Gems & Gemology





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Part 2

The Origins of Color In Gems and Minerals

By K. NASSAU, Ph.D.
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F. Idiochromatic Transition Metal Caused Color

In Part 1 of this series, an outline was given of some of the crystal field characteristics. It was noted how absorptions leading to color orginate in unpaired electrons on transition metal ions, and how the specific color depends on the environment around the transition metal ion, i.e., on the strength of the bonding and on the symmetry of the environment. The reason transition metals are so dominantly involved in causing color is that these are the elements that have unpaired electrons, and so have the ability to cause color. The most common transition metal, iron, constitutes 5% of the earth's crust.

An additional factor which can be important is variable valence. Thus copper in its divalent state Cu²⁺ (with

two electrons used in chemical bonding) has one unpaired electron and forms many colored cupric compounds; in the monovalent state, Cu⁺ (where only one electron is used in bonding), all electrons are paired off and the cuprous salts have no color. In the case of iron both divalent ferrous Fe²⁺ and trivalent ferric Fe³⁺ have unpaired electrons and both can cause color.

In Table 2 are given gem material colors caused by a variety of transition metals: since these are all idiochromatic ("self-colored") materials, the transition metal is an essential ingredient and cannot be omitted without both losing the color and changing the nature of the compound. Additional impurities acting in an allochromatic capacity (see the next section) can of course darken or

modify any of these colors, but the basic absorptions of the idiochromatic transition metal will always remain present as a component of the absorption spectrum.

The chemical composition of these compounds can be located in compilations such as M.H. Hey, "Chemical Index of Minerals," British Museum, London, 2nd Ed. 1962 (Appendix 1963); "Encyclopedia of Minerals" by W.L. Roberts, G.R. Rapp, Jr. and J. Weber, Van Nostrand, 1974; or any of the more recent "Dana" books.

Some caution must be used in assigning the colors to a specific transition element known to be present in idiochromatic materials, since some, such as copper in the cuprous state or iron in the ferrous state, can be colorless or close to it, and the color may really be caused by another impurity. A particiularly good example of this is the mineral vivianite $Fe_3(PO_4)$ • 8H₂0. This contains ferrous iron (Fe2+), and can be completely colorless when freshly mined but darkens

TABLE 2

Some Idiochromatic Colorations by Transition Metal Components in Gem Materials

Chromium: Uvarovite (green)

Manganese: Rhodochrosite, rhodo-

nite (pink), spessartite

(orange)

Iron: Almandite (red), lazulite (blue), peridot

(green)

Copper: Azurite, chrysocolla, turquoise (blue), diop-

tase (green)

rapidly to green, blue, and bluish-black due to the formation of some ferric iron (Fe³⁺) by air oxidation (see Section I below).

G. Allochromatic Color Caused by **Transition Metal Impurities**

The touchstone for allochromatic ("other-colored") materials is that they also occur in forms which show much less, or even no color. For example, blue, green, yellow, and pink sapphire to red ruby also occur as colorless sapphire (all Al₂O₃) and blue and green aquamarine, pink and yellow beryl, and green emerald also occur as colorless goshenite beryl (all $Be_3Al_2Si_6O_{18}$). This test is, of course, not foolproof, since some of the color-center and charge transfer materials discussed in the next two sections also occur in colorless form. as do the doped semiconductors of Section M.

In Table 3A are listed some wellestablished allochromatic gem and mineral colorations. It will be noted that a wide variety of colors can be produced by chromium or iron: this varies with the valence state, the strength of the bonding, and the symmetry of the crystal field as previously discussed.

It is of interest that emerald can be colored green either by chromium or by vanadium. Chromium by itself produces a very satisfactory emerald shade of green, which is probably not true of vanadium by itself, but nevertheless much naturally occurring chromium emerald also contains some vanadium. The vanadium may well be in unsuspected dominance in

TABLE 3

A. Allochromatic Coloration by Transition Metal Impurities

Chromium: Emerald, grossularite, hiddenite, Cr-jade, Cr-tourmaline (green);

ruby, spinel, topaz (red); alexandrite (red-green).

Iron: Aquamarine, tourmaline (blue, green); citrine (yellow); "greened

amethyst'' (green); jade (green-yellow-brown).

Manganese: Morganite, spodumene (pink). Nickel: Chrysoprase, Ni-opal (green).

Vanadium: V-Emerald (green); "alexandrite-colored" sapphire (natural and

synthetic) (green-red).

B. Same as A with Daylight Fluorescence Added

Chromium: Ruby (red color plus red fluorescence); emerald (green color plus

weak red fluorescence).

Cerium: Fluorite (bluish).

emeralds where the chromium concentration is too low to explain the depth of the coloration by itself.

An additional subtlety occurs with some chromium compounds which fluoresce red even with daylight illumination. This adds to the glowing red color in ruby and adds character to the green of emerald. Note that the red fluorescence can be "quenched" (extinguished) by impurities, e.g., by the iron present in many natural emeralds. Another case of daylight fluorescence listed in *Table 3B* is the bluish glow seen in some cerium-containing fluorite.

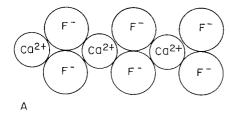
H. Color Centers

Not only can an unpaired electron cause color in its transitions between energy levels on a transition metal ion, but the same can occur in a color center. This is usually a "defect" in the crystal, which is able to "trap" an electron or a hole. By a "hole" is meant the absence of one electron; if

this is missing from a place usually occupied by a pair of electrons then it leaves behind an unpaired electron which can cause color. Some examples will clarify these concepts.

A well-known color center is the deep purple color in fluorite. There are several color centers that can form in fluorite, but the simplest is the "F-center". Fluorite consists of divalent calcium ions Ca²⁺ and monovalent fluoride ions F⁻in the ratio of two to one as shown schematically in *Figure 5a*. Because there are two F⁻for every Ca²⁺, the electric charges are balanced and the crystal is electrically neutral, as it must always be.

It is possible at times for an occasional fluorine ion F⁻ to be missing from the fluorite crystal as shown in *Figure 5b*. For the crystal to remain electrically neutral an electron can occupy the space left by the missing fluorine ion, i.e., it is "trapped" there and cannot escape except under special circumstances.



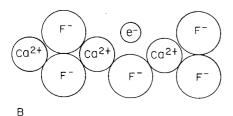


Figure 5. Fluorite (calcium fluoride) structure: a) normal; b) containing an "F center" where a fluorine ion is replaced by an electron.

Now this trapped unpaired electron can have energy levels just as described in Sections B and C for an unpaired electron on an ion. It can cause color when light is absorbed to produce transitions between these energy levels, and also fluorescence if the conditions are appropriate.

Color centers in fluorite can be formed during growth, by heating the crystal in calcium vapor (which results in the out-diffusion of some fluorine), by the application of an electric field (which can also remove fluorine), or by irradiation, e.g., with gamma rays or x-rays.

In the case of smoky quartz there is a "hole" color center. Here it is necessary to have aluminum ions, Al³⁺, replacing silicon ions, Si⁴⁺, in the

quartz crystal (SiO₂). Some alkali (e.g., Na[†]) or a hydrogen ion (H[†]) is near each Al³⁺ to maintain a neutral crystal. Most natural quartz contains some aluminum impurity in this way, but by itself this does not cause any color since there are no unpaired electrons.

If quartz containing such an impurity arrangement is irradiated with x-rays, gamma rays, neutrons, etc. or by being exposed to some radio-active materials producing such radiation, this can result in one of the paired electrons being knocked out of its

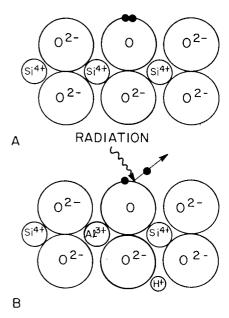


Figure 6. Quartz (silicon dioxide) structure: a) normal; b) containing an Al³⁺ in place of a Si⁴⁺ and an additional H⁺ to retain neutrality. Radiation ejects one of a pair of electrons from an oxygen ion leaving the unpaired electron "hole" color center of smoky quartz.

position on any oxygen ion, leaving an unpaired electron as shown in *Figure 6b*. Since an electron is missing, this defect center is called a hole, and here again there are energy levels and lightabsorbing transitions which result in the color of smoky quartz. This process does not occur in quartz without the necessary defect (*Figure 6a*).

The displaced electron in smoky quartz becomes trapped elsewhere in the quartz crystal without causing any additional light absorption. If, however, the smoky quartz is heated (say to 400°C), these displaced electrons can move around and return to occupy their original positions. This destroys the "holes," all electrons are now paired again, and the smoky quartz again becomes colorless.

The smoky color center formed in suitable aluminum-containing quartz during geologic periods of low level irradiation from nearby radioactive materials, and that caused by irradiation, say in a gamma cell in a few hours, are identical. After bleaching by heating, the color can again be restored by a new irradiation treatment.

Some color centers may be formed by special conditions during growth without the need for irradiation.

Somewhat similar is the case of amethyst. The presence of iron in quartz can produce a yellow color (citrine) or a green color depending on conditions. Some of this material (but not all) can yield the lilac color of amethyst on irradiation; heating returns amethyst to either yellow citrine or to the "greened" amethyst. Even though iron, a transition metal ion, is involved in the coloration of amethyst, this should not be considered an allochromatic color due to the iron impurity; the iron merely provides the defect which permits the special amethyst color center to occur.

Other color centers are listed in Table 4. It will be noted that some of these are quite stable to light exposure, while others fade rapidly. Also some of these color centers need energetic radiation for their formation (e.g., smoky quartz), while other materials can be colored even by ultraviolet irradiation (e.g., some "photochromic" hackmanite). These

TABLE 4 Color Centers

Essentially Stable to Light Exposure: Fluorite (purple), smoky quartz (brown to black), irradiated diamond (green, yellow, brown, black, blue).

Rapidly Fading on Light Exposure: Maxixe-type beryl (intense blue), irradiated topaz (brown), irradiated sapphire (yellow), U.V. exposed purple hackmanite (red).

Involving Transition Metal Ions, Stable to Light Exposure: Amethyst.

Other Colors Probably due to Color Centers: Halite (blue and yellow), pleochroic haloes in fluorite, zircon (brown), calcite (some yellow), celestite (blue), barite (blue), topaz (some brown), sapphire (some yellow), etc., etc.

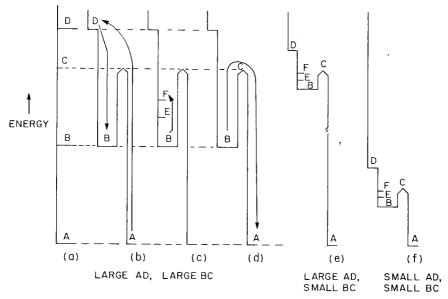


Figure 7. Energy level schemes showing energy barriers involved in color centers, phosphorescence, and thermoluminescence.

variations can be readily understood from the energy level schemes of *Figure 7*.

In Figure 7a is shown schematically what might be the energy level diagram of smoky quartz. Starting with colorless quartz in the ground state A, irradiation takes the system up to state D as in Figure 7b, and the system now drops down to state B with the release of some heat or light (the quartz of course must contain the substitutional aluminum precursor or the smoky color center cannot form). This is now a "trapped" state, confined by the energy "barrier" C.

As shown in *Figure 7c*, the smoky quartz of state B can now absorb light because there are absorption energy

levels such as E and F, the result of such absorptions being the smoky color. Note, however, that if sufficiently energetic excitation is supplied, e.g., by heating to 400°C, the barrier C can be surmounted and the quartz returns to the colorless ground state as in Figure 7d.

In the illustrations of Figures 7a to 7d the energy needed to form the color center (i.e., A to D) is large, and the energy to bleach or decolor the color center (i.e., B to C) is also large. Smoky quartz is a typical example, as is amethyst.

If the formation energy is large, but the energy barrier for bleaching is small (B to C), this produces the scheme of *Figure 7e*. An example is some irradiated brown topaz which fades rapidly after a few days' or weeks' exposure to daylight (which contains light energetic enough to surmount the barrier BC) or in a short time at temperatures as low as 200°C. Another example is Maxixe-type beryl which bleaches at temperatures as low as 100°C and in a 2°w days in daylight.

If the formation and the bleaching energies are both low, the diagram of Figure 7f is appropriate. Here, even short-wave ultraviolet light (about 5 eV) is energetic enough (AD is small) to produce the color center, which bleaches very easilv. energetic radiation than ultraviolet, e.g., gamma rays (from 100 eV to over 1 million eV) can still be used for the coloration, but the color nevertheless remains fleeting. An example is photochromic hackmanite which turns red ultraviolet irradiation bleaches rapidly in daylight and slowly even in the dark (the thermal excitation at room temperature is large enough to permit slow leakage over the very low barrier BC in this instance).

It might be mentioned that phosphorescence is a case similar to the last one, where the drop from C back to the ground state emits light, and room temperature is enough to permit rapid leakage across the barrier. Phosphorescence is shown by some fluorite, calcite and diamonds. Fluorescence and phosphorescence "lifetimes" grade into each other; rapid phosphorescence with a very small barrier would appear to be merely fluorescence.

If trap BC is a little deeper, how-

ever, the result is thermoluminescence which occurs when such a material is heated to permit the system to escape from the trap and produce the fluorescence at a fairly well defined temperature. Some calcite and much fluorite show thermoluminescence.

Phosphorescence and thermoluminescence, just as fluorescence, are not confined to color centers — but the energy level diagrams would nevertheless appear similar wherever such phenomena occur.

Positive proof that a specific color is due to a color center may require years of investigation using optical spectroscopy, paramagnetic resonance, and other scientific analyses. In the absence of such detailed work the fading of the color on exposure to light or heat and recovery of the color with irradiation remains the touchstone of the color center.

For some color center studies on Maxixe-type beryl, etc., see K. Nassau and D.L. Wood, *Lapidary Journal 27*, 1032 (Oct. 1973), and K. Nassau, *Lapidary Journal 28*, 20 (April 1974) and 1064 (Oct. 1974).

I. Molecular Orbital Caused Color

In the crystal field approach discussed in Sections B through H, the unpaired electrons remain localized on a single ion or at a defect. Where unpaired electrons are in orbits around two or more ions in a predominantly ionic type structure, or on two or more atoms in predominantly covalently bonded organic molecules, then "molecular orbital theory" is the appropriate treatment. The results of such a treatment nevertheless resemble

TABLE 5

Molecular Orbital Type Coloration

Α. Mixed Valence Charge Transfer Colors

Fe²⁺ — Ti⁴⁺: Sapphire, benitoite (blue)
Fe²⁺ — Fe³⁺: Magnetite, ilmenite (black), vivianite (blue-black).
Ti³⁺ — Ti⁴⁺: Rutile (blue to black).
Mn²⁺ — Mn³⁺: Hausmannite, braunite (brown to black).
Mn²⁺ — Mn⁴⁺: Manganite, bixbyite (black).
Cu¹ — Cu²⁺: Covellite (dark blue).
V⁴⁺ — V⁵⁺: Vanoxite (black).

B. Metal — Nonmetal Charge Transfer

Pyrite, marcasite, cobaltite, smaltite, sylvanite, etc. (all metallic in appearance).

Electrons Not on Metal Ions C.

a) S₂: Lapis lazuli — Lazurite (blue).

b) π electrons: Graphite (black).

c) Organic Pigments: Amber, ivory, tortoise shell (brown), coral (red, black); pearl (pink, greenish, blue-black); bitumen, asphalt, coal, etc. (brown to black); dyed materials.

the results of crystal field theory in that it also yields energy levels and selection rules which control the absorption of light and therefore the color. Several different types of molecular-orbital caused color can be distinguished; the three types listed in Table 5 are of significance in gems and minerals and are here briefly discussed.

There are several types of charge transfer mechanisms. A type of charge transfer of major significance in minerals occurs between two different transition element ions, or between two ions of the same element but having different valence states. Consider a divalent iron ion and a tetravalent titanium ion occupying adjacent aluminum sites in blue sapphire. If we take an electron from the divalent iron it becomes trivalent; if we give this electron to the tetravelent titanium, it also becomes trivalent:

$$Fe^{2+} + Ti^{4+} \rightarrow Fe^{3+} + Ti^{3+}$$

The reverse process returns the system to the original state:

$$Fe^{3+} + Ti^{3+} \rightarrow Fe^{2+} + Ti^{4+}$$

In magnetite the same can happen with only one element, namely iron. Magnetite is Fe₃O₄ or FeO • Fe₂O₃; it thus contains both Fe2+ and Fe3+. Let us use subscripts A and B to identify two specific iron ions. By moving one electron from the Fe_{Λ}^{2+} to the $Fe_{\mathbf{R}}^{3+}$, the two valence states become reversed:

$$Fe_{A}^{2+} + Fe_{B}^{3+} \rightarrow Fe_{A}^{3+} + Fe_{B}^{2+}$$

The reverse reaction restores the original situation:

$$Fe_A^{3+} + Fe_B^{2+} \rightarrow Fe_A^{2+} + Fe_B^{3+}$$

Now a certain amount of energy is involved in the hopping of the electron from one ion to another, and therefore light can be absorbed by this process. This usually leads to deep blue to

black colors such as in the blue sapphire colored by Fe²⁺ plus Ti⁴⁺ and in the black magnetite containing both Fe²⁺ and Fe³⁺. The latter process is also involved in the deep blue-black of the oxidized vivianite mentioned in the previous section. Examples are given in *Table 3A* and probably the majority of deep blue to black materials are colored by this mechanism. Detailed work would be needed on most of these very dark compounds to confirm that this is in fact the mechanism responsible for their color.

This type of charge transfer has been discussed by M.B. Robin and P. Day in "Mixed Valence Chemistry – A Survey and Classification" which appeared in "Advances in Inorganic Chemistry and Radiochemistry", Vol. 10, Academic Press, 1970, p. 247.

Another type of charge transfer involves a metal ion as well as a non-metal ion. An example is pyrite, FeS, and other metallic appearing sulfides, selenides, etc., such as those listed in *Table 5B*. In these compounds there is movement of an electron from the sulfur to the metal and back again, resulting in light absorption.

Some compounds, such as lazurite $(Na,Ca)_8$ $(Al, Si)_{12}$ O_{24} (S_2, SO_4) , which is the blue component of lapis lazuli, contain pairs of sulfur ions held together by electrons in orbit about both ions; such a grouping is written as S_2 . Here the electrons holding the sulfurs together have excited states and absorb light to produce the deep blue color. In graphite, which is one of the forms of elemental carbon, there are sheets of connected six-membered rings and some of the electrons, the

" π -electrons," are essentially free to move around the whole crystal of graphite in the plane of the rings. This produces electrical conductivity and almost complete absorption of light, hence the black color (see also Section K in Part 3).

Lastly there are a number of gem and mineral substances such as those listed in Table 5C which are colored by dye-like organic compounds of biological origin such as the conchiolin of pearl, coral, amber, and so on. Some of the dves used to color agate. turquoise, pearls, spinel doublets, etc., fall into this group (others being inorganic compounds of the idiochromatic type). Here also color originates in transitions involving electrons in organic molecules and is explained by the molecular orbital theory of dyes.

Further details on this subject may be found in "Color and the Electronic States of Organic Molecules" by S.F. Mason in *The Chemistry of Synthetic Dyes*, K. Venkataraman, Editor, Academic Press, 1970, p. 169.

J. Treatments that Change the Color of Minerals

With the background of the various causes of color discussed in the previous sections, it is possible to understand many of the color changes produced by treatments used on minerals and particularly on gem stones.

Heating can have a variety of effects. In some cases it destroys color centers, thus completely removing the color of smoky quartz, brown topaz,

and Maxixe-type beryl (in some brown topaz and all Maxixe-type beryl even exposure to light removes the color). In other cases, the loss of the color center leaves another color, as in amethyst turned either citrine color or "greened" by heating, depending on the type of the material. These changes can be reversed by irradiation as described in Section H above.

Another result of heating can be a change in valence. Thus yellowish carnelian, tiger's-eye, and some other iron-containing materials can be turned red by heating, the change being Fe²⁺ to Fe³⁺. In beryl the reverse appears to happen: golden beryl turns colorless and green aquamarine turns blue on heating due to the change Fe³⁺ to Fe²⁺ in a specific site, and this change can be reversed by irradiation. The blue color of aquamarine is due to Fe²⁺ in a different site in the crystal and this color is not affected by the heating.

Irradiation, performed most efficiently with gamma rays, produces the many color centers listed in *Table*

4. The stability of these colors depends on the depth of the trap as discussed in Section H. When pearls are darkened by irradiation the change is probably due to a chemical change in some of the conchiolin, not too different from a gentle charring process.

Some diamonds can be colored green to black by irradiation due to the formation of a color center. This is quite different from the green color found in some natural diamonds which is impurity caused (see Section M in Part 3); spectroscopic examination can distinguish the two types of green. Heating can convert this irradiated green into yellow or brown. Some diamonds can be colored blue by irradiation with electrons, again a color center. This is also different from the natural blue diamond in that it does not conduct electricity (see Section M). Very rarely a pink color has been obtained in diamond by irradiation.

Part 3 will appear in the next issue.

Developments and Highlights at GIA's Lab in New York

By ROBERT CROWNINGSHIELD

Heavy Carvings

As we have mentioned many times in this column, carved items not used in jewelry tax gem testing equipment, and we find the chore often quite time consuming. We continue to offer the service, however, in spite of the fact that there seems to be no limit to the requests. In *Figure 1* the writer and staff gemologist Dennis Maun search for a polished area and take a refractive index on the ear of a 180-pound carved horse, which proved to be nephrite.

Selective Dyeing of Calcite

In Figure 2 we see a hololith calcite bracelet with areas of an attractive green color produced by selective dyeing. Although we have illustrated this before, this piece was the most convincing as the color of green was not so sharp as we have noted before. We have recently seen similar calcite bracelets dyed with areas of brown.

Organics

Figure 3 illustrates an inexpensive though exotic hololith ring with white and yellow metal inset ornamentation.



Figure 1



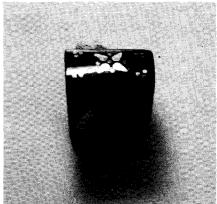
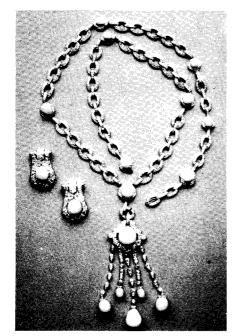


Figure 2 Figure 3



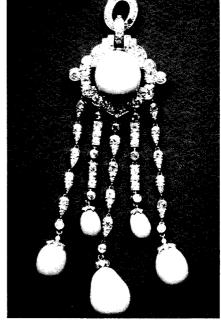


Figure 4 Figure 5

From our limited tests we concluded that it was probably water buffalo horn. Supposedly, many such articles are made in Thailand where the animal is plentiful.

Not so plentiful is another organic material which we all too rarely see. This is the lovely pink "pearl" found in the conch. Formerly, it must have been more common and particularly appreciated in France. We recently identified 15 beautiful matched pink pearls in a heavy platinum and old mine diamond chain necklace with two in similar clips, as seen in *Figures 14* and 15. The ensemble looked lovely when modeled on a aquamarine-colored gown.

Damage or Shattering Experiences

In Figure 16 we see all that remains of a once-magnificent blue zoisite. It had been worn in a ring for several years but was returned to the manufacturer for some minor tightening. Unfortunately, the workman who handled the job was unaware of the extreme sensitivity of Tanzanite to temperature change with the result that in the process somehow the stone was completely shattered. How completely was brought home to the writer when lapidaries pointed out that it would be impossible to salvage even a 1/2 carat stone from what was once more than 15 carats in weight. Again, it seems prudent to warn anyone who handles colored stones that Tanzanite along with the quartz gems, garnets and peridot are bad actors when it comes to rapid temperature change.

Peridot can be a bad actor in an-



Figure 6

other way too. As we see in Figure 17, all the small peridots in a lovely diamond, amethyst, green tourmaline, and peridot ring have been etched by the solutions used to remove the residue from the polishing operation. We did not learn the nature of the solution but assume that it was an acid. It was particularly unfortunate that this unhappy property of peridot could not



Figure 7

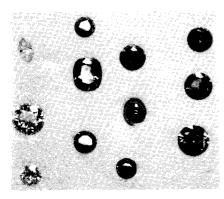


Figure 8

have been learned from a single ring instead of a whole line.

Forgotten But Not Gone — And Damaged Too

We sometimes forget that shortly after World War II the hottest imita-

tion of diamond was synthetic rutile. We rarely see it today. Rarer still are examples of synthetic rutile in other than the pale yellow color. Figure 8 illustrates in black and white this material that ranges in color from very light to dark yellow, green, blue, and orange. Forgotten too is the fact that this material, along with the heatsensitive stones mentioned above, has a tendency to fracture with rapid temperature change. This sad fact was learned by a jeweler who called to ask help in identifying a deep red-orange stone which had been damaged during repair of a ring setting. See Figures 9 and 10. In the Laboratory, the initial impression was that the stone was a fine zircon. Aside from the obvious fracture, no inclusions were present and no typical absorption spectrum

Figure 10

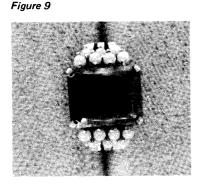






Figure 11

was observed. However, the extreme doubling due to birefringence (Figure II) served to identify it as an orange synthetic rutile and one that will be difficult to replace, it would seem. The photograph shows the square culet clearly doubled.

The devilish combination of thin girdle and thin crown angles worked its inevitable damage on a round brilliant-cut diamond shown in *Figure* 12.

A Gem Rarity

We wish to thank New York gem dealer Samuel Goldowski for the gift of a completely transparent, very dark blue lazulite weighing 0.48 ct. It is shown in *Figure 13*. It is highly dichroic, or rather trichroic, with a pure saturated blue, greenish-blue, and nearly colorless as the colors. The refractive indices are 1.616 – 1.645 for the extremes (alpha and gamma) with beta approximately 1.633, thus making the stone biaxial negative. The absorption spectrum (*Figure 14*) resembles that of turquoise, although with greater absorption in the red.

Imposturing Threesome

This brooch shown in *Figure 15* contains numerous natural sapphires, diamonds, and what appear to be



Figure 12.



Figure 13

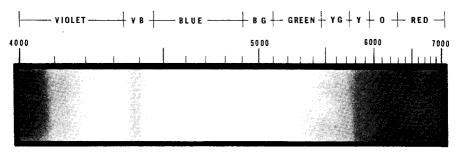


Figure 14. Dark Blue Lazulite (0.48 ct.).

good-sized, rather sleepy rubies. Magnification reveals that the rubies are quench-crackled synthetics which we have seldom seen mounted, and then only as single stones. The natural-appearing cracks produced by quench-crackling may be seen in two of the stones in *Figure 16*.

A Real Diamond Rarity

Black and white cannot begin to do justice to a fantastic true yellow diamond of nearly 6.50 cts. shown in Figure 17. Some time ago a cutter brought for testing two large yellow crystals, since it has been known that rough diamonds have been treated yellow by irradiation and an innocent cutter is duped into thinking he has a natural stone. At first glance, one of the crystals certainly appeared to be a treated color having the intense color we noted in the "Deepdene," which is perhaps the most famous treated diamond in existence. The other crystal, from which the heart-shaped stone illustrated here was cut, had a very intense slightly orangy-yellow color and showed absolutely no absorption bands in the spectroscope. Most socalled canary diamonds belong to the Cape series of yellow diamonds which owe their color to the presence of nitrogen. This type of intense yellow stone (usually only in melee sizes) belongs to a different class. They have been called "true canaries" by B. W. Anderson. Neither of these stones showed absorption bands, and the stone illustrated also showed no inclusions or blemishes beyond slight polish lines. All the more remarkable is the fact that the cutter was able to nearly match the stone with a colorless heart shape which had no flaws but showed whitish graining.

Flux-Grown Synthetic Rubies

The fact that both Gem Trade Laboratories of GIA have seen an in-

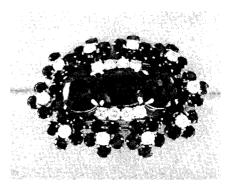


Figure 15



Figure 16



Figure 17

creasing number of flux-grown rubies since the last issue of Gems & Gemology suggests that serious jewelers and dealers must refresh their knowledge of these stones. Inasmuch as the new Kenya rubies may have wispy inclusions reminiscent of those in Chatham synthetic rubies particularly, it behooves everyone to be on guard. If the uncut crystals are being sold in the Orient, it is easy to see why serious mistakes can be made.

Acknowledgements

To Mr. Robert Schwager of International Cultured Pearls, Inc., New York, for a fine 5.09-carat black

diamond crystal. The firm is having a number of black diamond brilliants cut and plans to begin a promotion. The Laboratory has examined a number of the cut stones and finds them equal to those we have seen in the past. If the experience of lecturers who show specimens after their talks is any indication of potential sales, then black diamonds should be a successful item. When an audience is told that the lecturer has a black diamond to show among many other diamonds, it is the black that seems to capture the attention first.

To *Jerry A. Gewirtz*, Fir Lawn, New Jersey, for many colors of imitation stones which will be useful in classes.

Dunton Mine Tourmaline: An Analysis

By C.R. BEESLEY, G.G. GIA — New York Laboratory New York, New York

During this period of economic turmoil, complete with spiraling prices, dwindling supplies and increasing demands, it is reassuring to see new additions to the ranks of fine gem material. Actually it is a thrill under any conditions to witness the birth of a new gem or, as in the case of Maine tourmalines, the rebirth of an old mining locality.

Historically, Newry Mountain (Figure 1) has intermittently produced industrially important minerals and small amounts of gem tourmalines since the turn of the century. General Electric, Harvard University and various private collectors have periodically probed the Dunton Mine and attempted to relieve it of its hidden treasures.

It seems somewhat ironic that a nation as rich as the United States has contributed so little to the ranks of commercial gem materials. Despite this

lack of productivity, Maine has been one of the few areas of this country that has sporadically yielded gems of any consequence. However, in the fall of 1972, that non-productive record was shattered by a small group of amateur mineral collectors when they stumbled upon what may be one of the most important gem finds in America. The uniqueness of this particular rediscovery stems from the quality and quantity of the gem material being recovered. Maine tourmalines, once coveted by collectors as rarities of nature, have now become commercially available.

The significance of the reopening of the Dunton Gem Mine by Plumbago Mining Company will be its potential impact on the jewelry trade. Whether sufficient material exists to develop a lasting market is still uncertain. However, the quantity and quality of available material should insure the U.S. jeweler of the opportunity to develop

¹ See References for detailed historical and geological data.

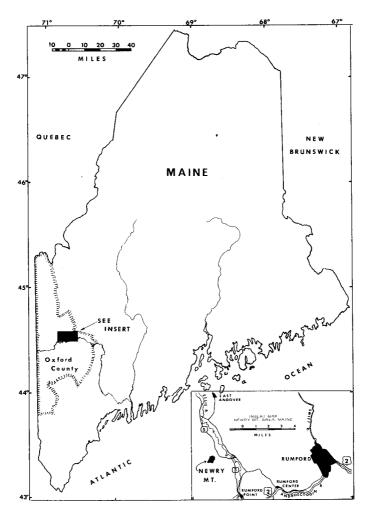


Figure 1. Location map of the Newry Mountain tourmaline deposits, Oxford County, Maine.

and promote this uniquely American product. Two of the most outstanding features of Maine tourmalines are the exceptional brilliance, possibly due to the presence of cesium, and the exquisite array of hues in which these gems occur. The colors range from green, yellow-green and greenish-blue at one end of the spectrum to pink

and purplish-red at the other. The colors do not occur with the same degree of frequency. To date, the purplish-red stones constitute the largest percentage of the available supply. The greens, greenish-blues and yellowish-greens, although fewer in number, are among the most exciting colors being produced. As is the case

with any gem material, color should be observed in a variety of lighting environments. There is a tendency for some of the purplish-red stones to exhibit a brownish color when examined in certain lighting conditions.

The clarity of the commercial supply ranges from stones that are free of inclusions when examined with the unaided eye to lightly (LI) and moderately (MI) included material. In the latter case these stones do not exhibit distracting or potentially damaging inclusions.

In addition to faceted stones ranging from calibrated sizes to rare museum quality gems in excess of 30 carats, a number of exquisite watermelon sections are available. These slices, consisting of a green rind and a purplish-red core, are an exciting addition to the repertoire of material available to the discriminating

designer. Equally dramatic is jewelry fabricated with combinations of green and pink faceted stones of similar tones.

Since part of the interest in this material may stem from its U.S. origin, it is important to examine those properties that are indicative of tourmaline from the Dunton Mine. Based on a cross-sectional analysis of Newry material (Table 1), it is apparent that very little variation exists between the refractive indices of Maine tourmalines and tourmalines from other localities. Typically, the refractive indices ranged from 1.62 to 1.64 and the specific gravity varied from 3.04 to 3.09. In general, increasing refractive indices and specific gravity were accompanied by a corresponding change in the depth of body color.

The most remarkable deviation from known tourmaline properties was observed during microscopic and ultra-

Table 1
Refractive Index Data for Newry Tourmaline

Color*			Most Common R.I.†		
			€	ω	
A.	Very light pink		1.620	1.639	
В.	Slightly brownish pink		1.620	1.640	
C.	Medium orangish pink		1.619	1.639	
D.	Slightly purplish pink		1.620	1.637	
E.	Intense purplish pink		1.620	1.636	
F.	Intense purplish red		1.619	1.635	
G.	Dark purplish red		1.620	1.634	
Н.	Very light yellowish green		1.621	1.638	
I.	Light yellowish green		1.620	1.636	
J.	Yellowish green		1.620	1.637	
K.	Very light bluish green		1.619	1.636	
L.	Light bluish green		1.620	1.638	
M.	Light blue-green		1.620	1.638	
N.	Medium blue-green		1.621	1.640	
O.	Dark blue		1.621	1.641	

^{*}Color determinations were based on examination of specimens in diffused south daylight (11:45 a.m.) on 23 May 1975.

[†]Refractive indices were determined with a G.I.A. Duplex II Refractometer and a G.I.A. Utility Lamp using a filter centered on 589.6 nm.

violet examination. Although ultraviolet fluorescence is not a standard test for tourmalines, the Newry material consistently displays a faint to moderate chalky blue reaction when examined in short wave ultraviolet. In order to ascertain if this reaction was unique to Newry material, Nafco Gems of New York City supplied a number of Brazilian and Mozambique tourmalines for a comparison study. With few exceptions, tourmalines from other locations exhibit a lack of ultraviolet fluorescence under both long and short wave radiation. All pertinent

ultraviolet reactions have been tabulated in *Table 2*.

The ultraviolet reaction can be altered during the heat treating process. Purplish-red stones that are heated to generate more desirable color result in a subsequent intensification of the bluish fluorescence. One test stone, which was unfortunately over heated, turned colorless and produced a strong blue fluorescence under short wave radiation. To date, the ultraviolet fluorescence of a natural colorless tourmaline has not been examined to determine if the fluorescence will equal the intensity of

Table 2

Analyses of Fluorescence in Tourmaline

LOCATION	COLOR	s w	LW
Newry, Maine	Very light pink (heat treated)	Strong blue	No reaction
	Brownish pink	Moderate chalky blue	No reaction
	Purplish red	Faint to moderate chalky blue	No reaction
	Green	Faint chalky blue	No reaction
	Colorless (heat treated)	Strong to very strong blue	No reaction
Brazil	Brownish pink	No reaction to faint chalky blue	No reaction
	Purplish pink	Very faint blue	No reaction
	Red	No reaction	No reaction
	Dark purplish red	No reaction	No reaction
Mozambique	Brownish pink	No reaction	No reaction
	Light pink	No reaction to very faint chalky blue	No reaction
	Brownish purple	Very faint blue	No reaction

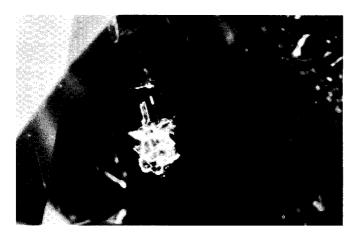


Figure 2

the heated materials. The collector would be well advised to test the fluorescence of any anticipated purchases prior to adding "rare" colorless tourmalines to his collection.

Without question, the examination of inclusions produced the most interesting observations (Figures 2, 3 and 4). The irregular module-like structure of a solid phase of unknown identity was encountered in a number of samples (Figure 2). Although we most

frequently associate three-phase inclusions with emeralds, a variation of the three-phase inclusion was encountered in most samples that were examined. In each case the configuration of cavities exhibited a typical tourmaline network, with the addition of an irregular solid phase deposited in the liquid-and-gas-filled framework (Figure 3). The most unusual, but least encountered inclusions were patches of fine needles yielding a pattern



Figure 3

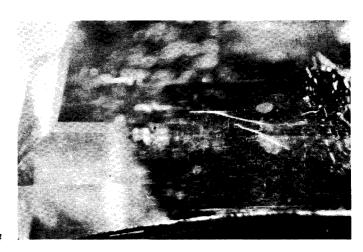


Figure 4

reminiscent of graphic granite or Egyptian hieroglyphics (Figure 4).

In the final analysis, the relationship of dollar value to country of origin should be one of academic interest. Beauty, in conjunction with the other physical attributes that contribute to a gem's desirability, should be the prime consideration in establishing value. As the international supply of gems continues to dwindle, the plight of the gem miner becomes even more difficult. The quest for gems is essentially a business of chance, devoid for the most part of deliberate, calculated and well-executed recovery operations.

Philosophically, the account of the rebirth of the Dunton Mine typifies colored stone mining operations throughout the world. When the last mining group discontinued its operations at Newry, they stopped just inches away from the most spectacular tourmaline deposit in Maine's history.

However, that element of chance has always been the adrenalin of the gem business.

Acknowledgments

The Plumbago Mining Company has made available to the Gemological Institute of America their Maine facilities as an extension of our New York Resident Class Training Program. Our thanks to Mr. Dean McCrillis and Mr. Dale Sweatt of Plumbago Mining and to Mr. Roland Naftule of Nafco Gems for their support and cooperation.

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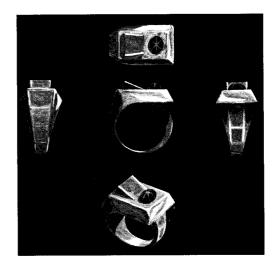
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Winner of Schuetz Design Contest Announced



Winner of the 1975 annual George A. Schuetz Memorial Fund Jewelry Design Contest is William Shoup of Tampa, Florida, who is affiliated with Sapphire Blue & Opals, Milpitas, California.

Mr. Shoup's design, shown here, is a ring made of a yellow gold ingot stretched and piercing itself, set with jade inserts and one golden-brown star sapphire oval cabochon. We congratulate him on his fine design and excellent rendering, and we want to thank all the other entrants for taking part in the contest.

Members of this year's Panel of Judges were J.B. Streeter of the GIA Staff in Los Angeles; Mrs. Sopha Albright, a jewelry designer in Los Angeles; Arthur Gleim, Gleim the Jeweler, Palo Alto, California; and Robert Spratford, C.A. Kiger Co., Kansas City, Missouri.

This contest was established in memory of George A. Schuetz, Sr., former president of Larter & Sons, Newark, New Jersey. Charles E. Butler, of Shreve, Crump & Low, Boston, Massachusetts; James B. White, of Jeweler Security Alliance, New York, New York; Arnold A. Schiffman, of Schiffman's Inc., Greensboro, North Carolina; Leo J. Dolan, of Diesinger & Dolan, Ardmore, Pennsylvania; and Ralph W. Landis, of Landis Jewelers, Camp Hill, Pennsylvania, are Administrators of the Schuetz Memorial Fund.

Any jeweler, jewelry designer, or aspiring jeweler or designer may enter the contest. Entries must be designs for items of men's jewelry (i.e., rings, belt buckles, cuff links, tie tacks, or other items suitable for wear by men), and they must be in the form of wax models or renderings; photographs or actual pieces are not acceptable. The \$300 prize may be used for any jewelry-related training at an institution of the winner's choosing.

Details on next year's Schuetz Design Contest will be available this fall from GIA in Los Angeles.

- Sue Adams

Developments and Highlights at GIA's Lab in Los Angeles

By RICHARD T. LIDDICOAT, JR.

Strange Opal

A jeweler had sold what appeared to her to be an Australian white opal to a woman who brought it back a year later. The appearance was transformed. It was now quite translucent near the surface with a very large white nontransparent core in the center and with lighter off-white patches of nontransparent white or off-white here and there throughout the stone.

After we had immersed it in water for several days, all of the patches disappeared and the white core had shrunk noticeably. The surface areas were all light brown and transparent. When we immersed it later in hot tap water, even the central white core disappeared and it became almost transparent brown. When immersed, some vague faint play of color could be seen.

The only explanation that made sense to us was that the opal was one of the very porous varieties of Mexican opal that absorbed a great deal of water. Possibly if the opal had been gently heated in a dry oven, the moisture would have been driven off, and the stone would have returned to a opaque white opal or semitranslucent opal that would resemble the Australian type.

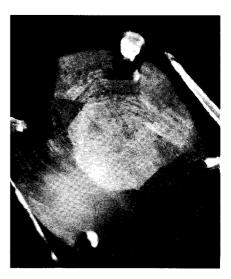


Figure 1.

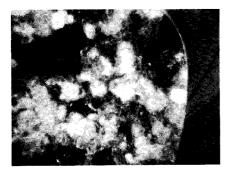


Figure 2.



Figure 3.

Damage to a Montana Sapphire

A jeweler sent us a blue Montana sapphire that was totally without polish. It is shown in *Figure 1*. The ring had been sold to a nurse who had worn it for about a year and noticed that it seemed to be showing less and less polish.

We could find no reason to account for the serious etching that had taken place. Had the ring been heated to very high temperatures, and covered with borax, we might have expected some such reaction, but to have this occur while apparently in the course of normal wear was unexplainable, as far as we were concerned.

Attractive Rock

A New York dealer sent us for testing a rather attractive cabochon with bright red and green grains. It is shown in reflected light in *Figure 2* and in transmitted light in *Figure 3*. The darker areas are green tourmaline and the lighter areas are ruby. There were minor amounts of other minerals included in this very unusual rock. We don't recall any combination involving ruby and green tourmaline in the past.

Some Notable Occurrences

When a blue sapphire is tested and shows no absorption line at 4500 Angstrom units, and is moderately to strongly fluorescent to short-wave ultraviolet (and negative to long-wave ultraviolet), the assumption would be that the sapphire is synthetic. No inclusions were visible. However, when the stone was immersed in methylene iodide, the color zoning showed it to be natural. This is one of the rare, almost iron-free blue sapphires that fluoresce similarly to synthetic sapphire.

Large Montana Sapphire

We were shown a 12.54-carat antique cushion-cut blue sapphire, believed by its owner to be the largest cut sapphire from Montana. It is an alluvial stone rather than being from the Yogo Gulch Mine. The largest sapphire reported from the Yogo Mine to our knowledge is only a fraction of that size.

Jadeite Spectrum

We were called upon to identify the glass with crystalline inclusions which

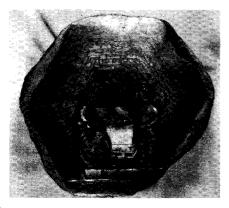






Figure 5

is sold as "metajade." We were surprised to encounter one that showed a spectrum that appeared identical to that of a naturally colored green jadeite.

Odd Fluorescence

We encountered a bangle bracelet of mottled brown and white nephrite jade. The refractive index was about 1.61 and the specific gravity near 3.00. X-ray powder diffraction proved that it was indeed nephrite. We were surprised by a medium orange fluorescence to long-wave ultraviolet.

Interesting Ruby in Zoisite Carvings

We received a huge carved object for identification, which proved to be a section of a semitranslucent ruby crystal in chrome zoisite. The carvings on the two sides of the flat crystal are shown in *Figures 4* and 5. The piece measured 5 1/2" x 6" x 3 1/3".

Emerald Inclusions

Charles Fryer was very much intrigued by the helical structure of

inclusions of a two-phase nature in emerald. This is very clearly shown in *Figure 6*.



Figure 6



Figure 7

Variscite

A rich green opaque stone was proved by x-ray diffraction to be variscite. We were surprised that the refractive index reading was approximately 1.60 instead of the usual reading encountered in variscite of near 1.56. The refractive index range is usually shown in tables at 1.56 to 1.59. Our experience has been that 1.56 is the usual reading for this massive material.

Oddity in Diamond Inclusion Reflection

An inclusion near a culet of a round brilliant-cut diamond can sometimes reflect in a large number of facets. We decided to photograph an inclusion that appeared four times as we were examining a diamond. It is seen in two adjoining facets across a facet junction and then doubled by reflecting from the table as the stone is viewed through the pavilion. This effect is seen in Figure 7.

Acknowledgements

We wish to express our sincere appreciation for the following gifts:

To the Association of Japan Gem Trust, Tokyo, Japan, for an interesting garnet rough for the reference collection.

To Barton Distributing, Inc., Billings, Montana, for a collection of faceted blue natural sapphires for our Gem Identification classes.

To Clyde Cooper, Cooper's Jewelry, Sycamore, Illinois, for five faceted natural emeralds for student test sets.

To GIA student *Elzora Eldridge*, Los Angeles, California, for a muchneeded diamond and sapphire ring which will be used in appraising mounted goods in the Diamond Course.

To Ernest Fordham, GIA student, Muskegon, Michigan, for a round brilliant-cut YAG for use in the Gem Identification class.

To Arthur Goldstein, GIA resident student, Canoga Park, California, for a large collection of broken cabochons of Eilat stone which will be put to good use in our resident stone testing sets.

To Ben Gordon, G.G. of Gordon Jewelry Corporation, Houston, Texas, for a large assortment of miscellaneous stones for resident course gem testing sets.

To *Hidenori Mochizuki*, G.G., Kofu, Japan, for a specimen of rough emerald crystals on a matrix from Colombia, which is now on exhibit in the student display case.

To *Joe Murphy*, G.G. and former GIA correspondence Diamond Instructor, Canoga Park, California, for a weight estimation chart to be used in our Colored Stone Course.

To Edward Oran, Gem International, Inc., Beverly Hills, California, for a lavender chalcedony from Taiwan, three actinolite cat's-eyes, and two amethyst oval brilliants for resident stone testing sets.

To *Dee Parsons*, cutter of rare minerals, Burbank, California, for a collection of rough willemite, beryllonite, rutile, euclase, anhydrite, cassiterite, diopside, cuprite, brookite, and fluorite, williamsite and quartz cabochons for class use.

To *David A. Patterson*, of Creative Crystals, Inc., Danville, California, for

a 1.73-carat synthetic alexandrite and several rough specimens of transparent green grossularite for the reference and research collection.

To *Dr. Frederick H. Pough*, eminent mineralogist and gem consultant, for numerous rough prehnite specimens for our Gem Identification classes and a red dravite crystal for research.

To Jules Sauer, Lapidação Amsterdam S.A., Rio de Janeiro, Brazil, for two turquoise cabochons from a new locality for the GIA reference collection.



Bibliophile Requests

GIA has a request from a bibliophile on gemology, who wants to buy a complete set of *The Gemmologist* and *Journal of Gemmology* for a reference library. Should you know of anyone having these journals and wishing to sell them, please contact: Mr. Joseph O. Gill, Jr., c/o S.S. DeYoung, Inc., 373 Washington Street, Boston, Massachusetts 02108.

Idar-Oberstein Announces 1975 Gem Design Competition

Idar-Oberstein, the world-renowned and oldest city continuously active in

the gem trade, announces the "German Jewels and Gems Award Idar-Oberstein 1975" contest for gem fashioning for ornamental purposes. The contest is open to all designers and craftsmen either professional or amateur. The entries are expected to be unconventional and creative; the deadline is August 18, 1975 (date of postmark). Details of the competition are available from:

Verband der Edelstein – Und Diamantindustrie E.V. D6580 Idar-Oberstein 2 Mainzer Strasse 34 Germany

Book Reviews

By ROBERT GAAL, Ph.D.

MINERALS OF THE WORLD, by Charles A. Sorrell. Published by Golden Press, New York, 1973. 280 pages. Hardbound price: \$5.95. Paperback: \$3.95

Charles A. Sorrell has written a small, handy, well-printed and clearly illustrated introduction to mineralogy which is very reasonably priced and deserving of wide circulation. though the price is particularly favorable, the fact that it is well put together, and the data appear correct, make it highly appealing for the student mineralogist and gemologist. The first 66 pages give a clear and concise overview of elementary classical mineralogy. It emphasizes chemical associations and crystal structures with a brief introduction to rocks and their geological relationships to major rock types. The use of acidic and basic for igneous rock classification is confusing, and felsic and mafic are preferred in modern usage. The remaining 191 pages of the text are a description of minerals based on chemical compositions according to the nonmetals or the radicals present. The most important and valuable feature of this systematic presentation is that the descriptive text and numerous color illustrations are on facing pages. This will provide the gem and mineral enthusiast with a unique "reference catalog," which helps simplify identification of each mineral and emphasizes the chemical relationship and crystal structure of minerals.

The author's stated purpose of the book was that it "was written to fill the gap between available popular books and the typical college textbook." Towards this end, the author has succeeded and possibly exceeded his goal, since the book could be used as a supplementary introductory text in mineralogy.

"Minerals of the World" is an excellent book for the amateur and serious student of gems and minerals since it is one of the very few books published containing so much information for the reasonable price of \$5.95. The paperback is also nice at almost half the price. This book is highly recommended for the serious gemologist.

WORKING WITH GEMSTONES, by V. A. Firsoff. Published by Arco Publishing Company, Inc., New York,

1974. Illustrated in black and white and color. 210 pages. Hardbound.

Price: \$8.95

"Working With Gemstones" is a generalized guide to many aspects of the lapidary art and craft. The book is divided into three parts; the first part discusses raw gem materials and is an introduction to gemology; the second and longest part deals with general lapidary in a simplified manner with some practical advice; the third part consists of miscellaneous information.

The sections on rocks and minerals and the optics of gems are a bit confusing and need close scrutiny, for example; jade is not "well known as an ornamental stone of volcanic origin"; "borazon is a gem comparable to and harder than diamond" - borazon is not a gem, it is an abrasive; silicon carbide's formula is SiC, not Si₃C; most scheelite fluoresces bright blue to bluish white in short-wave ultraviolet (2537 Å) becoming yellowish white with increasing molybdenum and does not "fluoresce lilac" as stated by the author; the description of polarization, asterism and pleochroism are fuzzy, e.g., "shifting colour or pleochroism which may be Englished as more colouredness." Numerous other inaccuracies can be quoted; however, one myth should be buried once and

for all; that is, the resurrection of the ghost of "Lodewyk van Berquem of Bruges, in Flanders," who in 1476, "found that diamond could be cut and polished with diamond." Faceted diamonds, i.e., pointed stones, were polished before 1476. The reader interested in the mythological character of van Berquem is directed to Godehard Lenzen's book "The History of Diamond Production and the Diamond Trade," Praeger Publishers, 1970, in which a painstaking study of source references indicated that van Berquem was a mythical character to whom was attributed the origin of diamond finishing!

One of the major beneficial features of the book appears to be the appendix with a list of world "suppliers of lapidary making equipment and rough gemstone material" and a bibliography in which one of the deans of gemology and the lapidary arts' name is misspelled, John Sinkana /sic/! The color plates are reasonably good reproductions which greatly enhance the book, even though their source is not acknowledged. The book may be of interest to the novice in the field; however, most of the information on the lapidary art can be found in greater detail in other books, such as those listed in the bibliography.

