods to obscure, glowing crystals.

Some puzzles: what causes the unsaturated, whitish fluorescence common in some calcite, aragonite, gypsum, barite and many other minerals? To what degree is red fluorescence in feldspars activated by Fe^{3+} as opposed to REE? What ions are responsible for the yellowish white fluorescence of borates? What balance of metal ions controls the varied colors (orange, yellow, red, blue) of sphalerite luminescence? Is Cd^{2+} responsible for the deep red fluorescence of yellow smithsonite? What about the blue-white or greenish white fluorescence seen in diopside and tremolite; or the "brown" fluorescence of some phlogopite, and the yellowish white fluorescence of polylithionite? Why does witherite fluoresce blue-white, and hydrozincite, blue? In how many minerals does Pb^{2+} or Ti^{4+} play a role? What is going on in the multicolor "Terlingua-type calcites? Happily, research addressing some of these questions is in progress, including several studies being presented at this symposium.

Single-Color and Multicolor Fluorescence in Calcite

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The orange-red fluorescence of calcite from Franklin and Sterling Hill, New Jersey is known to all fluorescent mineral collectors. Western collectors know of calcite with similar fluorescence at localities where zinc, lead, and sometimes copper and scheelite have been mined. This orange-red fluorescence has been extensively studied, and the activators identified; it is due to manganese and lead replacing calcium. Somewhat less known are calcite fluorescences in white, yellow and other colors, the activators of which are not known.

Among the most interesting aspects of fluorescence is the fact that some minerals fluoresce in one color when excited by shortwave ultraviolet and in a second distinctive color under longwave ultraviolet light. Calcite provides excellent examples of this phenomenon. Calcite from Santander, Spain fluoresces red and white; calcite from Guanajuato, Mexico fluoresces pink and white; and certain massive calcite from Franklin fluoresces red and violet. Calcite from Fohnsdorf,

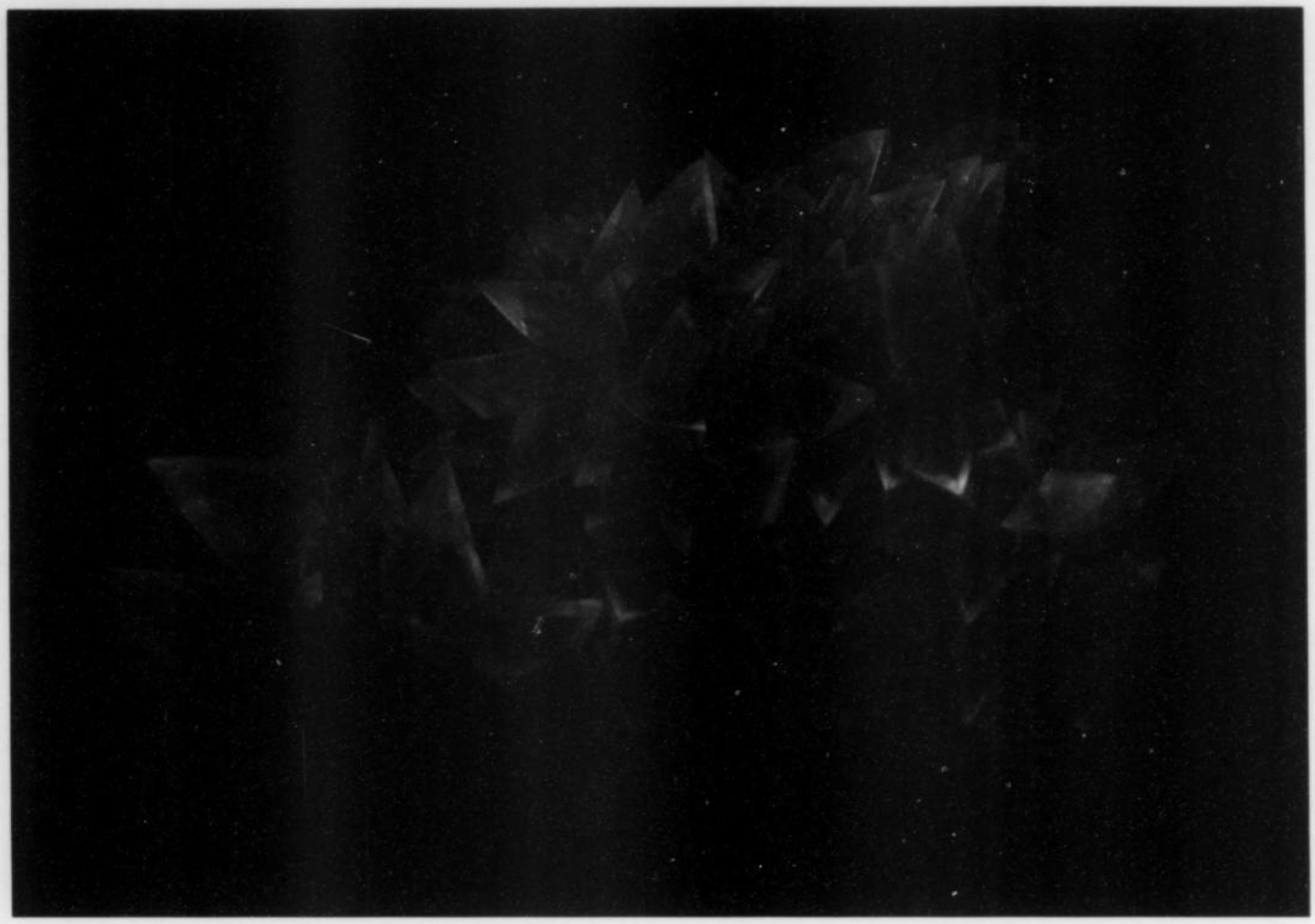

Figure 1. **Calcite crystal group, 4.5 cm, from the Waldo mine, Socorro County, New Mexico, fluorescing blue under longwave ultraviolet light. Compare the photo of the same specimen on page 17 fluorescing red under shortwave ultraviolet light. Photo by Peter Modreski.**

Austria, and northwestern Colorado fluoresces in bands of various colors under shortwave and different colors under longwave ultraviolet light.

Best known among minerals which show this two-color fluorescence is calcite from the mercury district of Terlingua, Brewster County, Texas. Under shortwave ultraviolet light its color is an intense blue-white. Removal of the ultraviolet light results in a phosphorescence of remarkable duration in the same color. This phosphorescence has been found to continue years after exposure to ultraviolet light. Complementary to this enduring phosphorescence, and perhaps related to it, is the slow build-up of blue fluorescence on exposure to shortwave ultraviolet light. Under long wave ultraviolet, the fluorescence is usually pink or pink-orange. The color under longwave ultraviolet is accounted for on the basis of a second color near orange-red being added to the blue color produced by the shortwave light. That blue plus orange-red can produce the colors noted under longwave can be demonstrated.

Not evident to collectors using standard ultraviolet sources is the fact that there is (as measured in one specimen), in addition to blue and orange-red, a broadband green fluorescence and a narrowband red fluorescence which can only be excited by ultraviolet wavelengths other than those provided by standard mineral lamps.

A second and somehow related phenomenon is also found in Terlingua-type calcite. Much of it is colored pink as seen under ordinary light. Rarely, it is colored green. Invariably, when these colors exist, it is these regions of the calcite which fluoresce as described above. If the daylight color of such calcite is green, exposure to sunlight will rapidly bleach the green to gray, and further exposure will finally change the color to pink.

Fluorescence in calcite from Terlingua has been known to collectors since the 1930's. It had been suspected that the remarkable fluorescence was due to mercury, since the calcite was removed in the process of extracting mercury ores. It is now known that this probably is not the explanation, since similarly fluorescing calcite is known from a number of localities where mercury is not found. The cause of the fluorescence, and of the daylight color, has not been positively established, but the following paper will present some hypotheses and plausible conjectures.

Luminescence Mechanisms and Activators in Terlingua-Type Calcite, and in Benitoite and Related Silicate Minerals

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A suite of calcite specimens having luminescence similar to notable samples from Terlingua, Texas, has been examined by luminescence spectroscopy methods (emission and excitation spectra), and analyzed with neutron activation for trace element composition. The emission spectra are all similar, but vary in the relative intensity of bands in the blue and red part of the spectrum. Excitation spectra of the blue emission suggest rare earth activation, probably either Eu^{2+} or Ce^{3+}. However the unusual "build up" of the blue emission upon first application of shortwave ultraviolet light cannot be due to simple activation or typical phosphorescence (or "afterglow"). A mechanism is proposed that includes the photoreduction of Eu^{3+} in the calcites into Eu^{2+} as ultraviolet light strikes the samples. As the Eu^{2+} concentration increases, so does the fluorescence. Upon cessation of ultraviolet exposure, trapped electrons can hop back onto the Eu^{2+} ions, converting them back into Eu^{3+} with continuing afterglow. Red emissions in the calcites is probably due to Mn^{2+} emission with Ce^{3+} sensitization, as suggested by the red band's excitation spectrum. Benitoite was also studied, because its blue emission spectrum looks very much like the blue emission of the calcite. However, in this case the excitation spectra suggest a charge-transfer excitation mechanism, presumably due to the TiO_6 cluster in the structure. The red emission of some benitoites appears to be (at least) sensitized by rare earths, but the activator has not been identified. Finally, silicates that may have similar types of luminescence mechanisms as in benitoite are considered.

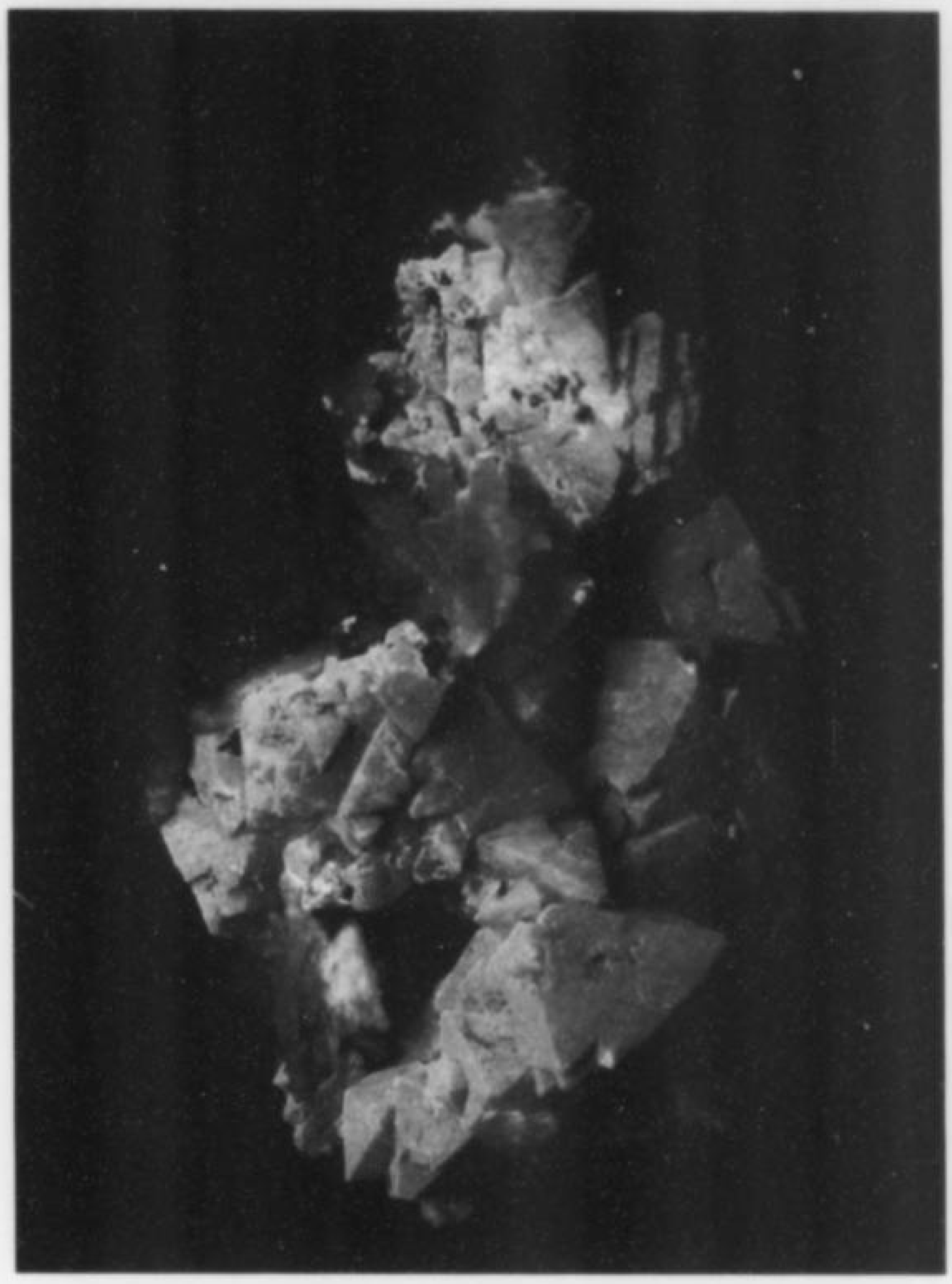

Figure 2. **Calcite crystals (fluorescing red) on scheelite crystals (fluorescing blue) from the Camp Bird mine, Ouray County, Colorado; 10 cm. Bryan Lees collection; photo by Peter Modreski.**

The Influence of Heating on the Luminescence of Calcite

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The dependence of the luminescence of calcite and dolomite on trace element activators and quenchers (e.g. Mn^{2+} and Fe^{2+}) is well-known, although quantification is incomplete. Recent cathodoluminescence (CL) work[1] on calcite with Mn and calcite with REE grown from solution over ~10 days shows that heating can also modify the luminescence of calcite. The present work extends the results to calcite with Mn grown rapidly (<30 minutes) from solution. Synthetic calcite was heated (1) in CO_2 at 1 atmosphere and (2) hydrothermally at ~500 bars in the range 75 to 400° C. Heating effects were measured using spectra collected from the samples before and after treatment. Changes in CL intensity are expressed in the ratio $I_R = I_{heated}/I_{unheated}$.

In rapidly grown calcite I_R increases with temperature up to ~5.5 in material heated hydrothermally at 400 °C whereas heating of 100 °C or below is almost ineffective (I_R ~1 ± 0.2). There is a plateau in I_R at ~300 to 400 °C. At temperatures greater than ~150 °C, I_R does not change after ~15 to 20 hours. Heating in CO_2 is less effective: I_R ranges up to ~3 at 400 °C. At 250 and 300 °C (in CO_2), I_R increases (slowly) even after heating for 300 hours. Individual starting materials differ in the magnitude of I_R at a given temperature but the effect is not related to the concentration of Mn. These data show that rapidly grown calcite is more responsive to heating than slowly grown calcite[1] and establish a temperature dependence of that response.

Experiments on natural calcite show that heating effects are not restricted to synthetic calcite. The response is more complex: both the wavelength and bandwidth of emission are modified by heating.

Mason[1] suggested that changes in the concentration of structural defects may be responsible for heating effects on CL intensity. An alternative hypothesis is that heating disperses clusters of the CL activator in which concentration quenching occurs. However, unit cell parameters and EXAFS spectra from selected synthetic samples failed to show differences between heated and unheated calcite, suggesting that there are no significant changes in crystal chemistry or local coordination of the activator. These results show that both trace-element chemistry and thermal history are important controls of luminescence in calcite.

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[1] *Chemical Geology*, **111**, 245–260 (1994).

Uranium-Activated Fluorescence in Minerals of the Franklin-Sterling Hill Area, Sussex County, New Jersey

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Uranium minerals are rare at the great zinc-iron-manganese deposits of Franklin and Sterling Hill, but uraninite has been found there, as well as several secondary uranium minerals including uranophane, metazeunerite, meta-ankoleite, metalodevite, uranospinite and znucalite. Most of these secondary uranium minerals (including the last four named above) fluoresce green under ultraviolet radiation due to the presence of the uranyl ion, UO_2^{2+}. Similar fluorescence has been observed locally in quartz, aragonite, monohydrocalcite and other minerals which were deposited under surface or near-surface conditions, and while this so-called "uranium-green" fluorescence has been assumed to be due to uranium, no proof has been offered. One of the major zinc ore minerals at Franklin and Sterling Hill is willemite, which typically fluoresces green; to the eye this fluorescence of willemite can be similar to that of uranium-bearing minerals, and there is considerable possibility for attributing green fluorescence at Franklin and Sterling Hill to either manganese-activated willemite or to the uranyl ion. A spectrofluorometer, however, can easily differentiate the two, and the spectra of several green-fluorescing secondary minerals from the two deposits are being examined for evidence to confirm the true activator. Manganese-activated minerals have a single, moderately broad peak in their emission spectrum (centered at about 523 nm in willemite), whereas uranyl-activated minerals exhibit a "fingerprint" spectrum with 4 to 5 or more sub-peaks (autunite, for example, has peaks near 500, 521, 545 and 571 nm). In well-crystallized uranyl minerals these sub-peaks are sharp and distinct, whereas in some uranium-containing minerals (e.g., opal) the sub-peaks may be broad and poorly resolved.

Possible candidates for uranium-activated fluorescence from the Sterling mine include chabazite and monohydrocalcite. Green-fluorescent chabazite was found in about 1990 at the 340 and 900 levels of the Sterling mine. The 340 level occurrence was in calcite associated with garnet, pyroxene, yellow-fluorescent powellite and an apatite-group mineral; the 900 level occurrence was as 2–3 mm rhombohedral crystals in cavities in gneiss. Monohydrocalcite, also fluorescent green, was found in a vein associated with johnbaumite on the 700 level of the Sterling mine, and also as clearly secondary surface coatings on the 900 and 1600 levels. The emission spectrum of monohydrocalcite exhibits a broad peak with slight structure; the maximum is near 500 nm, with a secondary peak near 520 nm. This spectrum appears to be consistent with uranyl activation.

Fluorescent Minerals of the Karnes Uranium District, South Texas

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Numerous papers have been written on the geology of the Karnes uranium district, which is about 45 miles south of San Antonio, Texas. The open pit mines of this district have produced uranium since the late 1950's. Zones of concretions containing crystals of calcite and gypsum have been sporadically referred to in the literature, but these occurrences have never been considered particularly significant. Many cross-sections through the mine areas were drawn during the intense mining activities of the 1970's, showing distinct concretionary zones. However, there has been no serious mention in the literature of the fine and possibly unique overburden mineral assemblage above the ore zone.

It can be argued that the Karnes uranium district is the best mineral collecting locality in Texas, and the diversity of fluorescent mineral colors, especially in the calcites, could well be the best outside of Franklin, New Jersey. The basis for such a claim is the variety of habits and the crystal quality of the calcite, gypsum, quartz and barite, and a list of fluorescent colors that includes red to pink, orange, yellow, greenish yellow, green, gold, cream, white, purple, purplish blue and brown. The calcites alone fluoresce red to pink, orange, yellow, greenish yellow, gold, cream and white; the fluorescent response appears to vary with crystal habit, and much of the calcite is phosphorescent.

Sadly, few collectors are even aware of this occurrence, and no serious study has been undertaken to compare other potentially similar areas throughout the world. This presentation will not only enlighten the mineral world to these observations, but will attempt to lay the groundwork and impetus for studies of other concretion-bearing, hypercalichified, tuffaceous sandstones with associated uranium ore. The presence of these near-surface concretions may have exploration value as possible ore indicators. Unfortunately, this important yet virtually unknown deposit may already be lost to a massive and long overdue open pit reclamation project.

The Fluorescent Characteristics of Coal; A Petrological, Chemical and Technical Perspective

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Coal is not a homogeneous material, a universal characteristic that is readily revealed under the microscope using reflected plane-polarized light. The microscopic organic constituents of coal, called macerals (from the Latin *macerare,* "to soften"), are analogous to rock minerals, although unlike rock minerals, macerals are neither crystals nor crystalline. Therefore macerals are recognized and defined by a combination of morphology, optical properties, botanical affinity, technological properties and inferred mode of preservation. There are three internationally recognized maceral groups, *liptinites, vitrinites* and *inertinites*; each group possesses a set of distinguishing characteristics, one of which has traditionally been *fluorescence.*

When irradiated with ultraviolet light (e.g., 365 nm), macerals of the liptinite group fluoresce under the microscope, and over the last 30 years this important characteristic has served to unify macerals within this group. However, for many years it was thought that fluorescence was in some way related to the hydrocarbon-generating potential of the liptinite macerals. It is becoming increasingly evident that the presence of conjugated double bonds within the molecular structure of a material (i.e., $C=C$; π-π, σ-σ bonds) act as the fluorophores. Spectral shifts in fluorescence (i.e., towards the red) associated with an increase in coal rank, are therefore attributable to the relative increase in the proportion of conjugated double bonds between carbon atoms. Recent improvements in analytical procedure have demonstrated that fluorescence is also not restricted to macerals of the liptinite group, but is a much more universal characteristic.

Has this led to a general obfuscation of coal maceral characterization and definition? Not at all! Recent technological improvements have opened the way to new sensitive and technologically important analytical techniques, and a possible renaissance for fluorescence microscopy, moving coal maceral fluorescence out of the domain of the scientist's laboratory into the world of the coal analyst and technologist.

Cathodoluminescence in the Study of Rocks and Minerals

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Luminescence excited by bombarding a solid with high-energy free electrons (known as cathodoluminescence or CL) was discovered over 100 years ago. A surprisingly large number of observations were documented by Crookes (1879, *Phil. Trans. Royal Soc.*, 641–662) using what would be considered very primitive vacuum and high voltage instruments. While cathodoluminescence was extensively researched in the quest for cathode ray tube phosphors, it was not until the early 1960's that the technique was applied extensively to petrographic and mineralogical analysis. Gradually, with the availability of commercial CL cells for use on petrographic microscopes, the technique gained acceptance and is now widely used, especially for carbonate rock analysis. Recently, the author has applied CL techniques to the study of (1) alkali syenites, (2) carbonatite dikes and associated fenite xenoliths, and (3) refractory products and slags from steel making. Examples of CL will be presented that show both the scientific value and beauty of the cathodoluminescence technique.

Alkali syenites from the Magnet Cove complex and the Granite Mountain syenite in central Arkansas have a very complex magmatic history that is revealed by CL. Primary feldspars, both K-feldspars and plagioclases, are activated by Ti and luminesce a bright blue. Where the feldspars have been subjected to fenitization or granitization they luminesce a deep red (Fe^{3+} activator) or bright greenish-yellow (Fe^{2+} activator), respectively. The degree of fenitization can often only be detected by CL. Other syenite minerals that show distinct cathodoluminescence include: sodalite (red), apatite (yellow to violet), fluorite (blue), wollastonite (yellow), calcite (orange), lorenzenite (green), rinkite (*mosandrite*) (green), synchysite/bastnaesite (red), and quartz (red and blue).

Carbonatite dikes from near Morillton in central Arkansas contain numerous xenoliths brought up from as deep as the upper mantle. These xenoliths range from fresh shale to gneiss that is extensively fenitized and replaced. CL examination of the carbonatites and cuttings from a deep oil well drilled in the area showed that the carbonatites were very extensive in the subsurface. Calcite (orange) and dolomite (red) forms a groundmass containing apatite (yellow to violet). CL observation of the distinctive zoned apatite crystals is the primary evidence used to distinguish the igneous carbonatites from sedimentary carbonate rocks. The xenoliths contain quartz (dull red and blue) and feldspars (bright red and blue).

Study of refractory materials used in glass furnaces and steel manufacture has revealed an extensive suite of artificial products that cathodoluminesce strongly. Research in this area is still in its infancy; the most extensive study on slag reaction products has been carried out by Dr. Musa Karakus at the University of Missouri-Rolla. The list of luminescing compounds is quite extensive; some of the minerals/substances observed were: spinel (red and green), corundum (red through blue), periclase (red through blue), hibonite (green and reddish violet), forsterite (red and purple), monticellite (blue and yellow-orange), melilite (blue), anorthite (blue and yellow), quartz and cristobalite (blue and red), mullite (red), oldhamite (orange), silicon carbide (orange), zircon (red to blue), and zirconia (yellow). Most of the slag/refractory species concentrate and incorporate trace activators from the steel and have become highly to intensely luminescent.

Activators for Cathodoluminescence in Minerals and Gems

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Cathodoluminescence (CL) in minerals is mainly of two types: impurity-center (*activator*) luminescence, and defect-

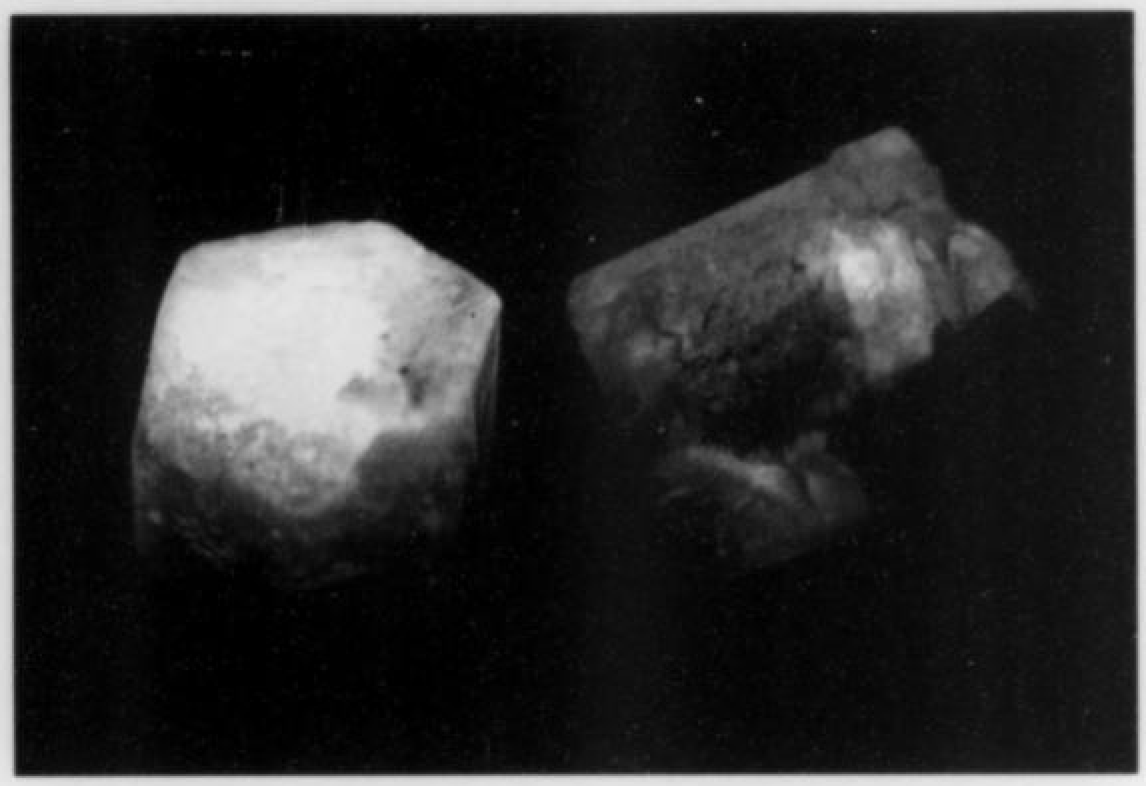

Figure 3. **Apatite crystals to 7 mm, from Mt. Antero, Colorado, under shortwave ultraviolet light. Peter Modreski photo.**

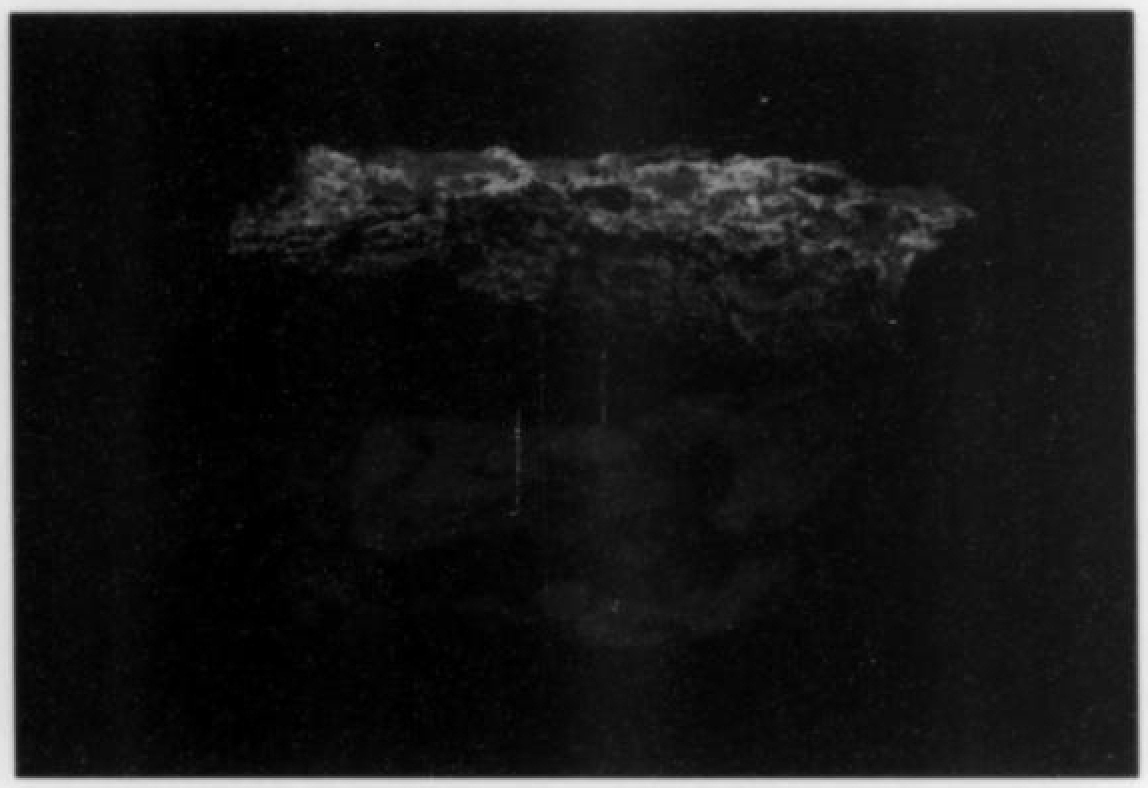

Figure 4. **Turneaurite (orange) and calcite (red), 25 cm, from Franklin, New Jersey, under shortwave ultraviolet light. Mark Leger collection; Henry Van Lenten photo.**

center (*intrinsic*) luminescence. The major impurity activators are the transition-metal ions Mn^{2+}, Fe^{3+} and Cr^{3+}, and the rare-earth element (REE) activators that mainly include Sm^{3+}, Dy^{3+}, Tb^{3+}, Eu^{3+} and Eu^{2+}.

Gem minerals that exhibit activator-induced cathodoluminescence include corundum, emerald, spinel, spodumene, chrysoberyl, zircon, garnet, topaz and feldspar. In gem exploration programs the use of CL enhances the recognition of sub-microscopic gem minerals that may occur in rocks or in stream sediment samples. The CL emission spectra for the gem minerals are usually diagnostic for identification.

Activation by Cr^{3+} in synthetic emeralds gives a broad-band emission in the red part of the visible spectrum. A sharp spike, at 683 nm, is usually resolved within the broad-band spectrum. The spectra of synthetic emeralds are similar to those of emeralds from most of the world localities including pegmatite emeralds and those found in the emerald belt of Colombia. However, emeralds from the talc carbonate schist (TCS) environments of Pakistan consistently display significantly different spectra, with the broad band shifted about 10 nm farther into the IR region and with a superimposed spike that peaks at about 740 nm. This unique CL emission differentiates the TCS emeralds of Pakistan from all other emeralds including synthetic types.

Activation from Fe^{3+} in minerals is most often encountered in feldspar, where it is an indication of crystallization under strong oxidizing conditions or high alkalinity of the crystallizing medium. The presence of Fe^{3+} activation in feldspars is used as an indicator for alkali metasomatism in mineral exploration programs.

Observation of luminescence produced by the REE activators in the minerals apatite, anhydrite, calcite, dolomite, fluorite, isokite and strontianite can be used for determining the dominance of light REE or heavy REE in the mineral.

Cathodoluminescence of Charoite and Associated Minerals

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Charoite, a rare and unusual alkali silicate, is characterized by intense purple hues and wavy fibrous habit. Its unique occurrence is restricted to pods within metamorphic and fenitic country rocks adjacent to the Murun igneous alkalic complex, Chara River Valley, Russia. Strongly folded fibers of charoite form continuous mats in monomineralic rocks or enclose other minerals such as complexly zoned K-feldspar, dalyite, aegirine, arfvedsonite, tinaksite, canasite, Sr-Ba carbonate, chalcopyrite, thorite and quartz.

As a portion of a larger study on the crystal chemistry of charoite (see *Geol. Soc. Amer., Abstracts with Programs, 26* (7), p. A-481, 1994), several charoite-bearing samples were investigated by cathodoluminescence (CL). Charoite-bearing samples contain strongly cathodoluminescent minerals. Charoite displays an orange-yellow CL, dalyite luminesces bright azure-blue, and K-feldspar luminesces crimson-red. The purple hue characteristic of charoite is attributed to the small but significant content of Mn^{2+}, whereas the orange-yellow CL denotes the presence of Mn^{3+} and the absence of Fe^{2+}. Ti^{4+} is responsible for the blue CL of dalyite. Significant amounts of tetrahedral Fe^{3+} replacing Al^{3+} result in the spectacular red CL of the potassium feldspar.

Illuminating Gems with Visible Monochromatic Lasers: What Can it Do for the Gemologist?

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A laser Raman microprobe permits non-destructive, pin-point (one micrometer diameter) laser irradiation of any given area (either on or below the surface) of a gem or other mineral sample. The sample is viewed in a high-magnification optical microscope while being irradiated. Typically, the 488-nm or 514-nm lines of an argon-ion laser are used to excite both inelastic scattering of light (called "Raman scattering") and fluorescence. The Raman spectrum and the laser-induced luminescence spectrum of a micrometer-sized area in the specimen are analyzed by wavelength with a high-precision optical spectrograph that is coupled both to the microscope and to a photon-sensitive detector (either PMT, CCD, or diode-array detector). The wavelength-resolution is dependent on slit width and wavelength, but bands as close as 0.03 nm from each other can be resolved. The procedure is non-destructive, requires minimal to no sample preparation, and can be applied to mineral grains *in-situ,* to raw precious stones, or to a faceted gem in its setting.

Raman scattering is observed between 100 and 4000 relative wavenumbers (the frequency of excitation corresponds to "zero relative wavenumbers", i.e., 0 Δ cm^{-1}), and provides definitive information on the molecular and crystalline structure of a gem. The positions of Raman peaks (in terms of Δ cm^{-1}) are independent of the wavelength of excitation, and a Raman spectrum is as conclusive as an X-ray diffraction pattern for the purpose of mineral identification. The Raman microprobe technique is useful for the characterization of real and synthetic gemstones, as well as imitations. For instance, alexandrite (chrysoberyl, $BeAl_2O_4$) has a strong Raman spectrum with about 20 bands whose most intense peaks occur at 480, 517, 547, 641, 679, 780 and 932 Δ cm^{-1}, whereas its imitation (corundum, Al_2O_3) has a totally different Raman spectrum with only 5 bands which are at 381, 418, 577, 646, and 751 Δ cm^{-1}. In addition, microscopically small regions of bulk specimens, such as mineral or fluid inclusions can be analyzed. For instance, we successfully obtained the Raman spectra for subsurface rutile needles (down to 3 µm in diameter) in rutilated quartz and rutilated garnet (note that the Raman spectra for the three TiO_2 polymorphs rutile, anatase, and brookite are distinctly different), but have so far been unable to obtain characteristic spectra of the very thin needles (rutile?, <1 um in diameter) or leaflets (hematite?, up to 7 µm width) in geological thin-sections of star ruby (note that hematite is one of the few minerals that is an extremely weak Raman scatterer).

The luminescence spectra can be recorded between the wavelength of excitation and 840 nm (note that we use green or blue light, not ultraviolet!). Such spectra provide information for characterizing the luminescent ions (e.g., Mn^{2+}, Cr^{3+}, trivalent rare-earth-element ions) and luminescent color centers in gems. We monitor the wavelengths, band shapes, and relative intensities of fluorescence emissions. For instance, the Cr^{3+} fluorescence in ruby (strong bands at 659, 669, and 675 nm, as well as extremely strong narrow bands at 639 and 694 nm) is several orders of magnitude more intense than the Raman bands of the corundum matrix. In contrast, the narrow-band fluorescence (about one hundred individual bands between 530 and 760 nm) caused by Sm^{3+}, Tb^{3+} and Dy^{3+} in many zircons is only half as intense as the Raman bands of the zircon matrix. The interpretation of fluorescence spectra can be complicated by the fact that the fine structure in the spectrum of any given trace element ion also depends on the host matrix, i.e., it is structure- and site-specific. We are presently investigating whether the combined interpretation of Raman and fluorescence spectra can be useful in providing locality-specific signatures of gems that could be used as "fingerprints."

A Combined Microscope/Fluorescence Spectrometer System for Mineralogical and Gemological Applications

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John R. Gilchrist
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Fluorescence techniques are often preferred for measurement analysis in many medical applications; they offer significantly higher sensitivity over absorption techniques, because small fluorescence signals are detected against zero background. Measurement in a cuvette or through an optical fiber bundle gives an average value over the measured area. Spot measurements under a microscope, however, allow one to measure the fluorescence signal from selected sample areas, the size of which can be varied from sub-micron to millimeter dimensions. The main advantage of using a microscope is the ability to view the object during the measurement, thus allowing the determination of a spatially and spectrally resolved map of sample fluorescence.

Until now, the measurement of steady-state fluorescence characteristics of microscopic matter have been limited by the requirement for filters, dichroic mirrors and neutral-density beamsplitters/quartz wedges in the optical light path. Measurements have generally been restricted to the monitoring of emission spectra because the microscope arrangements have used fluorescence "cubes" optimized for specific wavelengths such as the emission lines in the mercury spectrum. This has meant that only these lines can be used to excite a sample, and excitation spectra can therefore not be obtained.

Recently the quest for mapping of fluorescence excitation spectra, as well as emission spectra of small minerals, gems and microscopic matter, has led to the development of optical systems using neutral-density beamsplitters or quartz wedge plates for reflecting and transmitting light from the subject. Such systems are capable of making an excitation emission map of the fluorescence characteristics of a sample exhibiting strong auto-fluorescence. The major drawback of these systems has been the incorporation of neutral beam splitters which theoretically are capable of transmitting a maximum of 25% of the excited light onto the photomultiplier detector.

We have developed a novel infinity-corrected fiber optic coupling module (patent pending) which allows the direct coupling of a single photo-counting spectrofluorimeter system to be combined with an OLYMPUS=AE infinity-corrected research grade microscope.[1] In contrast to former designs, this system does not employ filtering of any kind in the optical pathway. Hence, the sensitivity of this instrument has been dramatically improved (typically 400% from 340–900 nm) in comparison to instrument designs using neutral beamsplitters. The spectrofluorimeter uses a continuous-operation xenon lamp which emits a continuum spectrum rather than the line spectra characteristic of mercury lamps.

The advantage of using fiber-optic coupling is that the lamp and spectrofluorimeter system are not mechanically coupled to the microscope system. This has distinct advantages in avoiding any vibrations from the lamp fans and the scanning of the monochromator.

A combination of research-grade spectrofluorimeter and microscope systems opens many possibilities for fluorescence characterization of microscopic matter, for instance, in the application areas of fluorescence fingerprinting of gems, spectroscopic assessment of Pb/Mo contents of scheelites, and in any other field involving fluorescence phenomena.

Demonstration of Mineral Fluorescence Excited by a 193-nm ArF Excimer Laser

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A laser is a source of coherent monochromatic light. When used to irradiate minerals and gems, an ultraviolet laser may produce much more brilliant and more distinctive colors of fluorescence in comparison to a conventional shortwave or longwave ultraviolet lamp, because of (1) its greater intensity, and (2) the ability to operate at a shorter (more energetic) wavelength than conventional ultraviolet lamps. The instrument to be used in this demonstration is an MPB model PSX-100, ArF excimer laser. It is a rapidly pulsed laser, emitting 3 ns (1 ns = 10^{-9} sec), 3.5 mJ pulses at a repetition rate of 100 Hz, for a maximum average power of 350 mW and a maximum peak power of 1200 KW. The beam dimensions are 3x3 mm.

An excimer laser is one in which the light emission comes from a gas molecule (e.g. ArF, argon fluoride) which is stable only in its electronically excited state. The PSX-100 laser is capable of operating with a variety of gas compositions, producing different wavelengths of ultraviolet light: XeF (351 nm), XeCl, (308 nm), KrF (248 nm), KrCl (222 nm), ArF (193 nm), and F_2 (157 nm). Helium or neon is used as the buffer gas medium. This laser, the smallest and most portable excimer laser available, is contained in a 30x26x21-cm (13.4 Kg) housing, is air-cooled, and operates on 110 VAC, consuming 1A of current. Its normal uses include applications to photochemistry, fluorescence spectroscopy, laser ionization mass spectroscopy, photoablation, micromachining and medicine.

Reports of the fluorescence of minerals excited by such a laser are almost unknown, and the phenomena observed first-hand during this demonstration may be among the first to be seen anywhere. The demonstration of this laser at the symposium is being cosponsored by the Optical Sciences Center of the University of Arizona and the Arizona Optics Industry Association, as well as MPB Technologies, Inc.

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[1] KIHLE, Jan (1995). The new possibilities of luminescence spectroscopy of microscopic matter, *in* D. L. Andrews and A. M. C. Andrews (eds.) *Frontiers in Analytical Spectroscopy.* The Royal Society of Chemistry, 56–60.

Note: The *Mineralogical Record* would like to thank Dr. Peter Modreski and the Fluorescent Mineral Society for providing information and specimen photography regarding fluorescent minerals.

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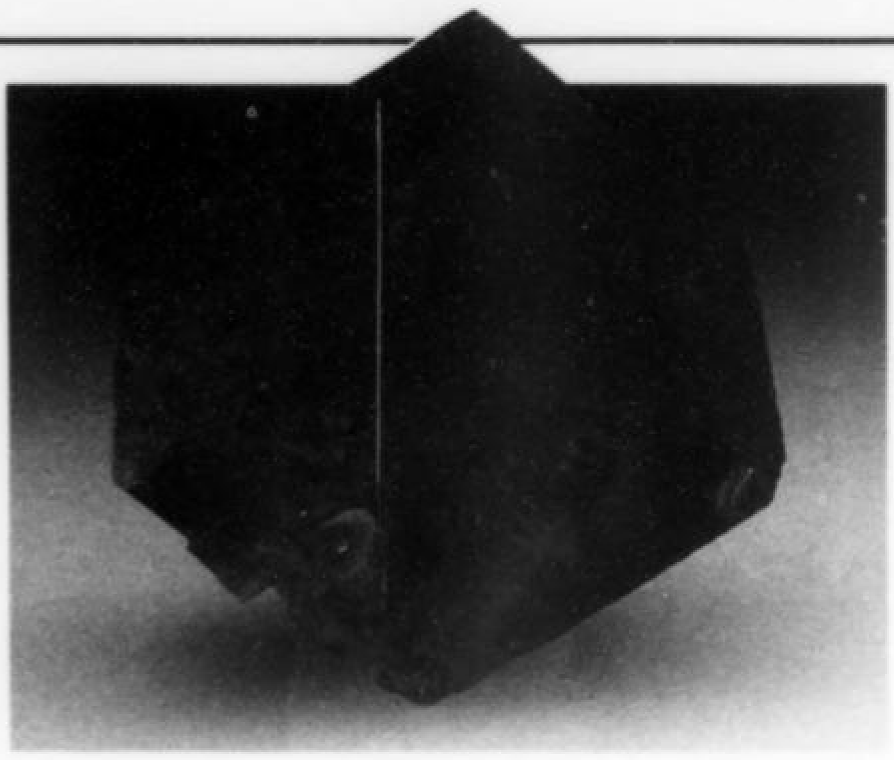

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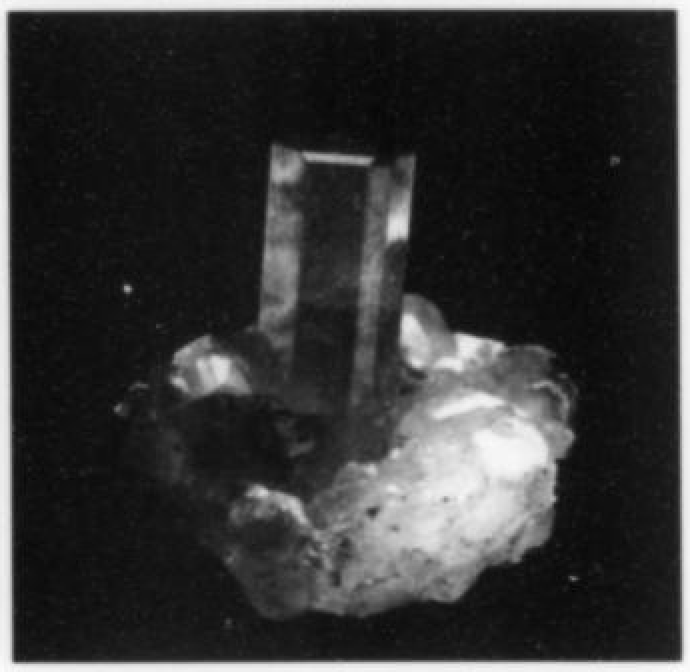

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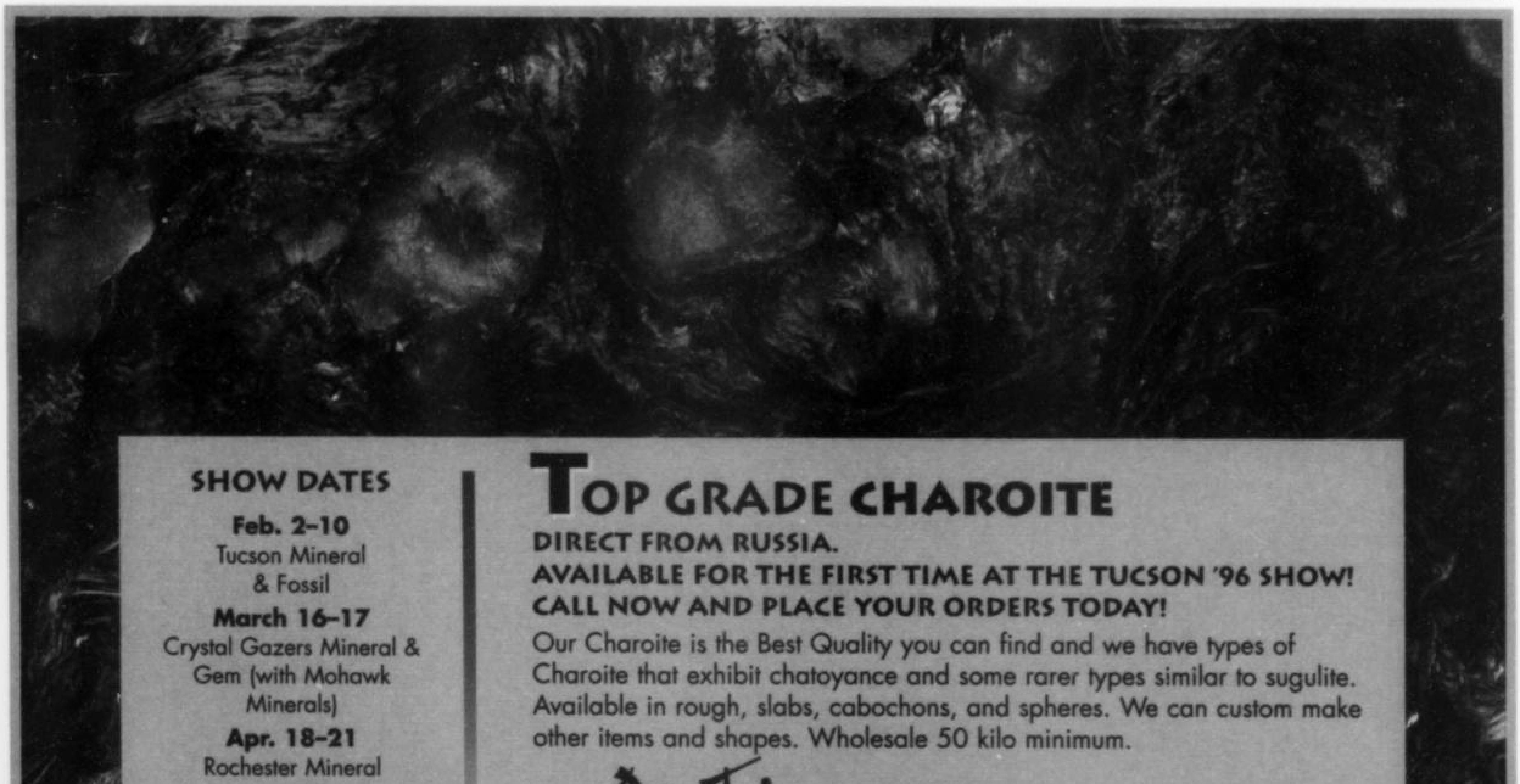

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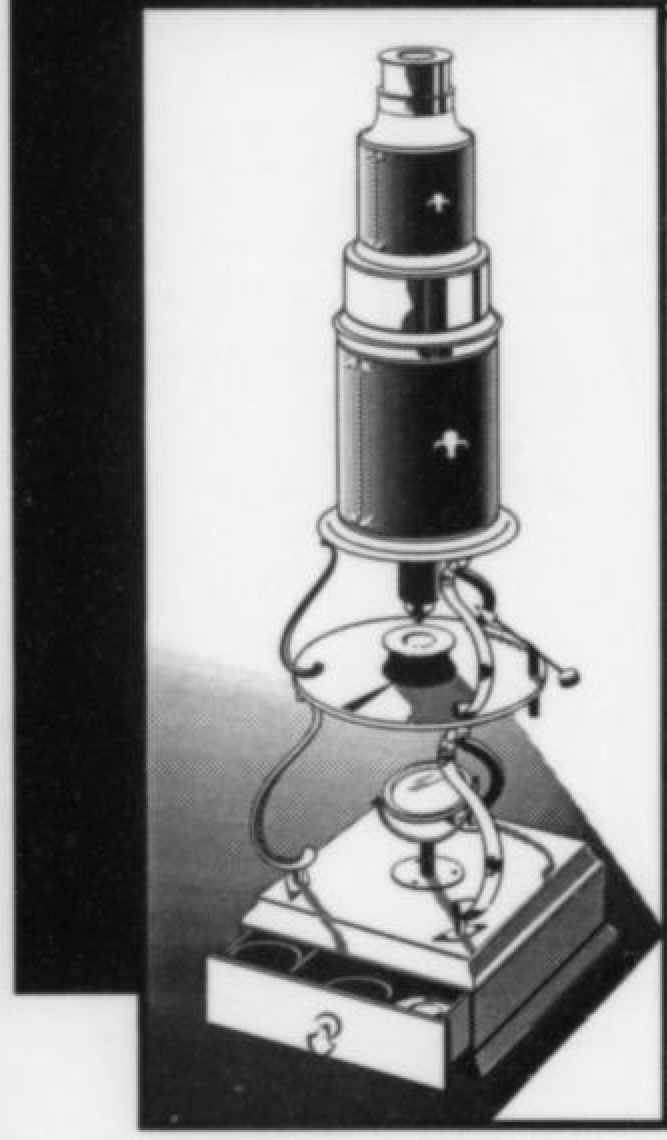

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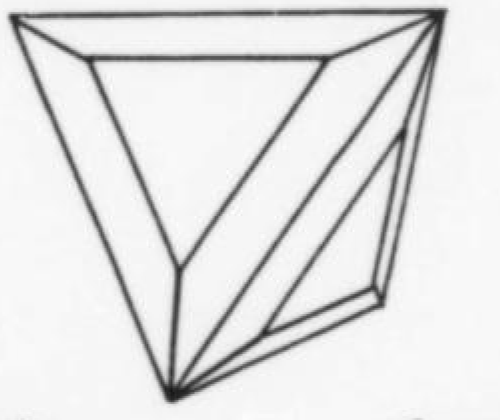

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The Billie mine borate deposit in California's Death Valley has produced large colemanite crystals and clusters, along with associated minerals, since first encountering ore in 1980.

LOCATION

The Billie mine, owned by the American Borate Company, is located in the Furnace Creek borate area of Death Valley National Monument, Inyo County, California. It is approximately 13 miles (21 km) southeast of Furnace Creek Ranch near the Dantes View Road off State Highway 190. The old mining town of Ryan is approximately 1 mile southeast, situated high on the side of the mountain. It is an impressive reminder of the previous borate mining activity which provided the primary impetus for the development of the Death Valley area.

HISTORY

Borates were discovered in Death Valley in 1873, only a couple of years after the discovery of the Nevada playa borates at Columbus Marsh and Teel's Marsh. Progress toward mining Death Valley borates occurred in 1881, when Isadore Daunet and his partners built the Eagle Borax Works near Bennett's Well. In the same year, Aaron Winters discovered borates on the playa near the mouth of Furnace Creek Wash. Winters sold his discovery to William T. Coleman, who built the Harmony Borax Works on the site in 1882.

Saltpans on the playa grew small crystalline balls of "cottonball" ulexite which were raked from the surface and processed into borax by boiling the ulexite in water, then cooling the solution to the ambient desert temperature. However, this process was ineffective at temperatures above 110°F (43.3°C). The high summer temperatures in Death Valley prompted Harmony Borax personnel to temporarily exit the site to operate a slightly cooler, small deposit at Amargosa, west of Tecopa, California, until ulexite processing could be resumed at Harmony.

The borax was transported by 20-mule-team wagons to railcar loading facilities at Mojave and Daggett, California. Problems with the summer heat, remoteness from supplies and length of overland wagon haulage made easily accessible borate deposits at Borate, near Daggett, California, more economically feasible. With the bankruptcy of William T. Coleman in 1888, the Harmony Borax Works ceased production.

Economics precluded any further development of the Death Valley borate resources until Francis Marion ("Borax") Smith nearly completed the length of the Tonapah & Tidewater Railroad from the California Eastern Railway (Santa Fe) connection at Ludlow to Death Valley Junction in 1907. Smith built the railroad to continue borate production more economically from Pacific Coast Borax Company's (predecessor to U.S. Borax Company) Death Valley claims, purchased along with the Borate claims (near Daggett) from Coleman's bankrupt estate.

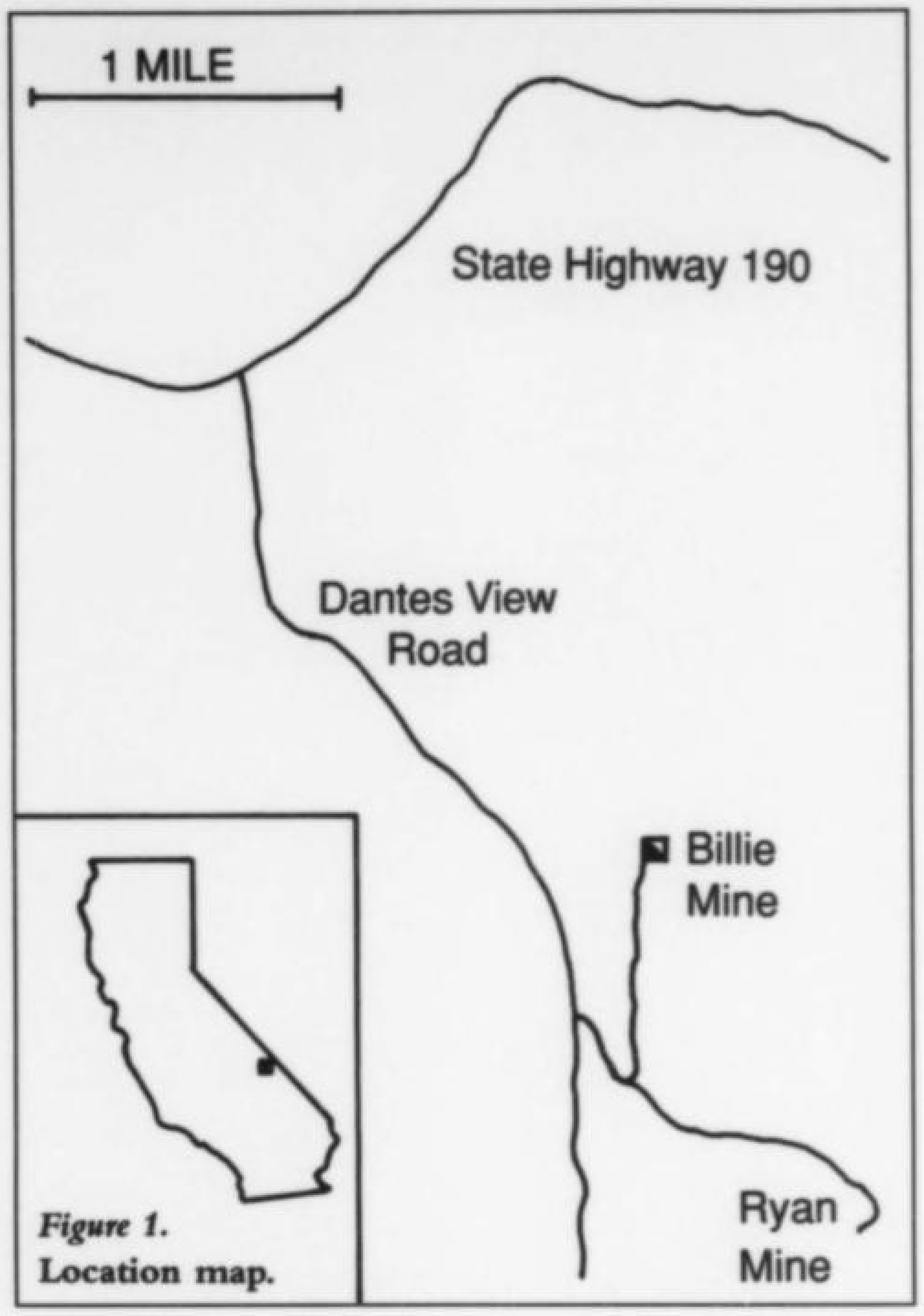

Figure 1. **Location map.**

Production from the Lila C mine near Death Valley Junction also began in 1907, and the rail was continued to the mine and the new mining camp of Ryan. The Lila C mine produced for seven years. Meanwhile, the rail was extended around the edge of the Greenwater Mountains into the Upper Furnace Creek Basin. The town of Ryan was also moved from the Lila C mine to its present location overlooking the upper Furnace Creek Wash.

Borates were produced from many small mines in the Ryan area. Some of the mine names were the Upper and Lower Biddy McCarthy, the Played Out, the Grand View, the Lizzey V. Oakley, the Widow #3 and #7, and the Monte Blanco. Production from all operating mines was discontinued in 1928 due to the discovery and development of the large borate deposit near Boron, Kern County, California (Anonymous, 1972).

Small tonnages of borates were mined for specialty uses in the 1950's and 1960's at U.S. Borax Company's Corkscrew mine and the East Coleman pit (McAllister, 1970).

During this time of low borate activity in Death Valley, the Kern County Land Company became interested in borates, staking and drilling the Billie claims in 1958. The Kern County Land Company also bought the controversial Boraxo #1 and #2 claims from U.S. Borax in 1960. The Boraxo #1 and #2 claims were originally claimed by the Pacific Coast Borax Company in 1900 as the Clara Lode. Mining began and the company applied to patent the claim, but overlooked an error in the patent information. Pacific Coast Borax, unaware of a title problem, ceased assessment work, and began paying taxes on the property (Minette and Muehle, 1974).

In 1919 Scott Russell, a promoter, noticed the error in the claim title, and assembled partners for his venture. Russell, Barlow, Monaghan, and Hill formed Death Valley Borax Company, moved in during the night, and overstaked the Clara Lode with the Boraxo #1 and #2 claims. When Pacific Coast Borax Company tried to re-establish physical possession, the Death Valley Borax Company crew of tough roustabouts removed the Pacific Coast miners, their equipment, and a small building from the claims. The Pacific Coast Borax legal department prevented further efforts to establish possession; consequently, in 1924 the courts upheld the Death Valley Borax Company claims. Mining claim patents were issued in 1931.

The Russell shaft was driven 18 meters during this period; then mining was suspended. The mine claims were later leased to operators but could not sustain continuous operation due to the limited availability of ore railcars. Economic ore shipment could only be accomplished on Pacific Coast Borax Company's railway, and they were not interested in the haulage of Death Valley Borax Company ore (Anonymous, 1972, 1978). In 1928, the entire Pacific Coast Borax operation was moved to Boron, California. The buildings of Ryan were left intact and for a few years the site was operated as the Death Valley View Hotel, complete with rail access for the guests and rail tours of the old workings (Jeff Moore, personal communication, 1986). The rail was later salvaged during World War II.

One of the lessees of the Boraxo claims during this time was named Thompson. He sank one of the shafts in the area, and the claims became popularly known as the Thompson mine (Anonymous, 1978).

Pacific Coast Borax purchased the mine in 1935, but was subsequently charged with restriction of trade in a government anti-trust suit in 1945 and ordered to divest itself of the property. It was not until 1960 that a purchaser could be found. Kern County Land Company bought the property, sank 37 meters of shaft, shipped the ore, then again became inactive. In 1967 Kern County Land Company merged with Tenneco Oil Company. Tenneco began open pit mining in 1970 and renamed the mine the Boraxo open pit mine (Minette and Muehle, 1974). The extent of the Boraxo pit dwarfed the earlier small shafts, which were completely removed by the mine workings. It is also far more notable for the size and volume of crystal specimens found in its vugs, which are on display in many museums around the country.

The Boraxo open pit mine ceased operation in 1977, 77 years after the original claim was filed (Anonymous, 1978). Borates are still visible in the bottom of the pit, but further excavation is considered uneconomical.

Tenneco also began the Sigma open pit and Terry open pit mines in 1975. When the ore of the small Sigma pit ran out, the pit was partially backfilled. Permission to access the Sigma #30 and #31 claims through U.S. Borax's White Monster claims was granted on a toll mining basis, and mining continued. In 1981 all personnel were assigned to the Billie mine.

A four-year moratorium on surface disturbance within Death Valley National Monument went into effect in 1976 to curb claiming activities. This also prevented the Billie claims from being developed as an open pit mine. Tenneco decided to continue development as an underground mine with the shaft outside the national monument utilizing 307 meters of drift per shaft level to reach the ore zone. Tenneco realized that large expenditures would be needed to finance this project and decided to leave the borate business. In 1976 Tenneco entered into a contract to sell its borate holdings to the American Borate Corporation. The contract was consummated in 1977, and the new partnership was known as the American Borate Company (Anonymous, 1981).

The Billie mine shaft-sinking operation began in 1977, and the development operation encountered the first ore in 1980. Mining was difficult, and the area possessed a high thermal gradient causing cases of heat exhaustion. The equipment and skills to operate the mine came from blending of hardrock, softrock, and coal mining technologies. Continuous mining machines were used as the main colemanite development mining system; drill-blast methods were used for probertite development mining, all access drift mining and all stope mining. Many problems occurred adapting the equipment to operate in the mixed limestone, claystone and mudstone rock types. The necessary changes were made and, with the construction of a fill plant and another ventilation shaft, the mine ran smoothly.

In the meantime, international monetary exchange rates had changed to the position of a strong worldwide dollar making foreign sources of borates less expensive. Consequently, the mine went into a standby status in April 1986.

The mine continued to be maintained by a small crew on the surface and underground. It was sold in December of 1990, and is now operating as a new joint venture.

GEOLOGY

General

The borate minerals in the Billie mine orebody are deposited in the lower main member of the Furnace Creek Formation, of Miocene age (Barker and Barker, 1985). The orebody formed from the effluent of volcanic springs in a small lake basin. The deposit is essentially a limestone breccia permeated with borate minerals, interbedded and surrounded with limey lakebed mudstones derived from Furnace Creek Formation weathered basalt, the Artist Drive Formation, and carbonate-bearing Paleozoic formations.

The orebody is mineralized with two main borate ore minerals, colemanite and probertite. A third borate ore, ulexite, occurs mainly in the upper part of the orebody. The original mineral of deposition is hypothesized to have been ulexite, a sodium-calcium borate with five molecular waters, but may have originally been deposited as probertite and colemanite. Due to heat and pressure from burial by later sediments, the ulexite had water forced out of its structure and recrystallized as probertite, a sodium-calcium borate with three waters.

Surface water percolated down faults through pyrite-bearing mudstone, reacting with the pyrite to acidify the water and charge the water with sulfate ions. The acidic percolating water dissolved the sodium-calcium borates and limestone ore. The water was gradually neutralized by reacting with limestone; ions then recombined as the calcium borate, colemanite, containing five molecular waters. The orebody continued to alter from probertite to colemanite, developing an envelope of colemanite around an inner core of probertite. The alteration to colemanite was more complete in the upper portions of the orebody than at the sides or the bottom, and the thickest areas of colemanite were usually near the upper margins of the orebody. Primary colemanite occurring within this system would also have experienced dissolution and recrystallization through this same process.

The stratigraphic thickness of the orebody averaged from 46 to 53 meters and the depth ranged from 46 meters to the shallowest ore, to 390 meters to the deepest ore. The block containing the orebody has been down-dropped by two fault systems which parallel the sides of the Furnace Creek Wash. Folding and faulting have oriented the long axis of the orebody to a N40–50°W direction with a dip of 20–30° southeast. The orebody extends for about 1,100 meters along that dip and averages about 200 meters wide (Norman and Johnson, 1980).

Many of the borate deposits of the Death Valley area occupied topographically high positions and have experienced different degrees of fault deformation and meteoric water leaching. The many differences between the deposits appear to suggest many avenues of deposit evolution. The Billie mine deposit occupies a topographic low and appears to be moderately affected by the major faults of the area, but it escaped the major deformation observed in the Sigma #30 and #31 claims and in the Boraxo pit. The depositional basin of the Billie mine occurs between the Plainview Fault and the Billie Mine Fault. A dextral fault on each side of the basin formed the deposit into a ship's-hull shape, with the south end lower than the north end. Faulting within the keel shape occurs at approximately 51-meter intervals, vertically across the ship's-hull shape with several feet of normal fault movement. Each subsequent block experienced slight downdip bedding-slip movement particularly in areas of high clay content.

Origin of the Deposit

The location and formation of the borate-producing springs and collecting basins continue to be controversial subjects in borate geology. The observation of evidence is difficult, due to the natural destruction of the original structures by the contemporaneous and later fault movements and the brecciation due to dissolution of the borates.

Borate-producing springs and borate collecting basins of Death Valley, California, occurred in areas undergoing tectonic extension, possibly associated with wrench fault movement at a triple-point continental plate junction. Crustal thinning allowed solutions from previously deep-seated sources to flow to the surface, in some cases creating deposits of rather rare mineral assemblages (Barker and Barker, 1985).

The springs were of unknown temperature, and the location of the springs has not been clearly observed within the collecting basin; but the lateral edges of the orebody are well preserved and show no features of disturbance by an external feeding system. Very little borate was observed in exposures outside of collecting basins; however, minor borates have been recorded as veinlets in a neighboring basalt formation and as granules and efflorescence in the Artist Drive Formation (McAllister, 1970). A basalt lava pillow structure interfingered with borate beds in the Sigma pit mine indicates that basalt surface eruptions accompanied borate spring activity in that deposit and possibly all the deposits in the Furnace Creek borate area.

Borates may have been deposited in a series of coeval fault sag basins, and subsequent complex fault activity allowed only a few deposits to be preserved. Projected shorelines of a series of basins can be traced from the Billie mine to the Boraxo pit and the Sigma-White Monster group of claims. Beyond this area the borate deposits generally occupied topographic highs in which leaching and erosion have removed most evidence of deposit margins or possible shorelines.

The Billie mine deposit basin began with the deposition of laminated mudstone and limestone with a conglomerate composed of pebbles and cobbles derived from local Paleozoic rock units. The borates are deposited above this layer in laminated beds of mudstone and limestone which became distinctly thinner and tightly laminated at the margins of the borate mineralization. Occasional rhyolitic ash tuff beds occurred in the borate zone and the laminated mudstone and limestone lateral of the borates.

Probertite is believed to be either the dehydrated secondary mineral after the primary mineral of deposition, ulexite, or along with colemanite, a primary mineral of deposition. In either case, the original texture of the beds was preserved in a more reliable state than in areas of colemanite mineralization due to lack of brecciation from dissolution and recrystallization. The probertite beds consist of mudstone beds laminated with beds of probertite containing limestone breccia. The limestone breccia occasionally exhibits reoriented laminae and fractures filled with probertite. The areas of pure probertite exhibit crude bedding partially delineated by clay.

The mudstone beds are sometimes continuous over large areas and are absent of graded beds, conglomerates and rip-up clasts. These observations indicate that the mudstone layers had been deposited slowly in a lake, providing a quiet environment necessary for thin continuous bedding within an area of low topography.

The brecciated limestone suspended in probertite indicates an environment of much higher energy. Chemical brecciation of the limestone occurred after deposition, but the initial brecciation and placement of the limestone indicates rapid deposition of the borates, which repeatedly brecciated and distributed previously formed limestone spring aprons. These aprons reformed after each borate episode, only to be distributed during the next episode. The absence of limestone cobbles at the tightly laminated margins of the orebody also indicates that the springs were within the deposition basin. The uniform spread of the brecciated limestone spring apron debris indicates that the borate springs were active along a linear area which migrated within the basin and were rejuvenated many times, as shown by the crude bedding formed by thin layers of clay within the probertite. Longitudinal pinching out of borate beds at the upper contact of the orebody indicates that the spring-producing areas eventually migrated out of the earlier producing areas.

Spring aprons within the orebody have not been observed, possibly indicating that the brecciation produced by renewed borate spring flow was not distinguishable from the brecciation produced by later dissolution and redeposition of the borates and faulting. The brecciation produced by the borate spring activity probably provided fractures and channels used by later percolating solutions to dissolve and recrystallize the spring-feeding area accompanied by the brecciation of dissolution. The chemistry within the spring-feeding pipes may also have crystallized colemanite directly from solution, but evidence for this theory is lacking.

Continuous faulting accompanied borate deposition and collecting basin formation, but faulting may have contributed much to the destruction of evidence of the spring-feeder system, particularly later, as more of the area became mineralized with colemanite. Nearly all of the fault tension of the orebody was released by deformation of the colemanite, leaving the probertite areas nearly free of faulting. The radiating, fibrous crystals of probertite interlock to form a tough, fault-resistant block which helped it retain its original texture. Probertite is more soluble and has less hardness than colemanite, but colemanite has better developed cleavages, better developed vug systems, and at times a sugar-like texture which allowed the rock to be more easily crushed and faulted.

The scant fossil record of pieces of reed-like plant material suggested a rapid rate of deposition. This may have destroyed fossil evidence; however, thicker mudstone beds which would have protected underlying fossils within the mudstone showed no increase in preserved fossils.

Mineralization

Most mines have relatively few cavities for active crystal growth. The Billie mine is exceptional in the number of crystal cavities encountered in mining and the variations of the colemanite crystals found in them. The survey of these crystals provided information for understanding more difficult problems, such as, the loss of sodium from the orebody and the increase in sulfate through colemanite recrystallization.

The percolating surface water seeped down faults through mudstones containing pyrite which reacted to acidify the water and charge it with sulfate. The slightly acid water easily dissolved probertite and colemanite and reacted with the limestone, gradually removing the limestone, liberating calcium ions and finally neutralizing the solution. Colemanite was then deposited from the solution. This process leached upper borate and limestone portions of the orebody, leaving limestone sinter, calcareous marl, and occasionally calcite and celestine. Similar occurrences of limestone sinter, calcareous marl, calcite and celestine in the region may also represent leached borate deposits.

The leaching occurred along a series of solution vugs; the larger vugs accounted for some of the brecciation and loss of bedding structure in the colemanite zone. Most bedding structure survived this mineralogical change, indicating that the recrystallization of colemanite proceeded quickly after the dissolution of the probertite, thereby preventing total collapse of the mudstone beds.

Partially dissolved probertite fibers have occasionally been observed penetrating crystals of colemanite at this interface, indicating a wandering focus of dissolution and recrystallization and a solution varying in amount, acidity, and dissolved borate. These factors suggest a limited amount and fluctuating supply of percolating water leaching the ore at any given time, perhaps affected by seasonal peaks in flow.

The ultimate destination of the liberated sodium ions is an obstacle in the formulation of a model of mineralogical change. The continuing change of probertite to colemanite requires that percolating surface water continue to supply calcium ions and remove sodium ions. The removal of sodium ions is hypothesized to occur by the circulation of water through vug systems in the lower orebody intersecting altered basalt aquifers across the bounding faults. This hypothesis is indicated to be correct by the recovery of a core of altered basalt near the lower edge of a central cross-section of the orebody. This also established the fact that as the water flowed through, the tendency was to recrystallize the borate at a lower level than it was initially dissolved.

MINERALS

Anhydrite $CaSO_4$

Anhydrite occurs as a massive replacement of colemanite, and has tan, gray and black coloring similar to colemanite ore. This similarity caused difficulty in recognition of the anhydrite, and subsequent dilution of the ore. The main difference between the minerals is the hardness, so that the continuous-mining machine's cutting heads sparked while cutting the anhydrite, also producing a faint sulfurous odor.

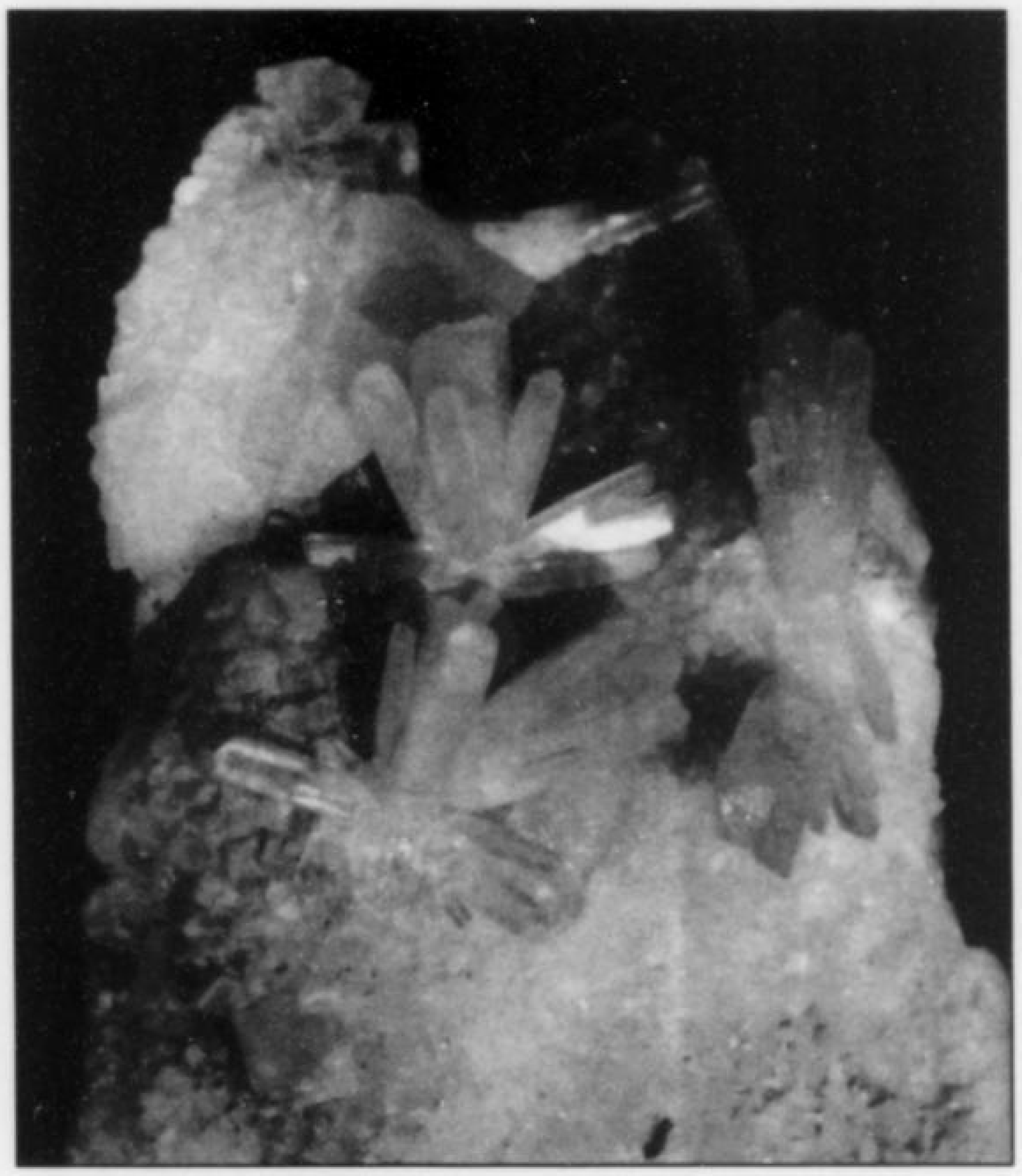

Figure 2. **Celestine crystals to 1.7 cm on colemanite, from the Billie mine (1360 S level, 2S drift).**

Celestine $SrSO_4$

Celestine occurs in white, clear, blue or pale green colors and in simple to complex crystal habits. The crystal sizes are usually less than 2.5 cm but have been observed up to 10 cm. Unusual crystal habits included thin, square-ended crystals sometimes occurring as pinwheels composed of small crystals. Celestine occurs in colemanite vugs away from the probertite margins and with calcite along the lateral edges of orebody.

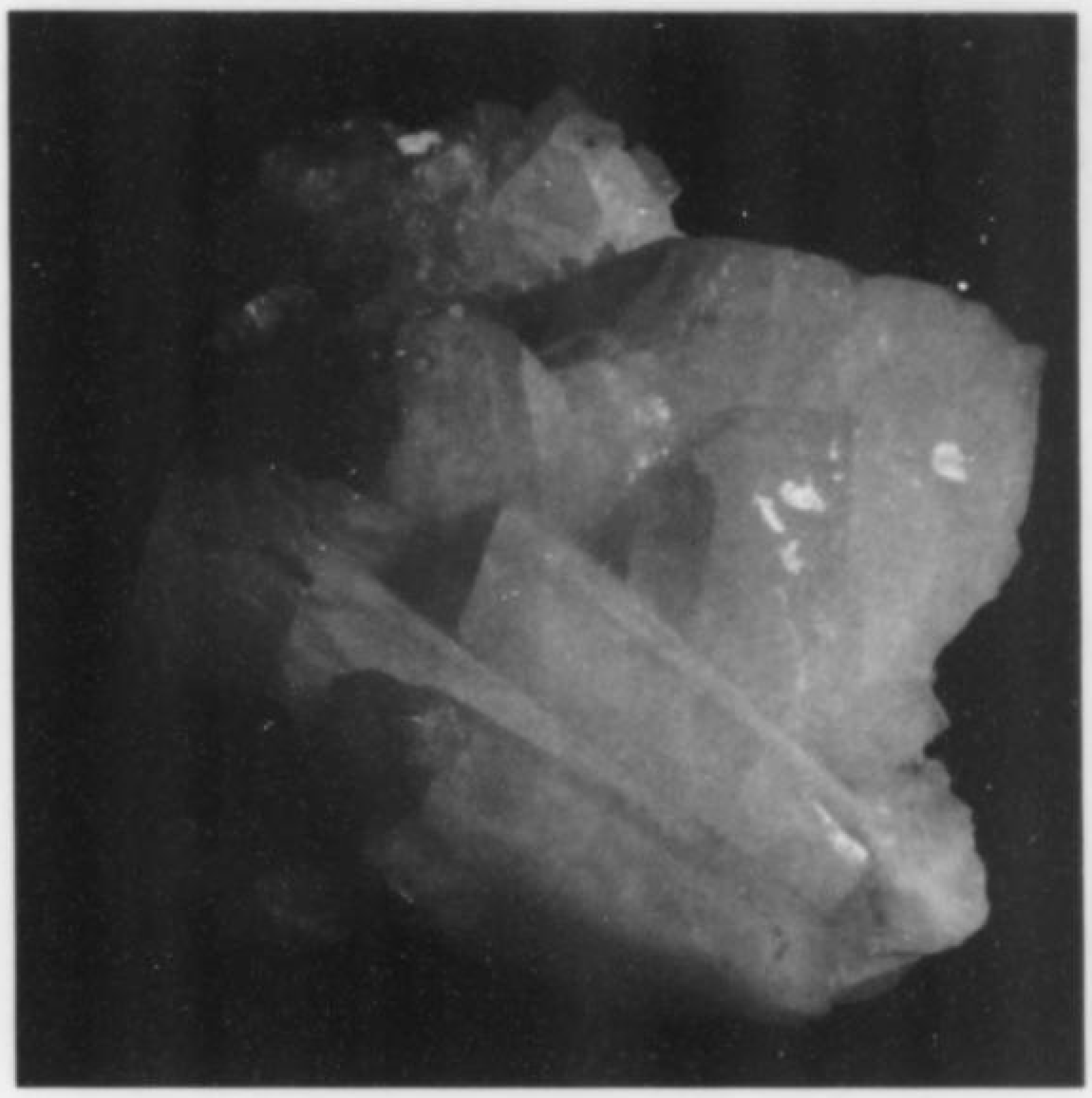

Figure 3. **Colemanite crystal group, 32 cm, from the Billie mine (1360 N level, 3E drift). The large crystal measures 20 cm.**

Colemanite $Ca_2B_6O_{11}{\cdot}5H_2O$

Colemanite from the Boraxo pit mine occasionally exhibits an amber zoning within the crystals. Some "root beer" colemanite crystals were collected on the White Monster claims, but no amber or brown zoning was observed in colemanite from the Billie mine. The amber zoning in the Boraxo pit colemanite was chemically tested and found to contain strontium, either as inclusions or as replacements of calcium within the crystal lattice.

Chemical tests of Billie mine colemanite have indicated that pointed, radiating crystals have a slightly higher content of included sodium than the lathe-shaped or equant crystals. This is of interest because the colemanite near the probertite and near areas of clay tends to be of more complex, pointed and radiating habits. Most crystals in other areas of the orebody are of a lathe-shaped or equant habit, indicating that dissolution and recrystallization of colemanite away from the colemanite-probertite contact continued after the initial change from probertite, winnowing vestigial sodium and moving the borate farther down the series of vugs.

The colemanite of the vug systems containing celestine tests low in strontium, and always correlates to faults, indicating that dissolution of strontium-bearing borates in a sulfate-bearing solution winnowed strontium from the borate solution by the crystallization of celestine. (Similar faults correlate to occurrences of anhydrite and gypsum, but are in the lateral margins of the orebody.)

Gypsum $CaSO_4 \cdot 2H_2O$

Gypsum was of only a limited occurrence in the Billie mine. One occurrence was in a vug of colemanite with gypsum on the colemanite, with the exposed gypsum partially dissolved and mixed with howlite. The other occurrence consisted of a few crystals on the lateral margin of the colemanite zone. The largest of the group occurred as a thin, semi-circular, single crystal 13 cm across.

Howlite $Ca_2B_5SiO_9(OH)_5$

Howlite also occurred in the Billie mine. Howlite is a borosilicate mineral well known from Tick Canyon, California, as microcrystalline nodules which can be cut by lapidarists into white porcelain-like slabs. Howlite in the Billie mine occurs as nodules similar to but slightly softer in hardness than Tick Canyon howlite, and decreases in hardness into the consistency of powder which, when mixed with water, runs like thick milk from newly mined vugs. Howlite occurred most often near the upper margins of the orebody and near the probertite-colemanite contacts.

Probertite $NaCaB_5O_7(OH)_4 \cdot 3H_2O$

Probertite from the Boraxo pit mine forms masses of radiating blades with clay included into the crystals. This is easily distinguishable from the Billie mine probertite, which forms masses of radiating fibers with little clay included into the crystals. Chemical testing has indicated that the Boraxo pit probertite had a higher content of calcium in its structure. The Boraxo pit probertite also looks similar to the Terry pit mine colemanite, which occurs in radiating masses in clay and limestone and tends to form blade-like cleavages. Chemical testing of the Terry pit colemanite indicates a sodium content higher than either Billie mine or Boraxo pit mine colemanite.

The probertite of the Billie mine contains a small percentage of strontium. No zones of celestine have been observed in the probertite.

Strontianite $SrCO_3$

Strontianite has been found in several areas. In two of the areas, strontianite was included into colemanite with active alteration of the exposed strontianite into celestine. These were the first confirmed occurrences of strontianite with borates in the Death Valley area. The strontianite identification was done through X-ray diffraction by John Longshore at Humboldt State University, Arcata, California.

Veatchite $Sr_2B_{11}O_{16}(OH)_5 \cdot H_2O$

Veatchite also occurs at the Billie mine (a species not previously confirmed in the Death Valley area). Veatchite, a strontium borate of rare occurrence, occurred sparingly in the Billie mine except for the 1360 level, 2S drift, where numerous vugs were filled with small (up to 5 mm) veatchite balls in colemanite vugs, occasionally occurring with celestine. This veatchite occurred in a fault zone and appeared to be limited to the area between two faults exhibiting a depositional setting similar to that of celestine. Higher quality specimens of veatchite were noticed in another area but were not salvaged due to a mistaken identity of the mineral. The veatchite was tentatively identified by Vince Morgan in 1982 and was confirmed through X-ray diffraction by John Longshore at Humboldt State University, Arcata, California.

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MINERALS OF THE SERAVEZZA MARBLE, TUSCANY, ITALY

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The Seravezza marble quarries in Tuscany are as interesting for their microminerals as the more famous Carrara marble quarries 20 km to the northeast. The mix of species is somewhat different, however, including such minerals as boulangerite, zinkenite, guettardite, robinsonite, baumhauerite, bindheimite and bournonite which are rarer or entirely absent at Carrara.

INTRODUCTION

The Seravezza quarrying district is located about 20 km southwest of Carrara, the famous marble deposit where over 70 mineral species have been found (Franzini *et al.*, 1987; Orlandi and Del Chiaro, 1989).

The cavity minerals of the Seravezza marble have received much less scientific attention; actually, just two papers, concerning guettardite and robinsonite from Seravezza, have been published (Bracci *et al.*, 1980; Franzini, Orlandi and Pasero, 1992). Our purpose here is to describe the geology of this interesting locality and the 51 mineral species which have been identified thus far (Table 1).

LOCATION

The town of Seravezza is located in Versilia, a district in the Tuscan province of Lucca, about 35 km north of Pisa and

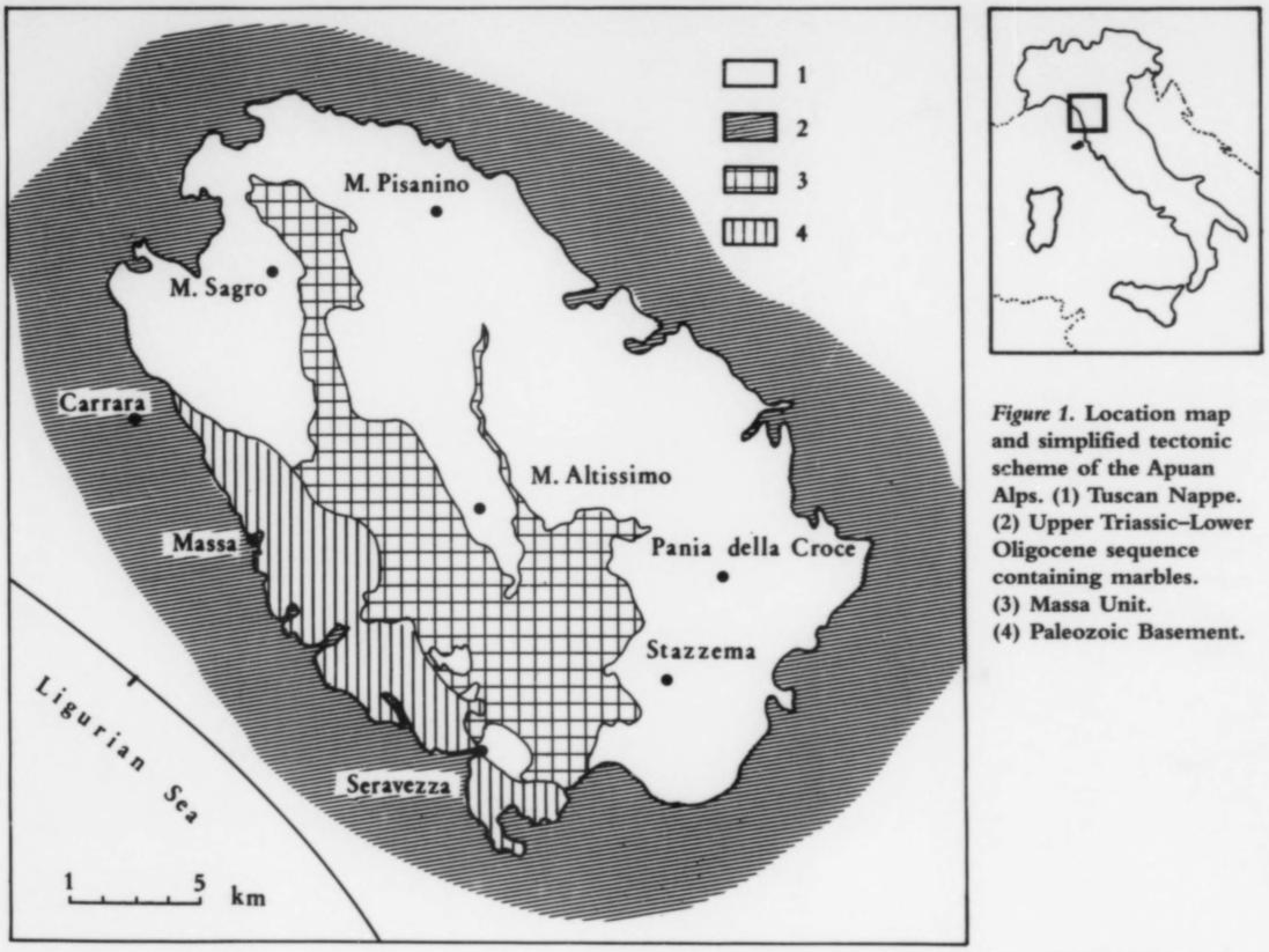

Figure 1. Location map and simplified tectonic scheme of the Apuan Alps. (1) Tuscan Nappe. (2) Upper Triassic–Lower Oligocene sequence containing marbles. (3) Massa Unit. (4) Paleozoic Basement.

20 km southwest of Carrara (Fig. 1). The marble quarries are on the eastern slopes of Monte Trambiserra (Pitone area) and on the southwestern slopes of Monte Ornato (Ceragiola and Costa areas).

The Pitone area hosts two quarries: a larger one, the Biagi quarry, and, further south, the smaller Tessa quarry. Quarrying activities there came to an end in 1984; only minor maintenance operations have taken place since then. The Costa area hosts several quarries, only one of which is active at the present time. The Ceragiola area includes the active Tognetti quarry, and the Bigi and Agostini quarries, which ceased operations in 1982–1983.

GEOLOGY

The Seravezza marbles crop out at the southwestern rim of the tectonic "window" of the Apuan Alps; they are part of an epizonal metamorphic complex originating from a Tertiary Tuscan sedimentary sequence. The Seravezza marbles are located along the southern boundary between the Massa Unit and the phyllitic Paleozoic basement, which hosts the main sulfide mineralization of the Apuan Alps (Carmignani and Giglia, 1975).

Other extensive marble outcrops occur in the northeastern and central part of the apuan metamorphic complex (Arni, Monte Altissimo, Isola Santa and Resceto). A few mineral specimens from this general area are beginning to appear and have been submitted by field collectors for identification; it is likely, therefore, that interesting finds will be reported in the future.

Figure 2. Typical cavities at the Ceragiola quarry. Orlandi-Del Chiaro photo.

Figure 3. **Pitone area quarries; Orlandi photo.**

CAVITY FORMATION

The minerals of the Seravezza marbles, like those of Carrara, occur in cavities generated by the deformation process during Tertiary metamorphism (Carmignani and Kligfield, 1990, and references therein). While the Carrara cavities are often tube-like with a diameter of about 10 cm and length up to several meters, the Seravezza cavities have an elongated, sometimes s-shaped cross-section only a few millimeters to a few centimeters wide and 10 to 30 cm high; the length can reach several meters (Fig. 2).

These cavities lie *en echelon* on definite horizons related to the schistosity surface of the first metamorphic phase, which was refolded during the second metamorphic deformation. A second schistosity surface associated with the folds above and lying at a small inclination can sometimes be seen. The elongated cross-sections of the cavities where mineralization occurs are emplaced at a high angle with respect to both the first and the second schistosity surfaces.

A model for the formation of the cavities is illustrated in Figure 4, which suggests that tension gashes have been produced by shearing stresses concentrated on certain horizons.

The structural data show that these phenomena are related to the late tectonic evolution of the Apuan metamorphic complex, and that they are consistent with the post-collisional processes which, in this area, appear as a southwest-dipping extensional shear zone and ductile extensional faults (Carmignani and Kligfield, 1990).

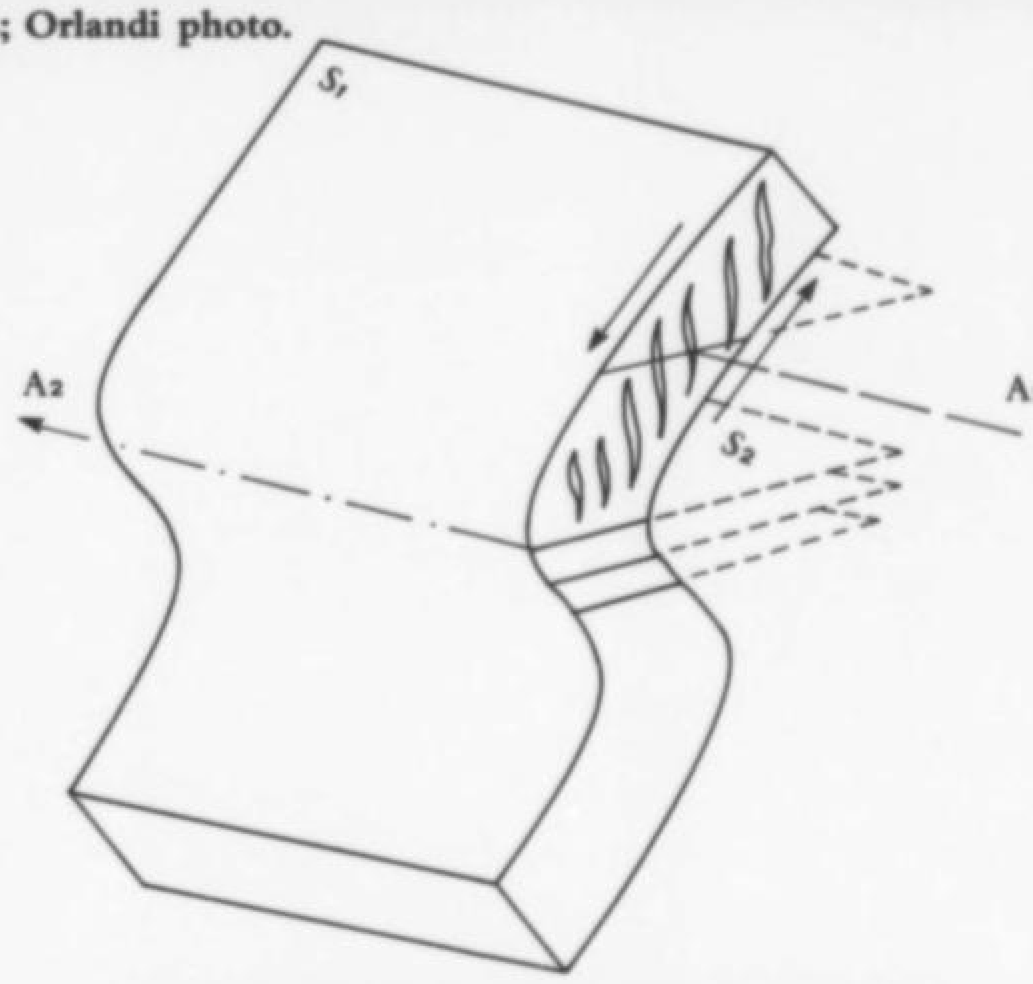

Figure 4. **Interpretive cinematic model, showing a tension-gashing process due to shear stress in marble horizons, creating the cavities in the Seravezza marble (after Giananti, 1984).**

The deformation process which opened the cavities brought about a pressure gradient around the cavity area, which activated the circulation of mineralizing solutions in the cavities. It is likely that at least part of the solutions were not of external origin, but originated from within the marble itself.

MINERALOGY

The first species deposited were: quartz (not common here), galena, pyrite, sphalerite, enargite, colusite and fluorite. The lead sulfosalts appear to have been deposited in a later phase, while smythite, marcasite, dolomite, gypsum and "wad" were deposited last.

Secondary minerals such as cerussite, hydrozincite, smithsonite, wulfenite, mimetite, etc. were formed much more recently during alteration processes caused by the circulation of surface water.

All the species described in this article were identified by X-ray diffraction methods. The minute dimensions of the crystals required, in most cases, the use of the Gandolfi camera to generate powder diffraction patterns and the Weissenberg camera for single-crystal diffraction patterns.

The chemical analyses of sulfides and sulfosalts were carried out on an ARLSEM-Q electron microprobe, using the following standards: natural galena for Pb and S; natural stibnite for Sb, natural chalcopyrite for Cu, metallic Cd for Cd and natural arsenopyrite for As and Fe.

The chemical formulas of the minerals listed below and on Table 1 are from Fleischer and Mandarino (1991). Table 1 lists the minerals reported from Seravezza, arranged according to Strunz's *Mineralogische Tabellen* (1978).

Adamite $Zn_2(AsO_4)(OH)$

Minute apple-green crystals of adamite in globular aggregates up to 1 mm have been found only once, at the Costa quarry.

Albite $NaAlSi_3O_8$

Albite occurs sparingly in various quarries as clear tabular crystals.

Anglesite $PbSO_4$

Just one crystal of anglesite, smaller than 1 mm, has been found near a fragment of altered galena.

Arsenopyrite FeAsS

Rare prismatic crystals of arsenopyrite with rhombic cross-section occur elongated on the *c*-axis, and are normally smaller than 1 mm. The color is pale lead-gray, sometimes tarnishing yellow. All known specimens were collected at the Costa quarry.

Azurite $Cu_3(CO_3)_2(OH)_2$

Rare azurite is normally associated with malachite. A few fairly showy microcrystal specimens of azurite up to 1 mm were collected at the Tognetti quarry.

Barite $BaSO_4$

Milky white, tabular crystals of barite to 1 or 2 cm occur sparingly in all of the Seravezza quarries.

Baumhauerite (?) $Pb_3As_4S_9$

A black, metallic, acicular crystal removed from a specimen collected at the Pitone quarry was found probably to be baumhauerite. Two chemical analyses and a Gandolfi camera powder X-ray diffraction pattern were obtained. Unfortunately the crystal is no longer available and further examination of the same specimen, containing both boulangerite and guettardite crystals, did not reveal any more baumhauerite.

The microprobe chemical analyses (Giananti, 1987, specimens 8a and 8b) gave results (shown in Table 2, samples 1 and 2) which are very close to those reported by Jambor (1967) for antimonian baumhauerite from Madoc, Ontario.

Bindheimite $Pb_2Sb_2O_6(O,OH)$

Like duftite, bindheimite has been found only in one specimen, as white earthy pseudomorphs after acicular crystals of lead sulphoantimonides.

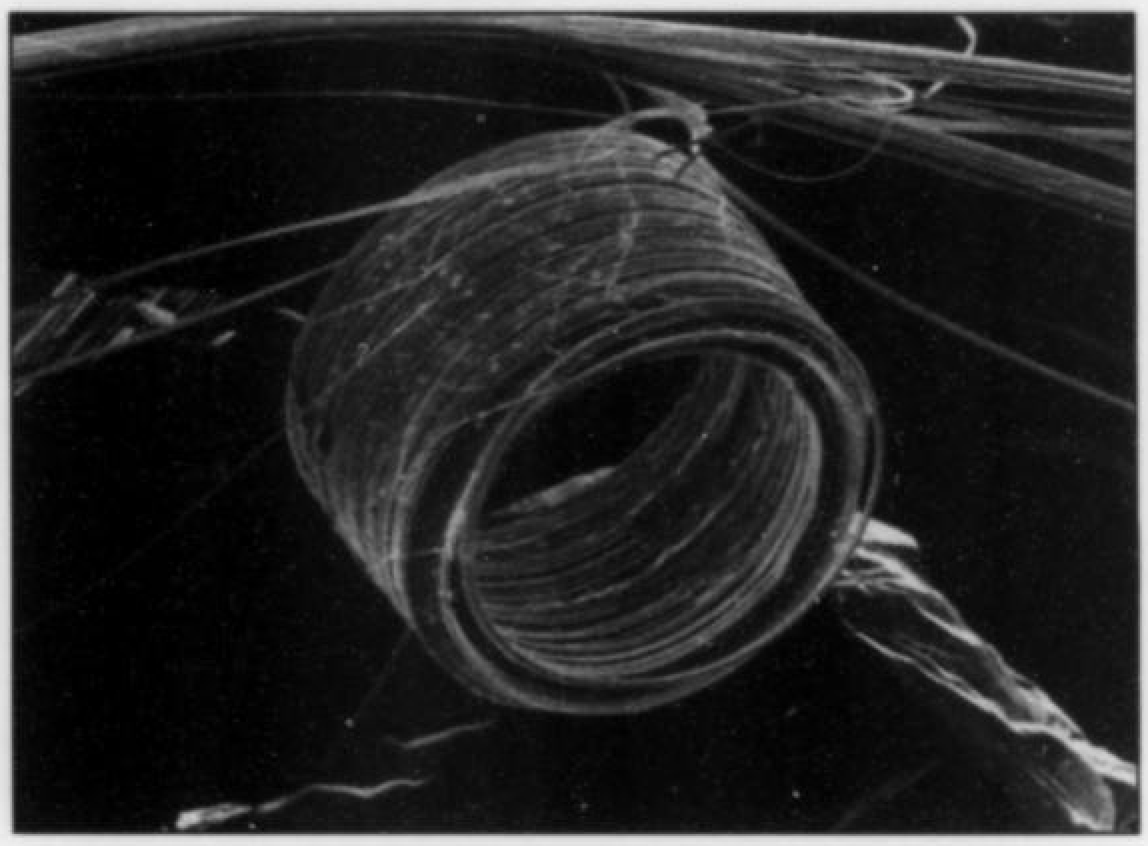

Figure 5. **Boulangerite, curved crystals 0.1 mm in diameter (SEM photo), from the Tognetti quarry. Del Chiaro collection; Orlandi photo.**

Boulangerite $Pb_5Sb_4S_{11}$

Boulangerite is common in all the Seravezza quarries, as acicular, extremely flexible crystals up to a few centimeters. The crystals are grouped in irregular or matted aggregates which are very dark gray, almost black, with a bright metallic luster. Some crystals may be thicker, stiffer and more brittle, and do not show the striations which are typical of zinkenite. Curved or curled crystals forming small rings and cylinders are not uncommon.

Microprobe chemical analysis (Giananti, 1987, specimen 19) gave the results shown in Table 2 (sample 6).

Bournonite $PbCuSbS_3$

Dark lead-gray, shiny metallic crystals of bournonite up to 2–3 mm, normally tabular and twinned, are uncommon. Square bipyramidal crystals have also been found, associated with minute crystals of tetrahedrite.

The chemical analysis of one crystal (Dalena, 1978) is shown in Table 2 (sample 3).

Calcite $CaCO_3$

Calcite crystals up to a few millimeters, but occasionally larger than 1 cm, line all the marble cavities. The crystals nearly always have a slightly elongated rhombohedral habit; the faces are often striated in a direction parallel to the crystal edges. Particularly interesting are some perfectly clear, twinned rhombohedral crystals which simulate a trigonal bipyramid.

Celestine $SrSO_4$

Transparent or white prismatic celestine crystals up to 1 mm, individually and in crystal sprays, are uncommon, but may be found more often in the Ceragiola quarries.

***Table 1.* Minerals found in cavities of the Seravezza marble.**

Mineral	*Composition*	*Rarity*	*Mineral*	*Composition*	*Rarity*
Native Elements			***Halides***		
Sulfur	S	Common	Fluorite	CaF_2	Uncommon
Sulfides and Sulfosalts			***Oxides***		
Sphalerite	(Zn,Fe)S	Very common	Bindheimite	$Pb_2Sb_2O_6(O,OH)$	Very rare
Chalcopyrite	$CuFeS_2$	Very rare	Quartz	SiO_2	Uncommon
Luzonite-	Cu_3AsS_4 - Cu_3SbS_4	Rare	Rutile	TiO_2	Rare
Famatinite			"Wad"	Mn oxides	Uncommon
Colusite	$Cu_{26}V_2(As,Sn,Sb)_6S_{32}$	Rare	***Carbonates***		
Sulvanite	Cu_3VS_4	Very rare	Smithsonite	$ZnCO_3$	Very rare
Tetrahedrite	$(Cu,Fe)_{12}Sb_4S_{13}$	Uncommon	Calcite	$CaCO_3$	Very common
Wurtzite	(Zn,Fe)S	Rare	Dolomite	$CaMg(CO_3)_2$	Very common
Enargite	Cu_3AsS_4	Uncommon	Strontianite	$SrCO_3$	Uncommon
Smythite	$(Fe,Ni)_9S_{11}$	Very rare	Cerussite	$PbCO_3$	Common
Millerite	NiS	Very rare	Azurite	$Cu_3(CO_3)_2(OH)_2$	Rare
Galena	PbS	Common	Malachite	$Cu_2(CO_3)(OH)_2$	Rare
Stibnite	Sb_2S_3	Uncommon	Rosasite	$(Cu,Zn)_2(CO_3)(OH)_2$	Rare
Pyrite	FeS_2	Very common	Hydrozincite	$Zn_5(CO_3)_2(OH)_6$	Rare
Marcasite	FeS_2	Very rare	***Sulfates, Molybdates***		
Arsenopyrite	FeAsS	Rare	Celestine	$SrSO_4$	Uncommon
Bournonite	$PbCuSbS_3$	Uncommon	Barite	$BaSO_4$	Uncommon
Baumhauerite	$Pb_3As_4S_9$	Very rare	Anglesite	$PbSO_4$	Very rare
Jordanite	$Pb_{14}(As,Sb)_6S_{23}$	Uncommon	Gypsum	$CaSO_4\cdot 2H_2O$	Common
Zinkenite	$Pb_9Sb_{22}S_{42}$	Uncommon	Wulfenite	$PbMoO_4$	Very rare
Robinsonite	$Pb_4Sb_6S_{13}$	Uncommon	***Arsenates***		
Semseyite	$Pb_9Sb_8S_{21}$	Very rare	Adamite	$Zn_2(AsO_4)(OH)$	Very rare
Boulangerite	$Pb_5Sb_4S_{11}$	Common	Duftite	$PbCu(AsO_4)(OH)$	Very rare
Guettardite	$Pb(Sb,As)_2S_4$	Uncommon	Mimetite	$Pb_5(AsO_4)_3Cl$	Rare
Realgar	AsS	Rare	***Silicates***		
Orpiment	As_2S_3	Rare	Orthoclase	$KAlSi_3O_8$	Rare
"Red acicular sulfoarsenide"		Uncommon	Albite	$NaAlSi_3O_8$	Common

***Table 2.* Analyses of some Seravezza sulfides and sulfosalts.**

Sample	*Pb*	*Sb*	*As*	*Cu*	*Zn*	*Fe*	*Cd*	*S*	*Empirical Formula*	*Note*
1	48.71	18.25	10.01	0.88				21.72	$Pb_3Sb_{1.9}As_{1.7}S_{8.6}$	Baumhauerite
2	48.07	19.42	11.18	0.03				21.66	$Pb_3Sb_{2.0}As_{1.9}S_{8.7}$	Baumhauerite
3	43.63	15.17	4.35	13.95	0.01	0.04	0.07	22.32	$PbCuSb_{0.6}As_{0.6}S_{3.3}$	Bournonite
4	39.42	24.72	12.29					23.92	$PbSb_{1.1}As_{0.9}S_{3.9}$	Guettardite
5	40.18	24.88	12.95					24.38	$PbSb_{1.1}As_{0.9}S_{3.9}$	Guettardite
6	55.48	25.34	1.06	0.08				18.25	$Pb_5Sb_{3.9}As_{0.3}S_{10.6}$	Boulangerite
7	51.31	29.41	0.55	0.03				18.39	$Pb_9Sb_{8.8}As_{0.3}S_{20.8}$	Semseyite
8					66.59	0.12	0.50	32.91	ZnS	Sphalerite
9					62.50	3.43	0.53	32.81	ZnS	Sphalerite
10					62.33	0.01	4.59	31.65	ZnS	Wurtzite
11					62.73	0.01	4.65	32.11	ZnS	Wurtzite

References: Dalena, 1978, for sample 3; Giananti, 1987, all other samples.

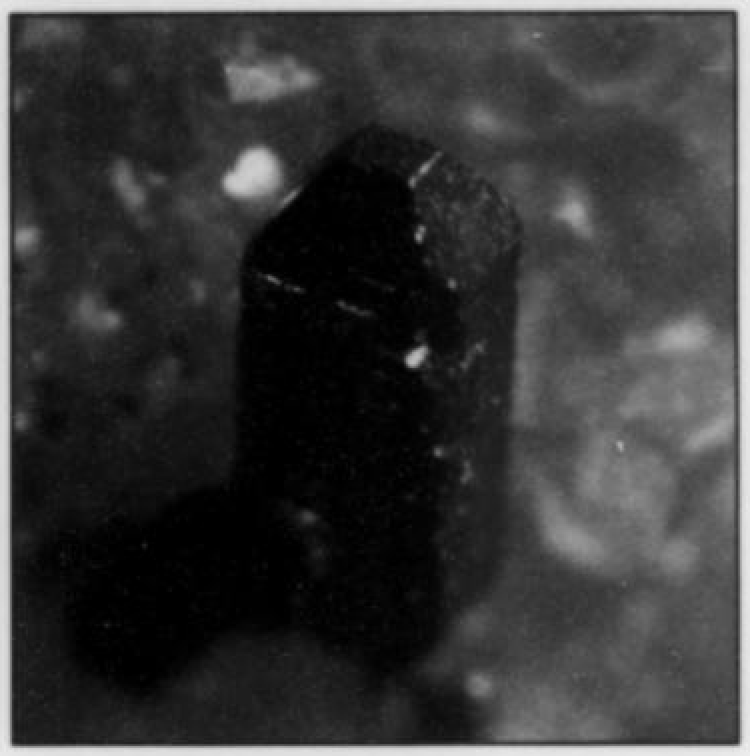

Figure 6. **Bournonite crystal, 0.5 mm, from the Ceragiola quarries. Deri collection; Orlandi photo.**

Figure 7. **Celestine crystal spray, 8 mm across, from the Tognetti quarry. Santarelli collection; Orlandi photo.**

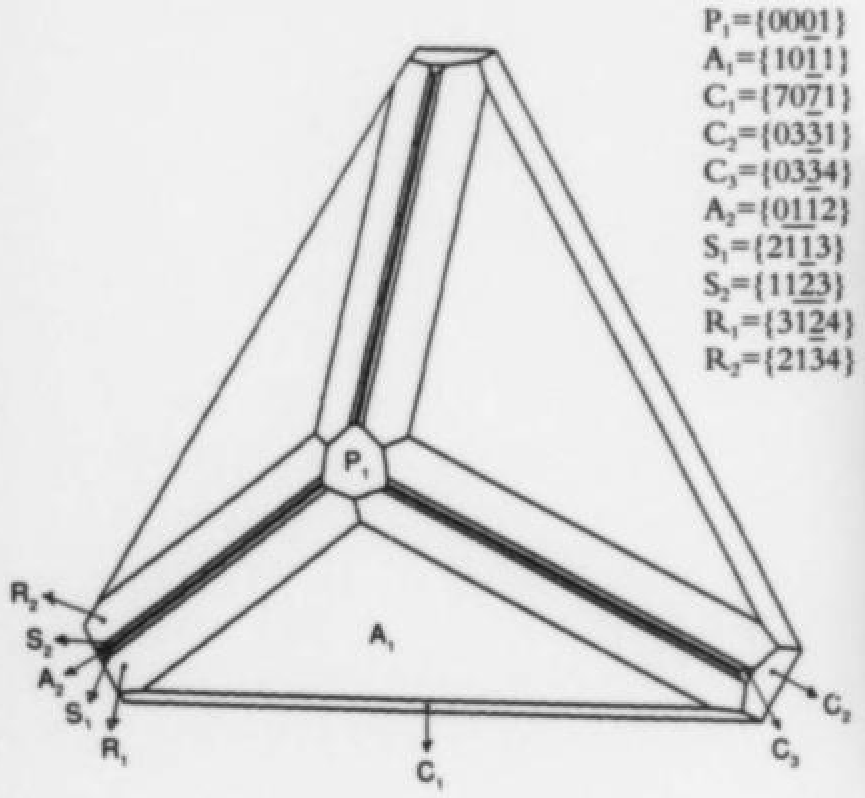

Figure 8. **Crystal drawing of a Seravezza calcite (courtesy of M. Ferrari and D. Tonacca).**

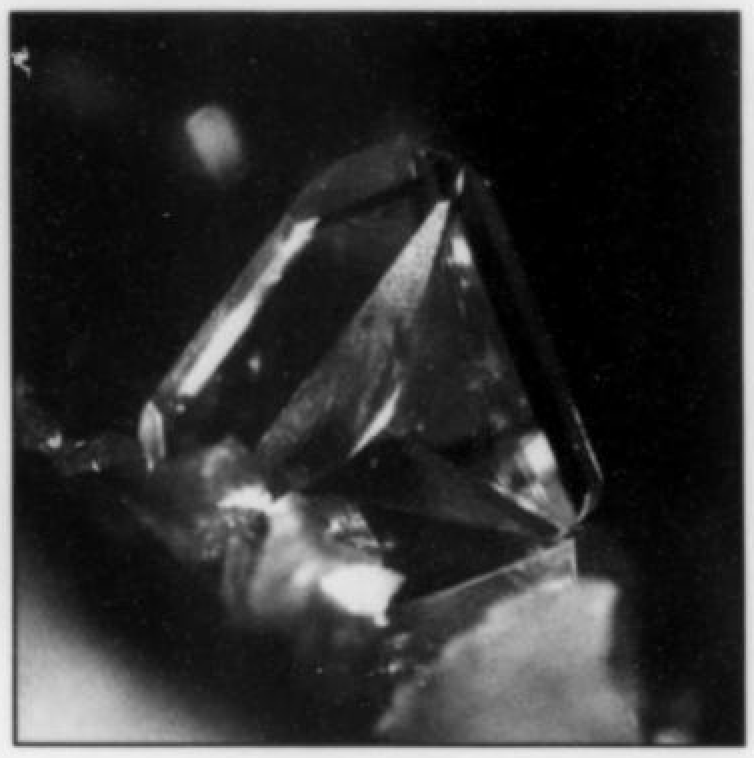

Figure 9. **Calcite crystal, 3 mm, from the Tognetti quarry. Deri collection; Orlandi photo.**

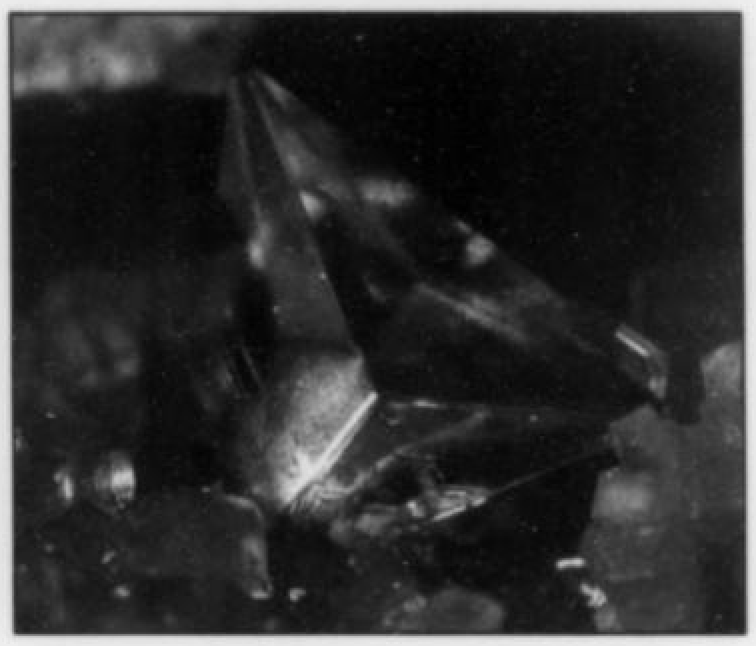

Figure 10. **Calcite crystal, 6 mm, from the Ceragiola quarries. Del Chiaro collection; Orlandi photo.**

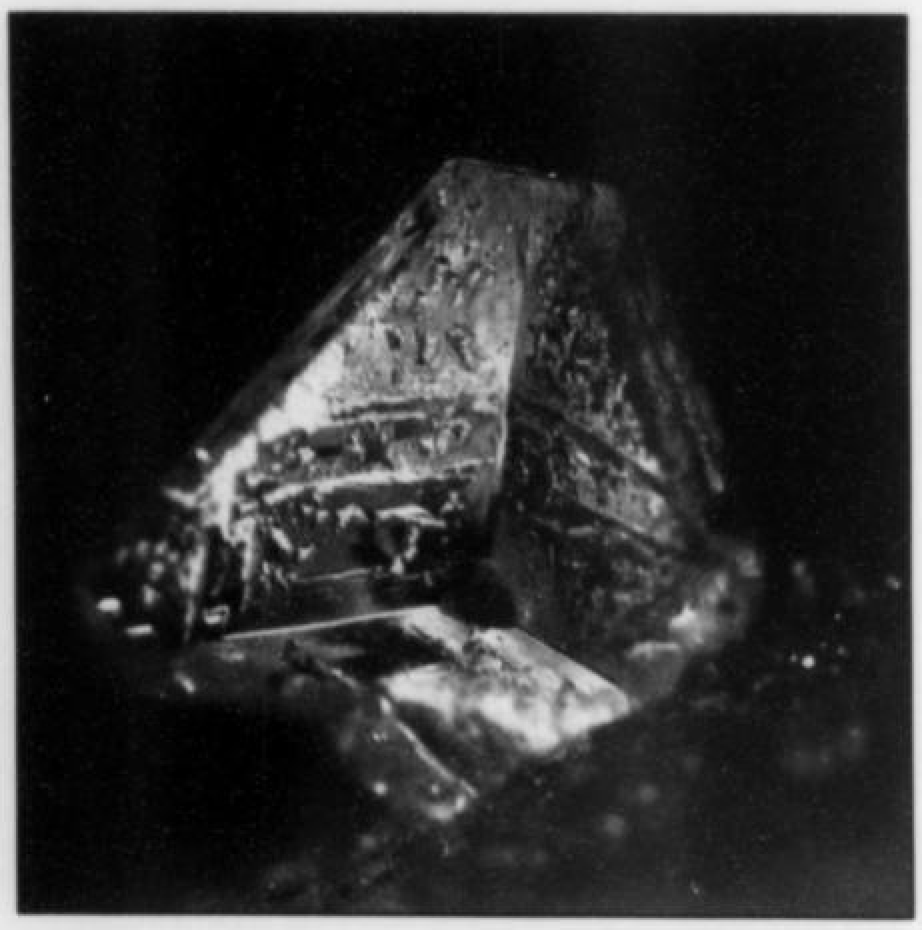

Figure 11. **Calcite crystal, 2 mm, from the Tognetti quarry. Del Chiaro collection and photo.**

Cerussite $PbCO_3$

Cerussite occurs rarely in transparent, tabular crystals up to 1 mm on altered galena. It is common as gray, glassy granules, often enclosing relict fragments of unaltered galena.

Chalcopyrite $CuFeS_2$

Chalcopyrite has very rarely been found as yellow, metallic, bisphenoidal crystals smaller than 1 mm.

Colusite $Cu_{26}V_2(As,Sn,Sb)_6S_{32}$

A few specimens of colusite crystals up to 4 mm, with typical tetrahedral habit, bronze-yellow color and metallic luster, have been found in the Costa and Pitone quarries. No chemical data are available on this species from Seravezza; in the Carrara marble both As-rich and Sn-rich members have been found (Orlandi *et al.*, 1981).

Dolomite $CaMg(CO_3)_2$

Dolomite is very common at Seravezza as white, isolated rhombohedral crystals with pearly luster, often in the typical saddle-like aggregates. Crystals are up to 1 cm long, sometimes with greenish or pinkish tinges.

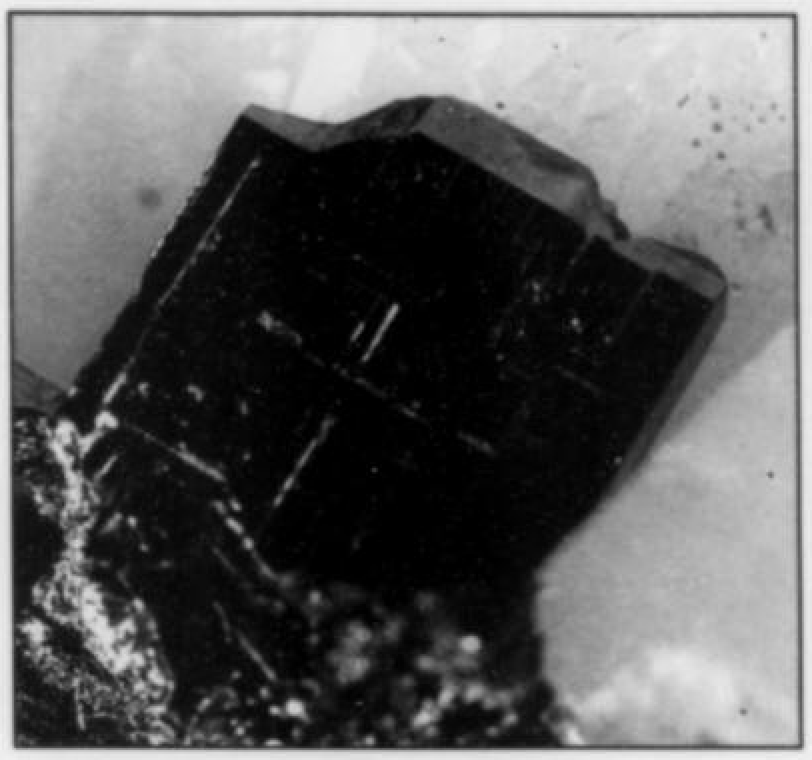

Figure 12. **Enargite crystal, 4 mm, from the Pitone quarries. Deri collection; Orlandi photo.**

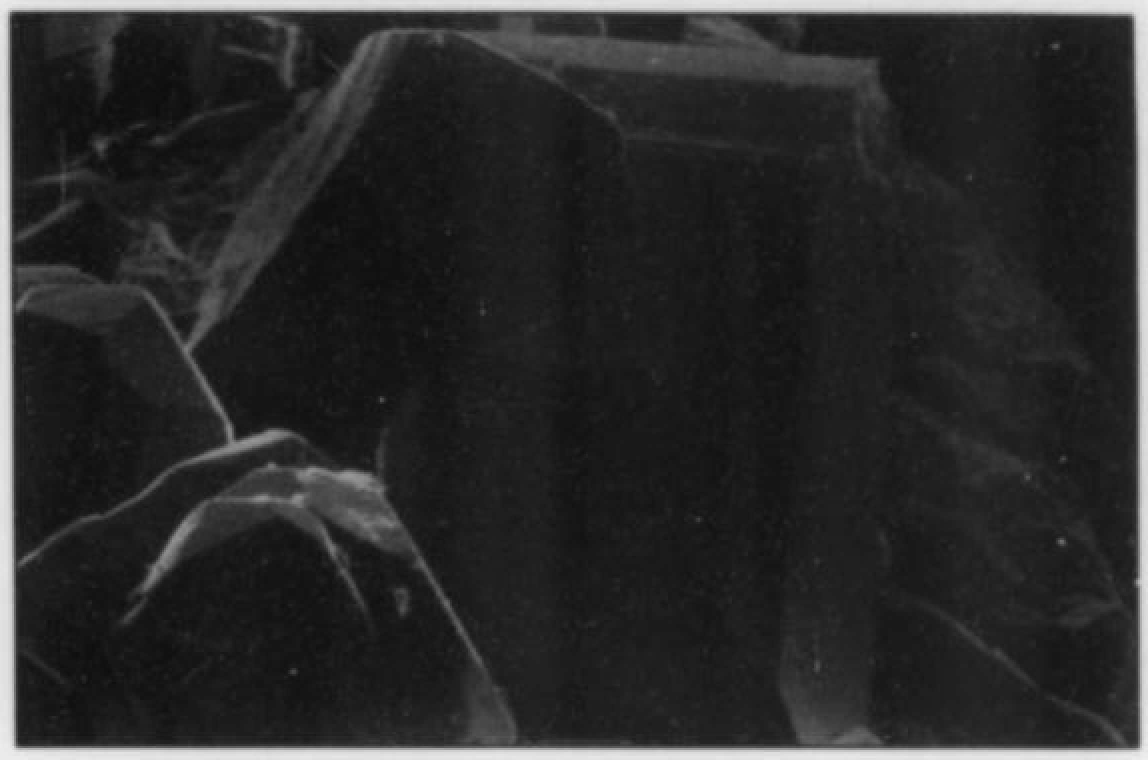

Figure 13. **Enargite crystals, 0.5 mm (SEM photo), from the Ceragiola quarries. University of Pisa collection; Orlandi photo.**

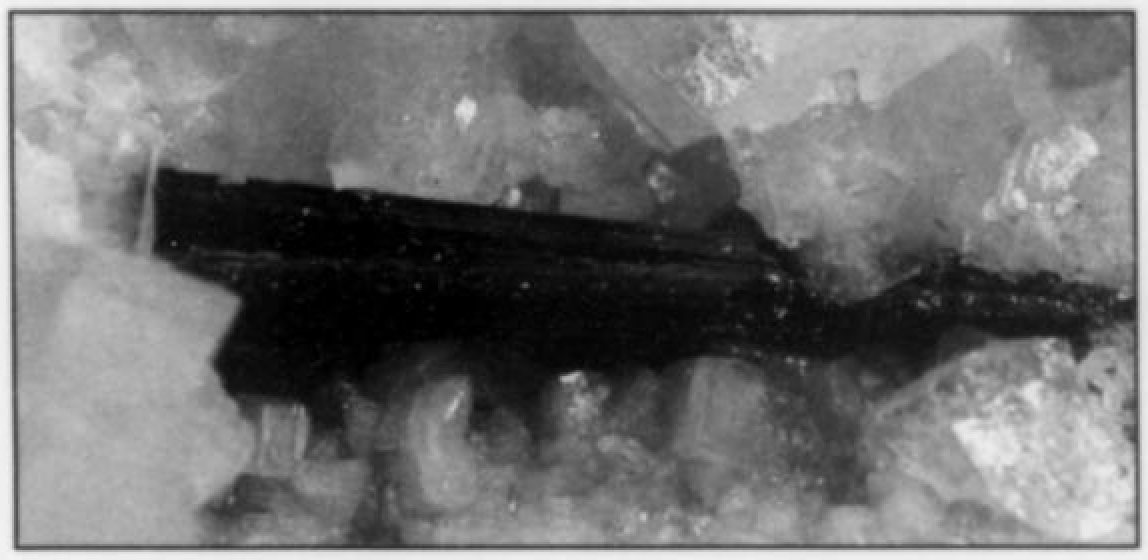

Figure 14. **Guettardite crystals, 2 mm, from the Tognetti quarry. Pellegrini collection; Orlandi photo.**

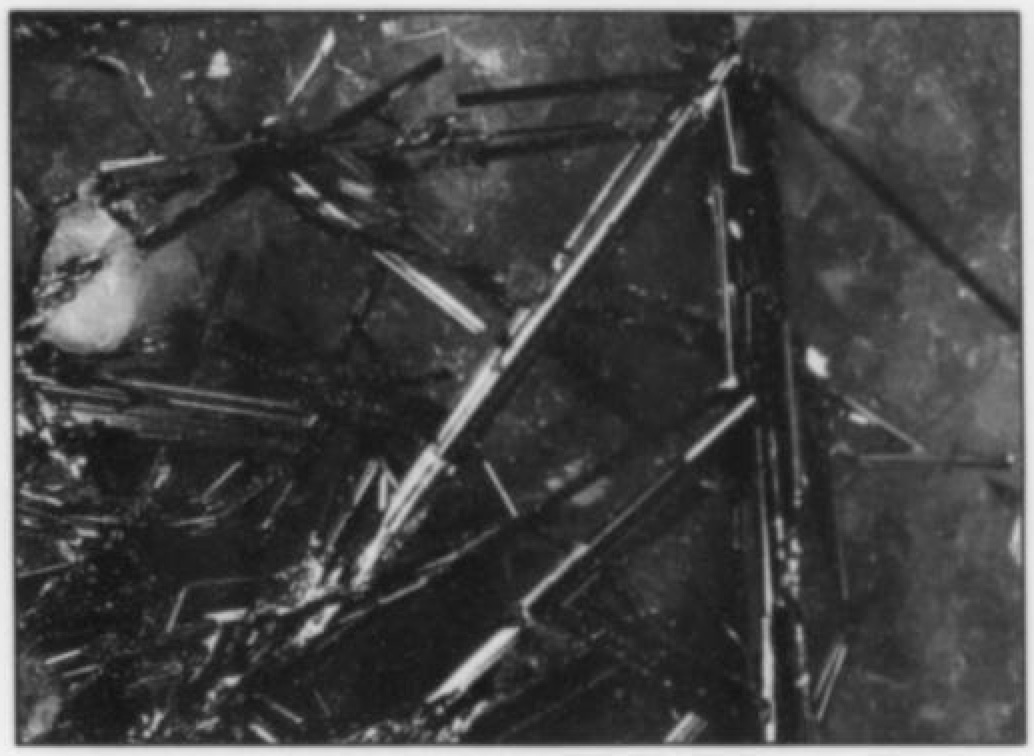

Figure 15. **Guettardite crystals, 3–4 mm, from the Pitone quarries. Del Chiaro collection and photo.**

Figure 16. **Guettardite crystals, 2 mm, from the Pitone quarries. Del Chiaro collection; Orlandi photo.**

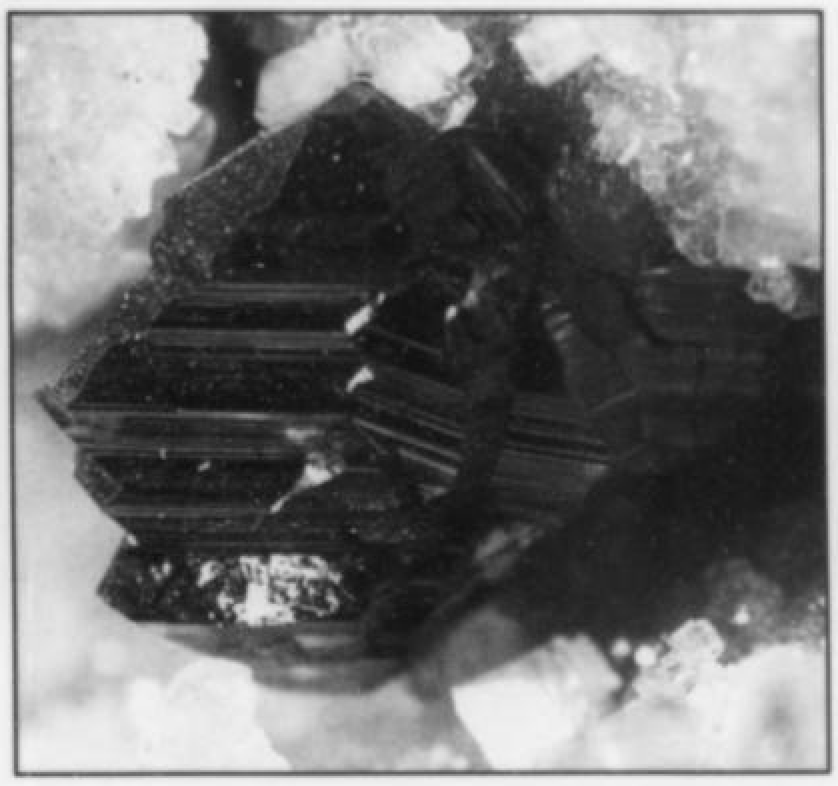

Figure 17. **Jordanite crystal, 3 mm, from the Ceragiola quarries. Deri collection; Orlandi photo.**

Figure 18. **Millerite crystals, 3 mm, from the Ceragiola quarries. Deri collection; Orlandi photo.**

Duftite $PbCu(AsO_4)(OH)$

Apple-green, earthy duftite associated with bindheimite has been found in a single specimen from the Tognetti quarry. This mineral appears to be the alteration pseudomorph of a sulfosalt in acicular crystals to several millimeters in length.

Enargite Cu_3AsS_4

Although uncommon, fine specimens of enargite, as tabular, pitch-black, 4–5 mm crystals with bright metallic luster, have been collected at the Pitone quarries. Enargite is frequently associated with stibnite, wurtzite, sphalerite and acicular crystals of lead sulfoantimonides.

Fluorite CaF_2

Fluorite occurs in small, colorless or, less frequently, purple cubes. Rather uncommon in the Seravezza area, it is rare in the Pitone quarries, but more common in the Ceragiola quarries.

Galena PbS

Galena is a fairly common mineral at Seravezza. The crystals are cubic, octahedral or cuboctahedral, and often twinned. Sometimes the crystals are deformed or flattened on the three-fold axis to yield an hexagonal outline, similar to those from Carrara (Franzini *et al.*, 1987).

Guettardite $Pb(Sb,As)_2S_4$

Guettardite occurs as prismatic to acicular or sometimes tabular crystals. The length-to-diameter ratio of the crystals is not as large as for boulangerite and zinkenite. The black color and metallic luster aid in visual identification of this mineral from boulangerite and zinkenite, which are lead-gray. Some rare, terminated crystals are tabular, with a rectangular cross section, showing the pseudo-orthorhombic symmetry of the species.

Guettardite is rare but has been collected both in the Ceragiola and in the Pitone quarries. Chemical analyses (Giananti, 1987, specimens 4 and 9) gave the results shown on Table 2, samples 4 and 5. The specimens above have been identified by X-ray diffraction patterns both on single crystals (Weisseberg and Buerger methods) and on Gandolfi camera.

Gypsum $CaSO_4 \cdot 2H_2O$

Clear crystals of gypsum up to 1 cm or more are common in all quarries.

Hydrozincite $Zn_5(CO_3)_2(OH)_6$

Rare hydrozincite is found in small, earthy white globules up to 3 mm in size, as an alteration product of sphalerite.

Jordanite $Pb_{14}(As,Sb)_6S_{23}$

Jordanite occurs as lustrous, lead-gray crystals up to 1 cm, with a pseudohexagonal, "bipyramidal" stepped habit. A rare species, it has been found more frequently in the Ceragiola quarries. Qualitative EDS analyses have shown a very low Sb content, indicating a chemical composition very close to the As end-member of the jordanite-geocronite series.

Luzonite Cu_3AsS_4 / **Famatinite** Cu_3SbS_4

The identification of luzonite/famatinite from Seravezza is based on Gandolfi camera powder X-ray diffraction patterns; no precise chemical data are available, so that attribution to either luzonite or famatinite is not possible at this time. The crystals, up to 1 mm in size, have a bisphenoidal habit, metallic luster and a bronze color, sometimes with a purple tinge.

The few specimens recorded have been found in the Ceragiola and Pitone areas; it is normally associated with zinkenite, stibnite and bournonite.

Malachite $Cu_2(CO_3)(OH)_2$

Rare in coatings, crusts and globules up to 1 mm, malachite occurs scattered near altered copper sulfides and sulfosalts.

Marcasite FeS_2

Marcasite is very rare, occurring as poorly formed, very brittle tabular metallic crystals; it has been found in association with zinkenite in the Ceragiola quarries.

Millerite NiS

Just one millerite specimen has been found at Seravezza; it consists of a spray of acicular crystals 3 to 4 mm long, showing the typical brassy yellow color and metallic luster.

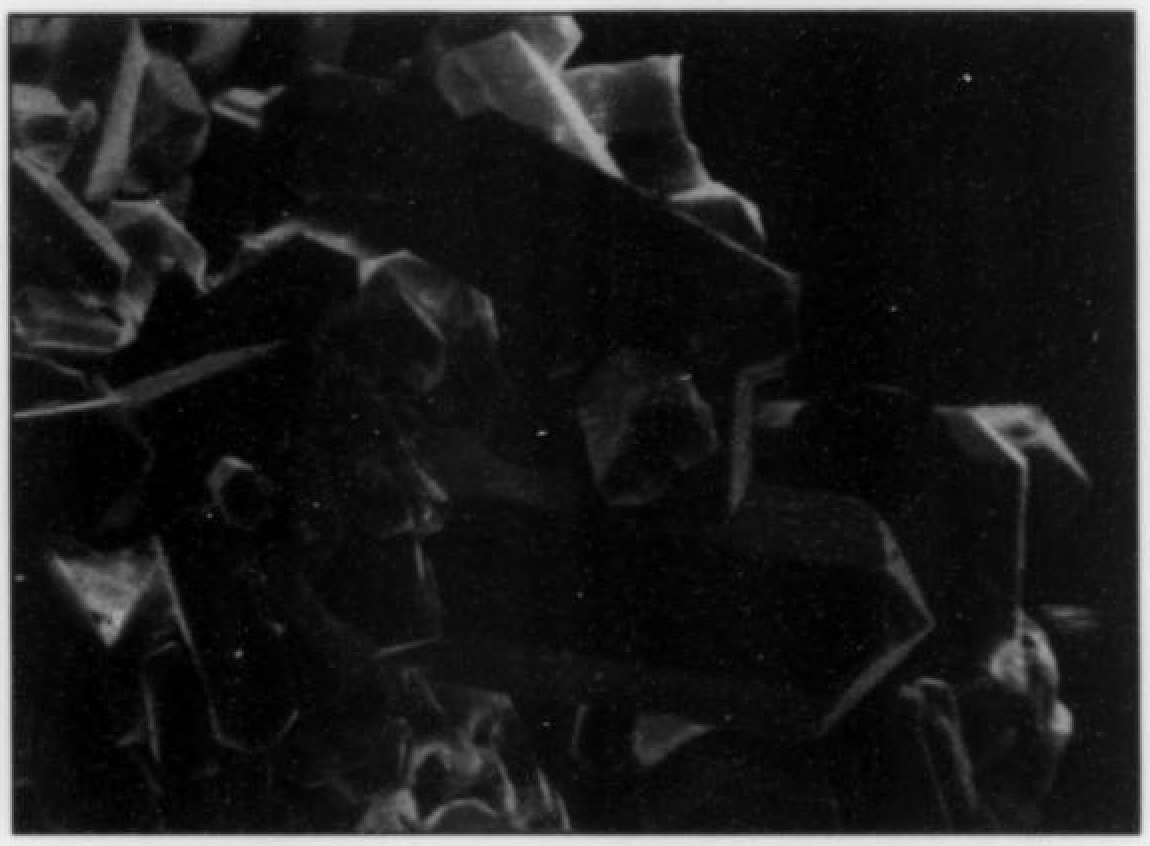

Figure 19. **Mimetite crystals to 0.07 mm (SEM photo), from the Ceragiola quarries. Del Chiaro collection; Orlandi photo.**

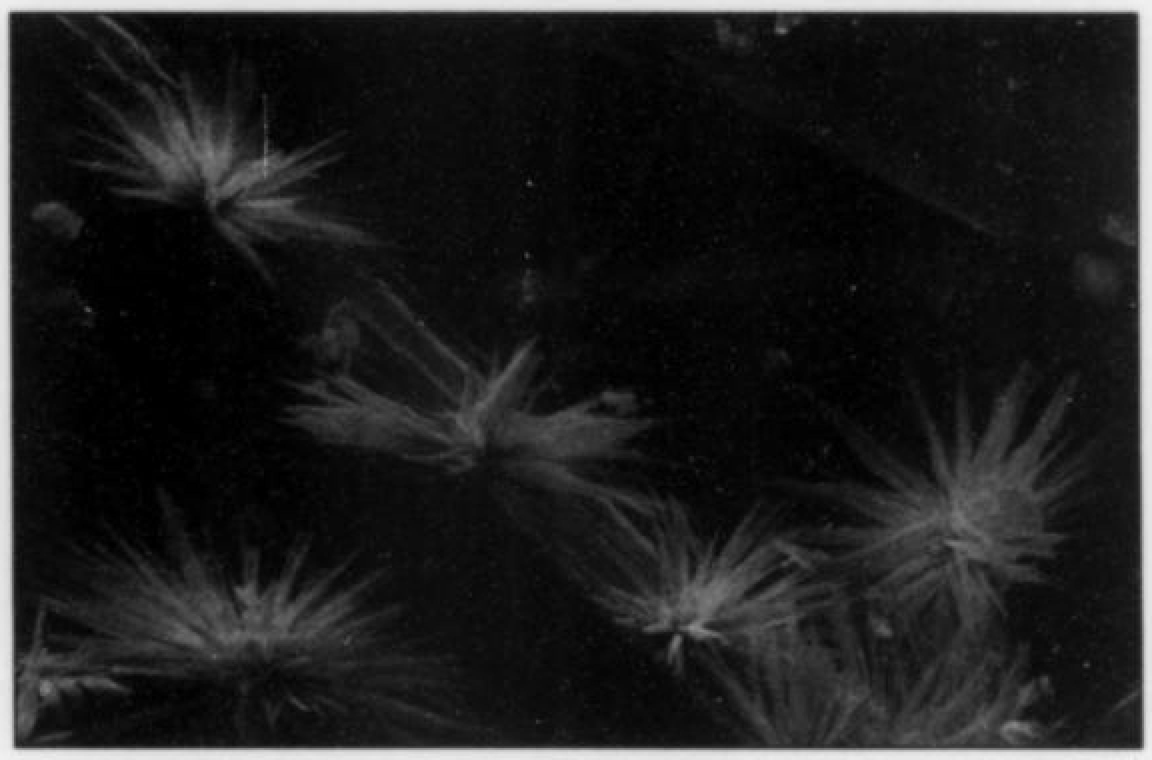

Figure 20. **Mimetite, 0.03-mm crystals on zinkenite (SEM photo), from the Ceragiola quarries. Del Chiaro collection; Orlandi photo.**

Mimetite $Pb_5(AsO_4)_3Cl$

Sprays of milk-white crystals of mimetite up to 0.1 mm occur occasionally on partly altered zinkenite crystals. Also, yellow prismatic crystals have been found rarely.

Orpiment As_2S_3

Acicular crystals of orpiment up to 1 mm, with the typical yellow color, are found at the same localities as realgar.

Orthoclase ("adularia") $KAlSi_3O_8$

The "adularia" variety of orthoclase has been found rarely at the Pitone quarries, as milky crystals up to almost 1 cm.

Pyrite FeS_2

Pyrite is the most common sulfide at Seravezza. It occurs as pyritohedral and, more rarely, octahedral and cubic crystals up to 1 cm.

Quartz SiO_2

Quartz is almost completely absent from the Pitone quarries and rather uncommon in the Ceragiola quarries, where it occurs (mostly in the Tognetti quarry) in crystals seldom larger than 1 cm.

Realgar AsS

Realgar is rare at Seravezza. Bright red, prismatic crystals up to 1 mm occur rarely in the Pitone and Ceragiola areas, and particularly in the Tognetti quarry.

"Red acicular sulfoarsenide"

This mineral, as yet unidentified, has an X-ray powder diffraction pattern very similar to that of robinsonite. A qualitative EDS analysis has shown the presence of Pb, As and S only. No single crystals suitable for a crystallographic study have been found. The brick-red acicular crystals are fairly widespread in several of the quarries, and are normally associated with jordanite, robinsonite and yellow sphalerite.

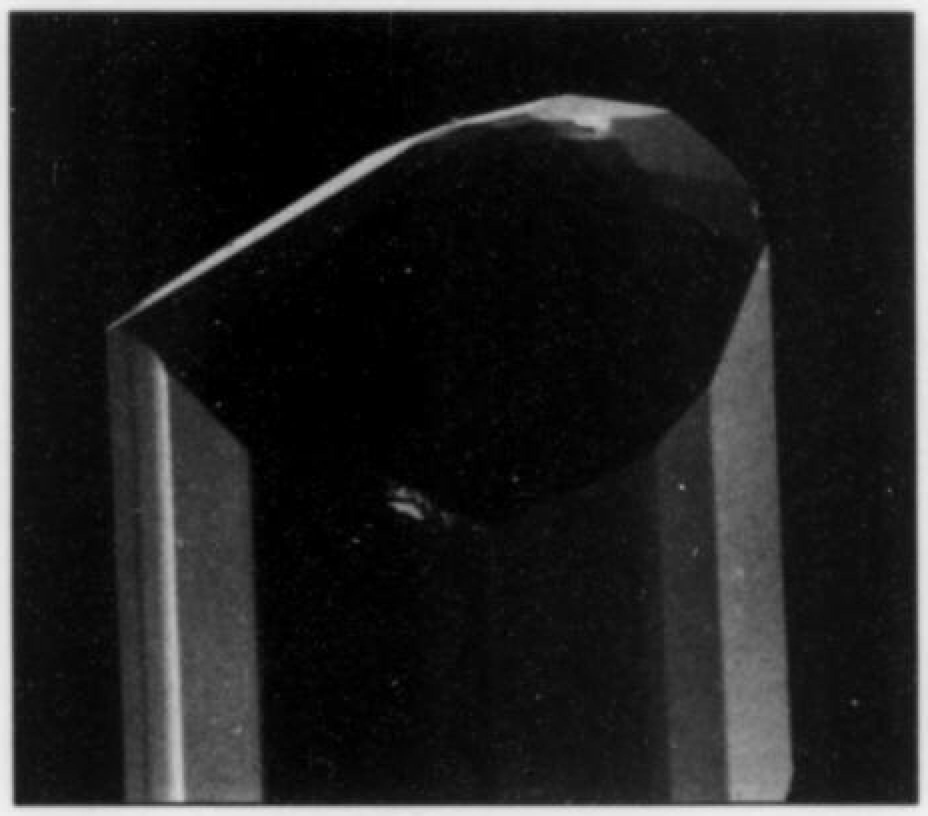

Figure 21. **Robinsonite crystal, 0.3 mm (SEM photo), from the Pitone quarries. University of Pisa collection; Orlandi photo.**

Robinsonite $Pb_4Sb_6S_{13}$

Robinsonite, a lead sulfosalt, shows a prismatic to acicular habit, with a length-to-diameter ratio similar to that of guettardite, and with a similar, or even brighter, metallic luster. The elongated prism faces of robinsonite are not striated; often the crystals are distinctly terminated by small shiny facets.

Robinsonite is rare; it has been found at the Pitone quarries, often with yellow sphalerite and, sometimes, with gypsum (Franzini, Orlandi and Pasero, 1992).

Rosasite $(Cu,Zn)_2(CO_3)(OH)_2$

Rosasite has been observed with malachite and azurite as an alteration product of sulfides and sulfosalts, forming coatings, crusts and, sometimes, globular aggregates of tiny blue crystals associated with bindheimite and duftite.

Rutile TiO_2

Reddish, prismatic crystals of rutile up to a few millimeters have been found rarely at the Pitone quarries.

Semseyite $Pb_9Sb_8S_{21}$

A few semseyite crystals about 1 mm in size have been found in the Ceragiola area. These crystals show a pitch-black color and metallic luster similar to that of enargite, but they are lenticular in habit and curved into a helix-shape. A microprobe chemical analysis yielded the composition shown in Table 2 (sample 7).

Smithsonite $ZnCO_3$

Smithsonite is very rare at Seravezza; it occurs in brownish to yellow rhombohedral crystals, smaller than 1 mm, sometimes with hydrozincite, on altered, skeletal sphalerite crystals.

Smythite $(Fe,Ni)_9S_{11}$

Very thin (0.01 mm), tabular, bronze-colored smythite crystals up to 2 mm have been found at the Ceragiola quarries. Normally the crystals lie on calcite crystals and do not penetrate them, thus indicating very late deposition in the cavities.

Sphalerite (Zn,Fe)S

After pyrite, sphalerite is the most common sulfide at Seravezza and has been found in all quarries. The crystals, up to 5 mm, are often ruby-red and complex in form; more rarely they can be tetrahedral and yellow in color. The red variety is associated with galena, geocronite and bournonite; the yellow variety with colusite, wurtzite and robinsonite.

Microprobe chemical analyses of an orange-red crystal and of a dark brown crystal gave the results shown in Table 2 (samples 8 and 9). This analysis suggests that the darker color is caused by a higher iron content.

Stibnite Sb_2S_3

Stibnite occurs in metallic, gray-black crystals, either with a stout prismatic habit or with a very thin acicular habit. The larger crystals, up to 3 mm in length, are prismatic with shiny, very seldom striated faces. Sometimes the prism is terminated by small, triangular, orthorhombic dipyramid faces giving the crystal a typical "bell tower" habit. The acicular crystals are often grouped in sheaf-like aggregates. Stibnite is sometimes associated with wurtzite and enargite. Moderately rare at the Pitone quarries, it is rather rare in the other Seravezza quarries.

Strontianite $SrCO_3$

White, acicular crystals of strontianite to 2 mm, forming sprays, spherules and sheaf-like aggregates, are common at the Ceragiola quarries, but are rare elsewhere.

An accurate determination of the interplanar distance *d*(132) by X-ray powder diffraction method gave the result of 1.982(2) Å. This value indicates a calcium-rich variety of strontianite, containing about 15 mole % $CaCO_3$ (Speer, 1983).

Sulfur S

Sulfur is fairly common in all of the Seravezza quarries, especially in the Tognetti quarry and in the Pitone area. The

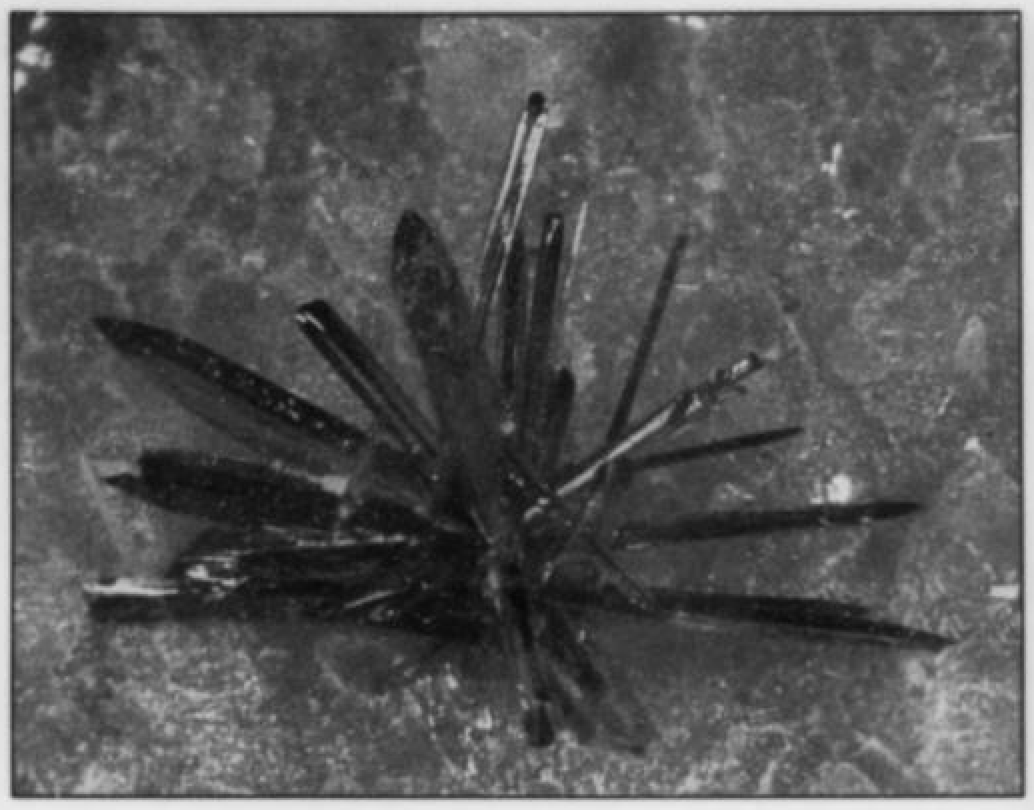

Figure 22. **Orpiment crystals, 3.5 mm, from the Pitone quarries. Del Chiaro collection and photo.**

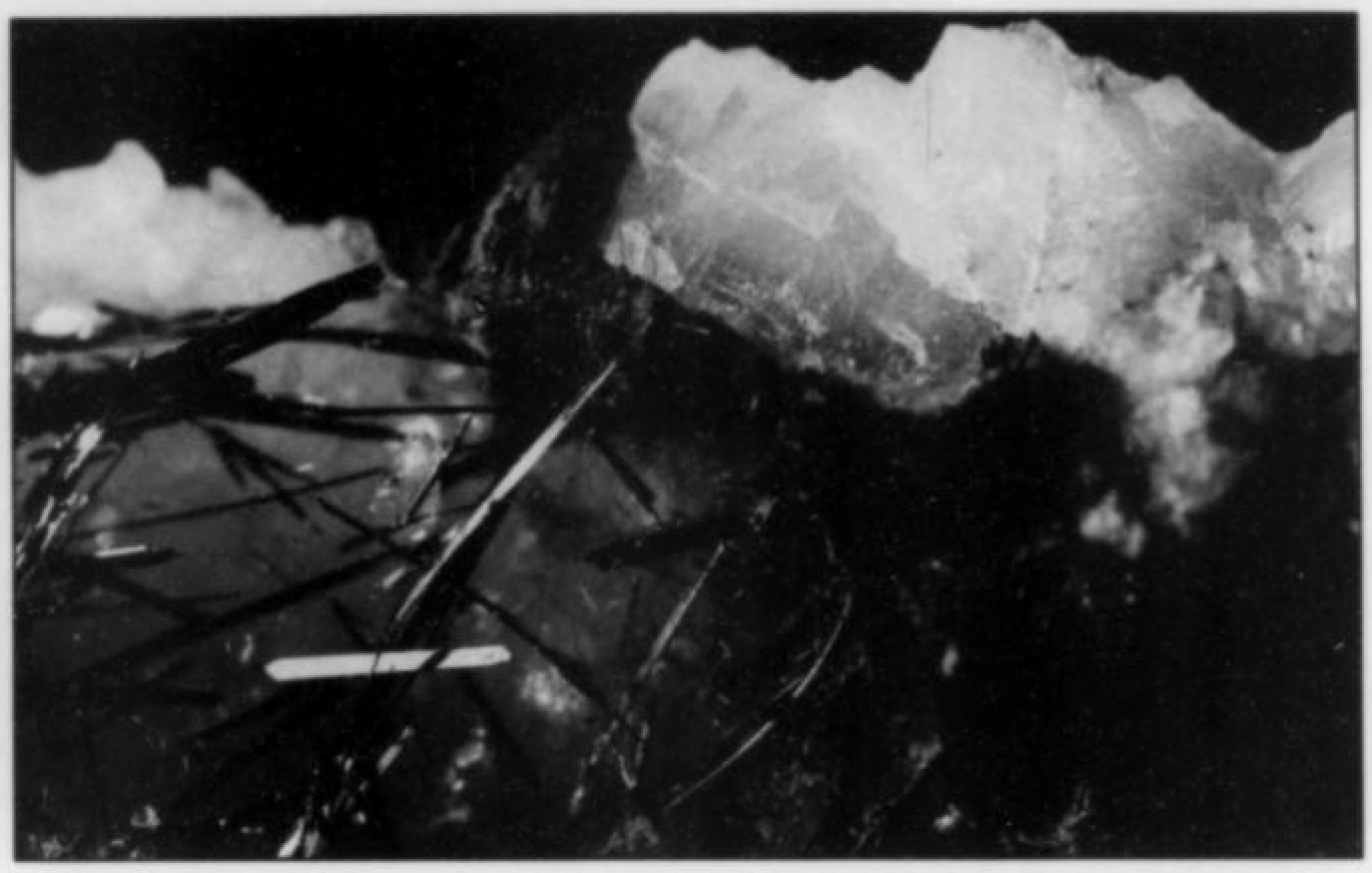

Figure 23. **Red acicular sulfoarsenide and robinsonite crystals, 2–4 mm, from the Pitone quarries. University of Pisa collection; Orlandi photo.**

Figure 24. **Rosasite spherules, 1.5 mm, from the Tognetti quarry. Deri collection; Orlandi photo.**

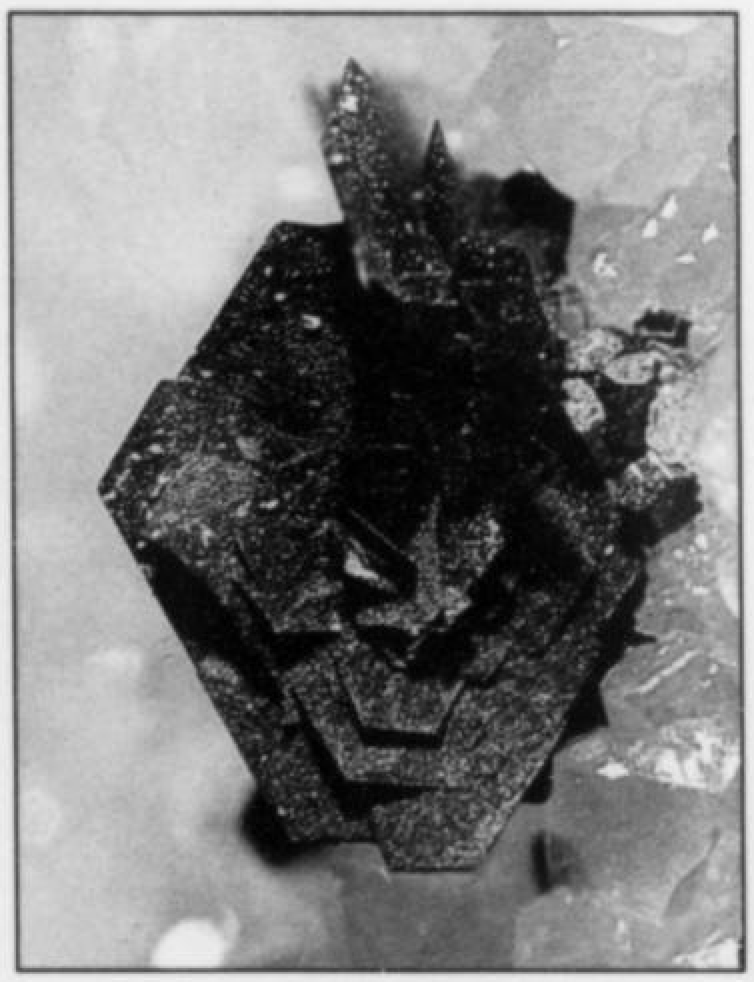

Figure 25. **Smythite crystals, 3 mm, with pyrite, from the Ceragiola quarries. Del Chiaro collection; Orlandi photo.**

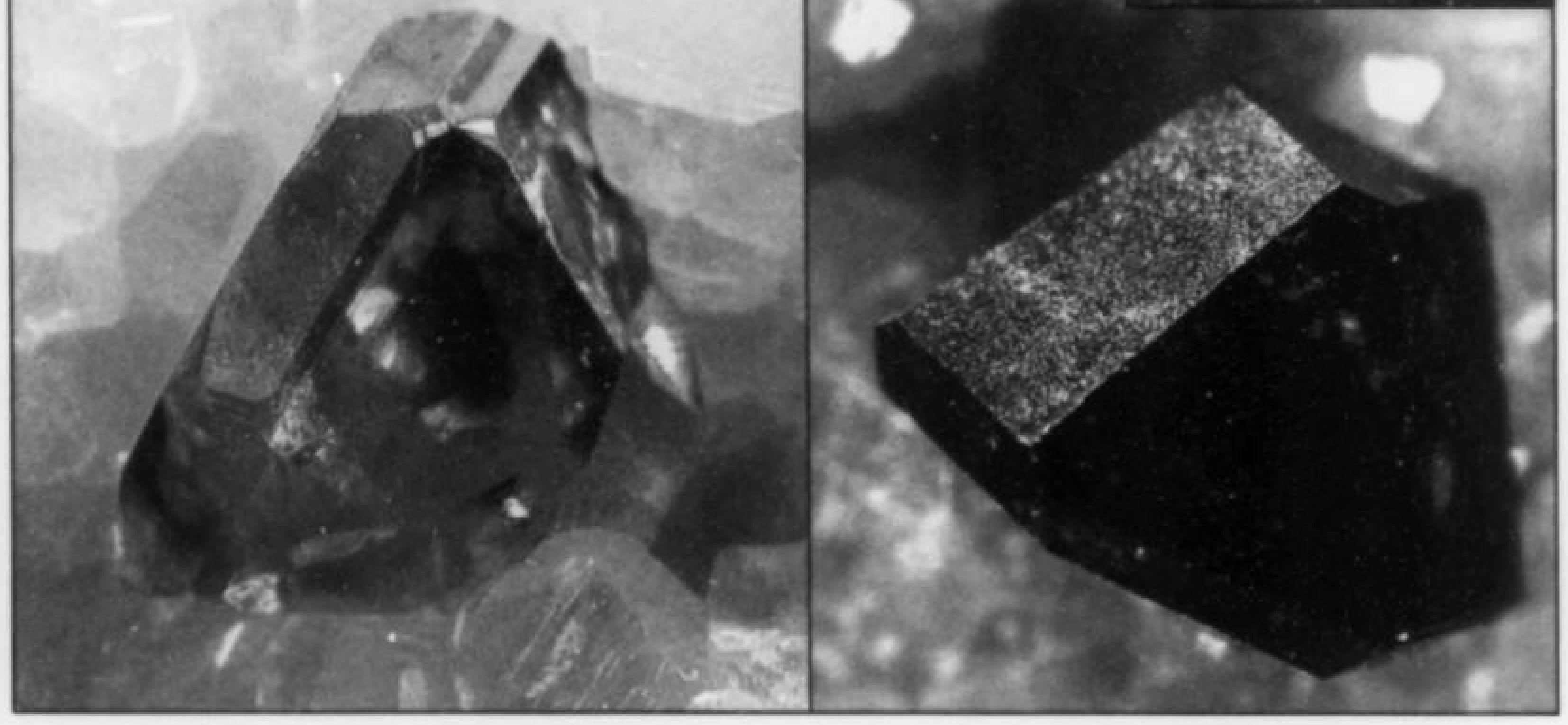

Figure 27. **Sphalerite crystals, 2 mm (left) and 3mm (right), from the Ceragiola quarries. Deri collection; Orlandi photo.**

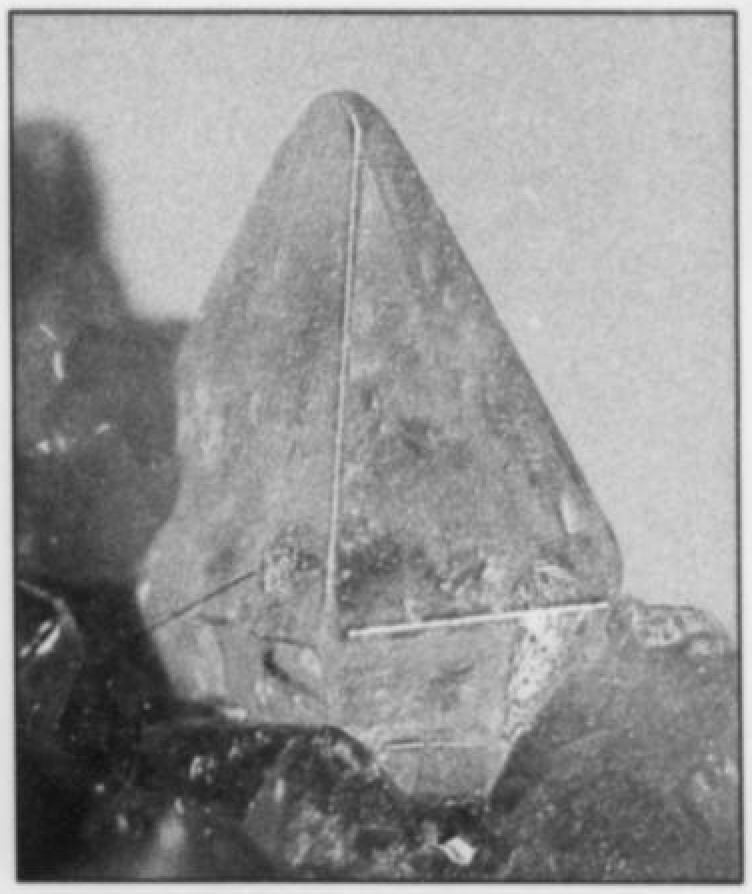

Figure 26. **Sulfur crystal, 2 mm, from the Pitone quarries. Del Chiaro collection and photo.**

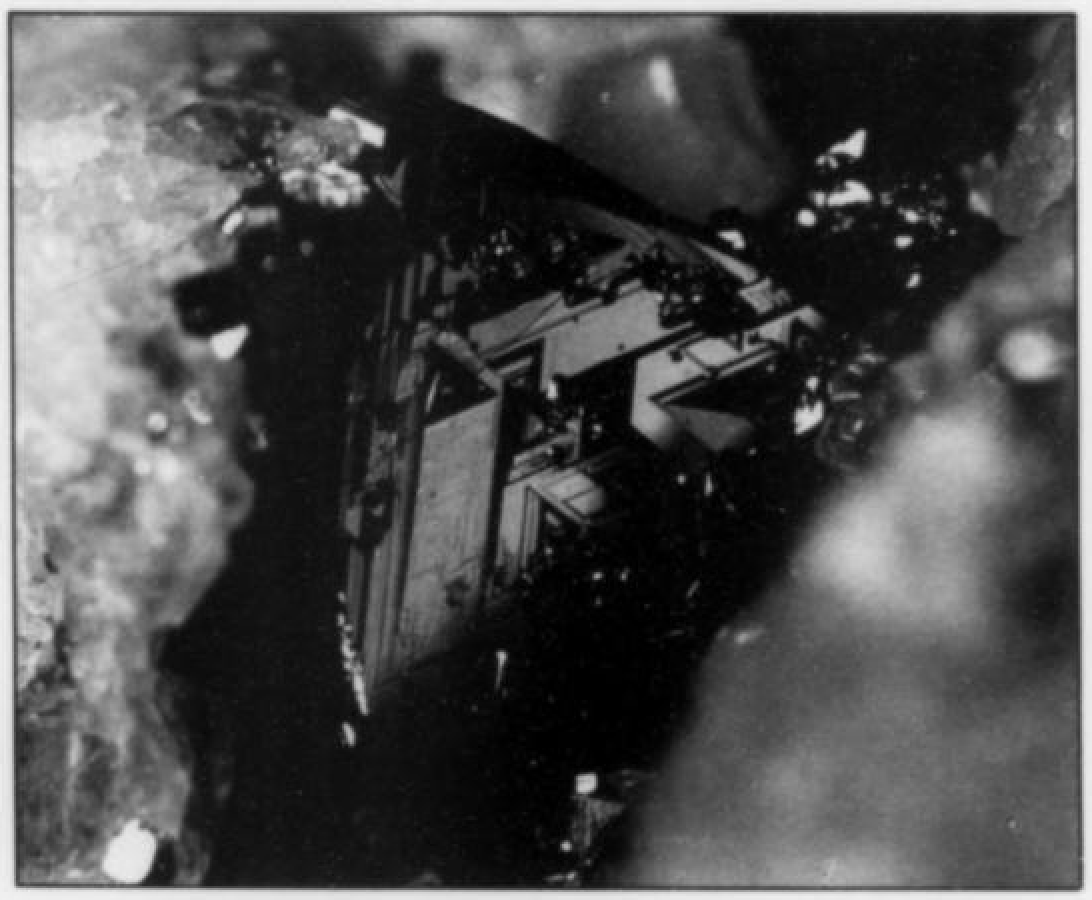

Figure 27. **Tetrahedrite crystal, 3 mm, with pyrite, from the Pitone quarries. Del Chiaro collection and photo.**

crystals, seldom larger than 4 mm, are normally rounded as if they had been gently melted or redissolved after deposition. This feature is common also to the sulfur of the Carrara cavities. Transparent, sharp, bipyramidal crystals with shiny faces are rare.

Sulvanite Cu_3VS_4

Just one specimen of sulvanite has been reported from the Ceragiola area, as cubic crystals of about 1 mm, black, with a shiny metallic luster, and occurring in association with yellow sphalerite.

Tetrahedrite $(Cu,Fe)_{12}Sb_4S_{13}$

Tetrahedrite is uncommon at Seravezza, but equally distributed in the different quarries. The crystals, up to a few millimeters in size, often show a tetrahedral habit, but very complex crystals with many different facets and an almost rounded habit have been found. An EDS qualitative chemical analysis has shown an As:Sb ratio of about 1:10, with significant Fe and Zn.

"Wad"

The general term "wad," meaning undetermined manganese oxides, can be assigned to brownish, earthy globules up to 1 mm in diameter, found sparingly in the Ceragiola area; the qualitative EDS analysis has shown Mn to be the dominant cation in this mineral.

Wulfenite $PbMoO_4$

Extremely rare at Seravezza, wulfenite has been found only once, at the Tognetti quarry, with other alteration products of galena as yellow tabular crystals less than a millimeter across.

Wurtzite $(Zn,Fe)S$

Wurtzite is moderately rare at the Pitone quarry, and very rare elsewhere at Seravezza. The crystals, which rarely exceed 2 mm in length, show the typical hexagonal pyramidal habit, sometimes flattened on the basal pinacoid. The most common color is red, but brown crystals and honey-yellow crystals have also been found. Microprobe chemical analyses of two crystals yielded the results in Table 2 (samples 10 and 11).

Zinkenite $Pb_9Sb_{22}S_{42}$

Zinkenite is uncommon in all the Seravezza quarries. The crystals are acicular, with a cross-section larger than that of the boulangerite crystals; typical, very distinctive longitudinal striations give the crystals as fasciculated aspect. The color is lead-gray, paler than that of boulangerite. Sometimes zinkenite has an alteration patina dulling its typical metallic luster.

This species has been identified by single-crystal Weissenberg camera diffraction analysis. The cell has a pseudohexagonal symmetry with the following parameters: $a = 44.2(1)$; $c = 8.60(5)$ Å.

Table 3. **Relative rarity of the Carrara and Seravezza minerals.**

Mineral	*Carrara*[1]	*Seravezza*	*Mineral*	*Carrara*[1]	*Seravezza*
Adamite	vr	vr	Hydrozincite	vr	vr
Albite	vc	r	Jordanite	r	r
Anatase	r	—	Kersterite	vr	—
Anglesite	—	vr	Litiophorite	r	—
Anhydrite	o	—			
Aragonite	vr	—	Luzonite-Famatinite	r	vr
Arsenopyrite	u	vr	Magnetite	uc	—
Aurichalcite	r	—	Malachite	uc	r
Azurite	c	vc	Marcasite	vr	vr
Barite	r	c	Millerite	—	u
Baumhauerite	—	u	Mimetite	vr	r
Bindheimite	—	vr	Muscovite	uc	—
Bornite	vr	—	Nordstrandite	vr	—
Boulangerite	r	c	Orpiment	vr	r
Bournonite	r	c			
Brookite	vr	—	Orthoclase (adularia)	c	r
Calcite	vc	vc	Pyrite	vc	c
Celestite	uc	r	Quartz	vc	r
Cerussite	vr	r	Realgar	vr	r
Chalcophyllite	vr	—			
Chalcopyrite	vr	r	"Red acicular sulfoarsenide"	—	c
Chalcocite	vr	—	Robinsonite	—	r
Clinochlore	uc	—	Rosasite	vr	vr
Colusite	r	vr	Rutile	c	vr
Connellite	vr	—	Sellaite	u	—
Cornubite	vr	—	Semseyite	vr	vr
Covellite	vr	—	Smythite	vr	vr
Cuprite	vr	—	Sphalerite	c	c
Dawsonite	vr	—	Stibnite	r	c
Digenite	vr	—	Stronzianite	r	r
Dolomite	vc	vc	Sulphur	c	c
Duftite	—	vr	Sulvanite	vr	vr
Enargite	c	c	Tetrahedrite	vr	r
Fluorapatite	r	—	Thorogummite	vr	—
Fluorite	c	r	Uraninite	vr	—
Galena	vc	c	Vaesite	u	—
Gibbsite	r	—	Volborthite	vr	—
Guettardite	—	uc	"Wad"	—	r
Gypsum	vc	c	Wulfenite	vr	vr
Halloyisite	vr	—	Wurtzite	r	r
Hematite	vr	—	Zinkenite	vr	c
Hemimorphite	r	—			

c = common, vc = very common, r = rare,
vr = very rare, u = uncertain, uc = uncommon,
o = only one specimen known

[1] Franzini *et al.*, 1992.

COMPARISON OF SERAVEZZA AND CARRARA

The Carrara and the Seravezza marble deposits, although similar in nature and origin, are rather different with respect to mineral association and relative abundance of the various species. At Carrara, the cavity minerals occur sparingly, in well-formed, individual crystals and crystal groups. At Seravezza, the mineralization may also occur as epithermal vein formations including the association of several sulfides (pyrite, sphalerite, galena) and sulfosalts (boulangerite, zinkenite, guettardite, etc.) which sometimes completely fill the marble clefts.

Concerning the various mineral species, firstly it should be noted that calcite in Seravezza and in Carrara occurs in very different habits, so that specimens can be readily assigned to one or the other locality by visual inspection. The calcite crystals from Seravezza have a very simple habit consisting of the most common rhombohedron; the faces are invariably marked by inverse hopper striations resulting from successive growth phases. The calcite crystals from the Carrara marble, on the other hand, have specular faces and complex habits in which the rhombohedron seldom predominates.

A second important difference concerns quartz crystals, which occur in most Carrara geodes and have been famous there for over a century for their beauty and perfection, but are very rare in the Seravezza geodes.

The relative frequency of the various other species at the two localities can be assessed by comparing Table 1 with the table for Carrara minerals (Franzini, Orlandi, Bracci and Dalena, 1992), and is summarized here in Table 3.

The significant presence of lead sulfoantimonides and arsenides (in particular guettardite, robinsonite, zinkenite and boulangerite) in the Seravezza marble is in contrast to their virtual non-existence in the Carrara marble. Since the cavities at both localities were formed during the same extensional post-collisional process, and can reasonably be considered to be of the same age, this difference can perhaps be explained by a difference in the chemistry of the circulating fluids.

The mechanism of remobilization, dissolution and recrystallization in the immediate vicinity of the cavities has certainly played an important role in the genesis of the minerals of the Seravezza marble, as it has for the minerals of the Carrara marble (Franzini *et al.*, 1987). In the Seravezza mineralization, however, the influx of elements from sources located outside the marble deposit, through large-scale fluid circulation, must also be postulated. At Seravezza, the mineralization is closely reminiscent, in various ways, of the neighboring sulfide and sulfosalts mineralizations in the underlying phyllic Hercynic basement (Bottino, Gallena, Santa Barbara and La Rocca mines); this fact suggests that a genetic relationships between these deposits is likely.

ACKNOWLEDGMENTS

The authors wish to thank the many mineral collectors who have been their constant and most valuable support in field research. The attention of collectors has been moving from the more showy quartz crystals to small, less obvious, sometimes rare minerals which may yield, after laboratory study, interesting information.

We thank, in particular, Messrs. Marco Baldi, Andrea Dini, Mario Galli, Giampiero Gramigni, Alessandro Lari and Sergio Mancini, who have supplied us with study material; Dr. Giancarlo Deri who loaned many of the specimens used for mineral photography in this article; Dr. Giovanna Vezzalini for the many electron microprobe analyses carried out at the Modena University; and Dr. Di Pisa for his revision of the structural geology aspects of the manuscript.

We would like to dedicate this work to our friend, the late **Dr. Giancarlo Brizzi**, who died tragically with his wife Massima on June 12, 1992. His enthusiasm and competence in the field of mineralogy has added a lot to our knowledge of many Italian localities, including Seravezza; he made available a number of the specimens used in this study.

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What's New in Minerals?

Denver Show 1995

by Thomas P. Moore

[September 15–17]

The hotel rooms were comfortable, the downstairs restaurant's food was good, the morning coffee was free, and for four straight days the weather was balmy—so there unfolded, with style and grace, Marty Zinn's big 1995 show at the Holiday Inn North in Denver. The Main Show, at the Denver Merchandise Mart, had its notworthy points too, including some fine displays on the theme of *calcite* and a small case of about 30 of Ralph Clark's amazing thumbnails. Most experienced parties agreed, however, that this Main Show was unusually flat in the "what's new in minerals" department. Well, you can't define feasts without famines, and there's still plenty between the two shows to report on here. And, like, *who cares* (you know?) that more new goodies happened to show up at the hotel than at the Main Show? I heard no complaints from any of those who, in the long run, count most: the hoards of excited children bussed in by local elementary schools to appreciate and learn from the beautiful things all over the Merchandise Mart's main hall and the side "tunnels." Off we go, then, mineraltripping . . . .

Dauntless prospector Ed Coogan (*Coogan Gold Company,* P.O. Box 1631, Turlock, CA 95381-1631) dug some new **gold** this year at a new site—given as "Eugene Mountains, Humboldt County, Nevada." At his stand in the hotel ballroom were about 20 nice gold thumbnails consisting of (a) slightly rough cubes, some of these with pronounced hopper growths, to 5 mm, (b) flattened octahedrons of the same size, and/or (c) shapely dendritic forms, of a medium-gold color and a good (though never brilliant) luster. Then, just down the road a piece, in the "Ten Mile District," Humboldt County, Ed went on to dig more quartz-enclosed gold of a different type: brighter, darker yellow, in highly flattened leaves composed of minute octahedrons in arborescent aggregates. There were perhaps ten thumbnails and small miniatures of these. Hats off to military retirees who become serious and skilled western gold prospectors!

Some excellent California **gold**, too, shone and preened for the kids (of all ages) at the Main Show. This included not only Wayne and Dona Leicht's (*Kristalle,* 875 N. Pacific Coast Highway, Laguna Beach, CA 92651) tremendous specimens of quartz-matrix gold of highest brilliancy from the Eagle's Nest mine (fine as these are, we've seen them before), but also some specimens, more surprising, from the Sixteen-To-One mine in Sierra County. Marketer Tom Woodfin (P.O. Box 1621, Alleghany, CA 95910) explained that the Sixteen-To-One has been in operation for 99 years, but has never had such a year as this one; for instance, in August a pocket was hit with 5,000 ounces of gold, this mostly as massive fillings of seams along faults, with arsenopyrite. Better for our purposes, some beautiful crystallized gold groups came from a 600-ounce pocket entered in June. These are very lustrous quartz-matrix specimens with bright, subhedral, flattened octahedrons to 2 mm, and curling crystalline leaves, making fine thumbnails and miniatures. In 1987, in the second *Gold Issue,* Wayne Leicht wrote of this mine, saying it was a shame that no good crystal specimens had ever been saved from it. But now, we're told, specimen-preservation efforts as careful as this one are likely to be made again when and if such pockets are struck.

In Utah's Lakeside Mountains, overlooking Utah Lake about 20 miles west of Provo, lies the "Pelican Point" locality for **goethite** pseudomorphs after pyrite, in sometimes enormous, sharp brown cubes and groups. We've known dimly about Pelican Point because it was worked as long ago as the 1930's, though in the early '50's it was abandoned. John Holfert of *Utah Minerals and Fossils, Inc.* (997 N. Chapel Dr. #4, Bountiful, UT 84010) did take some pseudomorph specimens out in 1978 but found them, at that time, prohibitively hard to clean. Now, thanks to a new Chicago Pneumatic air gun of which John is enamored, the specimens can be given a handsomely clean, crisp, rich brown appearance in no time. The pyrite originally occurred as striated cubes to 10 cm on edge, always very sharp; replacement by goethite is sometimes almost complete, sometimes limited to a thin skin, although all crystals have that same clean, sort of silky mahogany-brown aspect. John dug for nine weeks, 12 to 15 feet down, in shaly limestone to take out about 900 large specimens (the largest are cube groups 25 cm across) and thousands of smaller ones. Most specimens are loose crystals or clusters, but a few show remnants of a compact light gray matrix. There was a whole roomful of them—rapidly being depopulated when I stopped by—in the Holiday Inn.

1995 so far has not been the best of years for **rhodochrosite** at the Sweet Home mine, Alma, Colorado, although the *Collector's Edge* (P.O. Box 1169, Golden, CO 80402) did have, at its busy booth off the tunnel at the Main Show, a few nice new small specimens. The translucent, bright pink rhodochrosite rhombs to 1 cm are grouped in shapes after which the pocket (hit in August 1995) was named: the "Horseshoe Pocket." And there were a few exceptional holdover pieces—with razor-sharp gemmy pink rhombs to 2 cm on needle quartz, with tetrahedrite—from last year's astonishing "Corner Pocket," which was the rhodo gods' answer, at last, to the special prayers of thumbnail and miniature devotees.

But Bryan Lees of *Collector's Edge* has also been working lately at the Calumet iron mine, 10 miles north of Salida, Colorado, long known as the source of nice blocky striated epidote crystals to 5 cm across. In July 1995, a 5-foot-long clay-filled pocket was breached, and cleaned out inside of three weeks; it contained lovely **smoky quartz** crystals to 20 cm long, transparent and lustrous and on the "light" side for

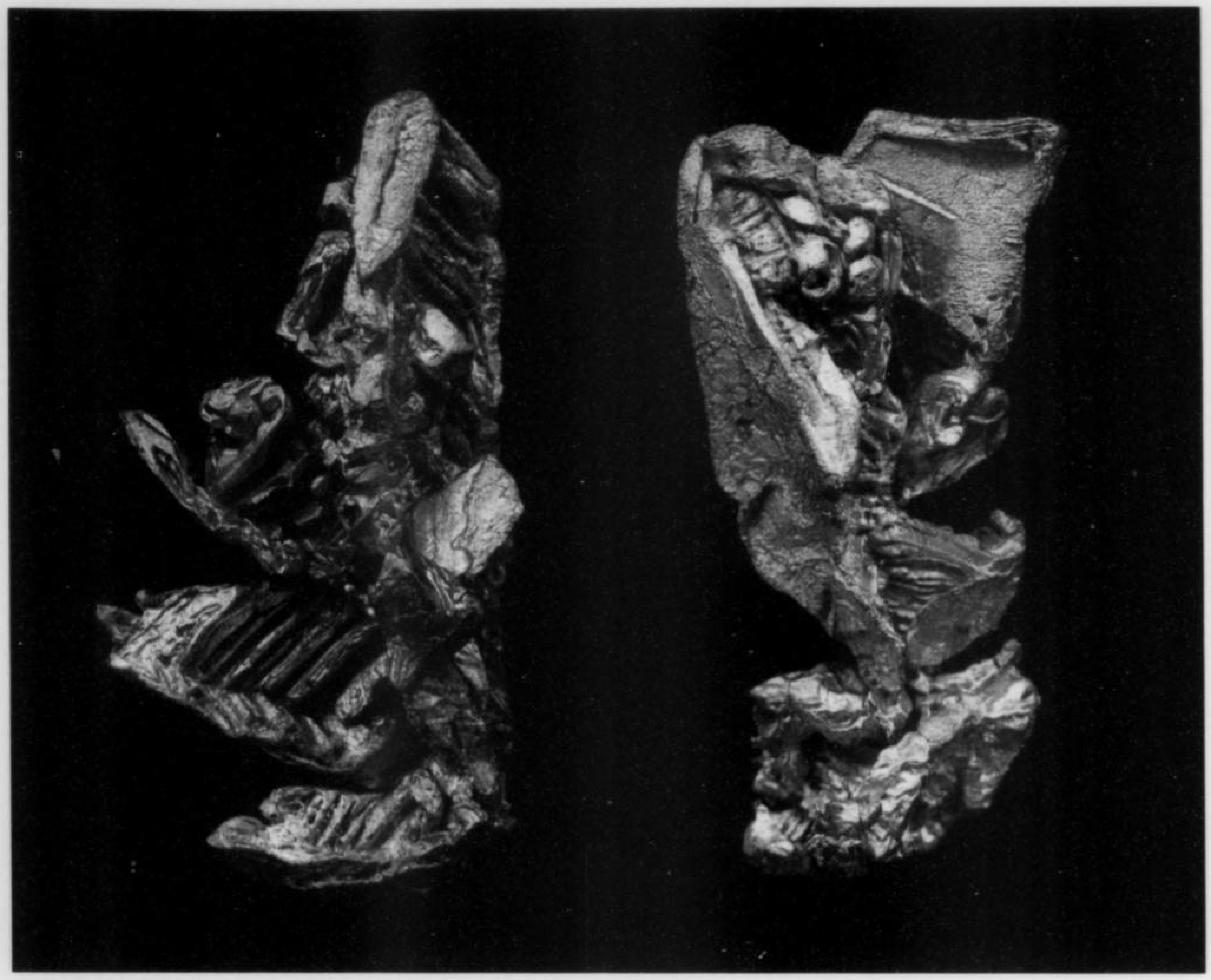


Figure 1. **Gold crystal groups, 3.0 and 2.8 cm, from the Eugene Mountains, Humboldt County, Nevada. Coogan Gold Company specimens; Jeff Scovil photos.**

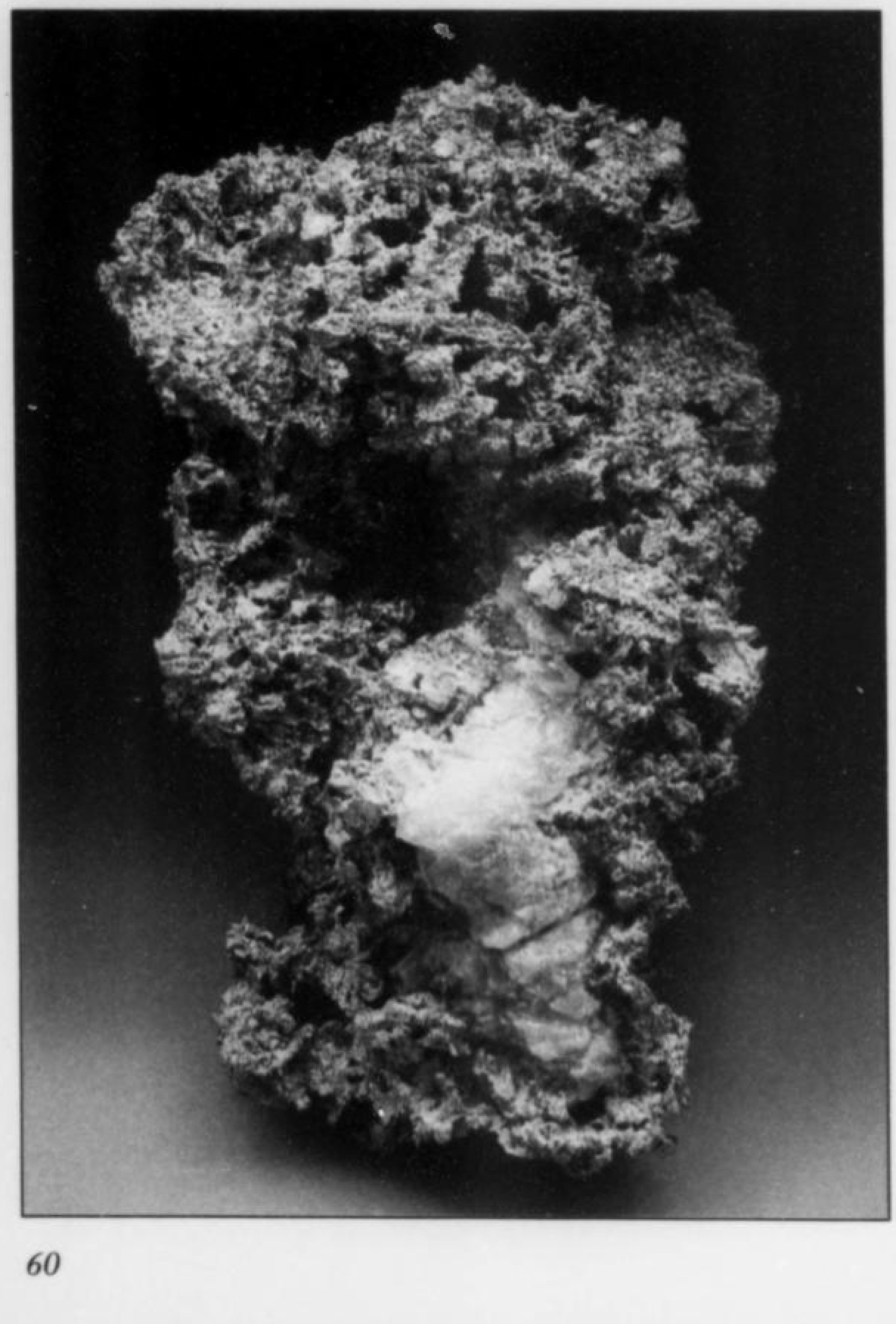


Figure 2. (left) **Gold with milky quartz, 15.2 cm, from the Eugene Mountains, Humboldt County, Nevada. Coogan Gold Company specimens; Jeff Scovil photo.**

smoky quartz. These rested on pocket linings of blackish-green **epidote** crystals, so we have a new and quite striking "association" phenomenon here: smoky quartz clusters resting on, and sometimes including, bright blocky epidote crystals. An exhibition case at the Main Show displayed some very large, attractive pieces, and *Collector's Edge* was selling ample numbers of specimens in all sizes.

Magnetite makes good groups of very sharp, submettalic black octahedrons, a little frosted and individually to 2 cm on edge, at the Republic mine, Hanover, Grant County, New Mexico—a fact which western U.S. collectors have apparently long been aware of, but I was not. So I had to admire the selection of small cabinet specimens, with black crystal groups leached out of calcite, in the hotel room of *George Stevens Minerals* (P.O. Box 44313, Tucson, AZ 85733). George says that the Republic is still an active iron mine, but its good magnetite specimens of this type, being hard to collect, are getting sparser.

One of the major what's-new excitements of this Denver Show was in fact an update-with-thrilling-additions of one of the major discoveries from the last Tucson Show: the extraordinary **chalcocite** (and other copper sulfide) speci-

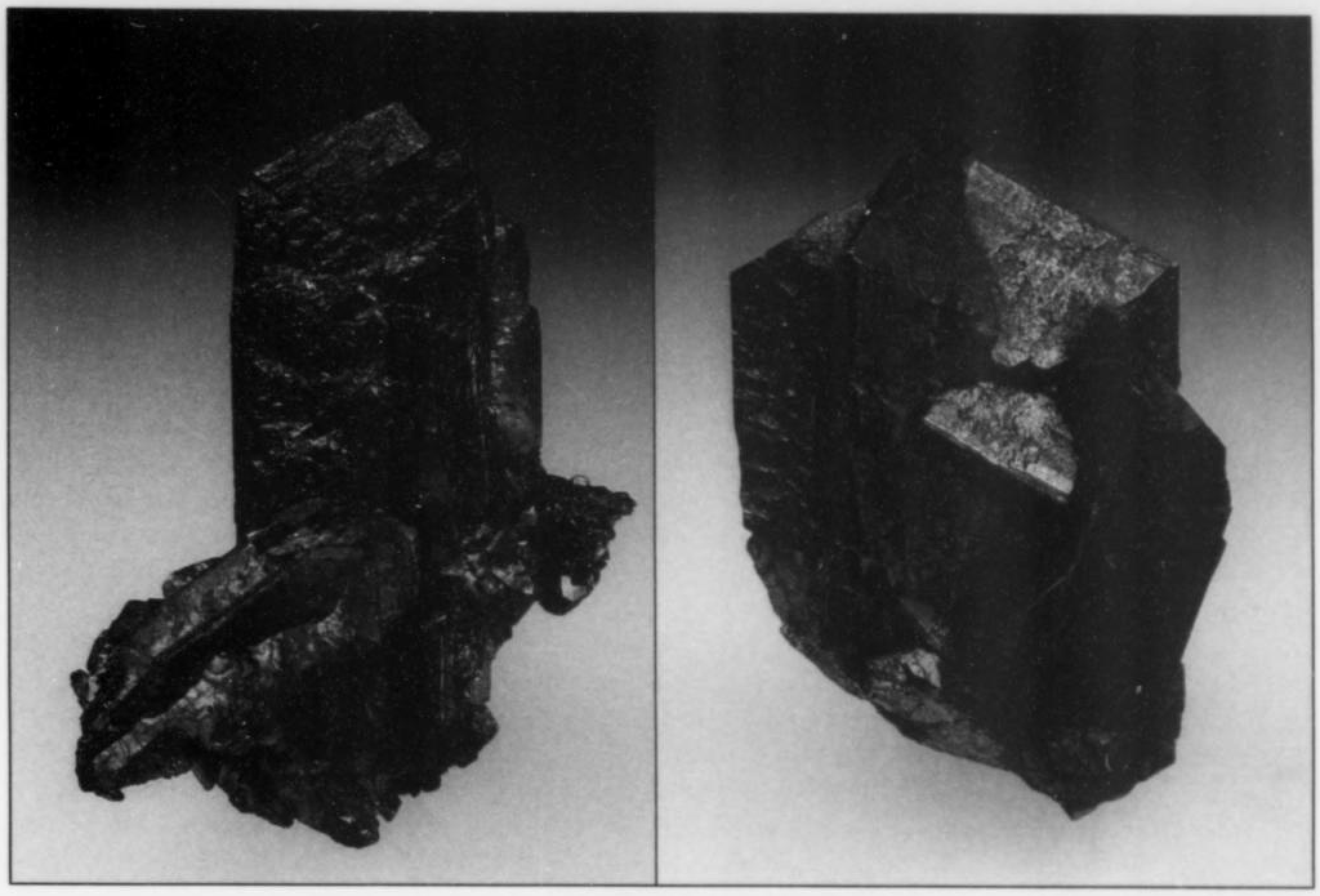


Figure 3. **Chalcocite crystals, 2.6 cm and 3.5 cm, from the Flambeau mine, Ladysmith, Wisconsin. Burminco specimens; Jeff Scovil photos.**

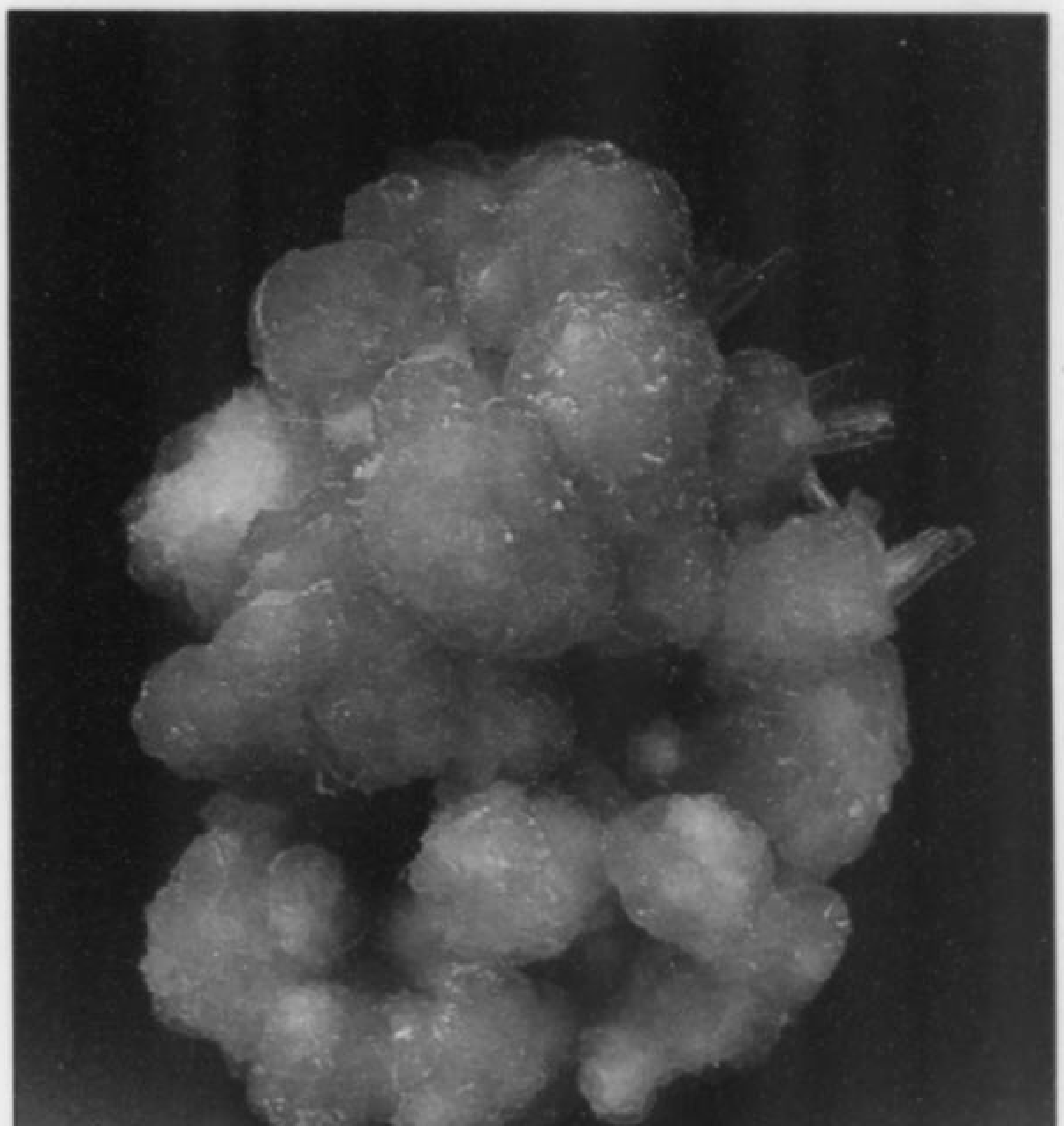


Figure 4. (right) **Smithsonite group, 6.8 cm, from Level 9 of the Potosí mine, Santa Eulalia, Mexico. Kerith Graeber collection; Jeff Scovil photo.**

mens now being dug from a supergene zone at the Flambeau mine, Ladysmith, Rusk County, Wisconsin. As before, the man in charge here is Casey L. Jones of *Burminco* (128 S. Encinitas Ave., Monrovia, CA 91016), who held court this time in a dazzlingly supergene-mineralized room at the Holiday Inn. Yes, there were more, hundreds more, of the small groups of slightly roughened, blocky to tabular chalcocite crystals tarnished a deep bronze by what has proven to be **bornite** coatings. But on Feburary 1st of this year (just as Tucson was about to begin), on the 1010 Level of the Flambeau mine, a drill bit suddenly plunged freely into a 10-foot pocket (now called the "Drill Pocket"). This pocket proved to contain chalcocite of the largest crystal size and best development yet found at the mine, and moreover with a gogeous metallic midnight-blue tarnish. The best pieces average fist-size, and are solid sulfide masses topped with intergrown, sharp, hexagonal chalcocite discoids to 1.5 cm across, uniformly of that brilliant iridescent blue. We now have to say that the best of these Wisconsin chalcocites are the peers of any chalcocites from anywhere in the world, and, thanks to the blue patina, resemble no others. Mining is still in progress, and the sexy (I mean the supergene) zone has not yet been left behind.

From Springfield I had some kind words to say for Dan and Shelley Lambert of the new dealership of *Lambert Minerals* (152 Colleen Cres., Ancaster, Ontario, Canada L9G 1J3)—and here they were again at Denver, not only with more of the Ontario **tremolite** and **ilmenite** mentioned before, but with two more, equally interesting items. For one, there were about a dozen thumbnails with good sharp tin-white **cobaltite** crystals to 1 cm sitting up pertly on greenish gray calcite matrix, from the small prospect at Elizabeth Lake, Espanola, Ontario. This cobaltite locality has been known for at least 25 years, and the pieces in the Lamberts' little hoard were collected about 15 years ago; it is fun to see good material like this come visiting again from the dead (for there's no current work going on at the place, and no current specimen production).

Further, the Lamberts had about 20 specimens, from thumbnails to a 10 x 12-cm matrix piece, of *green* **grossular** which was discovered three years ago at a place heretofore known only—but famously—for gemmy-orange grossular: the Jeffrey mine, Asbestos, Quebec. These new crystals are very vivid, sharp, gemmy, medium green dodecahedrons to about 3 mm across, well isolated in vugs and seams in a felsic rock. None others (probably) of this color have ever been found at the Jeffrey.

The crystal-diggers of *Crystal City, Inc.* (HC 63 Box 135-C, Mt. Ida, AR 71957) mainly dig Arkansas quartz, but there was a surprise at the back of the small ground-floor ballroom they occupied at the Holiday Inn: lovely, large specimens of green **smithsonite** on white to creamy yellow-white **aragonite**, from a single large pocket hit recently in an offshoot vein on Level 9 of the Potosi mine, Santa Eulalia, Chihuahua, Mexico. The pocket gave up about 40 pieces, including about 10 of highest quality. Most of them show only aragonite, in great snowy mounds of glistening microcrystals and/or coralloidal growths from which transparent colorless prisms to 5 mm bristle. In the elite, smithsonite-bearing pieces, glistening pale apple-green or prehnite-green microcrystalline smithsonite spheres to 1 cm across lie all over the aragonite, for a stunning color contrast. The specimens range from large miniature-size up to 20 x 30 x 30 cm, with most of the best ones being toward the top end of that range. This pocket reportedly has been wholly cleaned out.

Think of **chrysoberyl** from Brazil, and if you are classically minded you'll think of the beautiful gemmy yellow-orange or yellow-green sixling twins from Itaguaçu, in Espirito Santo, first brought out in the 1940's. The morphology is similar to the new chrysoberyls from Santa Tereza, Espirito Santo, which debuted at this show—except that the prism faces are more developed, so that the new ones tend towards more elongation than the old. Also, the color is distinctly different: a translucent to transparent brownish or grayish green, gemmy in small areas only; the luster is high, though, and the good "textbook" examples of cyclic twinning are as sharp as the Itaguaçu pieces.

Reportedly these chrysoberyls were taken in early summer of this year from a pegmatite prospect whose name, typically enough for a Brazilian gem pegmatite prospect, is unclear; some say it's Santa Tereza (a small town) while others say it's Fazenda Santa Isabel (a farm), Pancas (a town), Espirito Santo (and some add "Minas Gerais," although Espirito Santo and Minas Gerais in fact are separate Brazilian states). Mostly thumbnails and small miniatures, these specimens were in the hands of several people in Denver. The best I saw were some 4 x 4-cm sixlings and *groups* of sixlings with *Roberts Minerals* but there were also 15 fine ones, including one measuring 7 x 8 cm, in the room of Luis Menezes (R. Andre Cavalcanti, 761 Belo Horizonte, 30430 110 Brazil), and at the Main Show there were about 50 thumbnails with *The Rocksmiths* (5th & Toughnut, Box 157, Tombstone, AZ 85638).

Ken and Rosemary Roberts also were showing, with understandable pride, two (only!) specimens of prismatic **rutile** from Diamantina, Minas Gerais. Each is a single loose prism 7 cm long and 1.5 cm wide and thick, one with a modest girderwork of smaller prisms around the base. Both crystals are striated, sharp, terminated, undamaged, and brilliantly lustrous; the dark submetallic red overall color is gemmy on some striation ridges.

With *The Rocksmiths*, finally, an undoubted what's-new: nice small specimens of **rhodochrosite** from Brazil. Eldon Smith of Rocksmiths bought the whole contents of the pocket in question, discovered some months ago at the Marcello mine, Saõ Jose de Safira, Minas Gerais. Eldon says that this is a pegmatite prospect very near the famous Cruzeiro mine, but he has no further information just now. The rhodochrosite comes in pleasing medium-pink, largely opaque but occasionally translucent single rhombs to 1 cm, and small groups of these, on matrix. The matrix is odd: soft, almost friable packings of pale green sparkly 2-mm crystals that at first glance suggest diopside, but appear to be a (manganoan?) mica species (basally cleaved hexagonal sections can be seen with a loupe). The pale rhodochrosite-pink on this pale green spongy material makes for pretty specimens, the best of which are thumbnails for about $50.

The fastest fantasy-Concorde in the whole world now brings us in mere milliseconds to France, and then we get ourselves somehow to a snowy shoulder of Mt. Blanc, the highest Alp in Europe. For decades—probably centuries—there have trickled out from the hands of the *Strahlers* who hunt these heights such beautiful **pink octahedral fluorite** crystals as to rival the similar ones from the Göschener Alp, Switzerland. But supplies of course have never been lavish, and prices have always been high. Well, this past summer someone opened a pocket with gorgeous, *very* deep pink, gemmy-transparent, beautifully sharp fluorite octahedrons resting singly and in clusters of three to five on white weathered granite, this matrix sometimes showing shiny white flattened feldspar crystals to a centimeter or so. A few specimens also have excellent, gemmy, deeply smoky quartz prisms to 5 cm long. Although the best guess is that the best of this lot remains "in private hands" in Europe, Stefan Stolte of *Mineralien und Fossilien Galerie* (Fahrgasse 88, 6000 Frankfurt/Main 1, Germany) brought about ten excellent pieces to Denver, the most excellent couple of which are 8 x 10-cm matrixes with fluorite octahedrons to 2 cm on edge (around $5000).

At the Main Show, Victor Yount (8388 Lunsford Rd., Warrenton, VA 22186) had ten or so miniatures of a brand-new, weird-looking **jarosite** from Pozo Alfredo, Rio Tinto, Huelva, Spain. Opaque, creamy white, end-rounded "stalactites" to 1.5 cm high are grouped in wormy clusters, most of these stained light brown at the bases, some of the little jarosite worm-warrens resting on a dark Fe-oxide matrix.

Aesthetically coincidentally, the tour's next stop is to pick up on another worm-warren sort of specimen: flos-ferri **aragonite** from the ancient mines at Laurium (although the labels said "Sounion," the name of a cape just a few kilometers to the south), in Attika, Greece. Ernesto Ossola (8 rue de Luxembourg, 30140 Anduze, France) recently bought these ten specimens from a local collector at Laurium. They are delicate yet flamboyant, eccentric things, with thin curving tentacles of pure white to pale-green-stained aragonite waving upwards from soft limonitic matrixes. All are miniatures about 7-10 cm across the bases, the tentacles reaching to 6 cm high.

Leaving Europe, but remaining for one more paragraph with Ernesto Ossola, we come to his handful of specimens of **chalcostibite** from Gar el Anz, Casablanca Region, Morocco. Up to 12 cm-long metallic black blades with splintery surfaces (and every one bashed off at the terminations) rise from or penetrate buff-colored matrixes, or make flat-lying groups on solid chalcostibite. One can't decide whether they're ugly or pretty, but arguing for the latter judgment is the bright earthy-blue azurite alteration (with some green malachite spots in there too) on most surfaces. Sizes of specimens are from 4 to 15 cm, priced from $100 to $1000 . . . And these are superlative specimens, probably the top ones from anywhere, of an exceedingly rare sulfosalt species.

Back (again) at Victor Yount's stand at the Main Show, the former U.S. ambassador to Mali, William Dameron, stood ready to expound, with minutely detailed maps and all, on the interesting skarn mineralization at a site south of Sandare, Diakon Arrondissement, Nioro du Sahel, Mali. We know by now about the sharp brown-green dodecahedrons, often to very large sizes, of **grossular** from this place. Indeed they seem to get better with each show appearance, and did so here. But what's newer are Mr. Dameron's ten or so 15 x 15 x 15-cm loose blocky **vesuvianite** crystals from a newer dig in the area. These vesuvianites, like the best of the garnets, have a nice medium-glassy luster, although the faces are frequently deeply pitted, and their color, also much like the garnets', is a mottled medium-brown to epidote-green; in fact, the color-camouflage is such that one has to look twice to spot the 3-cm grossular dodecahedrons which grow on some faces of the vesuvianites. Anyway, these huge hunky crystals are, on balance, fairly attractive, and certainly fairly peculiar.

From the mysterious Jos gem-mining region of Nigeria, as we know, **emeralds** have intermittently come; but none I'd yet seen are any match for the four crystals being shown in the Holiday Inn by Cal and Kerith Graeber (P.O. Box 2347, Fallbrook, CA 92088). The color is halfway between deepest aquamarine and full emerald-green; the forms are very sharp, with pinacoidal and high-pyramidal end faces; one crystal is doubly terminated; the longest one is 1.5 x 2 x 12 cm. Best news comes last: they are fully, absolutely gemmy throughout, and this, with their swanky deep color, makes them absolute knockouts in the gem-crystal department. They are part of a very small lot which came out about five years ago.

More to the purposes of "casual" collectors, there was a fresh batch (dug, actually, in the late 1970's and hoarded until now) of fine **libethenite** crystals from the Mindola Open Pit, Kitwe, Zambia—see vol. 9, no. 6 for the writeup on this, almost surely the world's best locality for libethenite. Rod and Helen Tyson (10549-133 St., Edmonton, Alberta, Canada T5N 2A4) were selling this material for Stan Korowski, the man who collected it and wrote the original article. Most specimens are thumbnails, with very lustrous, very deep green crystals to 2 cm. Two habits are distinguishable: thin blades in tight parallel bundles with mosaic overgrowths, and sharp pseudo-octahedral blocky singles which sit up very smartly in open vugs in the gray, fine-grained argyllite matrixes. Prices were often in the high three figures, but, after all, these are world-beating specimens for their species, and relics besides: all active mining at the Mindola pit ceased about a year ago.

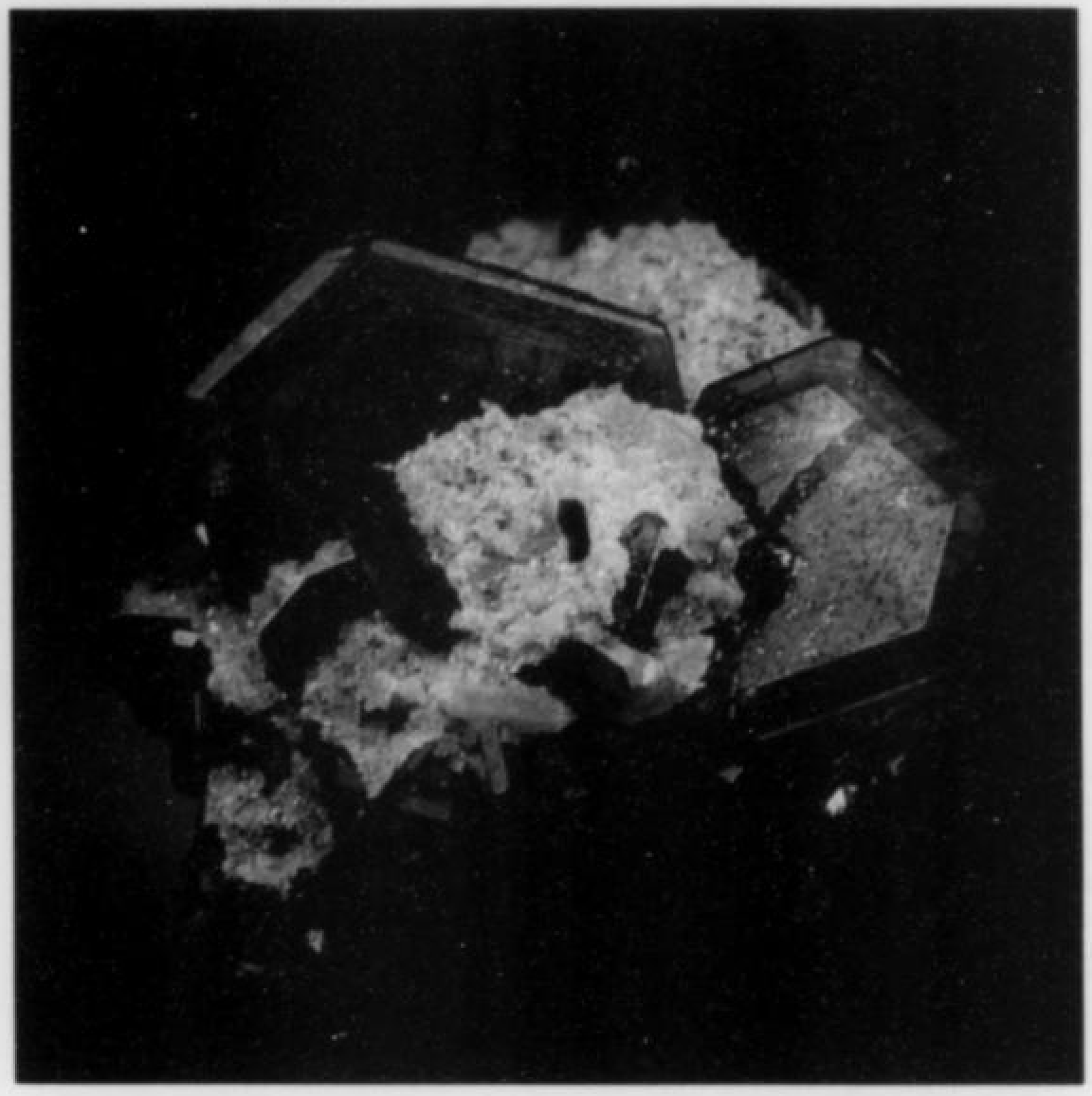
Petr Korbel of *Eastern Minerals* (Vysokoskolska 488/8, 165 00 Praha 6 - Suchdol, Czech Republic) had five promising samplings of a new find (two months old) of **scepter amethyst** from Obman, Yakutia, Russia. The largest specimen is a shapely 8-cm-long purple prism-topper with good amethyst color, grading in some areas to smoky. The opaque white "stem" is broken off about 2 cm down from the base of the scepter. The rest of the specimens are miniatures, and quite good ones too. Also, Petr had some opaque to translucent, greenish grayish white **apatite** in 2 x 3-cm prisms with good terminal faces, some associated with **magnetite** crystals, from a skarn at Dashkesan, Azerbaijan: these were found last summer.

The *KARP* dealership (P.O. Box 54, 272 80 Kladno, Czech Republic), whose own "eastern minerals" usually include something new and intriguing, had a small flatfull of loose pale **blue topaz** crystals of thumbnail size. Except for the rather dull luster, these look exactly like old (or new?) ones from the classic locality of Murzinka, Urals, Russia, but in fact they're from a place called Nura-Taldy, in central Kazakhstan. It is a greisen vein which hosts a tungsten deposit presently being worked. The word is that the topaz crystals are sometimes associated with cassiterite and wolframite, though no such extras showed up here. If you don't mind the unlustrousness, these are fine thumbnails for $10 or $20. Additionally, in the *KARP* room were *three flats* of fair to very good non-gemmy **emerald** crystals in the typical mica schist from the Malysheva mine, central Urals—these dug only a few weeks ago. And *you* can remember a time when you thought of these, regardless of quality, as old, unattainable "classics!

But the crowds constantly jamming the room of *Heliodor* (*Van Scriver-Pliaskov Minerals*) testified again to the fact that *this* is the place, above all others, to come for ex-Soviet Union specimens of high aesthetic caliber and, often, high scientific and/or what's-new interest too. Actually, *Heliodor* was a bit low, by earlier standards, on *new* Russian material this year. But browsing their cases, and, especially, eyeballing or even nosetipping their flats of small specimens, still yielded much satisfaction. For instance, there were some first-rate thumbnails of spinel-twinned **copper** in brilliant branching groups from the Frolowsky mine, Turinsk, near Bogoslovsk, Ural Mountains.; there were a couple of shining, loose, complete **zircon** crystals of mottled gray-buff color from Veshnovogorsk Vein #5, Middle Urals; there were many excellent *thumbnails* (a first) of the lovely pale orange twinned **calcite** from the Sarbayskaya quarry, Rudniy, Kazakhstan; there were superlative radial orange **stellerite** balls from the same place; and there was much Dal'negorsk material, etc., etc. And, here and in a few other rooms, there were **platinum** crystals; and hereby hangs a tale, still unfolding—

Figure 5. (left) **Grossular and vesuvianite crystal group, 6.3 cm, from Sandaré, Niaro du Sahal, Mali. B. and D. Dameron collection; Jeff Scovil photo.**

Figure 6. (below) **Fluorapatite crystal group, 3.2 cm, from Rio Grande do Norte, Brazil. Isaias Collins (*I. C. Minerals*) specimen; Jeff Scovil photo.**



Ever since the Pliaskov/Van Scriver dealership (now called *Heliodor*) brought the first three specimens of Siberian platinum crystals to Tucson in 1993, there has of course been much excited curiosity going around. How big do the crystals get? How do they occur, and how do they get out of Russia?? Will there be more??? So I sat down at this show with Star Van Scriver to receive The Scoop. It's of necessity a partial Scoop, but you may depend on its accuracy, as Star is both an honest man and, so far, *the* man best positioned to tell the story.

In Russia, the central government agency which oversees metal mining (and stockpiles precious metals, and backs the currency . . . a *serious* agency) is the Strategic Metals Reserve, a branch of the Ministry of Economics in Moscow. The platinum crystal locality, meanwhile, is near the village of Konder in far eastern Siberia, about 8,000 kilometers away. Somewhere between these, in a classified location, is the "branch agency" of the Strategic Metals Reserve that is responsible for the mines of this type in this region. The law is that 80% by weight of whatever is found at the mine must be sent to this intermediate branch-agency location, and 65% of *that*, in turn, must be sent back to Moscow. The 20% which remains at the source may NOT be sold to foreigners; indeed its disposition seems very unclear. But up to 35% of what the branch agency receives *may* be sold to foreigners, as may be some unspecified quantities of what ends up in the Moscow stockpile. Foreign buyers who come through, then, can deal only with these two government entities, far from the mine: Star has never visited the "Konder" site. Too bad—as no one at this site, it seems, distinguishes between nuggets and crystals; the distinguishing occurs, when it does, either at the branch agency or in Moscow. Although platinum crystals

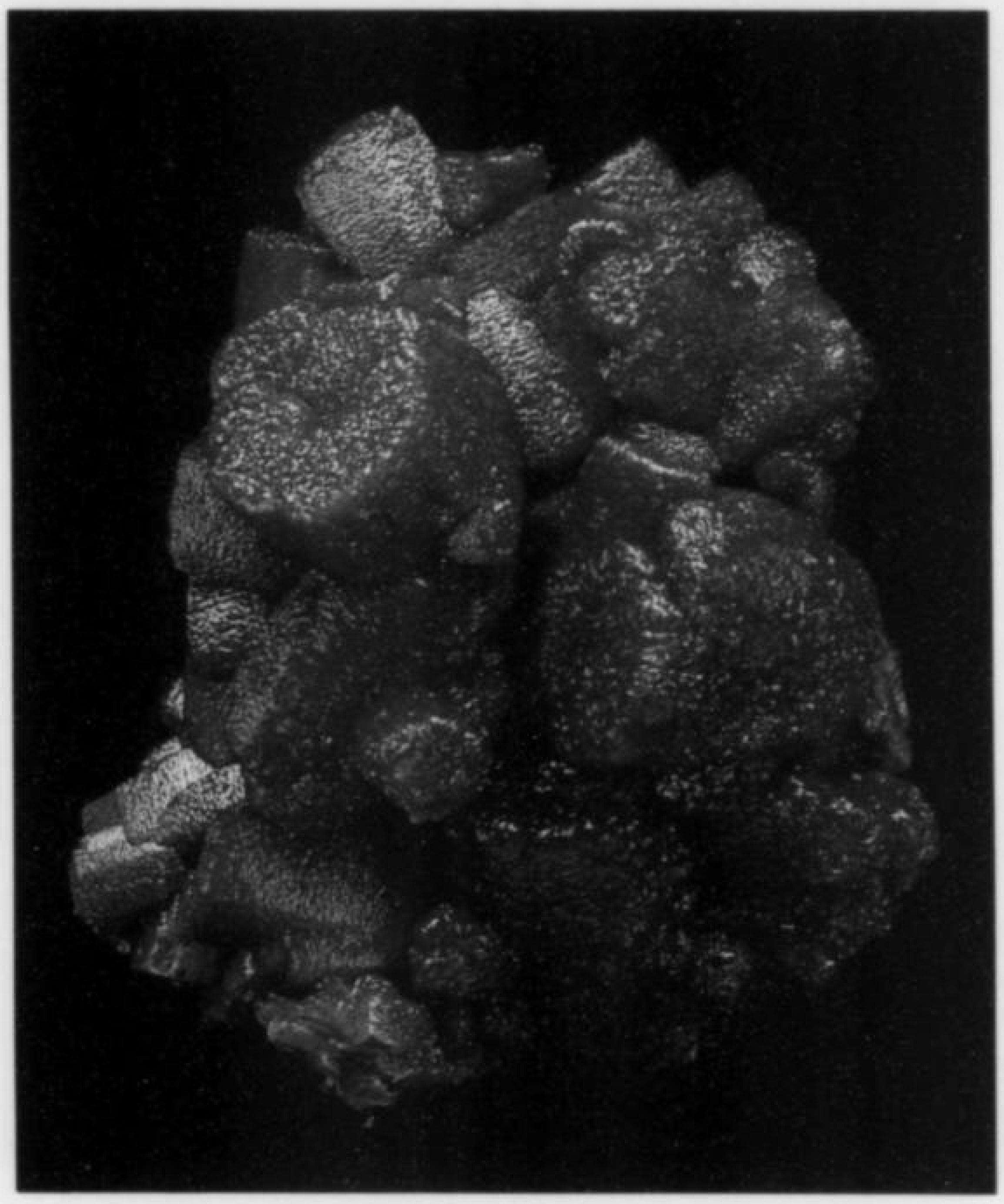


Figure **7. Pyromorphite, 10 cm, from the Bunker Hill mine, Kellogg, Idaho. Wayne Thompson Minerals; Jeff Scovil photo.**

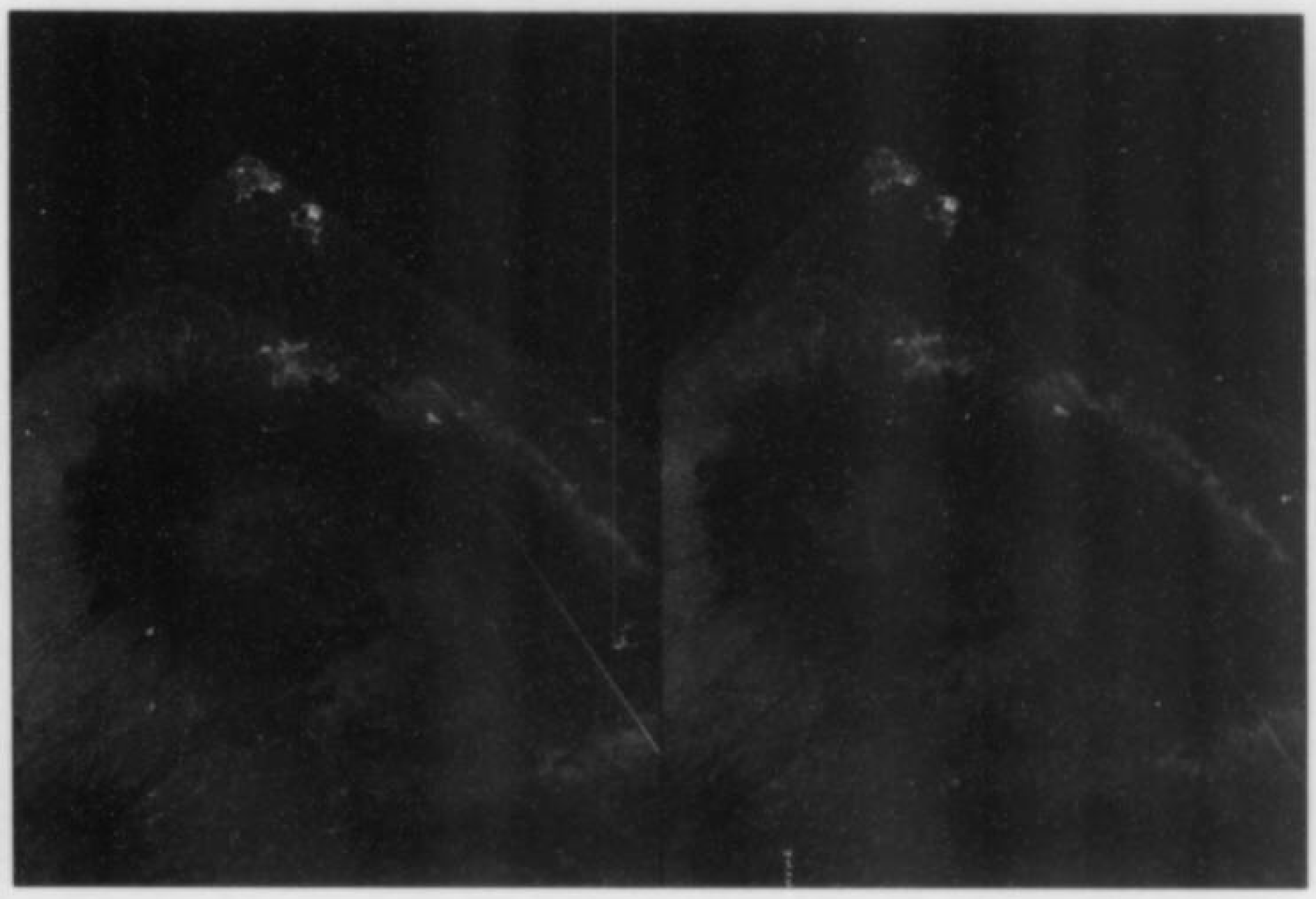


Figure 8. (right) **Papagoite, cuprite and copper in quartz, 2 cm, from the Messina mine, Transvaal, South Africa. Karl Sprich specimen; David Minster photo (stereo-pair).**

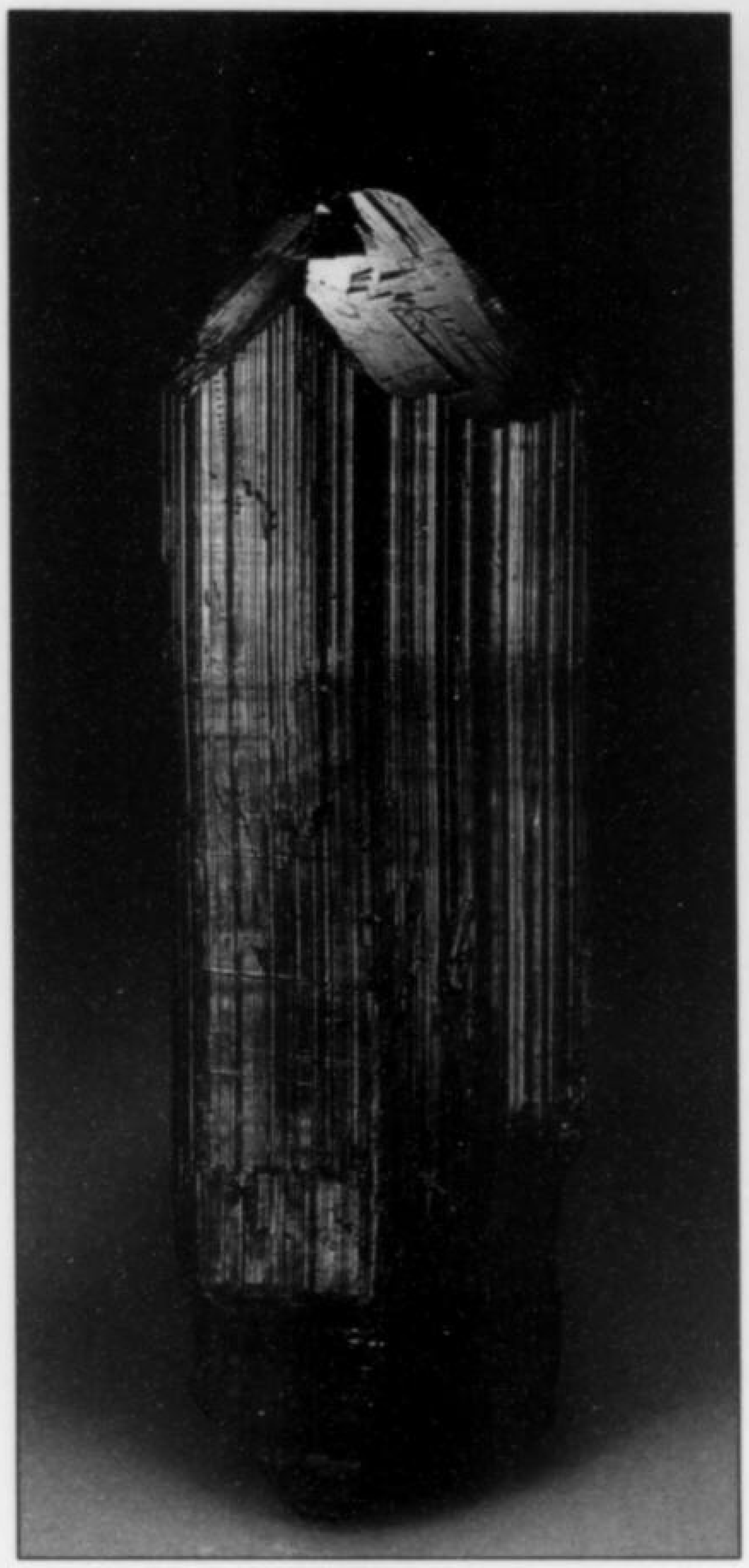


Figure 9. **Stibnite crystal, Lushi mine, Henan, China. De Trin Minerals specimen; Jeff Scovil photo.**

may now occasionally be seen in a few other dealers' hands, it is the Pliaskov/Van Scriver dealership, so far almost alone, which has trodden the bureaucratic-byzantine ways and brought crystals out of the country.

The mine is in a small alluvial river outwash which has been worked for two and a half years now, and the workings have processed between one third and one half of the deposit's apparent volume. It is reliably said that, besides platinum crystals, there occur here also euhedral crystals (mostly dodecahedrons and cubes) of platinum-group native metals like **palladium**, **osmium**, **iridium**, and the alloy **iridosmine**, in sizes much smaller than the platinums. Continued output of specimens—including any improvement in crystal size or any market appearances of crystals of the other rare metals—depends, in summary, on several undependable factors. Among the obvious ones are the internal politics and economics of the Strategic Metals Reserve (and ultimately of the Russian state as a whole); the increase (or lack of it) in awareness, along the pipeline in Russia, of the difference between nuggets and crystals; whether or not more alluvial deposits like this one are found and worked; and the ongoing bravery, pluck and luck of such western entrepeneurs as the Van Scrivers. This last variable, however, may be the least varying. Star is also about to begin (next May) his own serious mining operation in the Puiyva mine, in the Polar Urals, where those wonderful ferroaxinites sometimes emerge from under the permafrost.

We move on from Russia now to—you didn't guess it—Mongolia. Dave Lare of *Jeffrey Mining* (115 Boothloop, Henderson, TN 38340) has recently acquired about 10 cabinet specimens and several flats of miniatures of a new **fluorite** from Saybere, Mongolia. Their color is a pleasant, transparent lime-green to medium green, though a few have a purplish cast, and on a few others the fluorite crystals have purplish zones or even sharp purple lines along the cube edges. The slightly rough cubes can reach 3 cm. The specimens are often somewhat damaged, and, overall, not radically attractive as fluorite goes, but we are promised more, better, less damaged, better cleaned ones at Tucson this year.

Jeffrey Mining was also showing the best of a new strike of **elbaite** from Pakistan: the locality is given as the Asthor mine, near Shigar, Karakorum Mountains. Apparently these came out just a bit too late for the 1995 Tucson Show. What's most remarkable is the color scheme: the sharp, striated prisms and columnar groups are zoned perpendicular to the *c* axis in hues of pistachio-green to colorless to bright *blue*, and Dave Lare's biggest specimen, a spectacular columnar group 17 cm high, with a blue tip, has some very thin, pale pink "candy stripes" about halfway up. Some fine loose single prisms make appealing thumbnails to look at, too, in the room of *Trap Hills Minerals* (P.O. Box 247, Bergland, MI 49910).

At the Main Show, Dudley Blauwet of *Mountain Minerals International* (P.O. Box 302, Louisville, CO 80027-0302) was waiting for me with a short list of recent remarkables from Sri Lanka and other Asian locales. As I did not see specimens of these (they were not on hand), I will merely pass on his word about a 71.11-carat gem **taaffeite** crystal from Elahara, South Central Sri Lanka, this recently sold to the Smithsonian; and of floater, complete, clear gemmy brown **andalusite** crystals from Nawalapitiya, Sri Lanka.

Finally, I can deliver a sequel/clarification regarding the provenance of the giant, thick **stibnite** crystals from China that started appearing in Springfield, but whose source then wasn't clear. No, it *isn't* just a new kind of Xikuangshan mine, Hunan Province stibnite, but rather comes from the Lushi mine, Lushi Village, Henan Province, China—according, that is, to Dave Bunk, who seems quite confident of his information. No large new lots of this stibnite were on hand at Denver, by the way. As at Springfield, it's a case yet of monstrous, loose, exceedingly bright but heavily damaged prisms appearing in twos or threes at scattered dealerships here and there.

I'll conclude this report by saying what we show reporters too often leave unsaid about *other* minerals, besides what's-new finds, that make these huge shows such a pleasure to roam around in. I'm thinking chiefly of random amazements of one-of-a-kind specimens, which may pop up literally anywhere, of occurrences which we think of as impossibly "old," remote in their dignity when we meet them in large museum collections . . . but suddenly here one is, with old label (largely illegible), price (inaccessible, but we don't really grudge the specimen this), and story or stories attached (ask the dealer) . . . a piece of solemn History itself. At this show as at all of them, I enjoyed this experience many times, and so it's just as an example that I'll mention the Graebers' two specimens of **pyrosmalite** from Nordmark, Värmland, Sweden—a locality which stopped producing good specimens more than a century ago (and whose remains I have visited; having *been* there always helps—adds poignancy, maybe). One pyrosmalite is a small thumbnail, a sharp loose hexagonal olive-green crystal; the other is a 4 x 7-cm matrix with an even sharper crystal sitting up in the middle. Discoveries, appreciations, connections like *that* can make many an otherwise so-so show day sing with joy.

Finally, and even though this column normally doesn't even pretend to address micromounters, congratulations to *Carter Rich* (P.O. Box 69, Aldie, VA 22001) for having lovingly bought up and just as lovingly offered again for sale some hundred old micromounts, in old-fashioned cardboard boxes, with yellowing labels in the faint scripts of the men who'd made the mounts, men revered in this confraternity, including George Gilbert Rakestraw, George Washington Fiss, J. B. Brinton, George Letchworth English, and, getting into our own time, the late, much-beloved Neil Yedlin.

Enough already. My plane out of here leaves at 7:15 Sunday (tomorrow) morning. Until Tucson—!

Pretoria Show 1995

by David Minster

The Pretoria (South Africa) Gem and Mineral Club hosts a gem and mineral show at the Menlyn Shopping Centre each year in late September through early October to coincide with local school holidays. The site, an up-scale mall in an eastern suburb of Pretoria, has a special area called the Fountain Court which contains the facilities necessary for shows of this kind. The Pretoria Show attracts thousands of visitors including dealers and collectors from all over South Africa. Although rather small by international standards, the show serves as the conduit for a large quantity of South African minerals which eventually find their way to the European and American specimen markets. On alternate years (as this year) the Pretoria Gem and Mineral Club is joined by the other South African clubs to produce a "national show."

The show layout consists of a circle of showcases in the center exhibiting private mineral collections and lapidary items which are in competition for prizes and awards. Surrounding this exhibit area are outward-facing dealers' tables. Most of the mineral dealers here also show up at the Tucson and Munich Shows later, offering for sale the stocks obtained from local South African field collectors and other sources. A variety of fine specimens is usually available, from micromounts to museum-quality cabinet specimens.

This year *Karl Sprich* (70 Franschoek Drive, Oakdene Ext. 2, Johannesburg 2197) had just acquired some old collections of African minerals including fine green **tourmaline** crystals to *25 cm* long and 3.7 cm thick, from Mozambique; **rhodochrosite** crystals to 3 cm from the Kalahari Manganese Field (singles and clusters); and excellent **dioptase**. Much of this material is being saved for the Munich Show. Also available were **meteorites** from Namibia, including polished slabs and spheres, and pallasite meteorite slabs from Argentina; attractive ruby **corundum** in matrix from Madagascar and Afghanistan; **celestine** geodes and single crystals, **labradorite**, gemmy yellow **orthoclase** and **rhodonite** from Madagascar; a meter-long doubly terminated **quartz** crystal from Springbok (Northern Cape Province, South Africa); **ajoite** and **papagoite** in quartz from the Messina mine; very nice **pink zoisite** crystals on matrix from Pakistan; and **quartz** crystals from Brandberg, South Africa. Karl travels extensively and maintains a vast stock of mineral specimens from around the world.

Gondwana Resources (P.O. Box 1086, Rivonia, 2128) is another local dealer who has a large selection of quartz crystals and groups from the famous (in South Africa, at least) Brandberg locality, and also many **zeolites** from the Poona area, India.

Rolf Brandt (*Mineral Market,* 331 Cork Avenue, Ferndale, 1610) had interesting **quartz** crystals from a variety of localities; **rhodochrosite** crystals on matrix from the Kalahari Manganese Field; **cobaltoan calcite** from the Mashamba West mine, Zaire; various Indian **zeolites**; and a complete dinosaur skeleton embedded in a 25-cm matrix from Germany.

The above notes are only the highlights concerning the more unusual items; there were other dealers and many other specimens for sale. ▨

Letters

VANADIAN DRAVITE

I read with interest the recent letter (vol. 26, no. 2) from Jesse Fisher concerning vanadian tourmaline, which I had reported earlier (vol. 25, no. 4). As he notes, EDS is not necessarily highly precise. The analysis I reported previously, by Robert Gault at the Canadian Museum of Nature, was performed by WDS, and is more accurate. Although this analysis did indeed show a considerable amount of calcium, sodium is present in excess of calcium. I have subsequently discussed the analysis further with Dr. Gault, who assures me that the standard deviations for the measurements of sodium and calcium are quite small, and that he is quite confident that the material should be considered vanadian dravite. I would be happy to provide a copy of the complete analysis to anyone who might be interested. These data are of course only true for the crystal we studied. It would be interesting to see the results of analyses of more of these crystals. Although we may have exhausted the interest of the readership in this particular topic, I should note for those of you who have not seen any of these crystals that they are quite unique in color for a tourmaline, and are very reminiscent of vanadian grossular (*tsavorite*).

Mark N. Feinglos
Durham, NC

HAÜY MEDAL

On a recent trip to France my wife, Catherine Skinner, and I visited the Musée de Minéralogie of the École des Mines de Paris in order to see a fascinating exhibit in honor of the 250th anniversary of the birth of Haüy. On display were some of his measuring instruments, notebooks in which his calculations can be followed, crystal models, stacking models used to develop his law of rational indices and many specimens. As part of the exhibit an elegant Haüy medal has been crafted which can be purchased and a half-hour video of his life and work prepared. The video is in French but even a non-French speaker can learn a great deal from the tape.

I write to you on the supposition that you may wish to mention the video and medal in an editorial. Readers who are interested should contact the Curator of the Museum:

Dr. Lydie Touret
Musée de Minéralogie—
École des Mines de Paris
60 Bd. Saint-Michel
75272 Paris, Cedex 06 FRANCE

Brian J. Skinner

NAME GAME

Those interested in mineral names (many collectors) might take an interest in a recent article on the naming of bigger rocks, the contents of our solar system. The article, entitled "What's in a name?" appeared in the May, 1995, issue of *Sky and Telescope,* p. 28–33, and was written by John F. Kross; it contains an interesting sidebar, "Name games continue" by Govert Schilling. In addition to interesting text, there are a number of cartoons, somewhat similar in genre to that done by Wendell Wilson in *Mineralogical Record,* **8**, 347. Although these rocks are literally orders of magnitude greater than those the mineral collector admires, the naming situations provide many parallels.

Pete J. Dunn
Washington, DC

CROCOITE FIND

A remarkable find of crocoite was made at the famous old Adelaide mine in the Dundas district, Tasmania, in 1993. Dundas lies in a rugged mountainous rainforest about 12 km east of Zeehan on the Tasmanian west coast. Claims were first staked in the area in 1886, and crocoite was found at the Adelaide property in 1891.

The present proprietor of the Adelaide mine, Frank Mihajlowits (known locally as the "Crocoite King of Zeehan"), began prospecting in 1956 and took over the Adelaide mine in 1974. Since that time he has worked and reworked the old diggings, adits and shafts, mostly on his own. He has driven some new tunnels and kept the mine operational, but has recovered little worthwhile crocoite in the process. In recent years he has been joined by his son-in-law, Andrew Farrelly, and together they have prospected new ground and driven some new tunnels.

On May 14, 1993, after having driven an adit 50 meters into the hillside (at a level approximately 10 meters above the oxide enrichment zone), they intersected the upper end of an extraordinary crocoite vug measuring up to 1 meter wide and 14 meters long. The vug angles downward about 30°, so that its lower end is about 10 meters below its upper end. My wife and I were graciously permitted to inspect the vug just 12 hours after its discovery, a sight we will never forget.

Because of the difficulty inherent in mining out a vug from the upper end downward, Frank decided to drive a second adit 10 meters below the first one so as to intersect the lower end of the vug. In the process he hoped to

Figure 1. **A 30-cm (1-foot) pocket lined with crocoite crystals on black manganese oxide. Frank Mihajlowits collection; photo by Victor Kubiak.**

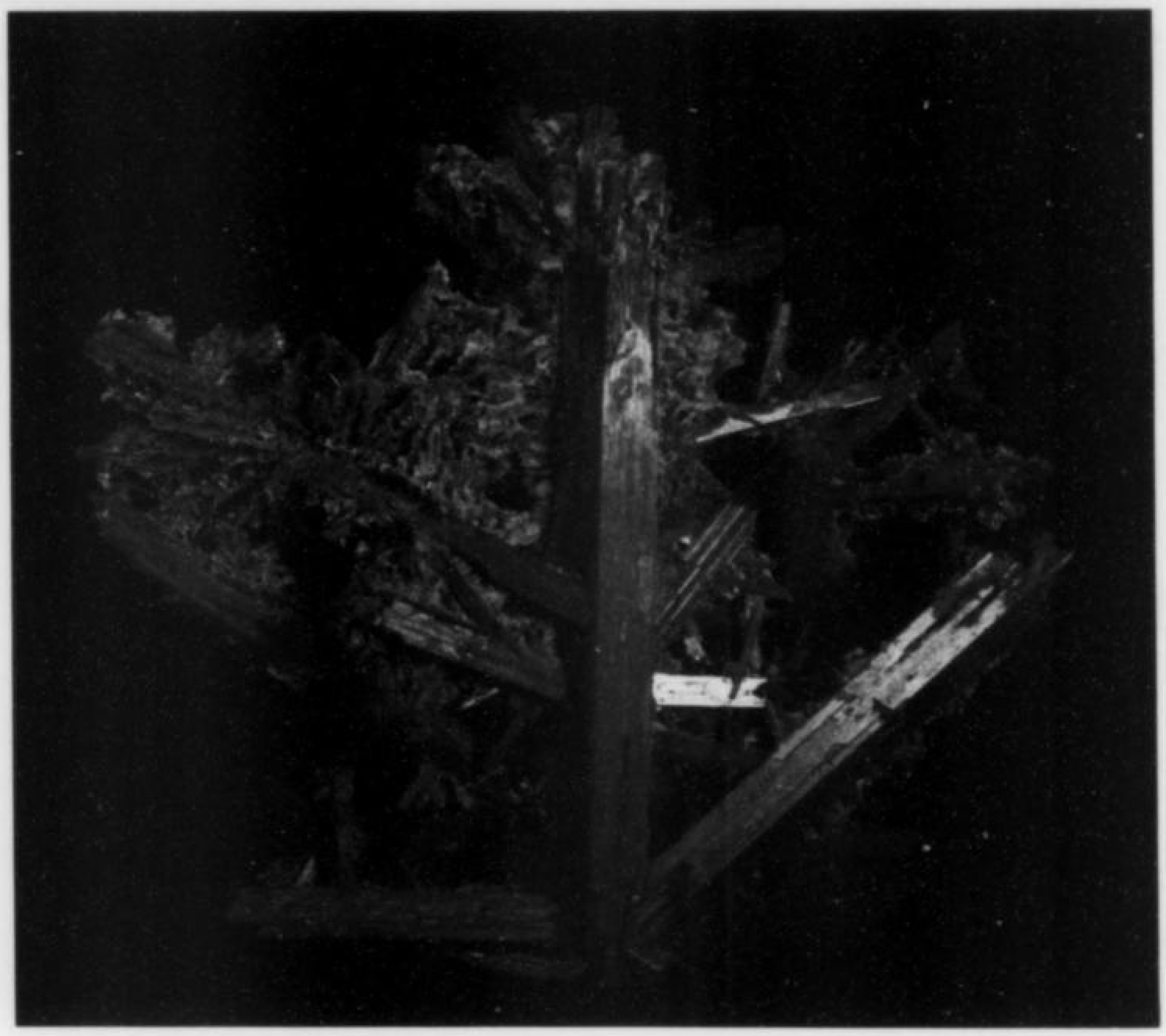


Figure 2. **Crocoite crystals on gibbsite, 8.5 cm. Ambros Kissling collection and photo.**

cross an old shaft, and perhaps also recover specimens of other minerals including white cerussite, yellow "chrome" cerussite, dundasite, siderite, phosgenite, pyrite, jamesonite and anglesite.

Among the first specimens removed from the pocket were matrix pieces bearing perfectly terminated, hollow crocoite crystals up to 8 cm long. The crystals have a brilliant orange to red color and clean, bright luster. The ferromagnesian gossan (goethite and manganese oxides) varies from black to pale brown to white as a result of gibbsite coatings.

Some large, spectacular specimens consist of entangled or intergrown masses of crocoite crystals, coated black but overgrown by a second generation of crocoite which is perfectly clean and deep orange in color. Other specimens have been recovered with striated crocoite crystals to 10 cm long and 1 cm thick, coated with gibbsite. [Ed. note: It is possible to chemically remove the gibbsite without damaging the crocoite.]

Although the Adelaide mine is not open to outside collectors, it should continue to produce excellent specimens of crocoite for some time, which will be distributed through various Tasmanian dealers including Frank Mihajlowits (143 Main Street, Zeehan, Tasmania 7469, Australia).

Ambros Kissling
GPO Box 419-E
Hobart, Tasmania 7001
Australia

NIOBIAN RUTILE

A comment on the niobian rutile described in vol. 26, no. 2, p. 123 by Gene Foord *et al.* from Topaz Valley: The description by Food *et al.* of hematite epitactic on niobian rutile seems incomplete. Figures 9 and 10 clearly show that the niobian rutile occurs as polycrystalline aggregates, as the authors point out, and that not all grains have the same orientation in the aggregate. Figure 10 shows further that not all grains occur in orientations which would be expected if they formed epitactically on hematite or ilmenite. Reversing the geometry, then, it is hard to imagine that a highly coherent outer rim of hematite could form on such an imperfectly oriented aggregate. It is also not obvious why the rutile aggregates are platy, unless some additional factor is at work.

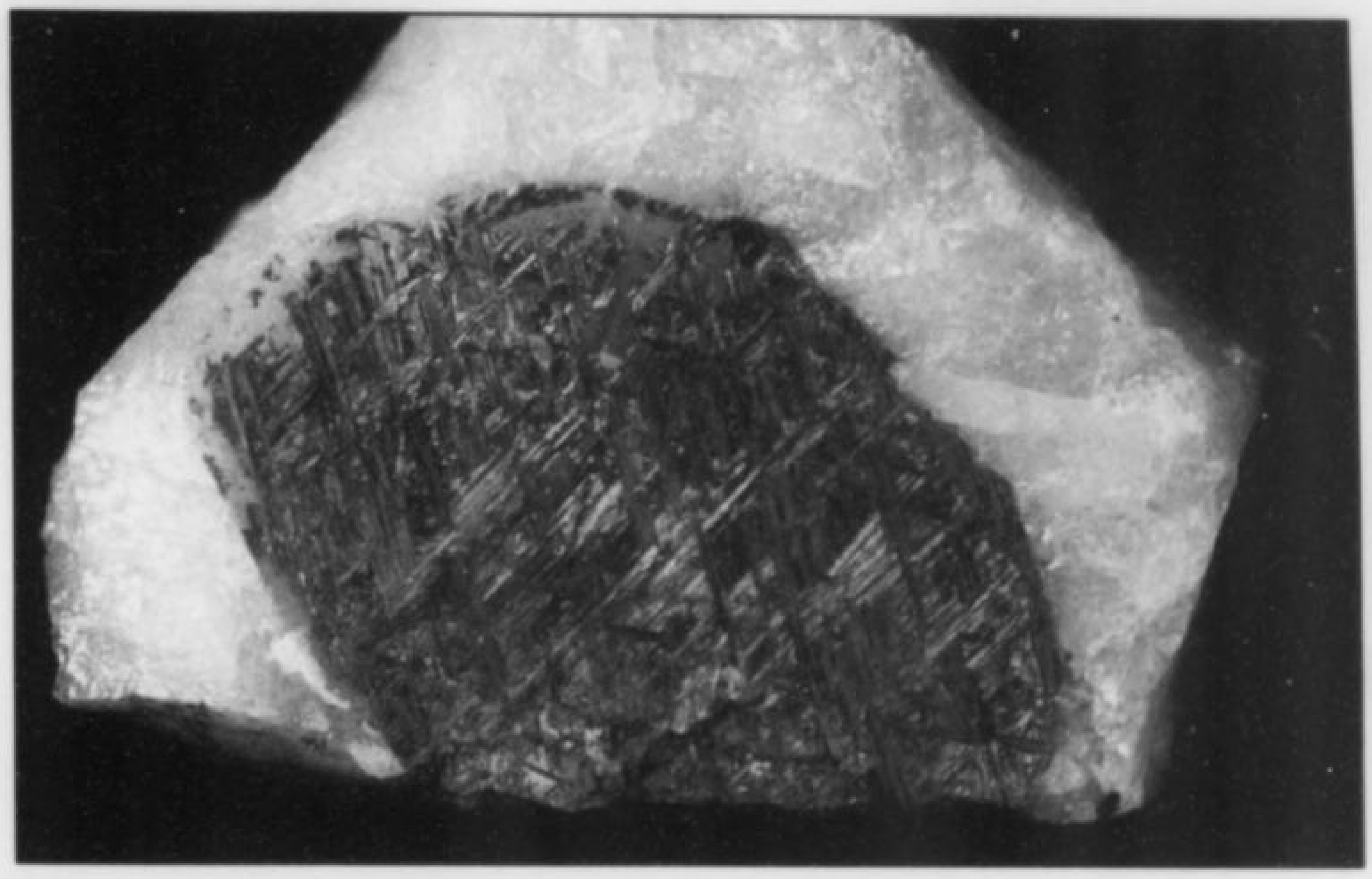


Figure 2. **Sagenitic assemblage (7 cm) of rutile crystals enclosed in vein quartz, with textural evidence that a precursor platy crystal, probably ilmenite, was replaced by rutile after the quartz enclosed it. Rowlandsville, PA. Oberlin College specimen T498, RPR photo.**

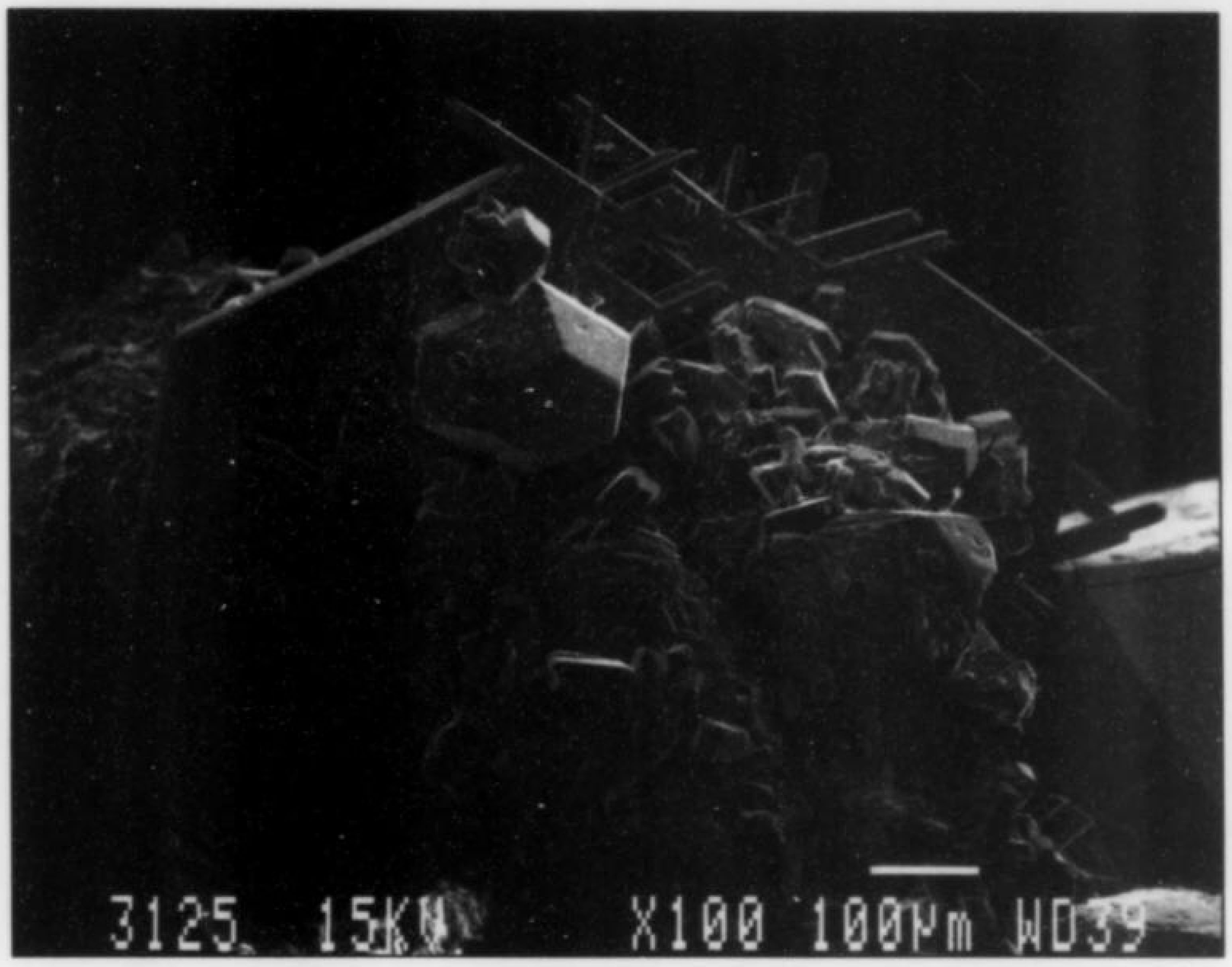


Figure 1. **Platy crystal, most likely ilmenite but possibly hematite or pyrophanite, totally replaced by oriented ilmenite. EDS analysis shows iron is not present in detectable amounts. Hornfels facies, Mont Saint-Hilaire. RPR specimen, SEM image and EDS analysis by Ruth Schultz Kramer, Institute of Materials Processing, Michigan Technological University.**

A reasonable hypothesis can be offered to explain these observations: there was a precursor for the niobian rutile, most likely (niobian?) ilmenite, which formed platy single crystals. The hematite grew epitactically on the edges of these ilmenite plates, forming the current rims. Thereafter, the ilmenite was replaced largely topotactically by niobian rutile to form the current association. The hematite was epitactic on ilmenite, but describing it as epitactic on the rutile is stretching the point.

Topotactic replacement of a platy precursor to form oriented rutile aggregates is common elsewhere (e.g. Mont Saint-Hilaire, see Figure 1 shown here). Sometimes replacement is incomplete, allowing the precursor to be identified as ilmenite. Topotactic replacement of a platy precursor is probably the origin of many sagenitic rutile aggregates as well. One interesting example, consisting of a plate of sagenitic rutile enclosed in vein quartz, is shown here in Figure 2. The quartz which enclosed the sagenitic rutile did not fill the spaces between the individual rods of rutile, which strongly suggests that the quartz enclosed an ilmenite plate, which only later was replaced by rutile. The structural relationships which make this topotactic transition an easy one mineralogically are described by Armbruster (1981).

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R. Peter Richards
Oberlin, Ohio

NEW PARADOCRASITE OCCURRENCES

In December 1993, while making a microscopic examination of stibarsen samples from Moctezuma, Sonora, Mexico, I noted some bright white metallic inclusions in some of the stibarsen fragments. In order to check the identity of the inclusions, a sample was sent to Dr. J. Wilson of Weber State University, in Ogden, Utah, for X-ray diffraction examination. The inclusions were tentatively identified by X-ray diffraction as *paradocrasite*, which had previously been reported in one sample only, from the Consols mine, Broken Hill, New South Wales, Australia (Anthony *et al.*, 1990). A portion of the sample from Moctezuma was then sent to Cannon Microprobe in Seattle, Washington, for microprobe analysis. Seven separate samples were initially analyzed and all contained some material consistent with the composition of paradocrasite.

From this experience it seemed possible that stibarsen ("allemontite") samples from other localities might also contain paradocrasite. During the next several months samples of purported

***Table 1.* Stibarsen specimens analyzed.**

Sample	*Locality*	*Method*	*I.D. By*	*Description*	*Samples Provided By*
GF	Broken Hill, NSW, Australia	X-ray diffraction Microprobe	B. Cannon	**Paradocrasite**, stibarsen (portion of type specimen)	Ben Leonard USGS—Denver, Colorado
GG	Atlin, B.C., Canada	Polished section	B. Cannon	**Paradocrasite** in stibarsen	Cureton collection
FX	Engineer mine, Atlin, B.C., Canada	Microprobe X-ray diffraction	B. Cannon J. Wilson	Stibarsen	Cureton collection
FQ	Bernic Lake, Manitoba, Canada	Microprobe	P. Cerny	Antimony	P. Cerny University of Manitoba
FT	Bernic Lake, Manitoba, Canada	Microprobe	B. Cannon	Bismuth, bismuthinite, pyrrhotite, sphalerite	P. Cerny
GB	Bernic Lake, Manitoba, Canada	Microprobe	P. Cerny	Arsenic, antimony, stibarsen	P. Cerny
GC	Bernic Lake, Manitoba, Canada	Microprobe	P. Cerny	Arsenic, antimony, stibarsen	P. Cerny
FU	Bernic Lake, Manitoba, Canada	Microprobe	B. Cannon	Bismuth, stibarsen, Bismuthinite, tetrahedrite	P. Cerny
GD	Carcross, Yukon, Canada	X-ray diffraction	J. Wilson	Arsenic, minor stibarsen	Cureton collection
FZ	Pribram, Czech Republic	X-ray diffraction	J. Wilson	Arsenic, stibarsen	Cureton collection
GA	Pribram, Czech Republic	X-ray diffraction Microprobe	J. Wilson B. Cannon	Antimony, arsenic, stibnite, sphalerite, paakkonenite	Cureton collection
FO	Pribram, Czech Republic	Microprobe	B. Cannon	Antimony	P. Cerny
FS	St. Joachimsthal, Czech Republic	Microprobe	B. Cannon	Bismuth in arsenic	O. Petersen, Geological Museum, Copenhagen, Denmark
GE	Allemont, France	X-ray diffraction	J. Wilson	Stibarsen, arsenic	Cureton collection
FV	Grube Samson, St. Andreasberg, Germany	Microprobe	B. Cannon	Stibarsen, antimony, loellingite	G. Ansell Geological Survey of Canada
FW	St. Andreasberg, Germany	Microprobe	B. Cannon	Arsenic, loellingite, stibarsen	Cureton collection
FP	Valtellina, Italy	Microprobe	B. Cannon	Arsenic	R. Pagano, Milano, Italy
FR	Hokkaido, Japan	Microprobe	B. Cannon	Arsenic, galena	H. Miura, Hokkaido Univ., Sapporo, Japan
GJ	Moctezuma, Mexico	X-ray diffraction	J. Wilson	**Paradocrasite**, stibarsen, antimony	Cureton collection
GH	Moctezuma, Mexico	X-ray diffraction	A. Roberts	**Paradocrasite**, stibarsen	Cureton collection
GK	Moctezuma, Mexico	*Microprobe	B. Cannon	**Paradocrasite**, stibarsen	Cureton collection
FY	Varutrask, Sweden	Microprobe	B. Cannon	Stibarsen, arsenic	M. Feinglos, Durham, North Carolina

*Approximately 35 additional samples from Moctezuma, Mexico, were microprobed.
All of the samples showed paradocrasite with stibarsen.

stibarsen were obtained from additional worldwide localities, both from my own collection and from supportive scientists and collectors. Microprobe and/or X-ray diffraction analyses were completed on approximately 60 samples from 14 locations. Of the 14 localities checked, paradocrasite was identified from three, including the type locality. (It is possible that two of the samples are from the same locality: they were given to me as (1) the Engineer mine, Atlin, British Columbia, Canada, and (2) Atlin, B.C., Canada; private communication, G. Ansell, 1994.) These samples were obtained at different times from different sources, and have a slightly different appearance.

Leonard's original analysis of the Broken Hill type material, performed 25 years ago with somewhat less sophisticated equipment, indicated 18.6% As and 82.9% Sb. Leonard provided us with a portion of the type specimen to analyze with our other samples. The results are as follows: The type specimen from Broken Hill contained 0 to 0.24% Hg, 14.7 to 17.1% As, and 81.9 to 86.4% Sb. Samples from Atlin contained 0 to 0.44% Hg, 10.3 to 14.6% As and 86.0 to 90.5% Sb. Samples from Moctezuma contained 0 to 0.03% Hg, 13.5 to 15.9% As and 86.1 to 86.6% Sb. All analyses totalled between 98.6 and 103.3%.

Samples showed a wide variance in the percentage of paradocrasite present, ranging from approximately 6–10% in the British Columbia samples and 4–98% in the Moctezuma, Mexico, samples to 90–97% in the original Consols mine, Broken Hill samples. Approximately 38 samples of Moctezuma stibarsen were analyzed by microprobe. All showed paradocrasite in widely varying percentages but the majority showed 55–90% paradocrasite. I have been unable to obtain samples from other stibarsen localities noted in the literature.)

In conclusion, paradocrasite, while still very uncommon, is shown by these results to be more widespread than previously thought. Work on additional material will likely reveal other localities for paradocrasite.

I wish to thank everyone listed in this report for their generosity and help. I particularly wish to thank Mr. Fred Kennedy of Rochester, Minnesota, for his assistance. Without Fred's encouragement this work would not have been completed. I also thank Gary Ansell of the Geological Survey of Canada for critical comments on the manuscript.

Incidentally, in the original description of paradocrasite, Dr. L. Lawrence of the University of New South Wales, Sydney, Australia, expressed doubt that the original paradocrasite came from Broken Hill, New South Wales. Since that time, Dr. Lawrence has done additional work on the ore samples in question and now agrees that the original paradocrasite did, indeed, come from the Consuls mine at Broken Hill, New South Wales (private communication, L. Lawrence, 1994).

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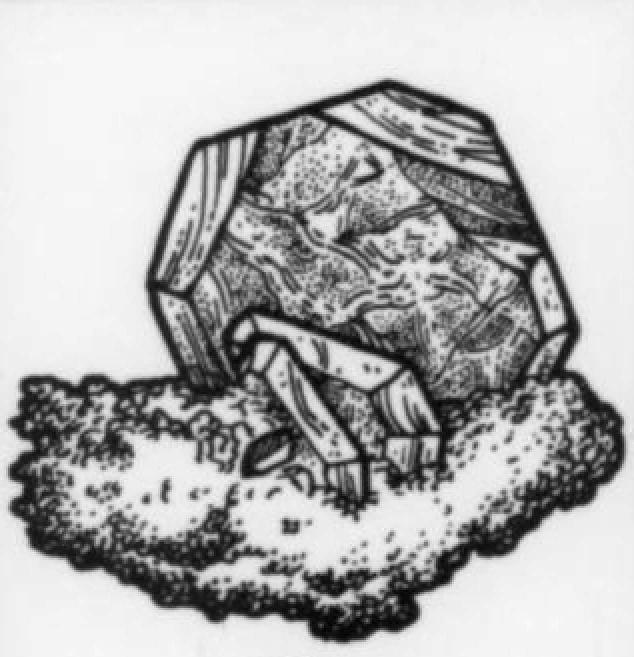

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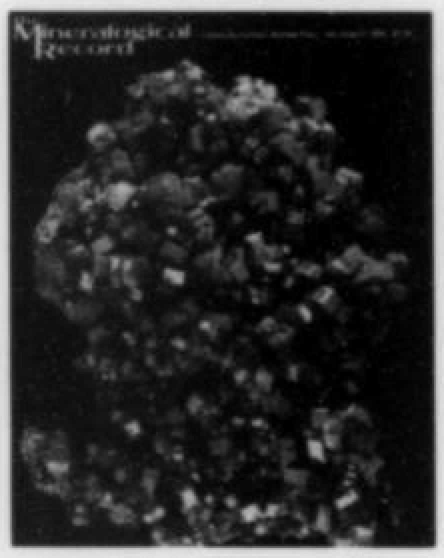

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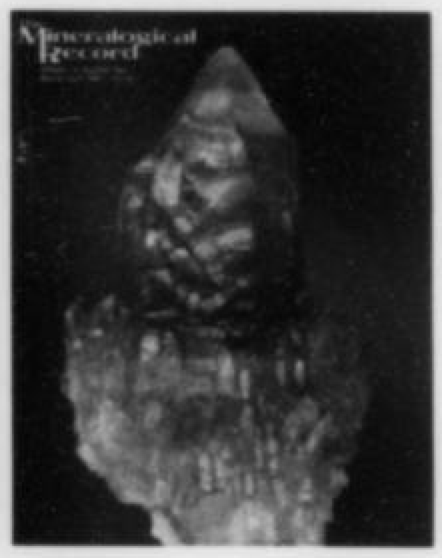

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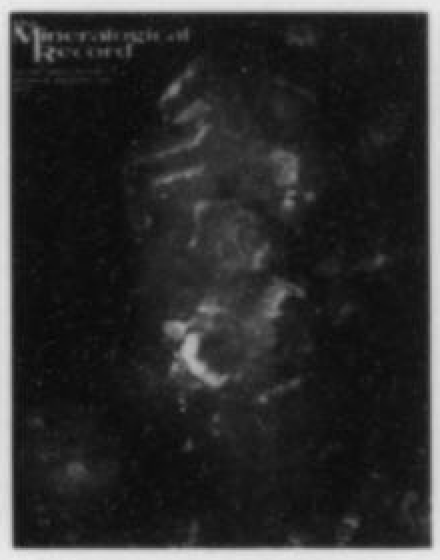

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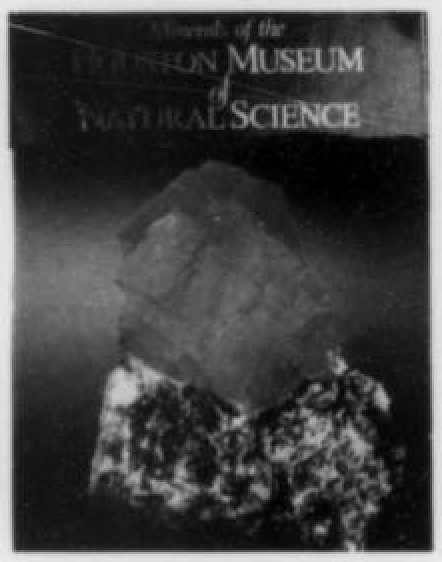

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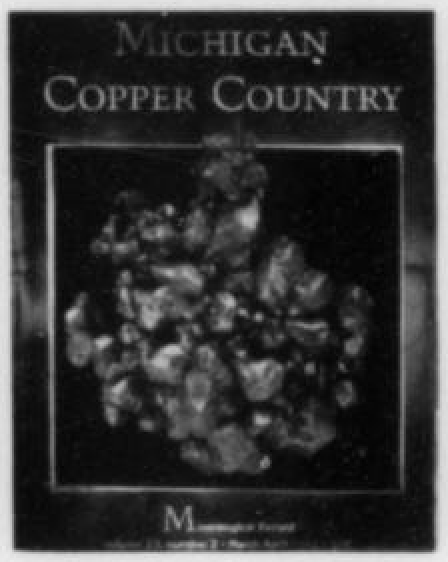

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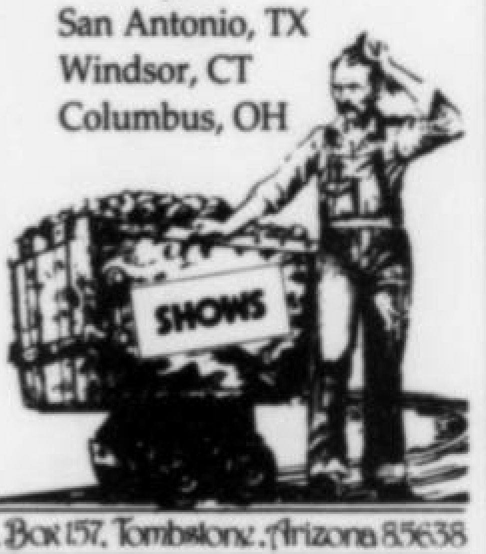

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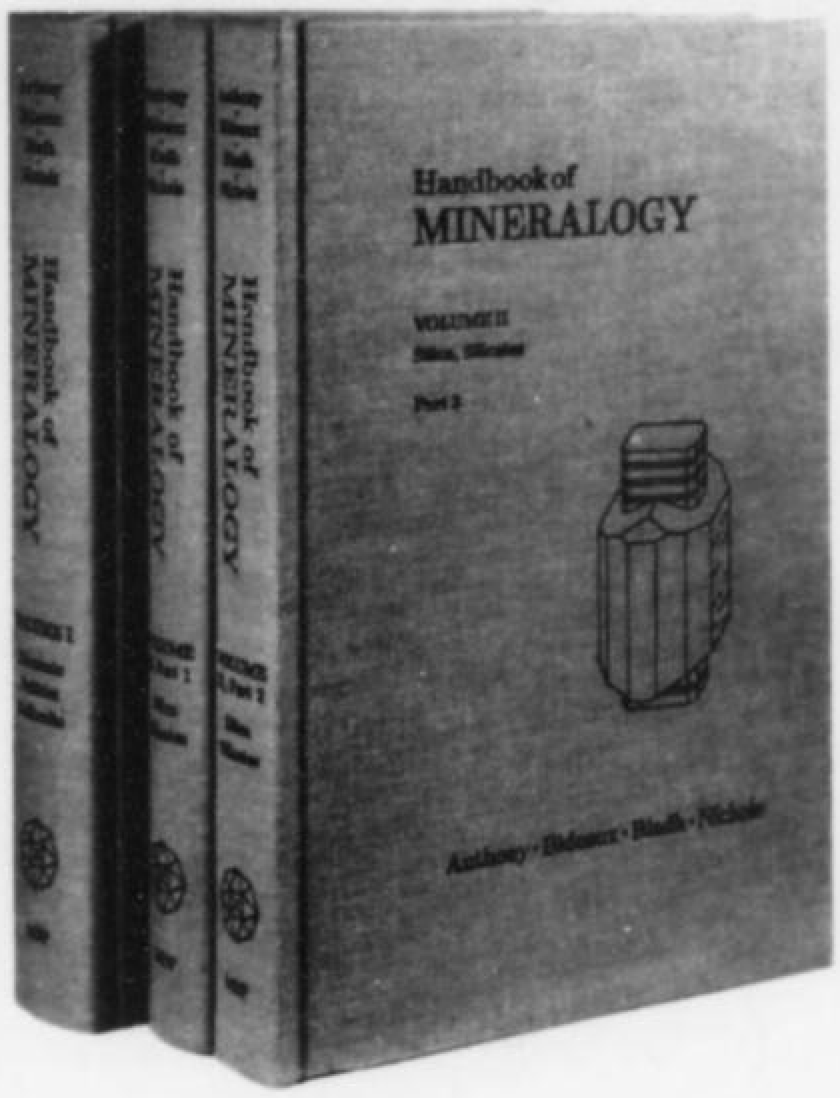

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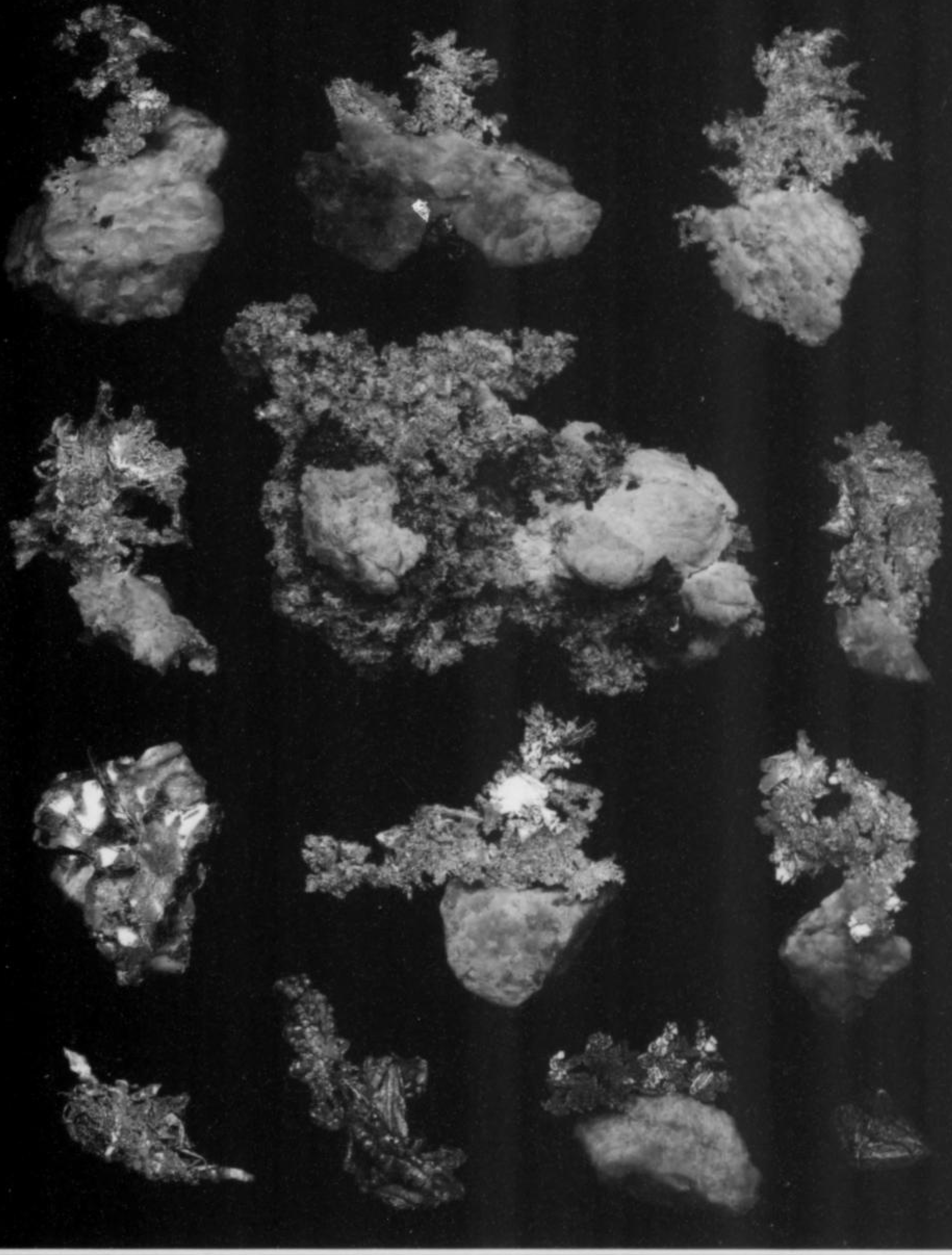

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