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ABOUT THE COVER: Diamonds represent the vast majority of gems sold worldwide. Colored diamonds are among the most valuable commodities of modern times. This brooch, designed by A. Shinde, contains fine yellow, pink, and colorless diamonds, as well as an 8.00-ct natural-color green diamond as the center stone.

A pressing concern in the gem trade is the recent commercial introduction of gem-quality synthetic yellow diamonds manufactured in Russia. The lead article in this issue examines several of these Russian synthetic diamonds and provides criteria by which they can be separated from their natural counterparts.

Brooch courtesy of Harry Winston, Inc. Photo by Michael Oldford.

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LETTERS

UNUSUAL NEW ALMANDINE GARNETS FROM BRAZIL

At our laboratory in São Paulo, Brazil, we recently received 11 samples of a "burgundy"-color gem material, including one faceted stone (figure 1). Our source suspected that the isometric material was either spinel or garnet (probably pyrope-almandine), and reported that it came from an alluvial deposit in the new state of Tocantins, in the northern part of the country.

Our initial examination revealed an R.I. over the limits of the standard gemological refractometer, which eliminated spinel. Hydrostatic determination of specific gravity yielded values between 3.95 and 3.97, which exceed those of pyrope (3.58 to 3.61). At this point, almandine seemed the likely candidate, but a hardness test using quartz and topaz points revealed a Mohs hardness of almost 8, which is greater than the highest value we could find reported in the literature for garnet (7.5).

X-ray powder diffraction analysis confirmed the cubic crystalline structure and revealed a lattice parameter of $A_0 = 11.508$, which is less than that of almandine (11.530). Qualitative chemical analysis by energy dispersive X-ray fluorescence indicated the presence of (in order of decreasing concentration)—Si, Al, Fe, Ca, Mn, and Mg, with traces of Cu and Zn.

To obtain a quantitative chemical composition, we performed neutron activation analysis on four samples. We irradiated 20 mg of material in a nuclear reactor for one minute, and an additional 100 mg for eight hours. Gamma-ray emission from the decay of the resulting radioisotopes was measured over periods of time varying from two minutes to 25 days. The weight breakdown obtained includes 22% Fe and 1% Mn; Co, Sc, and Zn showed trace values between 11 and 133 ppm, and Cr between 20 and 40 ppm. The precise determination of Ca could not be obtained due to interference from adjacent energy peaks generated by Fe, Sc, and Mn in the lattice.

Figure 1. These garnets, reportedly from the Brazilian state of Tocantins, revealed some unusual gemological characteristics but were found to be primarily almandine in composition. Photo by Ivan Leão Sayeg Filho.

The optical absorption spectrum obtained from this material includes peaks at 692, 574, 503, 460, 422, 398, and 365 nm, and differs only slightly from that reported for almandine.

We concluded that the samples are a member of the almandine-spessartine continuous series and consist primarily of almandine. The Ca and Mg components are probably responsible for the anomalous characteristics observed, most notably the high hardness. We hope this information will help *Gems & Gemology* readers with their identification of other samples from this highly varied gem group, as well as inform them of yet another new gem garnet locality.

MARIA SILVIA GORSKI AND
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MORE ON DISCLOSURE

Irradiate, burn, oil, coat, diffuse, paint, fill, or dye it. Enhancing gemstones to improve or alter their appearance is a common trade practice. Yet while discovery that a ruby has been heat treated may not surprise a gemologist, the consumer who purchased the ruby might not have so passive a reaction.

As a paralegal and a gemologist, I agree with your editorial titled "Stability Disclosure: Are We Going Far Enough?" (Summer 1993, p. 79). It is time we end our professional myopic view of what is fair for the ultimate consumer and look at our actions from their perspective.

However, there was an error in the editorial. You stated that the Federal Trade Commission has addressed the issue of enhancement. The quotation was instead from the Jewelers Vigilance Committee's proposed changes to the FTC guidelines, and has not yet been adopted by the FTC. Booklets distributed by the FTC to jewelers do include a note that "considered to be inhibited" by the guidelines are: "The sale, or offering for sale, of any diamond or other natural precious or semi-precious stone which has been artificially colored or tinted ... without disclosure that such artificial coloring or tinting is not permanent if such is the fact." Nevertheless,

Continued on p. 305

THE GEMOLOGICAL PROPERTIES OF RUSSIAN GEM-QUALITY SYNTHETIC YELLOW DIAMONDS

By James E. Shigley, Emmanuel Fritsch, John I. Koivula, Nikolai V. Sobolev, Igor Y. Malinovsky, and Yuri N. Pal'yanov

A group of gem-quality synthetic diamonds, grown in Russia using the "BARS" apparatus and now being sold for jewelry use, is examined. Study of seven yellow (five faceted, 0.11–0.51 ct) to orangy or brownish yellow as-grown samples, and three yellow to greenish yellow samples (all faceted, 0.14–0.21 ct) reportedly treated by post-growth annealing at high pressure and temperature, revealed distinctive gemological properties. These include: color and luminescence zoning, metallic inclusions, graining, and sharp visible-range absorption bands (some seen with a handheld spectroscope).

ABOUT THE AUTHORS

Dr. Shigley is director, and Dr. Fritsch is manager, of GIA Research, Santa Monica, California. Mr. Koivula is chief research gemologist in the GIA Gem Trade Laboratory, Santa Monica. Dr. Sobolev is director of, and Dr. Malinovsky is senior researcher at, the Institute of Mineralogy and Petrography, Russian Academy of Sciences (Siberian Branch), Novosibirsk. Dr. Pal'yanov is head of the diamond growth laboratory at the Design and Technological Institute of Monocrystals, Russian Academy of Sciences (Siberian Branch).

Acknowledgments: At GIA Research, Mike Moon and Sam Muhlmeister assisted in spectroscopy. Bruce Lanzl, and others in the GIA Gem Trade Laboratory, performed clarity grading, while Karin Hurwit provided assistance with the color descriptions and observations of X-ray luminescence.

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Developments in diamond synthesis make it increasingly likely that gem-quality synthetic diamonds will soon become available in the jewelry marketplace. Only a few months ago, Chatham Created Gems of San Francisco, California, announced that they would soon begin marketing synthetic diamonds from Russia for jewelry use ("Beware: Russia sells man-made diamonds," 1993). The quantity will be limited at first (see Nassau, 1993, for an analysis of the potential for synthetic diamond production in Russia), and subsequent Chatham statements have indicated that the original announcement was probably premature (Costan, 1993). Nevertheless, positive identification of any synthetic diamond is essential to maintaining confidence and integrity in the gem diamond industry.

In late 1990, GIA researchers had their first opportunity to examine synthetic diamonds produced in Russia (Koivula and Kammerling, 1991). Then, in May of 1992, one of the authors (NVS) provided GIA Research with 10 Russian gem-quality synthetic diamonds for detailed study. Most recently, in November 1993, we obtained four Russian yellow synthetic diamonds directly from the Chatham company. Independent of this research, during the latter half of 1993, the GIA Gem Trade Laboratory identified several synthetic diamonds among stones submitted by members of the jewelry industry for standard "origin of color" reports. Some of the cut stones found to be synthetic also appeared to have been treated by irradiation and subsequent heating (see International Colored Gemstone Association [ICA] Lab Alert No. 74, dated 13 August 1993; Moses et al., 1993a, 1993b). Evidence (cited in these references) suggests that all of the synthetic diamonds seen in GIA GTL recently, both

Figure 1. These synthetic diamonds—two as-grown crystals (0.78 and 0.88 ct), three as-grown faceted stones (0.18–0.51 ct), and two faceted stones treated at high pressure and temperature (0.14–0.21 ct)—were manufactured in Novosibirsk, Russia. They represent the core sample of this study. Photo by Robert Weldon.

the as-grown yellow crystals and faceted stones and the red treated samples, are of Russian origin.

We report here on a detailed gemological study of the 10 gem-quality synthetic diamonds—seven "as-grown" yellow to orangy or brownish yellow (two crystals and five faceted samples; see figure 1), and three reportedly treated yellow to greenish yellow (all faceted; see figure 1)—received in 1992. All were produced in Novosibirsk (a major technological city in southern Siberia, located approximately 3,000 km east of Moscow). We believe from the properties observed that the four yellow to orangy or brownish yellow synthetic diamonds recently loaned to GIA by Chatham Created Gems in late 1993, and the three yellow synthetic diamond samples seen briefly by GIA researchers in late 1990, represent the same type of synthetic diamond production. The three yellow to greenish yellow synthetic diamonds described here were reportedly heat treated ("annealed") at high pressure after synthesis in Novosibirsk to alter their color and to study other effects of annealing. We do not know their color before treatment, although we believe it was in the same range as the seven as-grown samples. Note that little information has been published on Russian synthetic diamonds treated by high-pressure/high-temperature annealing (Malogolovets et al., 1991; Teslenko, 1993); for brevity, such stones are referred to here simply as "HPHT treated."

Although all of the Russian synthetic diamonds described here are easily identifiable, some of their gemological characteristics (such as their ultraviolet luminescence and optical absorption spectra) differ significantly from what we and others have reported so far for yellow synthetic diamonds of other manufacture that are suitable for jewelry use.

BACKGROUND

Since 1971, gem researchers have regularly reported on the gemological properties and identifying characteristics of gem-quality synthetic diamonds (Crowningshield, 1971; Koivula and Fryer, 1984; Shigley et al., 1986, 1987, 1992, 1993a, 1993b; Ponahlo, 1992; Rooney et al., 1993; Koivula et al., 1993). Information on synthetic diamonds suitable for faceting has also appeared elsewhere in the scientific literature (see, e.g., Woods and Lang, 1975; Sunagawa, 1984; Burns et al., 1990; Lang and Moore, 1990; Collins, 1990; Kanda, 1990; Fritsch and Shigley, 1993).

Figure 2. A "split sphere" apparatus is used to grow synthetic diamond crystals at Novosibirsk. Left: This view of the apparatus opened reveals the internal spherical cavity, which holds the two sets of anvils and the central high-pressure cell. Right: The same apparatus is in a closed configuration at the start of an experiment to grow diamond crystals. Photos provided by N. V. Sobolev.

As discussed in these references, the gemological identification of synthetic diamonds is based on the conditions of diamond growth in the laboratory, which differ significantly from those in nature (in particular, growth time, chemical composition within the growth system, rapidity of cooling from high temperature, etc.). For example, with growth from a flux metal or alloy, metallic inclusions may become trapped in the synthetic diamond during crystallization. Furthermore, laboratory synthesis produces diamond crystals with a morphology different from that of natural gem diamonds. In particular, the synthetic diamond crystals we have examined always exhibit cube, and sometimes exhibit dodecahedral and trapezohedral, internal growth sectors (and external morphology), in addition to the octahedral sectors found in both natural and synthetic gem diamonds (Sunagawa, 1984; Shigley et al., 1987). The presence of several growth sectors, potentially containing different types and amounts of impurities, can lead to zonations of color, luminescence, and graining in synthetic diamonds that are different from those seen in natural diamonds.

The reports mentioned earlier have described synthetic diamonds grown by General Electric, Sumitomo Electric Industries, and (on an experimental basis) by the De Beers Diamond Research Laboratory. All of these manufacturers use the "belt" type of growth equipment (see Strong and Wentorf, 1972; Bundy et al., 1973; Nassau, 1980, pp. 170–193). However, the Russian synthetic diamonds described here were grown using a different apparatus. As a result, some of their gemological properties are different from those reported for these other productions. Nevertheless, they are sufficient to identify these stones as synthetic diamonds by means of standard gem-testing equipment and techniques.

GROWTH MECHANISM

The only economical process for growing large (1+ ct) single crystals of synthetic diamond is still the high-pressure/high-temperature flux method. General Electric, Sumitomo Electric, and De Beers researchers all use a reaction vessel in what is referred to as a "belt" type of apparatus mounted in a high-pressure hydraulic press, although the design details of their respective equipment apparently differ (see Nassau, 1980, pp. 170–193). When a metal solvent/catalyst is used as a flux, typical growth conditions are 1400° to 1600°C and 50 to 60 kbar. Such conditions are within the field of temperatures and pressures where diamond is the stable phase of carbon. With this type of equipment and these conditions, diamond crystals are produced by the "temperature gradient" or "reconstitution" technique (for more information, see Strong and Wentorf, 1972, 1991; Bundy et al., 1973; Burns and Davies, 1992). Growth periods for a 1-ct diamond crystal are reportedly on the order of five days or more (Shigley et al., 1986, 1987).

At Novosibirsk, synthesis of large, single diamond crystals is accomplished using a different type of high-pressure/high-temperature apparatus, known as the "split sphere" (also referred to by the Russian acronym "BARS"; Pal'yanov et al., 1990; Yelisseyev et al., 1992a, 1992b). In this type of growth apparatus, pressure is applied to two sets of anvils (figures 2 and 3). The outer set of eight anvils forms an octahedron-shaped cavity. Within this space, an inner set of six additional anvils is positioned to form a cube-shaped central cavity that contains the high-pressure cell in which the diamond crystals are actually grown (again, see figure 3). Diamond crystal growth experiments have been conducted at pressures of about 55 to 65 kbar and temperatures in the range of about 1350° to 1700°C. Transition metals (Fe, Ni, Mn, etc.) and their alloys are used as solvents/catalysts. The best-quality cuboctahedral crystals (grown up to 1.5 ct) reportedly have been obtained using growth rates of not more than 5 mg/hr. Thus, the conditions of pressure, temperature, time, and flux composition are similar to those used in the "belt" type of growth apparatus. However, the growth cell in the BARS equipment is smaller than that in the typical belt-type growth apparatus, so there is less space available to grow synthetic diamonds.

Experiments have also been carried out at

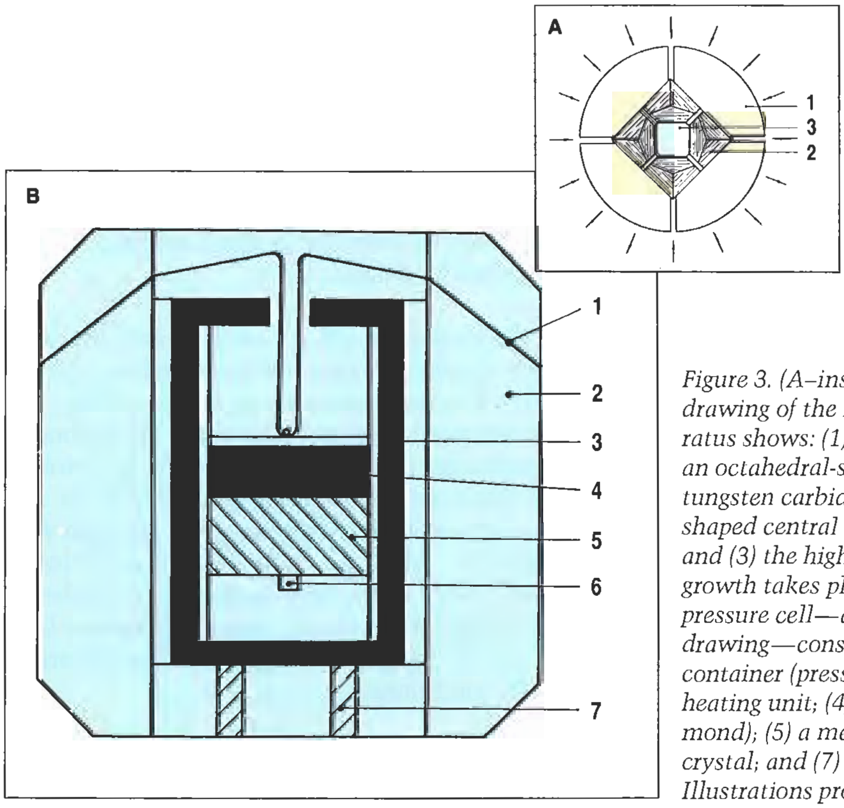


Figure 3. (A–inset) This simplified schematic drawing of the interior of the "split sphere" apparatus shows: (1) the outer set of anvils that form an octahedral-shaped cavity; (2) the inner set of tungsten carbide anvils that form the cube-shaped central cavity that holds the growth cell; and (3) the high-pressure cell in which diamond growth takes place. (B) The cube-shaped high-pressure cell—also simplified for this schematic drawing—consists of: (1) a thermocouple; (2) a container (pressure-transferring medium); (3) a heating unit; (4) carbon source material (i.e., diamond); (5) a metal flux solvent/catalyst; (6) a seed crystal; and (7) an electrical power supply. Illustrations provided by N. V. Sobolev.

Novosibirsk and elsewhere in Russia to study the effects of additional heating (or "annealing") at high pressure on synthetic diamonds produced using the BARS equipment (see Malogolovets et al., 1991; Teslenko, 1993). These experiments were conducted using the same "split sphere" growth apparatus. These researchers report that heating for four to five hours at up to 2000° to 2200°C and 70 to 80 kbar can both affect the color of the synthetic diamonds and produce changes in their visible and infrared absorption spectra. We do not know the exact treatment procedure used on the three yellow to greenish yellow synthetic diamonds described here, their condition before treatment, or whether the treatment was carried out before or after the samples were faceted.

MATERIALS AND METHODS

Ten synthetic diamonds were included in this study (see table 1 for descriptions of each) and subjected to all key tests. The four additional samples loaned by Chatham Created Gems (also in table 1) and the three yellow crystals seen in 1990 have the same gemological properties as the first seven in table 1; they are not discussed further here.

TABLE 1. Russian gem-quality synthetic diamonds examined during this study.

Sample no.	Weight (ct)	Shape	Color[a]	Clarity[b]
As-grown				
21476	0.78	Crystal[c]	Y	
21477	0.26	Round brilliant	oY	VS$_2$
21478	0.88	Crystal[d]	brY	
21481	0.20	Rectangle	oY	SI$_1$
21484	0.18	Hexagon	oY	VS$_1$
21485	0.51	Square	Y	VS$_1$
21486	0.11	Hexagon	oY	VS$_2$
HPHT-treated				
21474	0.17	Rectangle	gY	SI$_1$
21475	0.14	Round brilliant	gY	I$_1$
21480	0.21	Emerald	Y	VS$_1$
As-grown samples loaned by Chatham Created Gems				
21635	0.53	Princess	oY	I$_1$
21636	0.11	Round brilliant	Y	VVS$_1$
21637	0.32	Crystal[c]	brY	
21638	1.02	Crystal[d]	brY	

[a] *Color: Y—yellow, gY—greenish yellow, oY—orangy yellow, brY—brownish yellow.*

[b] *Clarity: Although the GIA Gem Trade Laboratory does not issue grading reports on synthetic diamonds, the faceted samples shown here (if natural) would receive these clarity grades on the basis of their inclusions and other clarity characteristics.*

[c] *Flattened cuboctahedron.*

[d] *Modified cuboctahedron.*

We used standard gemological testing equipment, including a binocular gemological microscope, a long-wave (366 nm) and short-wave (254 nm) Ultraviolet Products U.V. lamp unit (in a darkened room), and both a Beck prism and a Discan digital-scanning diffraction-grating spectroscope. Pye-Unicam 8800 and Hitachi U-4001 spectrophotometers were used to record absorption spectra at room and liquid-nitrogen temperatures over the range 250–850 nm. A Nicolet 60SX Fourier-transform infrared spectrometer was used to record infrared spectra over the range 400–25,000 cm^{-1}. Qualitative chemical analysis was carried out using a Tracor X-ray energy-dispersive X-ray fluorescence (EDXRF) system. The cathodoluminescence photos were taken using a Nuclide ELM-2B luminoscope. Luminescence spectra were obtained using a Milton Roy SLM Aminco AB2 series luminescence spectrometer. Excitation was used with a bandpass of 4 nm, and emission was recorded with a bandpass of 1 nm.

RESULTS

In contrast to the sample groups of gem-quality yellow synthetic diamonds we had examined before, the Russian samples described here exhibit greater variation in their gemological properties. In this section, we will describe the more representative features we have observed—some of which are merely indicators of synthesis, while others are proof. We emphasize that not all of these features are present in all 10 samples. Thus, they should not necessarily all be expected in other samples of this kind of synthetic diamond.

Color. The colors of all 10 samples and the four Chatham synthetic diamonds are listed in table 1, using GIA's current terminology for describing the color of fancy-color natural diamonds. The colors in these stones are similar to those of the Sumitomo and De Beers synthetic diamonds (Shigley et al., 1986, 1987), although the cause of the greenish yellow color is different (see later discussion). However, to our knowledge, none of the synthetic diamonds described in the above references had been exposed to post-growth high-heat/temperature treatment conditions.

Morphology. Each of the two crystals in the study sample (and the three pieces of similar material seen by us in late 1990) exhibited a combination of octahedral, cube, dodecahedral, and/or trapezohedral faces in different relative sizes and arrangements (see figures 1 and 4; for further information on the crystal morphology of natural and synthetic diamonds, see Sunagawa, 1984). The crystal morphology observed on these crystals is the same as that reported on other productions of synthetic diamonds (Shigley et al., 1986, 1987).

Microscopy. Examination of these Russian synthetic diamonds with a gemological microscope revealed many of the same kinds of diagnostic features we have reported previously in other gem-quality synthetic diamonds.

Color Zoning. One of the two crystals displayed an even yellow color. The other (no. 21478) exhibited some color zoning, with areas of lighter and darker yellow that were separated by graining (best seen using fiber optic illumination).

With only one exception (no. 21484), each of the faceted stones also displayed some form of uneven color zoning (as has been the case with other yellow synthetic diamonds; see Shigley et al., 1986, 1987, 1992). The appearance of the color zoning in a particular sample was influenced not only by the faceted shape and the viewing conditions, but also—more importantly—by the arrangement and relative sizes of the internal growth sectors in the original crystal, their orientation with respect to the faceted shape, and the amount of the growth sectors that remain after faceting. Color zoning was especially prominent in the HPHT-treated samples (see figures 5 and 6).

When most visible, this zoning appears (in transmitted light) as a near-colorless to light yellow, square or rectangular, central area surrounded by darker yellow areas, the latter often in a four-fold symmetric arrangement. Some typical patterns are illustrated in figure 7. In most cases, the position of the zoning appeared to correspond to the pattern of graining and uneven U.V. luminescence (see below).

Graining. We observed various patterns of surface and/or internal graining in all of the faceted Russian synthetic diamonds, although the surface graining was more difficult to see. For example, figure 8 shows an octagonal, or "stop sign," surface graining pattern on the table facet of the HPHT-treated synthetic diamond no. 21480 (for comparison, see pho-

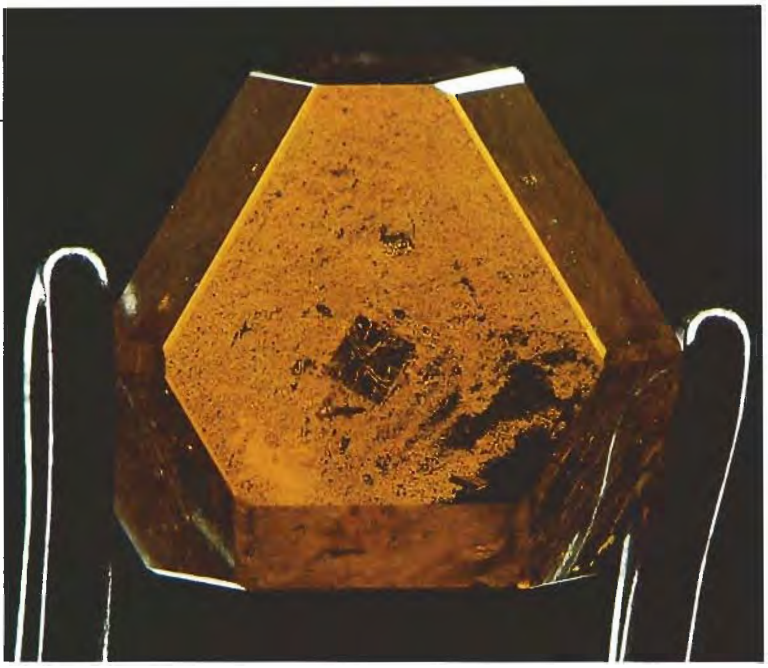
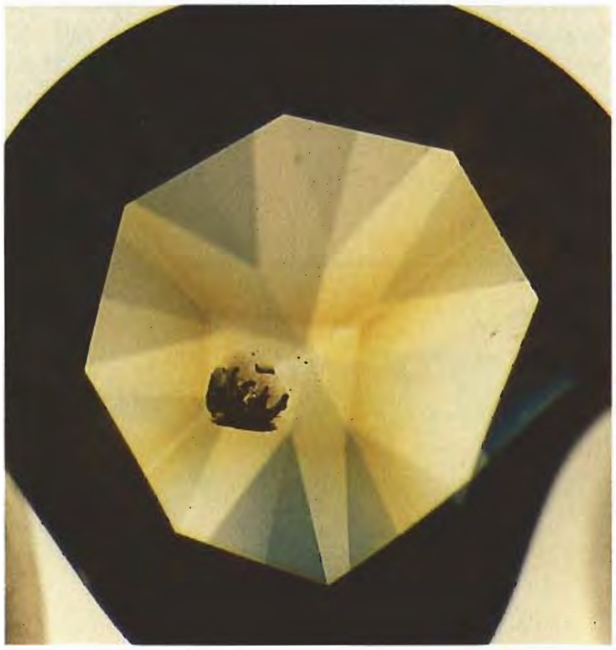


Figure 4. This 0.78-ct synthetic diamond crystal (no. 21476) shows the arrangement of crystal faces and the location of the seed (the black-appearing square area) on the octahedral face at the base of the crystal. Photomicrograph by John I. Koivula.

Figure 5. Distinct color zoning is seen when 0.14-ct HPHT-treated synthetic diamond no. 21475 is immersed in methylene iodide and viewed perpendicular to the girdle through the pavilion facets. Note the yellow outline of the rectangular area near the center. At each of the four corners of this area, a narrow yellow zone (slightly darker along both sides, and lighter along the center) projects outward toward the edge of the sample. The black-appearing area near the center is a metallic inclusion. Photomicrograph by John I. Koivula.



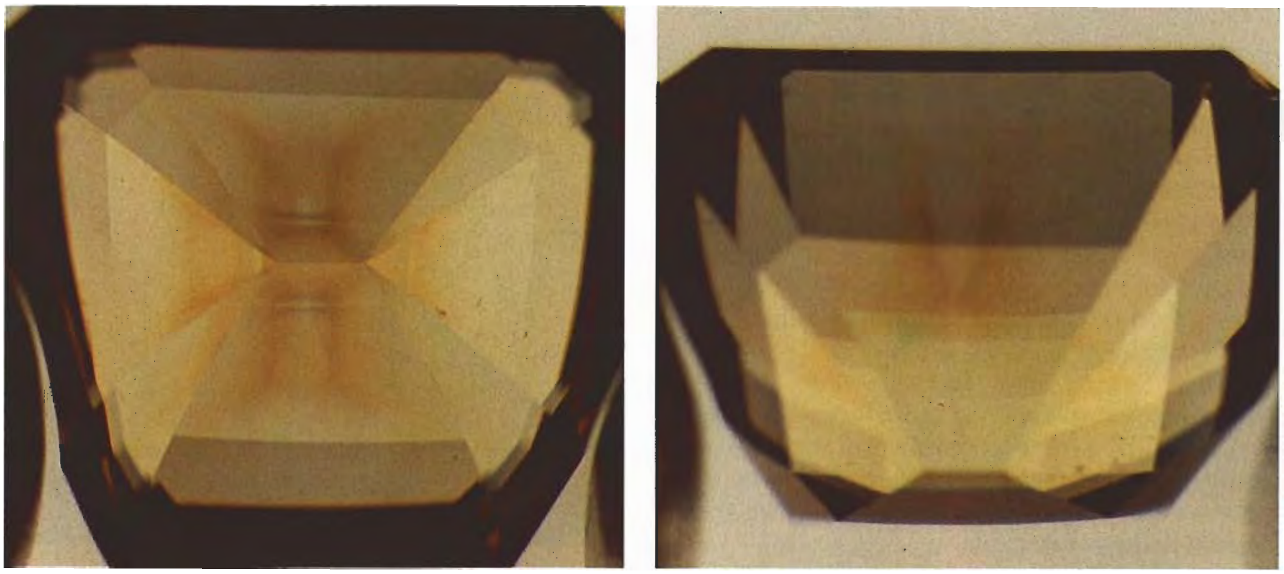


Figure 6. Distinct color zoning is also seen when 0.17-ct HPHT-treated sample 21474 is immersed in methylene iodide and viewed through the culet and the pavilion facets (left). Near the center, a square-shaped area is outlined in yellow. As the sample is rotated toward the girdle (right), a position is reached where this central area appears to broaden toward the crown facets. Photomicrographs by John I. Koivula.

tos in Shigley et al., 1986, 1987). This same sample revealed a pattern of internal graining in the form of a rectangle with graining lines projecting outward from each corner (figure 9; similar to the patterns described for color zoning). Other patterns, such as intersecting graining lines (or planes), were seen in other samples (see, e.g., figures 10 and 11).

Inclusions. Large rounded or elongate inclusions with a metallic luster were present in several of the faceted stones and both crystals (figures 12 and 13). In addition, most of the faceted stones exhibited numerous tiny pinpoint inclusions (figure 14). Most of the samples displayed a weak attraction to a simple magnet, and some showed none at all. We could not establish any relationship between the strength of the magnetic attraction and the size or number of the metallic inclusions present in a given sample.

EDXRF chemical analyses of the samples revealed the presence of nickel (Ni) and iron (Fe) in all but one of them (no. 21485, which contained only Ni), with the X-ray peak for Ni always being more intense than that for Fe (figure 15). Both elements have been reported previously in synthetic diamonds (see Shigley et al., 1987, 1992; Burns and Davies, 1992; Rooney et al., 1993). As expected, we noted no differences in the EDXRF spectra of the as-grown and HPHT-treated samples.

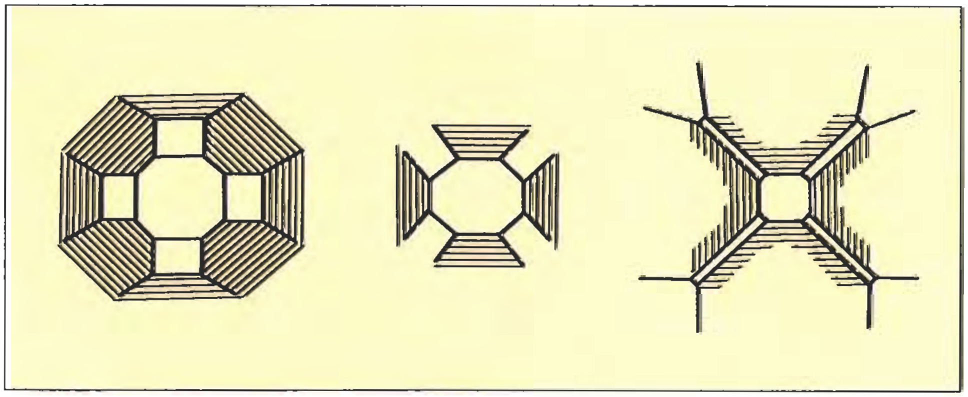
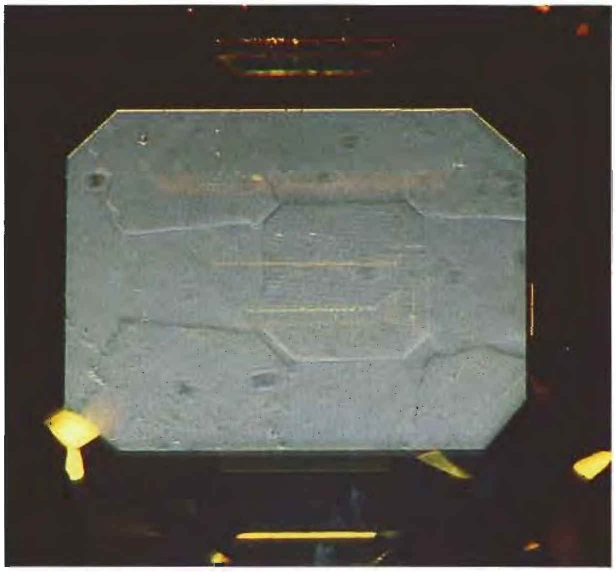


Figure 7. These three configurations are typical of color and luminescence zoning seen in the Russian synthetic diamonds examined. Patterns intermediate between these, or representing only a portion of one of them, have also been observed.

Appearance in Polarized Light. Examination of crystal no. 21476 with crossed polarizing filters revealed an anomalous birefringence (i.e., "strain") pattern in the form of a black or gray cross. Faceting of such a crystal might lead to more distorted-appearing anomalous birefringence where the cross pattern can no longer be recognized. In general, the eight faceted samples exhibited only weak anomalous birefringence in patterns that were usually difficult to see because of the small size of the samples and the fact that they were faceted.

Ultraviolet Luminescence. The U.V. luminescence of the 10 samples is summarized in table 2. Since luminescence in these synthetic diamonds occurs mostly in certain internal growth sectors or at the borders between sectors, the luminescence color and intensity that one observes may depend on the orientation of the sample and, for a cut stone, how the faceted shape intersected the growth-sector pattern of the original crystal (again, see figure 7). The observations we describe below are based on what we saw for those growth sectors of the sample that luminesced most intensely.

Figure 8. Indirect reflected light reveals octagonal surface graining on the table facet of HPHT-treated sample 21480. This octagon, from which four "arms" emanate, marks the intersection of the plane of the table facet and the arrangement of internal growth sectors in the synthetic diamond. The same growth-sector arrangement is visible in the cathodoluminescence pattern. Photomicrograph by John I. Koivula; magnified 25×.



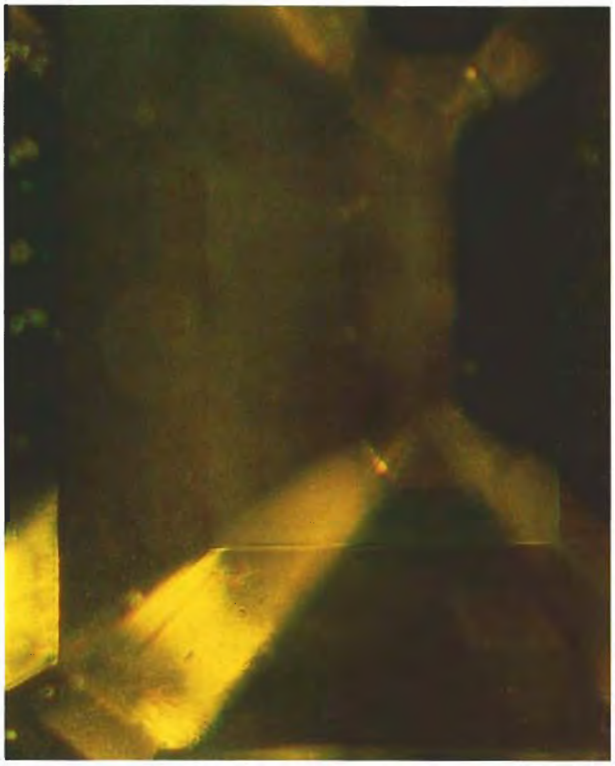


Figure 9. In sample 21480, internal graining is evident as a rectangular area seen beneath the table facet. Graining lines also project outward from each corner of the rectangle. The green seen in some parts of the sample is caused by luminescence to visible light. Note also the tiny pinpoint inclusions. Photomicrograph by John I. Koivula; magnified 35×.

Figure 10. Internal graining, in the form of intersecting lines, is visible through the pavilion facets of sample 21485. Similar graining patterns were seen beneath each of the four corners of the pavilion. Photomicrograph by John I. Koivula; magnified 25×.

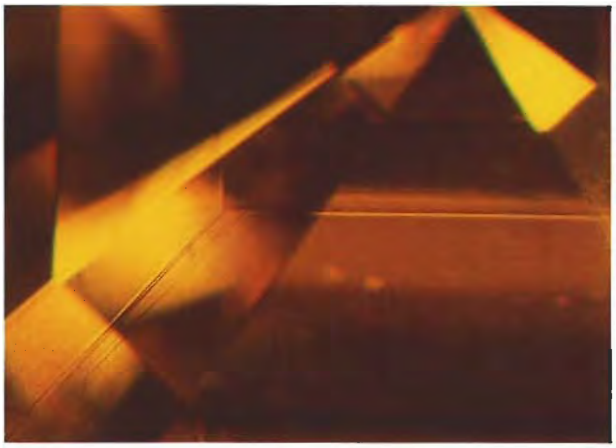


Figure 11. A different kind of internal graining, also in the form of intersecting lines, is seen through the pavilion facets of the same synthetic diamond shown in figure 10. Photomicrograph by John I. Koivula; magnified 40×.

Figure 13. This group of elongate, metallic inclusions beneath the crown facets of sample 21481 is typical of the metallic inclusions seen in some of the faceted Russian synthetic diamonds. Photomicrograph by John I. Koivula; magnified 35×.

In contrast to previous reports on other yellow synthetic diamonds (see, e.g., Shigley et al., 1986, 1987, 1992), only one as-grown sample (no. 21485) was inert to long-wave U.V. radiation but fluoresced to short-wave U.V. (this sample, incidentally, is the purest type-Ib sample; see discussion of infrared spectroscopy below). For all seven as-grown samples, the fluorescence to short-wave U.V. was

Figure 12. Opaque inclusions of flux metal (largest, 0.9 mm long) are seen here near the outer edge of crystal no. 21476. The elongate, rounded shape is characteristic of this kind of metallic inclusion in synthetic diamonds. Photomicrograph by John I. Koivula; magnified 20×.

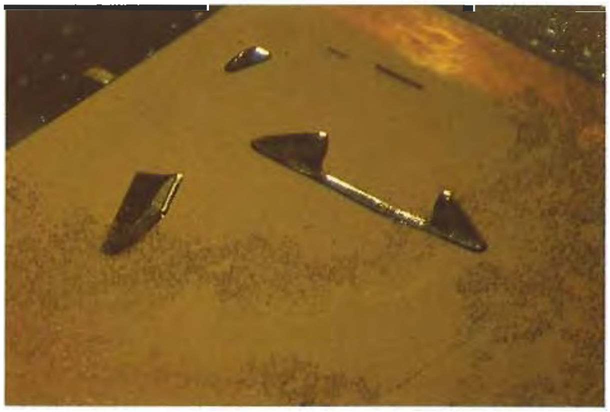


Figure 14. This large metallic inclusion, accompanied by numerous pinpoint inclusions, was seen beneath the table facet of HPHT-treated sample 21475 (see also figure 5). Note the rectangular area marked by graining; the border of this rectangular area is outlined by sectors that luminesce green to visible light. Photomicrograph by John I. Koivula; magnified 35×.

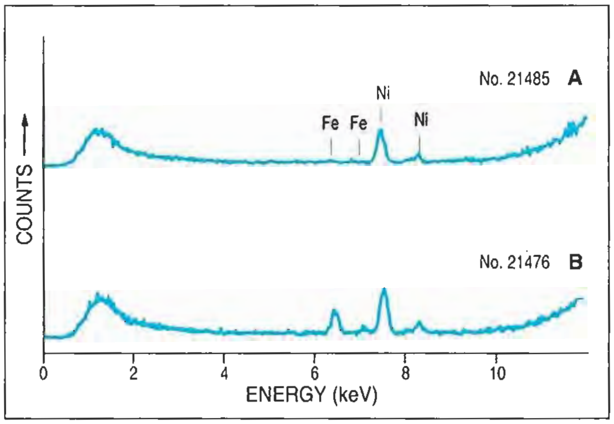
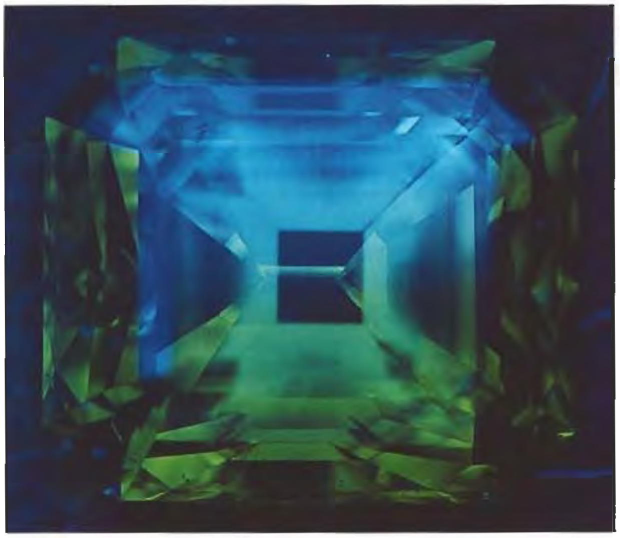


Figure 15. These two EDXRF spectra show the presence of nickel (Ni) and/or iron (Fe) in the metallic inclusions in these synthetic diamonds.

more intense than or equal to the long-wave U.V. reaction. However, all three HPHT-treated samples fluoresced more intensely to long-wave than to short-wave U.V. radiation, and their fluorescence to both wavelengths was greater than that of the as-grown samples (again, see table 2). Furthermore, these three samples exhibited moderate to strong yellow phosphorescence when either U.V. lamp was turned off. Figures 16 and 17 illustrate the uneven distribution of the U.V. luminescence that is typical of these synthetic diamonds. This pattern is similar, again, to that observed for the color zoning and graining.

Figure 16. Zoned long-wave U.V. fluorescence was observed in faceted as-grown Russian yellow synthetic diamond no. 21481. Some internal growth sectors (at the center and near the corners) are inert, but others fluoresce greenish yellow. The blue color is a reflection from the U.V. lamp off the crown facets. Photomicrograph by John I. Koivula.



Luminescence Spectroscopy. A three-dimensional plot of the emission as a function of excitation wavelength for sample 21480 (HPHT treated) is shown in figure 18. The greenish yellow fluorescence of the Russian synthetic diamonds appears in the emission spectrum as a broad band with an

TABLE 2. Ultraviolet luminescence of the Russian synthetic diamonds examined.

Luminescence behavior	As-grown crystals	As-grown cut stones	HPHT-treated cut stones
Long-wave U.V. fluorescence			
Color	Yellow	Greenish yellow to yellow	Greenish yellow
Intensity	Weak	Weak to strong[a]	Very strong
Appearance	Turbid[b]	Turbid	Turbid
Distribution	Uneven[c]	Uneven	Uneven
Long-wave U.V. phosphorescence			
Color	None	None	Yellow
Intensity			Moderate to strong
Duration			30–45 sec.
Short-wave U.V. fluorescence			
Color	Yellow	Yellowish green to green	Yellowish green
Intensity	Weak	Weak to strong	Strong
Appearance	Turbid	Turbid	Turbid
Distribution	Uneven	Uneven	Uneven
Short-wave U.V. phosphorescence			
Color	None	None[d]	Yellow
Intensity			Moderate to strong
Duration			30–60 sec.

[a] *As-grown sample 21485 was inert to long-wave U.V. radiation.*
[b] *A turbid appearance is also known as "chalky" fluorescence.*
[c] *An uneven distribution indicates that the fluorescence emission is related to the arrangement of internal growth sectors in the diamond. Some sectors fluoresce with a weak to strong intensity, while other sectors are inert.*
[d] *As-grown sample 21486 exhibited moderate yellow phosphorescence for about 30 seconds when the short-wave U.V. lamp was turned off.*

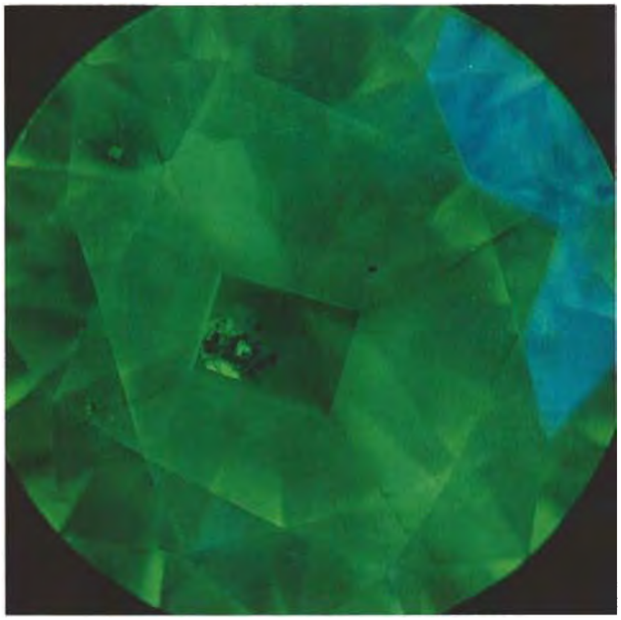


Figure 17. Zoned long-wave U.V. fluorescence was observed in greenish yellow HPHT-treated Russian synthetic diamond no. 21475. When compared to the pattern of color zoning (see figure 5), the darker yellow areas appear to be fluorescing greenish yellow, while the central colorless area is inert. The blue color is a reflection from the U.V. lamp off several crown facets. Photomicrograph by John I. Koivula.

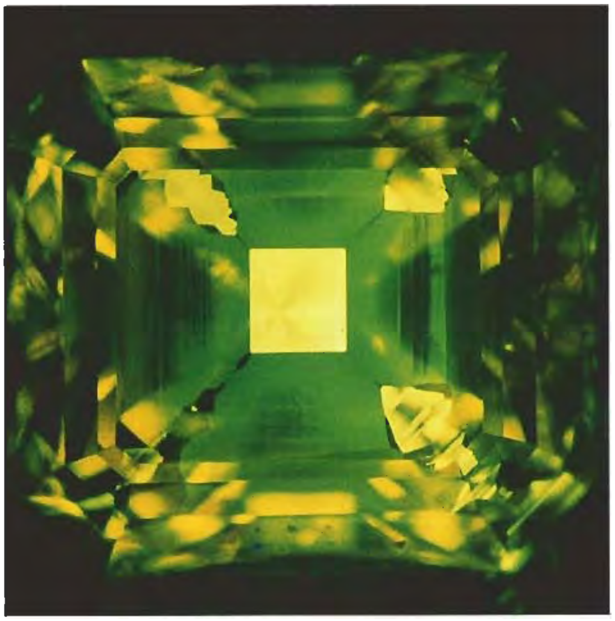


Figure 19. Cathodoluminescence of faceted yellow synthetic diamond sample 21481 (compare figure 16) readily reveals the arrangement of internal growth sectors, with some sectors at the center and the four corners luminescing yellow, and others emitting a greenish yellow. Note that the sectors that are not fluorescing to U.V. radiation in figure 16 are luminescing yellow here.

apparent maximum at around 550 nm. Small "dips" on the broad band seen in all the emission spectra are due to superimposed features that closely correspond to those noted in the absorption spectrum of the diamond at room temperature. Additional weak, sharp emissions were seen at approximately 748, 776, and 795 nm (not visible in figure 18 because of the vertical scale used). The general shape of the emission spectrum, and therefore the color of the fluorescence, remain essentially the

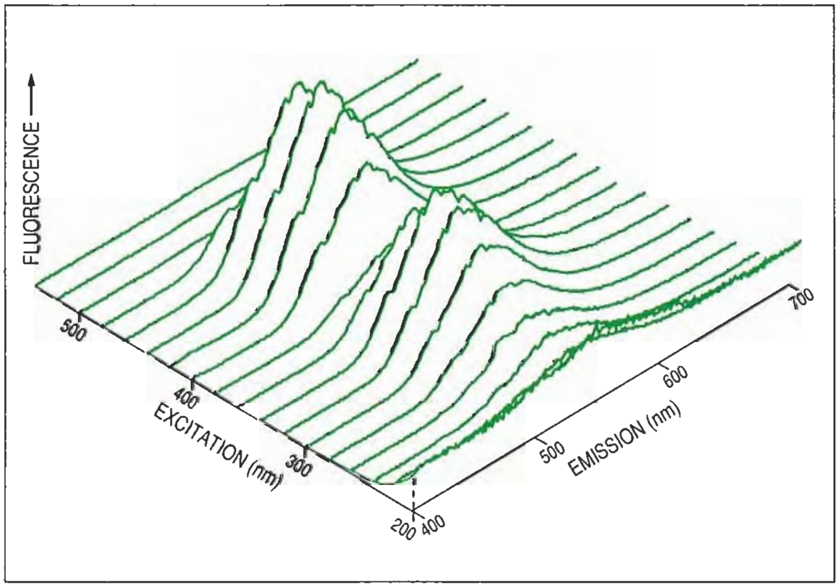


Figure 18. This three-dimensional plot shows the evolution of fluorescence emission (axis on the right) in HPHT-treated sample 21480 as a function of the excitation wavelength (axis on the left). Note that the general shape of the emission stays the same even when the excitation is changed. Artifacts at once and twice the excitation wavelength have been removed for clarity.

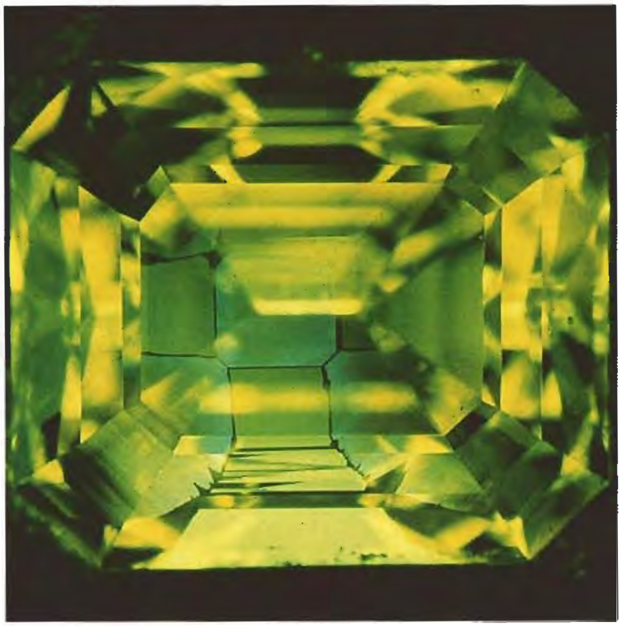


Figure 20. With cathodoluminescence, the different internal growth sectors in HPHT-treated synthetic diamond no. 21480 are seen to luminesce various colors that reveal the arrangement of sectors. Note that the same octagonal pattern seen in the surface graining of this stone (figure 8) is evident in the cathodoluminescence pattern, since both features are related to growth sectors.

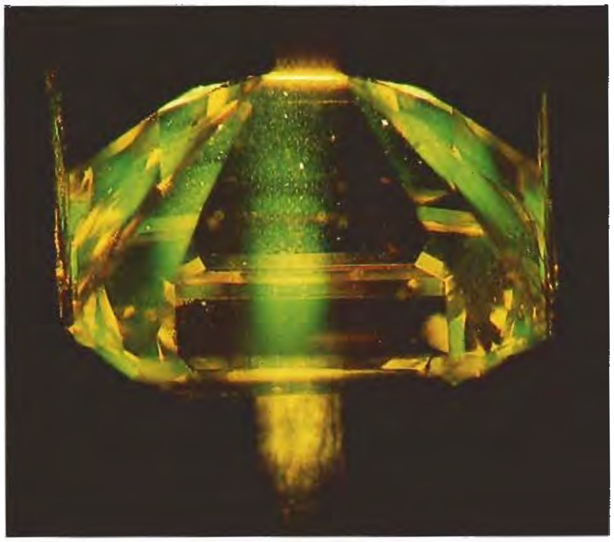


Figure 21. Green luminescence (also referred to as "transmission luminescence") is seen when faceted HPHT-treated sample 21480 is positioned over a strong visible (in this case fiber optic) light. Small pinpoint inclusions within the synthetic diamond are also highlighted. This luminescence to visible light was weaker in the other samples. Photomicrograph by John I. Koivula; magnified 10×.

same even when the excitation wavelength is changed. However, one can see that the emission intensity is stronger at the 365-nm excitation than at the 255-nm excitation. This confirms that the fluorescence is stronger to long-wave (365 nm) than to short-wave (255 nm) U.V. radiation. Maximum emission intensity is reached for excitation wavelengths of about 350 and 450 nm. The latter is situated in the visible range. Therefore, this diamond actually luminesces more intensely when excited with visible light in the blue range (about 450 nm) than when excited with U.V. radiation.

Cathodoluminescence. When exposed to a beam of electrons in a vacuum chamber, these synthetic diamonds emit cathodoluminescence. Typically, the uneven cathodoluminescence pattern, which closely resembles the U.V. fluorescence pattern, is directly related to the arrangement of internal growth sectors (see, e.g., figures 19 and 20). As we and others have reported previously, it is easier to see the growth sectors in a synthetic diamond with cathodoluminescence than with other luminescence techniques (see Woods and Lang, 1975; Shigley et al., 1987; 1993a; Lang and Moore, 1990; Ponahlo, 1992), because the luminescence that arises from the electron beam is more intense than that produced by exposure to U.V. radiation. Consequently, it is an excellent identification tool for this material.

Luminescence to Visible Light. All but two (as-grown nos. 21478 and 21484) samples also exhibited an unevenly distributed, weak to moderate intensity, green luminescence when they were positioned over a strong source of visible light (figure 21). It followed the general pattern observed for the other kinds of luminescence; areas that luminesced greenish yellow most strongly to both U.V. and visible light also had a darker yellow body color. We have not seen similar luminescence to visible light in other yellow synthetic diamonds (Shigley et al., 1986, 1987, 1992). Note also that the sample with the most intense green luminescence to visible light (no. 21480) still had a yellow body color. Thus, this luminescence makes no significant contribution to the body color of any of these samples.

Luminescence to X-rays. When exposed to X-rays (80 keV, 40 mA), the 10 samples emitted little if any luminescence as compared to a yellow, type-IaA, natural diamond (which luminesced weak yellow). This result is generally consistent with that reported by Koivula and Fryer (1984, p. 151) for G.E. yellow synthetic diamonds.

Absorption Spectroscopy (Handheld). In yellow synthetic diamonds examined previously (Crowningshield, 1971; Koivula and Fryer, 1984; Shigley et al., 1986, 1987), no sharp absorption bands were visible when the samples were viewed with a handheld spectroscope, even after the samples were cooled. However, all except two (nos. 21484 and 21486, both as-grown) of the Russian synthetic diamonds did exhibit one or more sharp absorption bands that could be seen with a spectroscope when the samples had been cooled to low temperature with a spray refrigerant (for further information on this technique, see Hofer and Manson, 1981). Table 3 includes a compilation of these sharp absorption bands. Note that the ease with which sharp bands can be seen will vary depending on factors such as the type of spectroscope used and the sample's viewing position. In addition, locations of sharp bands seen with a spectroscope can usually only be estimated. Thus, each absorption band listed in table 3 is shown with an accurate wavelength value, determined with the spectrophotometer, to prevent confusion with the information presented below.

The visible spectra for each of the seven as-grown samples displayed increasing absorption toward the ultraviolet, beginning at somewhere between 450 and 500 nm. Those for the two crystals and three of the five as-grown faceted stones also displayed a sharp absorption band, with weak-to-moderate intensity, at about 658 nm. An additional weak sharp band around 637 nm was observed in the spectrum of sample 21485; one at approximately 527 nm was seen in sample 21481.

The handheld spectroscope revealed quite different visible spectra for the three HPHT-treated synthetic diamonds. All three samples exhibited much less absorption below 450 nm, plus a number of sharp absorption bands between 470 and 600 nm when they were cooled with a spray refrigerant. The bands observed in each of the three samples were as follows: no. 21474—473, 477, 478, 481, and 547 nm; no. 21475—473, 478, 481, 547, and 553 nm; and no. 21480—473, 478, 481, 503, 511, 518, 527, 547, and 553 nm.

Ultraviolet-Visible Absorption Spectrometry. *As-Grown Samples.* Figure 22A presents the room-temperature absorption spectrum of an as-grown

TABLE 3. Absorption bands seen in the ultraviolet, visible, and near-infrared spectra of the Russian synthetic diamonds, listed by decreasing wavelength.

Wavelength (rounded to closest nm)	U[a]	T[b]	Handheld spectroscope (at LT)[c]	Comments
792	Y	Y		Ni-related[d,f,g]
767		Y		Visible in published spectrum but not discussed[d]
732	Y			Ni- and N-related[d,f]
711	Y			Ni- and N-related[d,f]
691	Y			Ni- and N-related[d,f]
671	Y			Ni- and N-related[d]
660	Y	Y		
658	Y		Yes	Ni-related[e,f]
649	Y			Ni-related[e]
647	Y			Ni-related[e]
639	Y	Y		
637	Y		Yes	Ni-related[e]
627	Y			Ni-related[e]
623		Y		
617	Y			Ni-related[e]
607		Y		
592		Y		
582		Y		
563		Y		
553	Y	Y	Yes	Ni- and N-related[d]
547	Y	Y	Yes	Ni- and N-related[d]
540		Y		Ni- and N-related[d,f]
527	Y	Y	Yes	Ni- and N-related[d,f]
520		Y		Ni- and N-related[d]
518		Y	Yes	Ni- and N-related[d]
516	Y	Y		Ni- and N-related[d]
511	Y	Y	Yes	Ni- and N-related[d]
506		Y		
503		Y	Yes	Ni- and N-related[d,f]
500	Y	Y		Ni- and N-related[d]
494	Y	Y		Ni-related[e]
491		Y		Ni- and N-related[d]
481		Y	Yes	Ni- and N-related[d]
478		Y	Yes	Ni- and N-related[d]
477		Y	Yes	Ni- and N-related[d]
473	Y	Y	Yes	Ni- and N-related[d]
468	Y	Y		Ni- and N-related[d]

[a] *U: Observed in the spectral curves of the as-grown samples (figures 23A–23B.*

[b] *T: Observed in the spectral curves of the HPHT-treated samples (figures 23C–23D.*

[c] *Absorption bands visible with either a Beck or Discan spectroscope when the sample is cooled to low temperature with a spray refrigerant.*

[d] *Observed by Lawson and Kanda (1993a, 1993b) in nitrogen-containing synthetic diamonds that were grown in nickel and subsequently annealed to 1600°-1900°C.*

[e] *Observed by Collins and Spear (1982).*

[f] *Observed by Yelisseyev et al. (1992) in nitrogen-containing synthetic diamonds that were grown in nickel-iron.*

[g] *Observed by Vins et al. (1991) in nitrogen-containing synthetic diamonds that were grown in nickel-iron and subsequently annealed above 1400°C.*

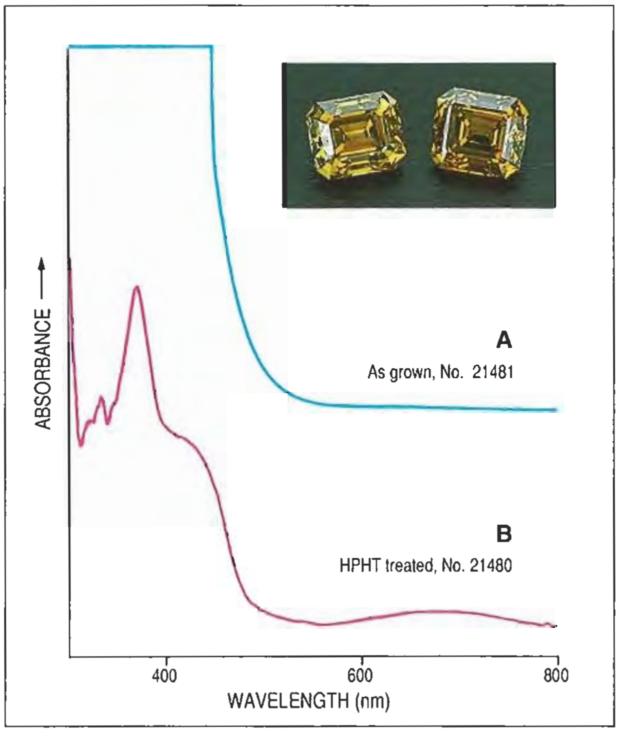


Figure 22. The room-temperature absorption spectra of orangy yellow as-grown sample 21481 (stone at right in photo) and yellow HPHT-treated sample 21480 (stone at left) reveals increasing absorption toward the ultraviolet, which gives rise to the yellow color in both synthetic diamonds. Less absorption below about 500 nm in the HPHT-treated sample explains why it is lighter yellow than the as-grown sample. The broad absorption region between 600 and 800 nm causes the green component in the color of some of the samples. Although too weak in spectrum B to affect sample 21480, it was sufficiently intense in the spectra of HPHT-treated samples 21474 and 21475 to produce a greenish yellow body color. The two spectra are offset vertically for clarity; both have been normalized by dividing the measured absorption by the path length of light through each sample.

sample. The yellow color is caused by an absorption that continuously increases from the near-infrared toward the ultraviolet, becoming very intense at wavelengths less than 550 nm.

The low-temperature absorption spectra in figure 23 illustrate the variety of sharp absorption bands noted in all of these synthetic diamonds (again, see table 3). In the seven as-grown samples, the important spectral features can be categorized as follows:

1. A weak, sharp band at 527 nm, present in two samples (see, e.g., figure 23A).
2. A group of up to six bands, from 617 to 658 nm, with intensities that were always in the same relative proportion to one another. One or more bands of this group were present in all the as-grown samples. The strongest band, and sometimes the only one visible in the spectrum, is at 658 nm (again, see figure 23A and B). The remaining bands are at 617, 627, 637, 647, and 649 nm.
3. A group of four distinct, moderately broad absorption bands from 671 to 732 nm (with the last being the most intense) that were observed in three of the as-grown samples. The bands are at 671, 691, 711, and 732 nm. One or more of the bands in this group were present in the spectra of all the as-grown samples.
4. Weak, sharp bands at 468, 473, 494, and 500 nm, seen in only one sample.
5. A weak, sharp band at 792 nm seen in the spectra of two samples.

HPHT-Treated Samples. The spectra of the HPHT-treated synthetic diamonds were quite distinctive, and featured an even greater number of absorption bands. Comparison of the two room-temperature spectra in figure 22 shows that, for like sample thicknesses, the HPHT-treated sample exhibits less absorption in the region where there was "total absorption" for the as-grown samples (i.e., below about 550 nm). Therefore, HPHT-treatment increases the transparency of these synthetic diamonds in the 300 to 500 nm range. In particular, two broad absorption bands, one at about 400 nm and one with an apparent maximum at about 425 nm, are present in figure 22B. The general shape of the absorption is a continuous increase toward the ultraviolet, which again explains the dominant yellow color.

Superimposed on this dominant feature is the broad band with an apparent maximum at 700 nm. It is particularly well defined in the spectra of the greenish yellow samples (see figure 23C). This broad band, and the more intense absorption below 550 nm, are responsible for the transmission "window" in the greenish yellow region of the spectrum (at about 560 nm) and, hence, the greenish yellow color of sample nos. 21474 and 21475. This broad band is weaker in the spectrum of sample 21480

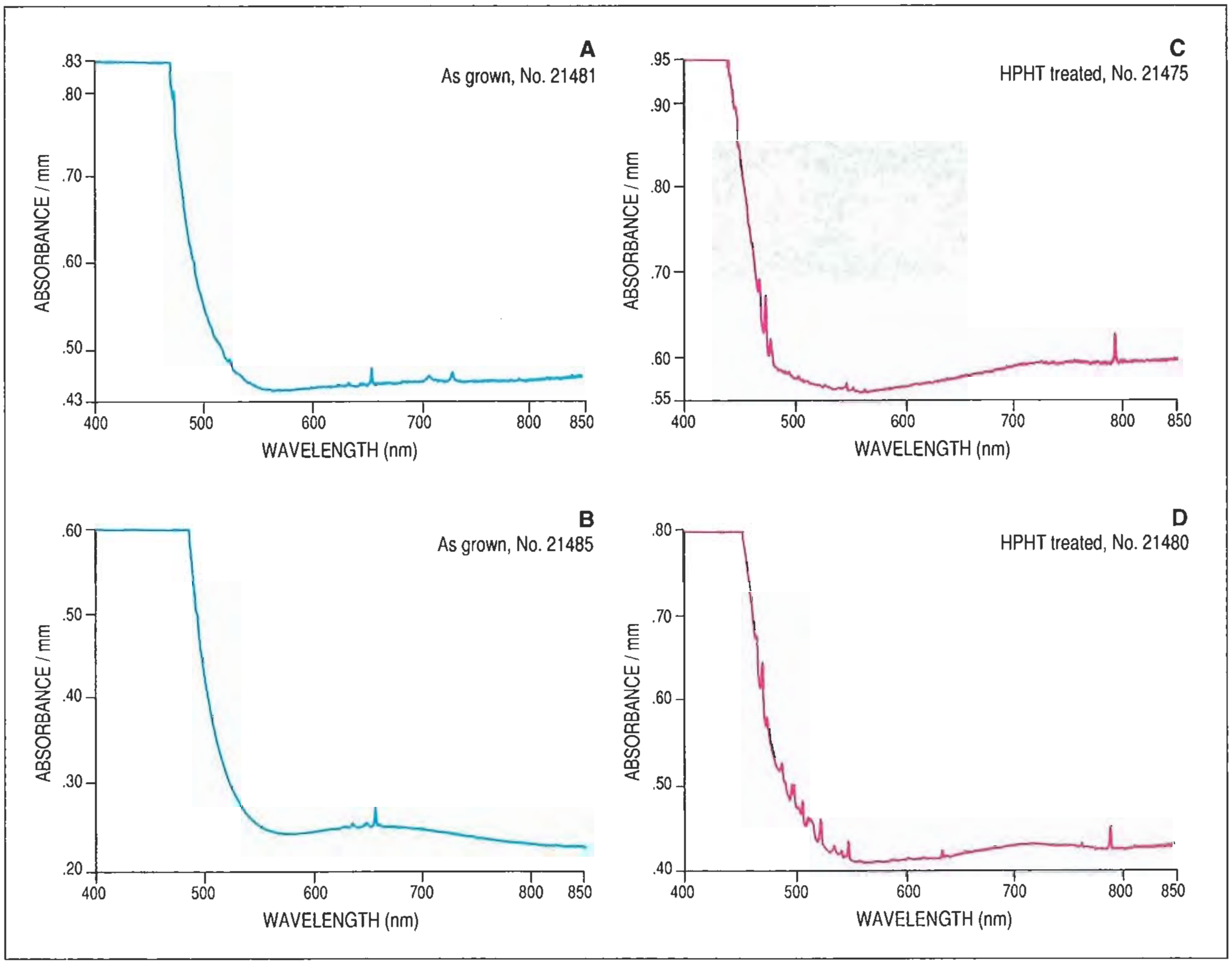


Figure 23. These visible-range absorption spectra of two yellow as-grown and two HPHT-treated Russian synthetic diamonds were recorded at liquid-nitrogen temperature. In addition to the increasing absorption toward the ultraviolet and the weak broad absorption region centered at about 700 nm (evident in spectra B, C, and D), all four spectra display a number of sharp absorption bands, which are listed in table 3. To normalize the absorbance values for the four spectra, we divided them by the appropriate approximate path length of light through the sample. Because of the vertical scale chosen to illustrate these four spectra, some weak absorption bands described in the text, and listed in table 3, may not be visible here.

(figures 22B, 23D), which may explain why this sample is yellow and not greenish yellow.

The spectra of the HPHT-treated samples, like those of their as-grown counterparts, show a number of sharp bands in the visible and near-infrared ranges, although most of these bands are at different positions (again, see the four spectra in figure 23), and there are even more of them. We noted the following bands in the spectra of the HPHT-treated samples:

1. A single sharp band at about 494 nm, seen in two samples (figures 23C and D).
2. A series of sharp bands that span the wavelength range from 460 to 660 nm. At least part of this series of bands is present in the spectra of all three HPHT-treated samples. In sample 21480, in which these absorptions were most intense, we were able to distinguish 25 sharp bands (see table 3 and figure 23D), as well as an apparently unrelated weak band at 767 nm. The more intense of these absorption bands can be seen with the handheld spectroscope (using a spray refrigerant). Although some of them might be close to absorption lines seen in the spectra of natural colored diamonds (such as the H3 absorption band at 503 nm), the pattern that

the bands form in the spectra of synthetic diamonds is unique, and helps identify them as part of the system under discussion.

3. The 792-nm absorption, which was observed only as a weak feature in two as-grown samples, was present in the spectra of all of the HPHT-treated samples as a sharp, relatively intense peak (figures 23C and D), even at room temperature.

The spectra of the HPHT-treated samples did not show the group of six bands, with the strongest peak at 658 nm, that was described above for the as-grown samples.

Infrared Absorption Spectroscopy. The mid-infrared absorption spectra of selected Russian synthetic diamonds are partially illustrated in figure 24. All as-grown samples showed a mixture in variable proportions of type-Ib (singly substitutional nitrogen) and type-IaA (paired nitrogen atoms) diamond. In addition, the infrared spectra of several of the as-grown samples revealed some weak type-IaB features. Since the peak heights of the absorptions in the "nitrogen region" (approximately 1344 to 1000 cm^{-1}) are equal to or less than those of the neighboring intrinsic diamond absorptions (between approximately 3900 and 1400 cm^{-1}), it appears that these synthetic diamonds contain only moderate amounts of nitrogen. A feature at 1050 cm^{-1} was observed in all of the as-grown samples, but was absent from the spectra of HPHT-treated stones.

In contrast, all of the HPHT-treated samples proved to be nearly pure type-IaA diamond. The presence of a weak, residual 1344 cm^{-1} peak indicates that only a very small proportion of type-Ib nitrogen remains in the HPHT-treated samples.

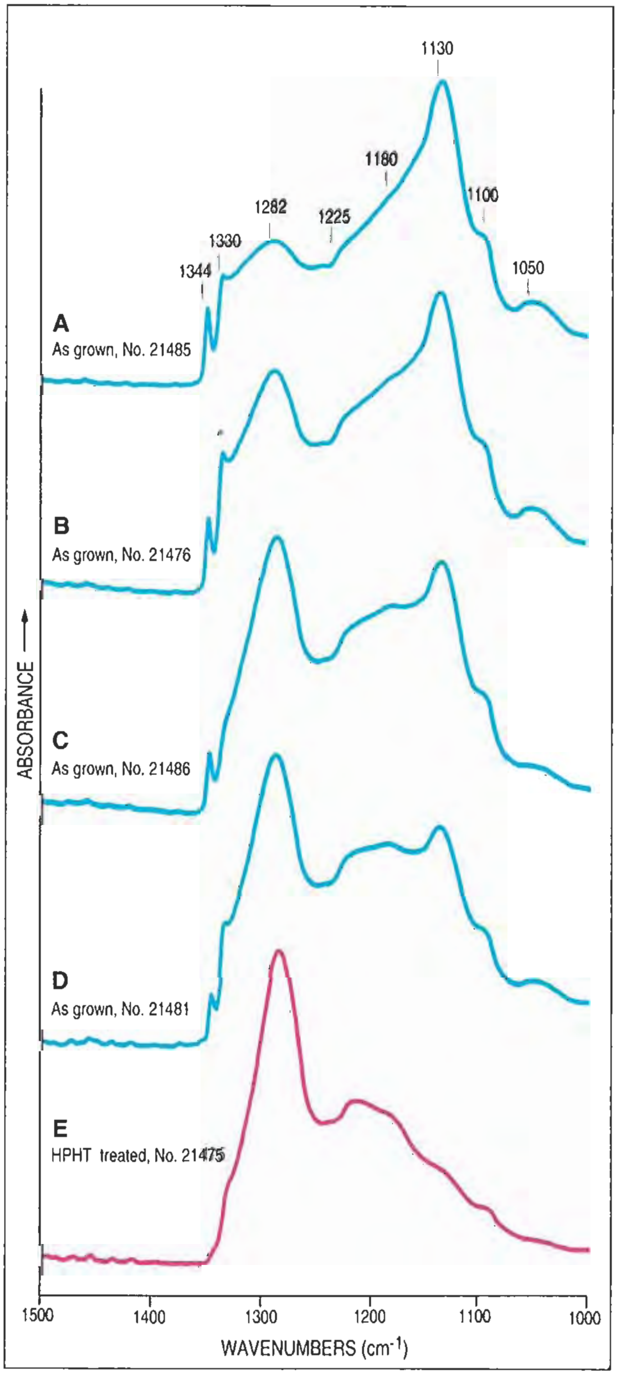


Figure 24. These mid-infrared absorption spectra (in the "nitrogen region") of four as-grown synthetic diamonds and one HPHT-treated sample reveal the different diamond types represented. Type-Ib diamonds are characterized by a sharp band at about 1344 cm^{-1} and a broader band at 1130 cm^{-1}. Type-IaA diamonds have a broad band at about 1282 cm^{-1} and weaker bands at about 1225 and 1180 cm^{-1}. Type-IaB diamonds have a sharp band at about 1330 and a broader band at about 1180 cm^{-1} (see Field, 1992, p. 683). The spectra of the four as-grown synthetic diamonds show a range from an almost-pure type-Ib (A) to a mixture of type-Ib with, finally, a dominant component of type-IaA (D). Spectra A, B, and D also show a minor type-IaB component. The spectra of the three HPHT-treated stones are identical to one another in this region of the infrared, and are typical of an almost pure type-IaA diamond (E). The five spectra have been offset vertically for clarity.

DISCUSSION

Comparison to Other Synthetic Diamonds. Overall, we observed much greater variability from sample to sample in the Russian synthetic diamonds we studied than in any previous group of gem-quality synthetic diamonds. This is probably because of the growth technique used, and the fact that only one stone may be grown at a time, with considerable variability possible between production runs. Even so, we observed that these Russian synthetic diamonds have some gemological properties that are similar to, and some that are different from, other yellow and greenish yellow synthetic diamonds that we have examined.

For example, we have seen the yellow and greenish yellow colors described here in other synthetic diamonds (although, as discussed below, produced by different factors). In addition, the cube, dodecahedral, and trapezohedral faces identified on the Russian synthetic diamonds have also been reported on crystals of other gem-quality synthetic diamonds (Shigley et al., 1986; 1987; see also Rooney et al., 1993). The identification of cube faces and related internal growth sectors proves that these Russian samples are synthetic.

The color zoning, graining, and weak anomalous birefringence patterns seen in these Russian samples (but varying somewhat from one sample to the next) are generally similar to what we have observed in other yellow synthetic diamonds; thus they remain diagnostic identification features. Note, however, that the patterns of color zoning differ somewhat from those we have illustrated previously, probably because of the growth conditions used in Novosibirsk.

Metallic inclusions are among the most conspicuous diagnostic features of gem-quality synthetic diamonds (Shigley et al., 1986, 1987). In other yellow synthetic diamonds, we typically observed these metallic inclusions near the outer edges of the crystals (where they were subject to removal by faceting). In these Russian synthetic diamonds, however, the metallic inclusions were also frequently located deep within the crystals, often near the original seed. This was also true with the yellow and treated-red synthetic diamonds examined recently that we also believe to be of Russian origin (see Moses et al., 1993a, 1993b).

We never observed long-wave U.V. fluorescence of any intensity in other yellow synthetic diamonds, although almost all did exhibit weak-to-strong short-wave U.V. fluorescence, often zoned in intensity, primarily yellow to greenish or orangy yellow (Shigley et al., 1986, 1987). Thus, these Russian samples (both as-grown and HPHT treated) are the first synthetic diamonds we have examined that display long-wave U.V. fluorescence, in this case weak to very strong yellow to greenish yellow. (For the HPHT-treated samples, the fluorescence is more intense to long-wave than to short-wave U.V.; the reverse is true for the as-grown samples.) Thus, a simple check for short-wave, with no long-wave, U.V. fluorescence will not permit rapid identification of these Russian samples (in contrast to other yellow synthetic diamonds). Nonetheless, the uneven intensity of the U.V. fluorescence (and, similarly, of the cathodoluminescence) still reveals the different internal growth sectors characteristic of synthetic diamonds.

U.V. fluorescence is closely related to diamond type. Among our samples, pure type-Ib diamonds show no long-wave U.V. fluorescence. As the proportion of type-IaA increases, so does the intensity of the long-wave U.V. fluorescence. When the type-Ib and type-IaA components are roughly equal, the intensity of fluorescence to both long- and short-wave U.V. is roughly equal. The fluorescence behavior of the three HPHT-treated samples is typical of type-Ia diamond with no significant type-Ib component.

The three HPHT-treated samples, and one as-grown sample (no. 21486), exhibited moderate to strong yellow phosphorescence to both short- and long-wave U.V. Previously, we noted weak yellow phosphorescence to short-wave U.V. from the greenish yellow De Beers synthetic diamonds (Shigley et al., 1987) and from portions of one of the two 5-ct color-zoned yellow Sumitomo synthetic diamond crystals (Shigley et al., 1992).

Also distinctive of the Russian synthetic diamonds is the weak to moderate green luminescence to visible light seen in most of our samples , a feature we have not seen in other synthetic diamonds. This luminescence may be due to Ni-related defects present only in these Russian samples.

Cause of Color and Spectral Features. *U.V.-Visible Absorption.* The general increase in absorption toward the ultraviolet in the as-grown material is typical of type-Ib synthetic yellow diamonds (see Shigley et al., 1986, 1987). It produces a brownish to orangy yellow color. The lighter yellow color of all three HPHT-treated diamonds is due to the reduced absorption in the 400- to 500-nm range. The greenish component of the color of two of these stones is contributed by the additional broad absorption band with an apparent maximum at about 700 nm. This band is very weak in the as-grown samples, and so has little if any effect on their color. Because the absorption of this band in the HPHT-treated samples is not overwhelmed by the "type-Ib" nitrogen-related absorption, it plays a more important role in the coloration of these samples. Combined with the increasing absorption toward the ultraviolet, it defines a region of transmission around 560 nm in the yellow-green.

The 700-nm broad band may be a vibronic structure associated with the 793-nm band (C. Welbourn and P. Spear, pers. comm., 1993, based on their examination of our spectra). The 793-nm band has been reported in type-Ib synthetic diamonds grown in nickel and subsequently annealed at 1700°C (Lawson and Kanda, 1993a, 1993b). The well-known greenish color in low-nitrogen, non-HPHT-treated synthetic diamonds (typical of certain types of diamond grit) is due to a broad, nickel-related absorption with an apparent maximum and superimposed sharp peak at 885 nm (Collins, 1990). This feature is very different from the broad band with an apparent maximum at 700 nm seen in the HPHT-treated Russian material. It has never before been described as a cause of a greenish component in yellow synthetic diamonds.

The presence of sharp bands, some of which can be seen with the handheld spectroscope, is one of the new and important characteristics of the Russian production. Most of the absorption features described here, although essentially new to gemology, are not unknown to science.

The series of six absorption bands (from 617 to 658 nm, with the strongest at 658 nm) seen in the as-grown samples was first reported by Davies (1977), but at the time it was wrongly attributed to radiation damage. Collins and Spear (1982) discovered that this series, like the 494-nm band, was caused by Ni-related defects. Collins et al. (1990) later demonstrated that these defects occur only in the octahedral growth sectors of synthetic diamonds, where the nitrogen concentration is relatively high (100 to 300 ppm).

The group of four bands from 671 to 732 nm in some as-grown samples, and the series of sharp bands identified between 460 and 670 nm in our HPHT-treated samples, were first reported by Collins and Stanley (1985) in synthetic diamonds heated in the range 1700°–1900°C. At the time, it was hypothesized that they represented intermediate states of nitrogen aggregation. Only recently, Lawson and Kanda (1992, 1993a, 1993b) demonstrated that these bands are produced exclusively in diamonds grown using nickel or nickel-containing alloys and, therefore, are presumably all nickel-related defects. Similar results were obtained simultaneously, but independently, by Nadolinny and Yelisseyev (1992). It is interesting that Lawson and Kanda (1993a, 1993b) also describe yellow-to-green synthetic diamonds. Their green samples contain low concentrations of nitrogen, with nickel dominantly in a positive charge state, whereas their yellow samples contain more nitrogen, with nickel apparently dominant in a negative charge state. Therefore, Lawson and Kanda believe that many of the features observed in Russian synthetic diamonds are due to color centers involving not only nickel, but also nitrogen, presumably as dispersed atoms and A aggregates (see table 3).

Thus far, nickel-related absorption bands have been reported exclusively in synthetic diamonds (Collins and Spear, 1982; Lawson and Kanda, 1993b), so their presence can be considered proof of synthetic origin. They are particularly useful to the gemologist, since those located in the visible spectrum can be seen with a handheld spectroscope if the stone is cooled by a spray refrigerant. For example, the detection of the sharp band at about 658 nm helps identify a yellow diamond as synthetic.

We do not believe that any of the absorption bands we observed in the Russian samples described here are a result of radiation treatment.

Infrared Absorption. These Russian samples are the first gem-quality synthetic yellow diamonds we have examined that show a mixture of type-Ib with type-IaA diamond, although the occurrence of both type-Ib (dispersed) and type-IaA (aggregated) nitrogen has been reported in small, nongem diamonds grown for research purposes that were synthesized at relatively high temperatures (Kanda et al., 1990; Vins et al., 1991; Kanda and Yamaoka, 1993). All other gem-quality synthetic yellow diamonds we have examined have been pure type Ib.

The infrared spectra indicate that almost all of the dispersed nitrogen present in the as-grown crystals aggregates during HPHT-treatment to form exclusively A aggregates (pairs of nitrogen atoms). The conversion of type-Ib dispersed nitrogen to A aggregates was first reported by Chrenko and others (1977; see also Evans, 1992). Changes similar to those reported here have also been described by Lawson and Kanda (1993a, 1993b). To the best of our knowledge, this is the first report of the formation of A aggregates in as-grown crystals. The feature at 1050 cm^{-1}, rarely seen in natural diamonds, has been attributed by the same authors (1993b) to a defect related to a positively charged nitrogen ion.

Natural diamonds with strong infrared absorption due to type-IaB nitrogen often have the familiar 415-nm "N3" band in their visible spectrum. However, we did not observe this band in any of the Russian samples, even those with the strongest type-IaB character.

Comparison to Natural Diamonds. As with other productions of synthetic diamonds, these Russian samples exhibit several features by which they can be distinguished from natural diamonds of similar color. Specifically, the patterns of color zoning and graining—characteristic of synthetic diamonds—have not been seen in natural diamonds. Metallic inclusions, too, are distinctive of synthetic diamonds (Shigley et al., 1986, 1987). Although both metallic sulfide minerals and metallic iron have been reported in natural diamonds (Sobolev et al., 1981), these inclusions are neither Ni-containing nor Ni-rich, as is the case with the Russian synthetic diamonds examined here. GIA researchers have never encountered an Fe-rich metallic inclusion in a faceted gem-quality natural diamond.

Although metallic inclusions are of diagnostic value, the presence of tiny pinpoint inclusions should not be used as an indication of synthesis because they can occur in both natural and synthetic diamonds with similar appearance.

When comparing the color and absorption spectra of these synthetic and similar natural diamonds, it helps to distinguish between yellow and greenish yellow samples. Most natural yellow diamonds are type-Ia, with blue, yellow, or green U.V. fluorescence (long-wave > short-wave) and an absorption spectrum with a 415-nm and other sharp bands of the "Cape series" (Collins, 1982; Liddicoat, 1987). Type-Ib natural yellow diamonds (sometimes referred to as "canary" diamonds) invariably display some type-Ia character in their infrared spectra, fluoresce yellow or orange-yellow to U.V. radiation (in some cases, with short-wave > long-wave), and have an optical absorption spectrum that lacks sharp absorption bands (Collins, 1982).

The green coloration in greenish yellow type-Ia natural diamonds has several possible causes. These include the broad absorption centered about 620 nm due to the GR1 band, which is produced by exposure to radiation either in nature or in the laboratory. Alternatively, natural yellow diamonds with strong H3 (503 nm) and H4 (496 nm) spectral bands may exhibit a greenish color as a result of these two color centers luminescing to visible light. Often, the color in yellow to greenish yellow diamonds is concentrated along graining planes that luminesce green (or blue) to visible light. Again, the greenish hue of two of the HPHT-treated samples is not due to either GR1 absorption or green luminescence to visible light.

The Russian synthetic diamonds are either type Ib+IaA (and sometimes a little IaB) or nearly pure type IaA. They exhibit yellow to greenish yellow U.V. luminescence, but with a zonation different from that of their natural counterparts. Their absorption spectra contain sharp bands in wavelength positions that are different than those seen in natural diamonds. These sharp bands, due to Ni, are sometimes visible with a handheld spectroscope. For the most part, they are located where few if any bands are seen in the spectra of natural yellow diamonds (except the bands at 496, 503, and 594 nm seen in some natural- and treated-color yellow diamonds).

Effects of HPHT Treatment. The yellow to greenish yellow treated synthetic diamonds described here are the first HPHT-treated synthetic diamonds we have examined. The possibility of treatment could increase the challenge that identifying synthetic diamonds poses for gemologists. In the present case, HPHT treatment appears to have affected the color, the U.V. luminescence, and the visible absorption spectra. Fortunately, HPHT treatment also gives rise to other diagnostic gemological properties; for example, some additional sharp bands are visible at low temperature with the handheld spectroscope. Moreover, it does not alter either the graining or the zoning of color and U.V. luminescence, which patterns remain the same as those seen in the as-grown samples. Finally, it is important to note that we have seen no evidence to date that HPHT treatment can produce a near-colorless synthetic diamond from type-Ib starting material.

CONCLUSION

The gemological properties of these Russian samples, grown by the BARS technique, expand the documented criteria for identifying gem-quality synthetic yellow diamonds. In these Russian samples, we observed the characteristic metallic inclusions as well as zoned U.V. luminescence, uneven color, and/or graining patterns related to the arrangements of internal growth sectors.

These Russian synthetic diamonds also exhibited some properties that we had not seen before in other synthetic diamonds. First and foremost, all but one fluoresced to long-wave U.V. radiation, and the HPHT-treated stones fluoresced stronger to long-wave U.V. radiation than to short-wave U.V. (as is typical of fluorescing natural diamonds). One of the as-grown samples, and all three HPHT-treated samples, showed yellow phosphorescence. As a result, U.V. luminescence (i.e., short wave > long wave) can no longer be considered diagnostic for synthetic yellow diamonds. However, the presence of sharp absorption bands between about 460 and 560 nm, and about 637 and 658 nm, are distinctive of Russian synthetic diamonds. Many of these bands can be seen with a handheld spectroscope. The sharp bands, in some cases quite numerous, in the visible absorption spectrum are due to the fact that nickel can enter the crystal structure of diamond and there give rise to one or more color centers. Heat treatment of these yellow synthetic diamonds at high pressure can produce a greenish yellow color.

There is one final point of interest: the significant variation in gemological properties from one sample to the next. Even considering that only 10 stones were studied, this variability was greater than what we have observed in other yellow synthetic diamonds. Several factors may be responsible. The small chamber in the BARS apparatus means that only a few good-quality synthetic diamond crystals (perhaps just one) can be grown at a time (as opposed to batch growth, which is possible with the "belt" apparatus). Each synthetic diamond crystal is, therefore, grown under slightly differing conditions of temperature, pressure, time, system chemistry, and so on. The concentrations of nitrogen and nickel are also likely to vary between crystals. Variability in the conditions of HPHT treatment will also affect the different gemological properties. Thus, gemologists are warned that it may be a challenge to establish simple identification criteria for gem-quality Russian synthetic diamonds that will be valid in all cases.

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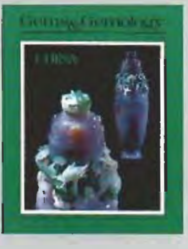

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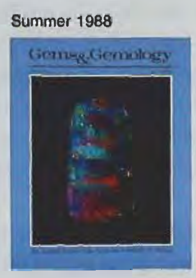

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HEAT TREATING THE SAPPHIRES OF ROCK CREEK, MONTANA

By John L. Emmett and Troy R. Douthit

Renewed interest in large-scale commercial mining of Montana sapphires motivated a detailed study of the heat treatment of sapphire from the Rock Creek deposit. During the course of this systematic study, over 75,000 stones were processed. It was found that approximately 65%–70% of the pale blue, pale green, and near-colorless sapphire could be converted to well-saturated blue and yellow colors. Some improvement in clarity was noted as well. Yellow hues were easily developed by heating in oxidizing atmospheres and were relatively insensitive to time and temperature. Blue hues were developed by processing in reducing atmospheres. The relatively high iron content of Rock Creek material restricts the range of reducing conditions that can be used to achieve optimal coloration because of hercynite precipitation in the sapphire.

ABOUT THE AUTHORS

Dr. Emmett and Mr. Douthit are principals in the firm Crystal Research, Pleasanton, California.

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The sapphire deposits of Rock Creek, Montana, have been known since the late 1890s. In fact, from 1906 to 1943 they were mined almost continuously to provide corundum for industrial applications. While most sapphires from this deposit are of gem clarity, the hues in which they typically occur—pale blue, pale green, pink, pale yellow, or near colorless—are not commercially desirable. Although natural blue, yellow, and pink sapphires with good color saturation are found at Rock Creek, the quantities are too small to justify commercial mining for these gems alone (figure 1).

In principle, heat treatment can improve color, clarity, or both in sapphire (Nassau, 1981, 1984; Themelis, 1992), and for many years now sapphires from various localities have been successfully enhanced in this fashion. Rock Creek sapphires have been heat treated locally and in Asia since at least 1977, but the results have been highly variable (G. Billings, pers. comm., 1993). As part of their overall evaluation of the commercial viability of the Rock Creek deposits, Skalkaho Grazing Inc. retained the authors to undertake a detailed, systematic study of the response of this material to heat treatment. This article presents quantitative as well as qualitative results of our efforts to develop optimal heat-treatment processes for the Rock Creek sapphires (figure 2). It also provides an explanation of various aspects of the physical processes involved in sapphire heat treatment.

HISTORY AND BACKGROUND

Sapphire was discovered in Montana in 1865. George F. Kunz (1894) attributes the discovery to Ed Collins, a gold miner who was working on one of the gravel benches, or "bars," just above the Missouri River near Helena. By 1895,

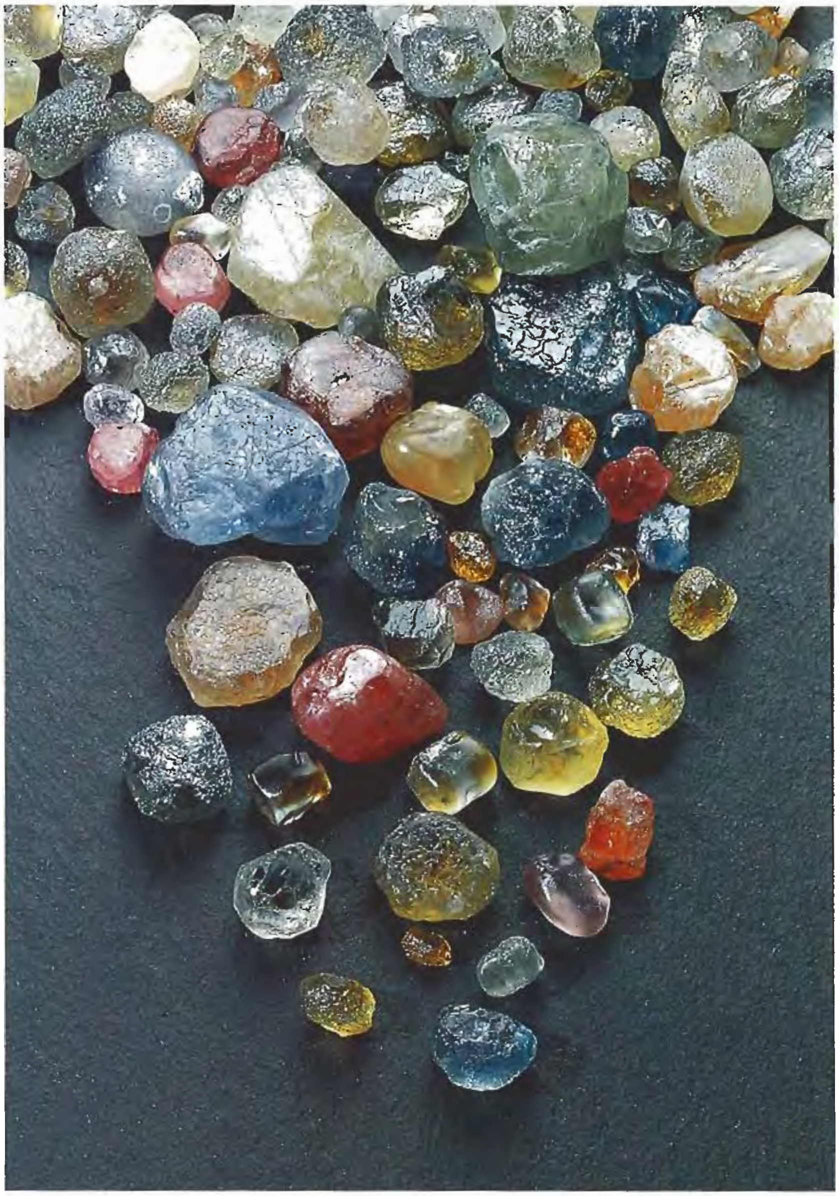


Figure 1. These rough sapphires were assembled from material mined at Rock Creek to show both the size range (here, 0.5–15 ct) and color range from this Montana deposit. Note that the largest—and the well-saturated—stones featured here represent a very small percentage of the total production. Photo © GIA and Tino Hammid.

the relentless search for gold in Montana had resulted in the discovery of most of the significant deposits of sapphire that had sufficient clarity to be classed as gem material. Of the many deposits discovered, four have been mined on a more or less substantial basis: Rock Creek, Dry Cottonwood Creek, Yogo Gulch, and the gravel bars of the Missouri River, most notably Eldorado Bar (figure 3). Detailed accounts of these deposits, including some fascinating historical material, are contained in Pratt (1906), Clabaugh (1952), Sinkankas (1959), and Voynick (1987). At Rock Creek, Dry Cottonwood Creek, and the Missouri River bars, all of the sapphires found to date have been in secondary, or placer, deposits. Although the sapphires from these three deposits are similar in color—primarily near colorless, pale green, pale blue, pale yellow, pink, and orange—they differ from one deposit to the next in such characteristics as size, dominant crystal morphology, and quantitative trace-element composition. Historically, stones from these three deposits have been sold primarily for industrial purposes: the manufacture of wire-drawing dies, watch bearings, and other precision instrument bearings. Only a negligible portion of these sapphires have been sold for jewelry use because of the pale, rather uninteresting natural colors.

Rock Creek is unique in that it was the only placer deposit in Montana rich enough to be mined for sapphire alone in the years from discovery to

Figure 2. The 3.08-ct sapphire in this ring illustrates the depth of color achieved in the larger Rock Creek sapphires with heat treatment. Photo © GIA and Tino Hammid.

World War II (Clabaugh, 1952). The main mining area is located in Granite County, about 16 miles (26 km) southwest of Philipsburg, in and along two tributary gulches on the north side of West Fork Rock Creek (again, see figure 3). The westernmost gulch is known as Anaconda Gulch; Sapphire Gulch, called Myers Gulch before the onset of sapphire mining, lies about 1$^1/_2$ miles to the east. Sapphire has also been found in most of the smaller gulches that drain into the Anaconda and Sapphire gulches and in the long meadow along West Fork Rock Creek extending eastward from the mouth of Anaconda Gulch. Farther north, sapphire has been found in the Quartz and Cornish gulches as well. Sapphire has not been reported south of West Fork Rock Creek.

Enormous quantities of sapphire have been mined from Rock Creek. We were able to review mining records for 10 years of production during the period 1906–1923, which show cumulative shipments to customers of 38 metric tons from the Anaconda and Sapphire gulches alone (J. Higgins, pers. comm., 1993). Records for specific weekly shipments in 1907 reveal an average of 1,000 pounds (455 kg) per week. This number is even more impressive when one notes that the material shipped was deemed sufficiently clean and fracture free to be used for precision industrial applications. Rock Creek continued to produce and ship large quantities of sapphires until 1943. Shipping documents from 1936, for example, show substantial sales to such concerns as Diamond Tool Company of New York; Industrial Jewel Company of Waltham, Massachusetts; Eugene Deshusses of Geneva, Switzerland; and General Electric Company of West Lyons, Massachusetts (J. Higgins, pers. comm., 1993).

The mining of sapphire in Montana for industrial applications was effectively terminated by the development of large-scale production capabilities for synthetic sapphire, most notably by Union Carbide in the U.S. and Hrand Djevahirdjian in Switzerland. Using the Verneuil flame-fusion growth process, these companies produced a very uniform, high-quality synthetic sapphire, in volume, at such low cost that the industrial use of natural crystals was quickly abandoned. Since 1943, there has been little interest in commercially mining the Rock Creek deposits. A portion of the deposit, known as the Gem Mountain Sapphire Mine, has been operated for many years as a fee digging area for hobbyists and individual gem miners, and it is now operated as a fascinating tourist attraction where individuals can screen sapphires from sapphire-bearing ore mined by the operators.

Skalkaho Grazing owns the portion of the deposit that encompasses the long meadow at the mouths of the Anaconda and Sapphire gulches, and it is this area that the company is evaluating to determine the economic feasibility of large-scale gem mining. During the summers of 1972 and 1973, the Day Mining Company drilled and assayed the portion of this meadow that is at the mouth of Anaconda Gulch. In addition to the drill core samples, they mined a large ore sample of approximately 3700 cubic yards which yielded 47 ct per cubic yard, or a total of approximately 35 kg (J. Higgins, pers. comm., 1993). These and subsequent studies conservatively calculated a recoverable reserve over 25 million carats for the portion studied. Since only the portion of the long meadow adjacent to the mouth of Anaconda Gulch was sampled, it is probable that the total sapphire recoverable from the whole meadow substantially exceeds this figure. However, after careful study of the sapphire sample, including cutting and appraisal of the stones, the

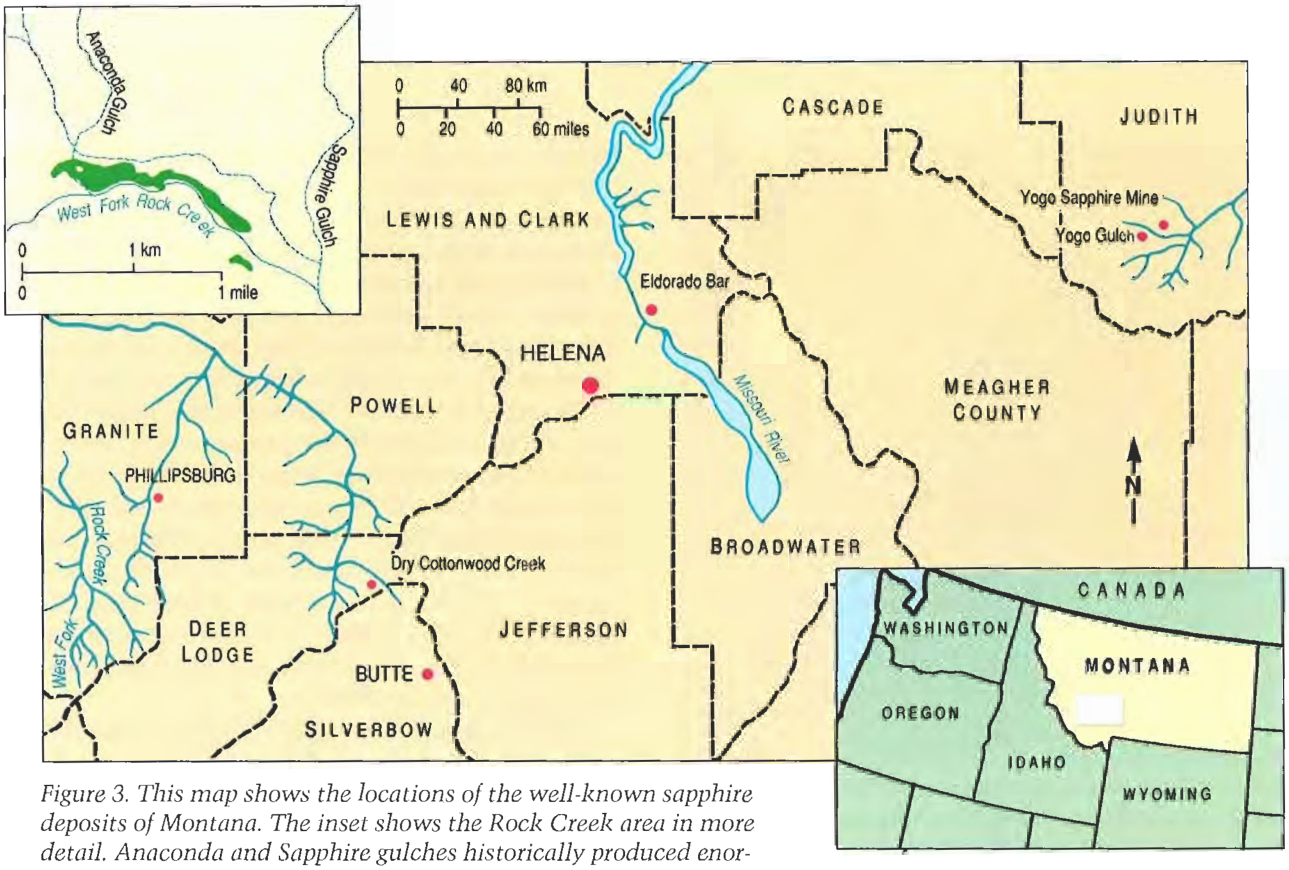


Figure 3. This map shows the locations of the well-known sapphire deposits of Montana. The inset shows the Rock Creek area in more detail. Anaconda and Sapphire gulches historically produced enormous quantities of sapphire. The meadow region along West Fork Rock Creek at the mouths of the Anaconda and Sapphire gulches was never mined commercially. The sapphire discussed in this article is from the meadow property. Artwork by Carol Silver.

Day Mining Company decided not to develop the deposit because the yield of commercially valuable colors was too low to be economic. Note, though, that commercial heat treatment was in its infancy in the early 1970s, and was not being applied to Montana sapphires.

DESCRIPTION OF THE ROCK CREEK SAPPHIRES

Sapphires found at Rock Creek range up to about 15–20 ct, although stones over 10 ct are found only occasionally. The early production records referred to previously (10 years in the period 1906–1923) indicate that crystals seldom exceed 6 ct (8.4 mm), with almost 75% in the range 0.1–2.2 ct (2.2–6.5 mm; see figure 4). These stones are typically near colorless, pale blue, pale green, pink, and pale yellow. Some show both pale yellow and pale green or blue in the same stone; these are locally referred to as "pintos." A few stones in highly saturated hues are also recovered. The approximately 35 kg recovered by Day Mining Company was graded for hue as shown in figure 5. Day Mining concluded that only 8% had sufficient color saturation to be marketable as gems. Therefore, 92% of the stones recovered are near colorless or of pale hue.

The best characteristic of Rock Creek sapphire is its clarity: Most stones, as mined, are sufficiently transparent and free of fractures and large inclusions to be faceted (see, e.g., figure 6). While a large proportion (90%) of the stones have at least some inclusions (fine rutile needles or silk), only 5%–10% of these stones contain enough inclusions to substantially reduce visual clarity. These rutile inclusions can be dissolved by heat treatment both to increase clarity and induce a blue coloration.

A small portion of Rock Creek sapphire crystals show sharp and distinct crystal faces. On the great majority of crystals, however, the faces are abraded or corroded, giving an overall appearance of rough, almost spherical pebbles. Careful examination reveals that the original crystals are hexagonal cylinders or modified hexagonal cylinders. Thus, they usually show both the unit prism $\{11\bar{2}0\}$ and the basal pinacoid $\{000\bar{1}\}$. These forms are often

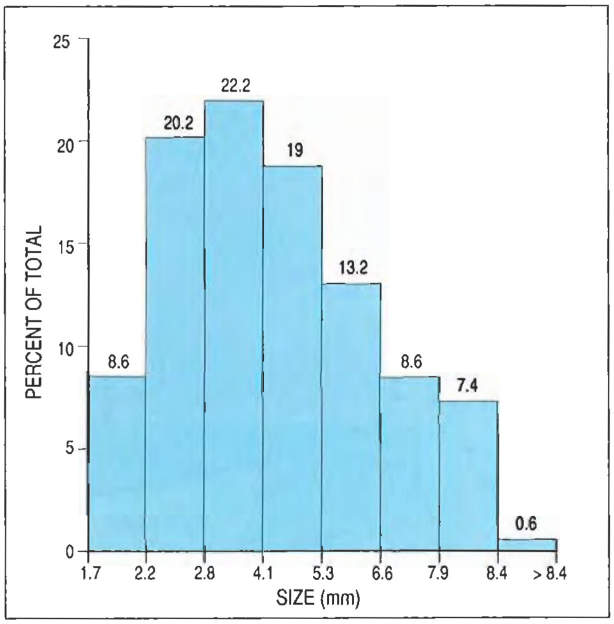


Figure 4. Rock Creek sapphires over 8.4 mm (about 6 ct) make up only 0.6% of mine-run material. The vast majority range from 2.2 to 7.9 mm (0.1 to 2.2 ct). This histogram of sapphire size was assembled from production records for 10 years of mine operation within the period 1906–1923; it represents a total of 38 metric tons of rough sapphire shipped from the Anaconda and Sapphire gulches, as graded through square-aperture screens. For example, the 22.2% bar represents those stones retained on a sieve with holes 2.8 mm square and passed through a sieve with 4.1-mm holes. Data courtesy of J. Higgins.

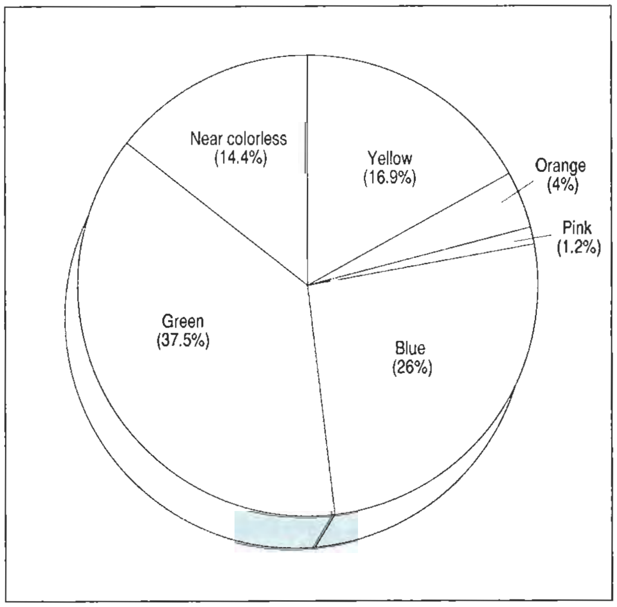
modified by the unit rhombohedron $[10\bar{1}1]$ and the second order pyramid $[22\bar{4}3]$. While a small percentage of the crystals occur as thin hexagonal plates or long prisms, most appear as slightly flattened spheres in which the c-axis is about 0.7 to 0.8 times as long as the a-axis—well suited to the faceting of standard round brilliants.

EFFECTS OF HEAT TREATMENT ON CLARITY AND COLOR

Clarity Enhancement. It is the scattering of light, rather than the absorption or direct transmission of light, that is responsible for a lack of clarity in normally transparent gem materials. Anything in the gem (like a fracture or an inclusion) with an index of refraction different from that of the host material will scatter light by reflecting it off its surfaces, thus reducing the clarity of the host. In general, heating to high temperatures alone will not improve the clarity of a stone that has multiple fractures, as it will not close and seal a significant portion of the fractures. However, heating the stone to a high temperature for 10–20 hours does usually produce enough solid-state diffusion bonding to partially heal some fractures. This process strengthens the stone so that it can subsequently be cut without disintegration. Note that fracture filling is often part of the heat-treatment process, with borax or other boron compounds being used. However, the use of such fracture-filling materials is not part of the work described in this article. On rare occasions, iron-stained fractures in sapphire may become somewhat less visible if heat treated at high temperatures (1800°C), because at such temperatures iron oxides decompose and vaporize out of the fracture (Sata, 1984).

More commonly, sapphire crystals contain very large numbers of microcrystals of another mineral (Gübelin and Koivula, 1986) that are often so small (0.5–20 μm) and so numerous that they appear as a cloud or haziness to the unaided eye, substantially

Figure 5. This chart is adapted from color grading done by Day Mining Company on a large sample of sapphires obtained at Rock Creek in 1972. With the exception of the fractions marked orange and pink, the colors are quite pale on the average. Day Mining Company determined that 8% of the total material had sufficient color saturation to be marketable as gems. Data courtesy of J. Higgins.



reducing the clarity of the host gem. In many cases, when the stone is heated to high temperatures, the microcrystals will dissolve back into the sapphire and remain in solid solution as the stone cools rapidly (relative to geologic processes), thus substantially improving the clarity. It is worth noting at this point that it is not necessary to melt the microcrystals to dissolve the material back into the sapphire. Since diffusion into solid sapphire is the limiting diffusion rate, it does not matter, temperatures being equal, whether the inclusion is solid or liquid. Rutile, for example, has a melting point of about 1830°C, yet rutile needles 1–5 µm in diameter will dissolve rapidly into sapphire at 1600°C. In this case, a combination of the finite solubility of TiO_2 in sapphire at 1600°C and the unusually high diffusion rate of Ti^{4+} determines the apparent rate of dissolution.

In the specific case of Rock Creek sapphire, as noted above, we find that the great majority of the stones as mined possess unusually high clarity. However, stones that appear somewhat brown or green usually contain a small amount of exsolved rutile as fine needles (Bratton, 1971; Phillips et al., 1980) and another phase of small (5 µm), compact, euhedral crystals of an as-yet-unidentified material. While the rutile needles easily dissolve into the sapphire, the unidentified crystals do not. Since the quantities of these unidentified microcrystals are very small relative to the rutile needles, heat treatment that dissolves the rutile produces extraordinarily high clarity in the sapphire. Natural-color Rock Creek stones with highly saturated colors, if they are heat treated at all, are processed solely to dissolve the rutile.

Color Enhancement. To understand the color transformations that can be induced by various heat-treatment processes, it is necessary first to understand the origins of color in sapphire. Inasmuch as there are at least seven causes of the yellow coloration alone (Nassau and Valente, 1987), in this article we will address only those agents that are directly responsible for the coloration of the Rock Creek material.

Absolutely pure sapphire is composed only of aluminum and oxygen (Al_2O_3). Such material has a transparency range from approximately 160 nm in the far ultraviolet to 5500 nm in the infrared region of the spectrum. Thus, pure sapphire is colorless. All color in sapphire is the result of impurities (other elements) or other point defects in the crystal (Kröger, 1984; Fritsch and Rossman, 1987, 1988). These other point defects can be, for example, missing atoms (a vacancy in the lattice), additional (interstitial) atoms, or charge carriers such as extra electrons.

Figure 6. Although all of these natural-color Rock Creek sapphires (0.32–1.04 ct) exhibit high clarity and consequently are quite bright, only the rare, more saturated, blue stone would find a ready market. Photo © GIA and Tino Hammid.

Heat treatment can induce chemical reaction among the existing impurities and other point defects in sapphire, thus producing entirely different absorption spectra and corresponding transformations in color. Specifically, heat treatment can potentially induce any or all of the following processes:

1. Change the valence state of an impurity, thus changing the absorption spectrum
2. Induce isolated impurities to form pairs that absorb differently from the unpaired impurities
3. Dissolve exsolved minerals, which can bring new impurities into solution, adding new absorptions
4. Exsolve or precipitate impurities out of solution, thus changing the combination of absorbing impurities in solution

For an understanding of the terminology and techniques of heat treatment discussed here, see box A, on thermochemistry.

BOX A: THERMOCHEMISTRY

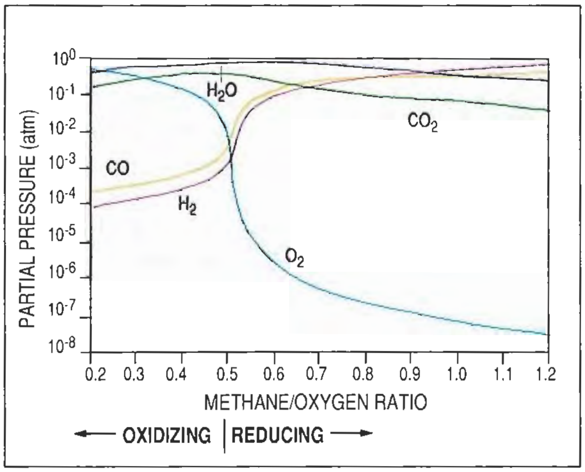


Figure A-1. This chart shows the partial pressures of the major products of combustion of methane and oxygen at 1700°C. Oxygen partial pressure is controlled by manipulating the methane/oxygen ratio of the gases fed in to fire the furnace. Note that hydrogen partial pressure increases rapidly as the reducing regime is entered. Thus, reductions in furnaces burning hydrocarbon fuels with oxygen or air are always done in the presence of hydrogen, which strongly participates in the solid-state chemical reactions in sapphire. (At low oxygen partial pressures and high temperatures, O_2 *is largely dissociated into oxygen atoms. To simplify presentation, we have plotted the oxygen partial pressure equal to* $pO_2 + {}^1/_2\, pO$*.)*

In the discussion of sapphire heat treatment, we use the terms *oxygen partial pressure* and *hydrogen partial pressure* to describe the atmosphere inside the furnace. *Oxygen partial pressure* simply means that portion of the total gas pressure that is attributable to oxygen. For example, the oxygen partial pressure of air is 0.2 atmospheres (atm), since oxygen makes up about 20% of the air. At high temperatures, both the valence state of the impurities and the concentrations and types of other point defects in oxide crystals (such as sapphire) can be changed by changing the oxygen partial pressure, thus changing color. The point defects with which we are most concerned are missing oxygen or aluminum atoms (vacancies), extra oxygen or aluminum atoms (interstitial atoms), or extra electrons or holes. As the oxygen partial pressure is raised, oxygen vacancies decrease and oxygen interstitials increase. Likewise, aluminum interstitials decrease and aluminum vacancies increase. Since all of these responses to the change of oxygen partial pressure are initiated at the surface of the crystal, how is the inside of the crystal changed? Some of these point defects are highly mobile at high temperatures and can move in or out of a crystal by diffusion. Oxygen does not really diffuse in or out of the sapphire crystal as the diffusion rate is far too slow. Rather, the effect of oxidation or reduction on color, in response to changes in the oxygen partial pressure, is achieved by diffusion of these much more rapidly moving point defects (Dutt and Kröger, 1975).

The hydrogen partial pressure in the furnace is also important, because hydrogen atoms are so small that they can diffuse rapidly into sapphire and participate in solid-state chemical reactions. Other typical furnace gases, such as N_2, CO, CO_2, H_2O, etc., do not diffuse into sapphire to any significant degree because their atoms are relatively large.

How are furnace atmospheres controlled? Sapphire is often heat treated in furnaces that burn natural gas, propane, oil, or charcoal with air and/or oxygen. The stones are exposed to an atmosphere made up of the high-temperature combustion gases. For example, if the furnace burns natural gas, which is mostly methane, with oxygen, the combustion reaction is essentially

$$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$$

As written, the formula indicates that there is exactly enough oxygen to burn all of the methane to water vapor and CO_2 (methane/oxygen ratio = 0.5); thus we have a neutral flame. If we have more than enough oxygen, excess oxygen appears in the combustion gases. If we have insufficient oxygen to complete combustion, both carbon monoxide (CO) and hydrogen (H_2) exist in the combustion gases, and the oxygen partial pressure (pO_2) is very low. Figure A-1 shows the partial composition of the furnace gases at 1700°C as the methane/oxygen ratio is varied from oxidizing to reducing. Thus, by changing the ratio of methane and oxygen fed in to fire the furnace, both the oxygen and hydrogen partial pressures of the combustion gases making up the furnace atmosphere can be controlled over a wide range, but not independently. However, the furnace temperature is somewhat dependent on the methane/oxygen ratio of the gas firing the furnace. For example, if the ratio is very high or very low, one usually cannot maintain the furnace at the high temperature desired. Electrically heated furnaces can provide any furnace atmosphere independent of temperature, as described in the article.

In other heat-treatment approaches, stones are packed in charcoal or sugar in partially sealed crucibles to create reducing atmospheres (Nassau, 1984; Themelis, 1992). While the charcoal or sugar exists, the oxygen partial pressure is very low. In fact, it is lower than is optimal for high iron-content sapphire. In the presence of carbon, the oxygen partial pressures at 1300°C and 1800°C must be less than 10^{-16} atm and 10^{-14} atm, respectively. What is generally not recognized about these types of reductions is the important role of hydrogen. In temperate climates, dry charcoal usually contains 8%–12% water. As the temperature is raised, water is driven off but it is also split by the water-gas reaction with carbon as follows:

$$C + H_2O \longrightarrow CO + H_2$$

This creates an atmosphere that has almost equal amounts of carbon monoxide and hydrogen. Thus, reductions conducted in a charcoal environment are usually accomplished more by hydrogen than by equilibration with the extremely low oxygen partial pressure defined by excess carbon. A related situation exists with sugar, starch, or other organic materials. Sucrose sugar, for example, is approximately $C_{12}H_{22}O_{11}$. When heated to high temperatures, it decomposes, creating an atmosphere with almost equal amounts of carbon monoxide and hydrogen. Under such conditions, the oxygen partial pressure is low but, again, reductions are usually driven by hydrogen.

Hercynite precipitation ($Fe^{2+}Al_2O_4$) constrains reduction conditions in high iron-content sapphire such as the Rock Creek material. Figure A-2, adapted from Meyers et al. (1980), shows the phase diagram of iron oxides and Al_2O_3 at 1500°C. High oxygen partial pressures are referred to as "oxidizing conditions"; low oxygen partial pressures as "reducing conditions." A "deeper reduction" means that we have lowered the oxygen partial pressure, for example, from 10^{-6} atm to 10^{-7} atm. At high oxygen partial pressures (very top of diagram), iron remains in the sapphire in solid solution (within the sapphire crystal structure) up to rather high concentrations. As the oxygen partial pressure is reduced, iron spinel (hercynite) precipitates out of the corundum phase. As the oxygen partial pressure is further reduced, metallic iron precipitates. Excellent identification and imagery of the phases associated with these processes are presented in the paper by Moon and Phillips (1991). Thus, hercynite precipitation limits the depth of reduction that can be used to treat high iron-content sapphire.

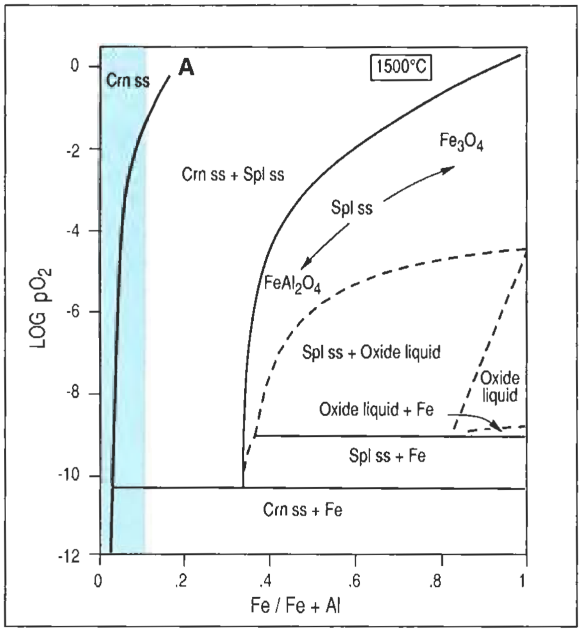


Figure A-2. The phase diagram of aluminum oxide and iron oxides is shown at 1500°C as a function of composition and oxygen partial pressure (Meyers et al., 1980). The vertical axis is the oxygen partial pressure in the furnace atmosphere. For example, −4 means that the oxygen partial pressure is 10^{-4} atm. For gem sapphire, we are interested in only the far left (blue shaded) portion of the chart. A typical Rock Creek sapphire would correspond to about 0.025 on the horizontal axis. At high oxygen partial pressure, above the phase separation boundary (marked A), iron remains in solid solution in sapphires. As the oxygen partial pressure is lowered below the phase separation boundary, iron begins to precipitate as hercynite ($Fe^{2+}Al_2O_4$) particles, and then as metallic iron particles. Hydrogen in the reducing atmosphere shifts the phase separation boundary to the left. Key: Crn ss = sapphire solid solution, Spl ss = spinel solid solution, Fe = metallic iron. (Figure reproduced with permission of its authors and The American Ceramic Society.)

Temperature-time profiles for heat-treatment processes are usually determined more by the desire to achieve longevity in the muffle tubes and heating elements of the furnace than by any special requirement of Rock Creek sapphires. At 1700°C, the diffusion of point defects responding to changes in oxygen partial pressure, hydrogen diffusion, and rutile dissolution require less than one hour to equilibrate in a 15-ct stone. Thus, one hour at this temperature is quite sufficient. The high resistance of sapphire to thermal shock–induced fracture would allow heating to 1700°C in one hour or less, and cooling at a similar rate. However, furnace components may deteriorate rapidly under such conditions, so the rise and fall portions of the heat-treatment cycle are determined more by economic decisions than by thermo-chemical ones.

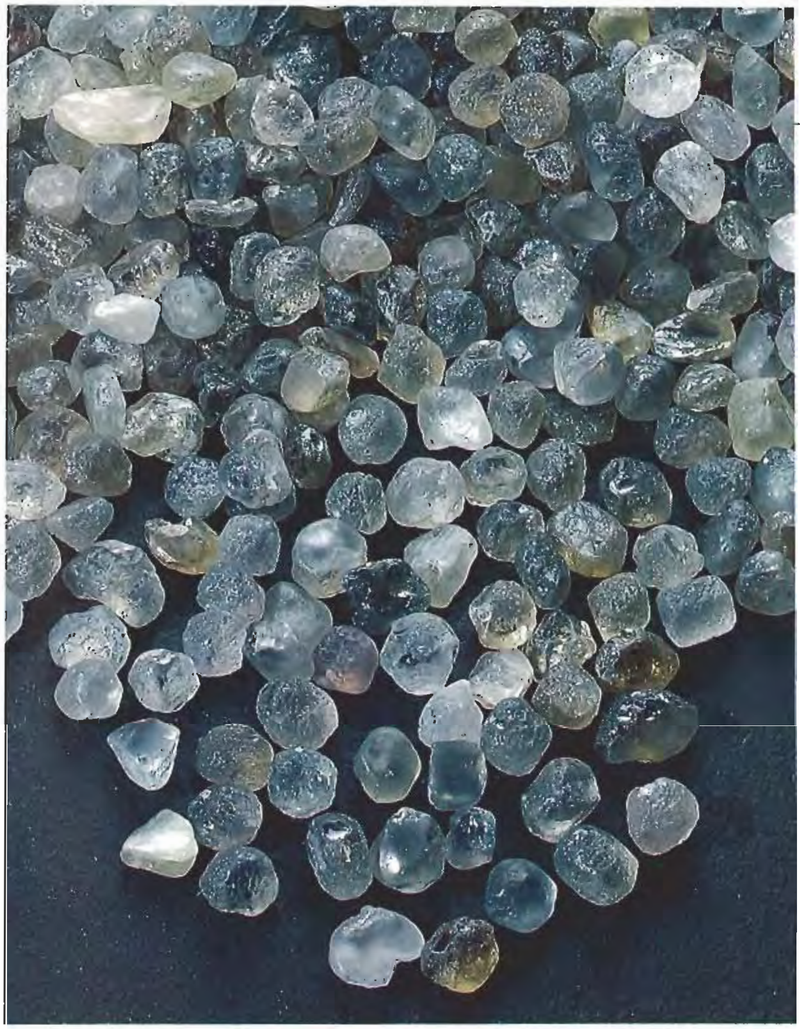


Figure 7. This sample of rough Rock Creek sapphire has been graded for size (average 4.5 mm), but the near-colorless, pale green, and pale blue colors are typical of the great majority of Rock Creek sapphires. The heat-treatment experiments focused on this color range of material and produced the heat-treated rough and faceted stones illustrated in this article. Photo © GIA and Tino Hammid.

As with almost all chemical reactions, heat increases the reaction rate. Thus, the heat of heat treatment is applied to achieve reaction rates that are rapid enough to be useful. In principle, a specific solid-state chemical reaction in sapphire can be achieved at 1600°C or at 1750°C, with treatment for different lengths of time. In practice, temperatures are chosen between 1300°C and 1900°C for the convenience of the treater or to optimize a specific chemical reaction over other competing reactions.

Far more important than the temperature is the atmosphere to which the stones are exposed inside the furnace. Since sapphire is an oxide, at high temperature its point-defect structure and the valence states of dissolved impurities are quite sensitive to the oxygen partial pressure of the furnace atmosphere (Kröger and Vink, 1956; Kröger, 1974). Low oxygen partial pressures promote the reduction of impurity ions, such as the partial reduction of Fe^{3+} to Fe^{2+}. High oxygen partial pressures drive the reaction in the other direction, that is, Fe^{2+} to Fe^{3+}. The hydrogen partial pressure in the furnace atmosphere is another important variable. Among the chemically reactive gases, only hydrogen atoms are small enough to diffuse rapidly into a sapphire crystal and actually take part in solid-state chemical reactions (El-Aiat and Kröger, 1982; Norby, 1990). Some chemical reactions in solid oxides—including, for example, sapphire and zircon, which require reduction (i.e., of the valence of a particular ion)—will not proceed without hydrogen regardless of how low an oxygen partial pressure is maintained. Thus, the major variables available to the heat treater to manipulate the color of sapphire are the oxygen partial pressure, the hydrogen partial pressure, the temperature, and the time held at that temperature. The temperature and time held at temperature are of far less importance than the oxygen and hydrogen partial pressures, as time and temperature are chosen only to assure that a desired chemical reaction goes to completion. However, it is the oxygen and hydrogen partial pressures that determine what type of chemical reaction proceeds and thus whether a Rock Creek sapphire, for example, changes to yellow or blue.

MATERIALS AND METHODS

For this study, Skalkaho Grazing supplied us with 15.7 kg of rough sapphire. These stones were a portion of the smaller rough of a 110-kg lot separated by Skalkaho Grazing in 1989 from ore mined in the meadow at Rock Creek in 1982 (J. Higgins, pers. comm., 1993). They were partially color graded by Skalkaho Grazing and could be characterized as pale blue, pale green, and near colorless; thus, they represented the corresponding hue groups of figure 5 but with highly saturated stones removed—that is, about 75% of the mine-run material. The stones were not separated by hues but were thoroughly mixed so that any sample from the lot contained all the hues described. We graded these stones for size through circular-hole diamond sieves and found a very narrow size distribution which averaged 4.5 mm (0.73 ct). In the experiments described below, where individual lots of rough stones were processed, every effort was made to ensure that each small experimental group was fully representative of the entire lot. Figure 7 shows a typical sample of this material. It is an accurate representation of the entire lot in both size and color of the individual stones.

In addition to the material described above, Skalkaho Grazing also supplied small quantities (10–30 grams) of rough stones from yellow and pink hue groups of figure 5. These stones were used primarily for spectroscopic studies. The large quantities of this material necessary for heat-treatment process development were not available at the time.

To determine the most effective heat-treatment conditions—temperature, time at temperature, and the composition of the furnace atmosphere (as discussed above)—we conducted more than 115 separate experiments. For each experiment, we used a fresh 50-gram lot (~340 pieces) of the rough Rock Creek sapphire previously described. When more critical comparisons of two different heat-treatment conditions were required, we increased the lot sizes to 100 grams (~680 pieces), 200 grams (~1,360 pieces), or 400 grams (~2,720 pieces) to ensure valid results. We made color assessments both visually and with a spectrophotometer. For the visual assessments, we not only sorted each heat-treated lot on a light box containing 5,000K fluorescent lamps, but we also made comparisons by viewing several different lots on the light box at the same time. We used the spectrophotometer both to make precise color determinations and to determine accurately the differences in the absorption spectra after heat treatment. Because the spectrophotometer requires samples with parallel polished surfaces to yield quantitatively comparable results, we had individual sapphires ground and polished on two sides to produce wafers from 0.6 to 2.0 mm thick. Five hundred such wafers were prepared for spectroscopy, chemical analysis, and inclusion studies.

Since natural gemstones are rarely as spatially uniform in color as liquids or glasses, special precautions must be taken to ensure reproducible measurements if accurate comparisons of before-and-after heat-treatment spectra are to be made. To accomplish this, we had an individual mold mounted on an aluminum plate constructed for each individual wafer. The wafer could be removed from this mounting and replaced repeatedly with high positional accuracy. A special kinematic mount was installed in the sample compartment of the spectrophotometer to hold the aluminum plates accurately in the measuring light beam, which was truncated to a rectangular cross section of 1.5 × 2.25 mm. The resulting spectra represent an average of the absorption coefficient over the 1.5 × 2.25 mm area of the sample and through the sample thickness.

We recorded the absorption spectra with an Hitachi U-2000 scanning spectrophotometer, at a wavelength resolution of 2 nm. The spectrophotometer was controlled, data were archived, and color calculations were performed by a Gateway 486 66MHz personal computer, using Spectra Calc software from Galactic Industries Corporation. A wafer of high-purity single-crystal synthetic sapphire, similar in size and thickness to the natural-sapphire wafer samples, was run before each sample to assure a correct baseline and to eliminate the effects of surface reflectivity. Using these techniques, we recorded 112 spectra on 60 different wafers of Rock Creek sapphire.

It is well known that sapphire is pleochroic; that is, different colors will be observed by viewing light that has passed through a crystal in different directions (Webster, 1983). In general, different absorption spectra will be recorded depending on whether the light propagating in the crystal has its polarization parallel or perpendicular to the c-axis of the crystal. Thus, a complete description of the absorption of light in sapphire requires two spectra. For clarity in presentation in this article, we illustrate only the spectrum in which the polarization of the light is perpendicular to the c-axis. This corresponds to the color observed viewing along the c-axis of the crystal with either polarized light or natural, unpolarized light.

To aid in the identification of the spectral features and to determine the possibilities for improvement by heat treatment, we obtained partial chemical analyses on the Rock Creek sapphires. These analyses were performed by Steve Novak of Evans East, Plainsboro, New Jersey, using secondary ion mass spectroscopy (SIMS). Since, with the exception of iron, the relevant impurities have concentrations in the range of a few to a few hundred parts per million atomic (ppma), SIMS was chosen for its sensitivity to low concentrations and for the availability of some ion-implant standards in sapphire. In all, 36 SIMS analyses were conducted on 25 samples of Rock Creek sapphire.

For research work, as well as for routine processing of ruby and sapphire from various localities, we use electrically heated furnaces manufactured by Thermal Technology, Inc. of Santa Rosa, California. The type 1000A series of furnaces (figure 8) use graphite heating elements and graphite insu-

Figure 8. The Crystal Research heat-treatment experiments were conducted using a Thermal Technology Group 1000A graphite hot zone furnaces identical to this one. The cylindrical device to the right is the furnace itself. The furnace body, muffle tube extensions, and end plates are water cooled, which is why this 2200°C-capable furnace is so compact. The equipment rack to the left contains a 20-kw power supply, a programmable temperature controller, and the gas flow controls. Photo courtesy of Thermal Technology, Inc.

lation, and can achieve temperatures far above the melting point of pure sapphire (2052°C). The heating element and insulation are enclosed in a water-cooled metal shell that forms the outside surface of the furnace. Nitrogen gas flows through the furnace body over the hot graphite to prevent combustion with the oxygen in the atmosphere. The furnace separates the heating element from the sapphires with a muffle tube assembly. The muffle tube is made from high-purity Al_2O_3 ceramic. The sapphires to be treated are placed inside the muffle tube, where any type of process gas can flow continuously over the stones. High-purity commercial cylinder gases are used. The flow is controlled by pressure regulators and flow meters of the ball and tube type. Thus, any type of atmosphere from pure oxygen to pure hydrogen or carbon monoxide can be used at any temperature below the collapse point of the ceramic tube (realistically, about 1950°C). Because the furnace is heated by electricity and not by the combustion of hydrocarbon fuels, highly reducing conditions can also be achieved without hydrogen in the furnace atmosphere. Temperature control is maintained with a type-C thermocouple connected to a Eurotherm Model 818P microprocessor temperature controller. Accurate temperature measurement of the sapphires is achieved by embedding a ceramic black-body cavity in the sapphires which is viewed with an optical pyrometer through a quartz window in the furnace body (McGee, 1988).

RESULTS

Yellow in Rock Creek Sapphire. Iron is probably the most common impurity in sapphire. Iron oxide, Fe_2O_3, is structurally similar to aluminum oxide (sapphire). The iron in Fe_2O_3 is Fe^{3+} and can substitute for the Al^{3+} of sapphire. Up to approximately 5 atomic % (at.%) iron can be incorporated in sapphire at geologic temperatures. This relatively high solubility of iron, combined with the fact that it is ubiquitous within the earth's crust, virtually assures that any natural sapphire contains some iron.

In the Rock Creek sapphires, iron is the dominant impurity. Measured concentrations of iron range from 0.2 at.% to 1.4 at.%, with 0.7 at.% being typical (see table 1). The concentration of iron in Rock Creek sapphires is typically 100 times that of other impurity elements. Figure 9 shows the optical absorption spectrum of a pale yellow sapphire in which iron is the only color-producing impurity. This spectrum has several major features. First, there are three relatively narrow absorption bands centered at 377, 388, and 450 nm, and three broad bands centered at 540, 700, and 1050 nm. The bands at 388, 540, 700, and 1050 nm are assigned to the single Fe^{3+} ion, whereas the bands at 377 and 450 nm are assigned to Fe^{3+}-Fe^{3+} ion pairs (Ferguson and Fielding, 1971, 1972; Krebs and Maisch, 1971). By pairs, we mean two Fe^{3+} ions that are close enough together in the lattice that they act as a single specie in absorbing light. Only those absorption bands in the visible region of the spectrum (450, 540, 700 nm) cause color. Since the single Fe^{3+} ion bands at 540 and 700 nm are very weak in sapphire with iron concentrations typical of Rock Creek (see table 1), they have little impact on the color of these stones. Thus, for a sapphire containing iron as the only color-causing impurity, the Fe^{3+}-Fe^{3+} pair absorption band at 450 nm is the primary cause of color. This is the absorption feature often seen when observing sapphire with a handheld spectroscope (Liddicoat, 1981).

Since the probability that two Fe^{3+} ions are close together in the lattice increases approximately as the square of the Fe^{3+} concentration, the strength of the 450-nm absorption also increases approximately as the square of the Fe^{3+} concentration. Thus, the 450-nm absorption band is a sensitive indicator of the amount of Fe^{3+} in the crystal. However, the absorption strength of the 450-nm band, per ion pair, is not high in sapphire nor is the band wide. Thus, this band produces only a pale yellow coloration in sapphire with iron concentrations typical of Rock Creek. The yellow color produced by iron alone is a clean, almost pure yellow that does not tend toward orange. The color coordinates of the sapphire in figure 9 are shown in table 2. Iron as Fe^{3+} in Rock Creek sapphire can also contribute to green when combined with other color-producing impurities (discussed below).

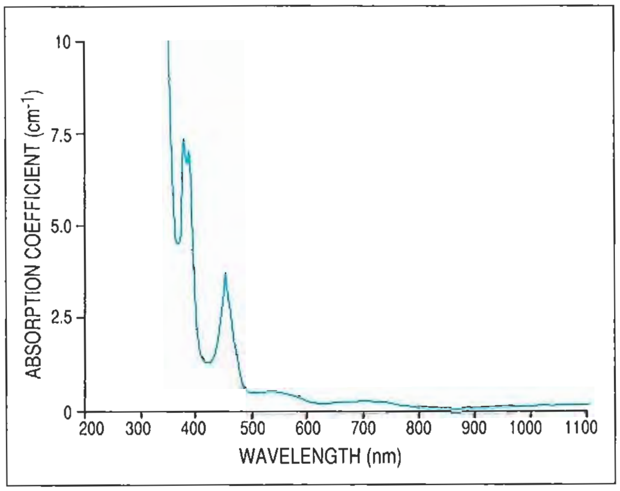


Figure 9. Iron causes the pale yellow coloration of some sapphires, primarily by absorption from Fe^{3+}-Fe^{3+} pairs, as evident in this absorption spectrum. The narrow peak at 388 nm and the broad bands at 540, 700, and centered at 1050 nm are assigned to Fe^{3+}, while the narrow peaks at 377 and 450 nm are assigned to Fe^{3+}-Fe^{3+} pairs (Krebs, 1971; Ferguson, 1971, 1972); see table 2.

Can heat treatment dramatically alter the color of Rock Creek sapphire colored by iron alone? Only to a limited degree. Heating in an oxidizing atmosphere simply assures that all of the iron is present

TABLE 1. Partial chemical analyses of Rock Creek sapphire.[a]

Sample no.	Color	Na	Mg	Si	K	Ca	Ti	Cr	Fe	Ga
313	Near colorless	0.0110	32.0	25.0	0.0060	0.470	42.0	1.60	0.670	13.0
323	Near colorless	0.1700	42.0	54.0	0.0180	0.600	42.0	3.70	0.670	12.0
324	Pale blue	0.1200	27.0	27.0	0.0650	0.910	32.0	1.80	1.180	14.0
331	Pale blue	0.0069	26.0	23.0	0.0032	0.370	32.0	15.00	0.810	13.0
337	Pale green	0.0044	55.0	37.0	0.0069	0.850	60.0	8.20	1.290	17.0
344	Pale green	0.0250	47.0	55.0	0.0190	0.630	55.0	0.85	1.090	12.0
345	Pale green	0.0012	36.0	26.0	0.0017	0.460	54.0	0.20	0.810	12.0
352	Pale green	0.0046	41.0	23.0	0.0025	0.560	54.0	6.60	0.920	12.0
309	Pale blue	0.0460	89.0	29.0	0.0140	0.500	80.0	1.30	0.730	8.7
310	Pale blue	0.0130	61.0	23.0	0.0210	0.290	61.0	5.30	0.790	6.6
319	Pale blue	0.0060	89.0	28.0	0.0063	0.390	71.0	26.00	0.710	8.4
320	Pale blue	0.0140	61.0	45.0	0.0110	0.310	59.0	24.00	1.400	9.0
321	Pale blue	0.0087	48.0	23.0	0.0065	0.240	41.0	4.60	0.850	8.1
351	Pale green	0.0028	48.0	18.0	0.0040	0.220	43.0	20.00	0.770	6.7
423	Yellow spot	0.0046	22.0	11.0	0.0011	0.190	11.0	12.00	0.280	5.9
423	Colorless area	0.0021	16.0	13.0	0.0004	0.130	15.0	11.00	0.300	5.9

[a] *These analyses were performed by Steve Novak of Evans East, Plainsboro, NJ, by secondary ion mass spectroscopy (SIMS). SIMS was chosen because it was important to have accurate measurements in the range of a few to few hundred parts per million atomic (ppma) range to compare quantitatively with the absorption spectra. The data are presented in ppma except for iron, which is in the units of atomic percent (i.e., parts per hundred).*

as Fe^{3+}, producing the "pure" pale yellow color just discussed. Heating in a moderately reducing atmosphere converts a small portion of the Fe^{3+} to Fe^{2+}. Yet detailed studies of this process have shown that, even in highly reducing atmospheres, the ratio of Fe^{2+} to Fe^{3+} rarely exceeds 10^{-3} (Koripella and Kröger, 1986)—and absorptions of Fe^{2+} alone in small concentrations have little impact on color. However, if the total iron concentration is high enough, a strong wide absorption band centered at about 875 nm appears as a result of reduction that has been ascribed to Fe^{2+}-Fe^{3+} pairs (Ferguson and Fielding, 1971, 1972). While detailed proof of this assignment is lacking, the arguments for it appear reasonable. The short-wavelength tail of this band provides some absorption in the 650–750 nm region, giving a bluish or greenish cast to an otherwise yellow stone. If the stone is heated in a much more strongly reducing atmosphere, microcrystals of hercynite (iron spinel, $FeAl_2O_4$) precipitate (Meyers et al., 1980; Moon and Phillips, 1991; see thermochemistry box A). These microcrystals add a gray hue and reduce clarity (see, e.g., figure 10). Further reduction leads to the precipitation of both hercynite and metallic iron, eventually producing total opacity and a reflective black exterior.

Figure 10. Overreduction of high-iron sapphire, such as that from Rock Creek, leads to hercynite precipitation; this makes the material, like the sample shown, a translucent gray. Prior to heat treatment, this wafer (5 mm in diameter and 0.34 mm thick) was colorless and transparent. Photo © John L. Emmett.

We have seen that iron, in concentrations typical of those seen in Rock Creek sapphires, produces only a pale yellow; yet there are many Rock Creek stones with a strong orangy yellow color (see figure 1), which is usually limited to the central region of the crystal. Figure 11 shows a wafer cut from such a natural-color crystal. To understand the origin of this coloration, we measured the absorption spectrum through both the yellow area and the colorless portion of this stone (see figure 12). To compare these absorption spectra, we simply subtracted the

TABLE 2. Color coordinates in C. I. E. L*, a*, b* space as related to the absorption spectra.[a]

Sample no.	Color	Figure no.	Illuminant A	Illuminant D65
S191AR	Medium yellowish green	18	79.3, −4.8, 7.8	79.7, −9.7, 10.5
S213AR	Pale yellow	9	93.6, 2.2, 29.1	92.7, −7.2, 31.3
S229AR	Medium blue	17	63.1, −1.5, −27.6	64.7, 3.2, −25.2
S389	Light blue	24, curve A	34.1, −8.3, −16.2	35.8, −7.1, −12.7
S389	Light blue with some gray	24, curve B	28.2, −7.4, −13.5	29.7, −6.8, −10.3
S454	Pale greenish brown	19 and 20 (curve A)	34.4, 5.2, 14.4	33.6, 0.0, 15.0
S454	Medium blue	20 (curve B) and 21	24.4, −7.7, −28.1	26.7, 0.1, −24.7
S462	Strong orangy yellow	11 and 12, on yellow spot	77.8, 39.7, 106.7	71.2, 35.8, 101.2

[a] To relate color to the absorption spectra, the color coordinates for the various spectra are presented here. The color system chosen is the C.I.E. L, a*, b*. Two light source types or illuminants were used. C.I.E. illuminant A represents incandescent light; illuminant D65 is one representation of natural daylight. Comparing the color coordinates for the two illuminates allows one to judge the amount of color change under different illumination. The color coordinates were calculated for a 2° observer, and for light making a single pass through a 4-mm-thick sapphire in all cases. For understanding of these color coordinates and conversion to other color coordinate systems, see Billmeyer and Saltzman (1981).*

Figure 11. This 0.9-mm-thick wafer was cut and polished from a natural unheated Rock Creek sapphire to illustrate the presence of yellow in only a portion of the stone, a feature that is relatively common in material from this locality. Photo © John L. Emmett.

spectrum of the colorless area from that obtained through the yellow area (figure 13).

From this differential spectrum, two important conclusions can be drawn. First, the Fe^{3+} concentration in the central yellow spot is essentially the same as in the colorless area of the stone. That is, subtraction of the colorless-area spectrum from that of the yellow spot almost completely eliminates all the Fe^{3+} absorption features at 377, 388, and 450 nm. Thus, Fe^{3+} is not responsible for the strong yellow coloration. Second, the strong broad absorption band that starts at 600 nm and extends through the blue and violet portion of the differential spectrum is responsible for the strong yellow coloration. While not completely understood, it appears to be associated with impurity-initiated point defects in the sapphire crystal (Kvapil et al., 1973; Mohapatra and Kröger, 1977; DuVarney et al., 1985; Boiko et al., 1987). If a divalent impurity such as magnesium (Mg^{2+}) replaces aluminum (Al^{3+}) in the sapphire lattice, there is a point defect created at the site which has insufficient charge. Such point defects are often referred to as color centers (see, e.g., Fritsch and Rossman, 1988). When sapphire is heat treated under highly oxidizing conditions, a hole (the opposite of an electron) is created in the lattice which has an effective electrical charge of +1. This hole combines with the Mg^{2+}, providing the +3 charge required at that lattice site. Therefore, the strong broad band in figure 13 appears to be the optical absorption associated with this Mg^{2+}-hole pair. Since the yellow area is usually in the center of the crystal, it appears that the chemical environment must have changed during the growth of these sapphires. Chemical analyses carried out on these stones indicate that the yellow coloration forms in those portions of the crystal where the concentration of magnesium substantially exceeds the con-

Figure 12. These are the absorption spectra of the sapphire sample shown in figure 11: (A) measured through the colorless area of the stone; (B) measured through the yellow area.

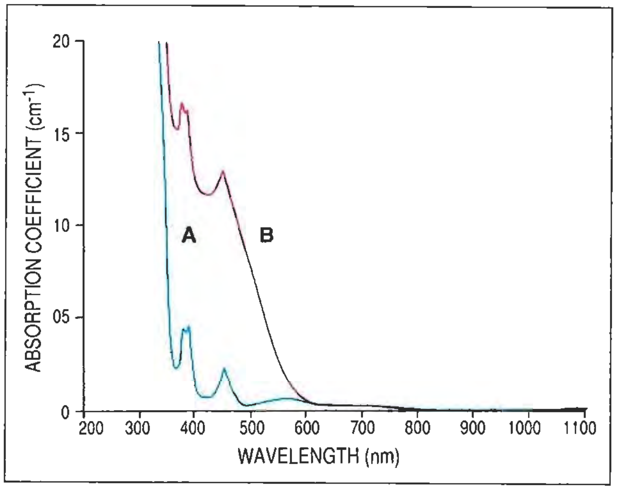
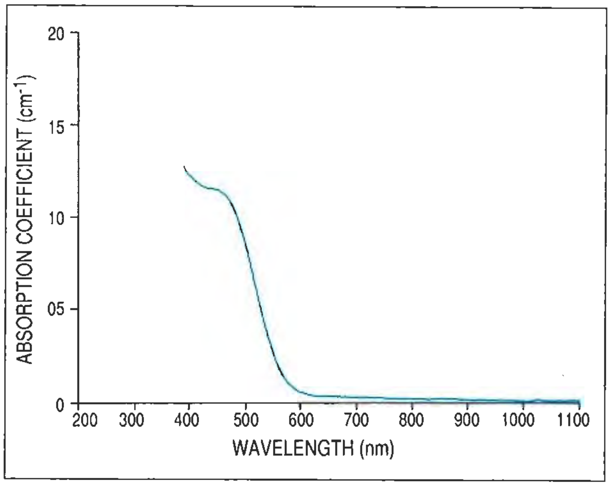


Figure 13. This absorption spectrum is the differential (B–A) of the two spectra shown in figure 12. Since the narrow absorption peaks of iron at 377, 388, and 450 nm are completely missing from this spectrum, it can be concluded that the iron concentrations in the colorless and yellow areas of the stone are identical. Thus, the yellow coloration does not result from iron.



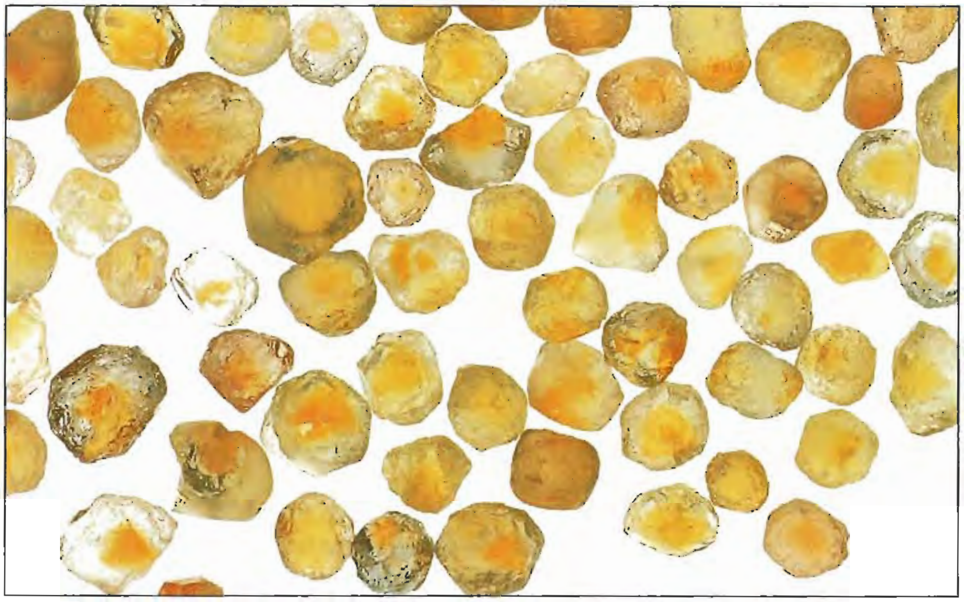


Figure 14. The yellow coloration of these stones was produced by heating the near-colorless, pale blue, and pale green material of figure 7 to 1200°C in a highly oxidizing atmosphere. Note the localization of the coloration in the crystals. The yield of such yellows from the material in figure 7 is 15%–20%. Photo © John L. Emmett.

centration of titanium (see table 1).

The interaction in a crystal of point defects and impurities is rarely as simple as single isolated centers like the Mg^{2+}-hole pair. It is quite possible that the absorption spectrum of this point defect is modified by association with the major impurities, or by the formation of point defect clusters (Koripella and Kröger, 1986). To understand the origin of this coloration more fully, we have studied the absorption spectrum of high-purity, single-crystal synthetic sapphire intentionally doped with magnesium and heat treated under highly oxidizing conditions. In this material, we observed absorption spectra that are nearly identical to that in figure 13. This point defect, or color center, cannot be bleached in oxidizing atmospheres up to 1850°C. However, the strength of the absorption is greatly reduced by heating to 1500°C at lower oxygen partial pressures ($pO_2 = 10^{-4}$ atm; Mohapatra and Kröger, 1977). Differential spectra, recorded through the yellow areas of natural stones equilibrated at two different oxygen partial pressures ($pO_2 = 1$ atm and $pO_2 = 10^{-3}$ atm), again yield absorption spectra nearly identical to that in figure 13.

The strong orangy yellow coloration produced by this point defect is very different from the pale pure yellow of iron-produced coloration. These different yellow colors are compared in table 2, where color coordinates are calculated for both the iron-colored sapphire of figure 9 and the point-defect-colored area of the stone in figure 11.

Since the strength of the yellow coloration is sensitive to one of the main variables (oxygen partial pressure) under a heat treater's control, this coloration can be enhanced or reduced. Good blue stones from Rock Creek often exhibit yellow centers. The yellow center is easily removed by heating the stones under slightly reducing conditions. We have found also that heat treating a sample of our near-colorless, pale blue, and pale green stones at 1200°C in a pure oxygen atmosphere will produce some highly saturated yellow stones (figures 14 and 15). Just as in the natural-color stone, the yellow coloration is usually confined to the central region of the crystal. Thus it appears that this heat-treatment process simply raises the equilibrated oxygen partial pressure for those Rock Creek stones that were equilibrated at a lower partial pressure in nature. For a 400-gram lot of our experimental Rock Creek sapphire described previously, 60–80 grams, or approximately 400 to 545 stones, were judged to have sufficient color saturation in a large enough region of the crystal to cut commercially valuable gems. Thus, the yield of good yellow stones from the pale-hued study material found at Rock Creek is about 15%–20%.

Pink and Orange in Rock Creek Sapphires. It is well known that chromium, as Cr^{3+}, is responsible for pink sapphire and (in greater concentrations) deep red ruby. In addition, the valence state of chromium—and thus the depth of color—in sapphire cannot be changed by heat treatment. Therefore, heat treatment cannot produce a more intense pink or red in the significant quantities of pale pink sapphire produced at Rock Creek. However, it can produce a pinkish orange, or "padparadscha," color, as well as orangy yellow and

Figure 15. These stones were cut from heat-treated sapphires like those shown in figure 14. Note the high clarity and broad range of color saturations. Photo © GIA and Tino Hammid.

bright orange (figure 16), by inducing the yellow coloration previously discussed into the pink stones. At the present time, we do not have good quantitative yield statistics on these colors, as sufficient quantities of pale pink stones are not yet available for testing.

Blue and Green in Rock Creek Sapphires. If sapphire contained only a small amount of Fe^{2+}, or only Ti^{4+}, it would remain colorless. However, when both Fe^{2+} and Ti^{4+} are present at the same time and are on neighboring lattice sites, an intense blue is created (Townsend, 1968; figure 17). This type of absorption is caused by intervalence charge transfer (Burns, 1981; Nassau, 1983; Fritsch and Rossman, 1988).

Since neither Fe^{2+} nor Ti^{4+} is easily incorporated into sapphire, most natural sapphire is not blue. In fact, the solubility of Ti^{4+} in sapphire is so low at normal temperatures that the majority of the titanium in natural sapphire is exsolved as titanium-containing microcrystals. Thus, much natural sapphire with both iron and titanium, and the sapphire of Rock Creek in particular, contains the iron as dissolved Fe^{3+} and most of the Ti^{4+} as exsolved TiO_2 microcrystals. Under certain conditions, Fe^{2+} and Ti^{4+} can enter sapphire at the same time and their solubility together is greater than the solubility of either alone (Roy and Coble, 1968; Ikuma and Gordon, 1983). This enhanced solubility results from mutual charge compensation—that is, one Ti^{4+} ion plus one Fe^{2+} ion have a total charge of +6, which equals that of the two Al^{3+} ions they replace. Thus, the incorporation of these two impurities as pairs during crystal growth does not require formation of substantial point defects.

Figure 16. When yellow coloration from heat treatment like that used on the stones in figure 14 is induced in pale pink stones that contain a low concentration of chromium, this range of colors is produced. While the percentage of pale pink stones from the deposit that can achieve these colors is not high, the number of stones is still very large. Photo © GIA and Tino Hammid.

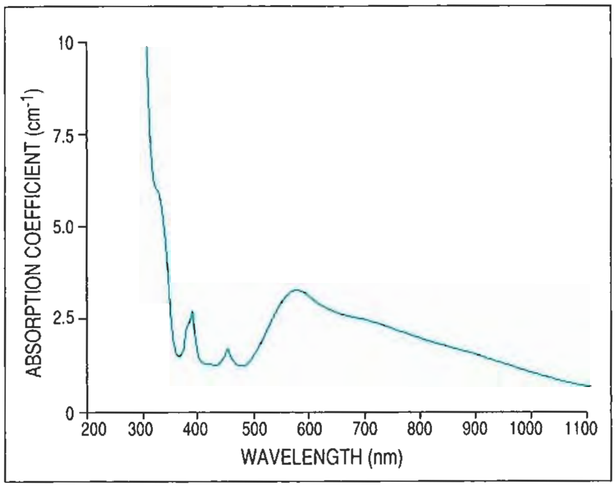


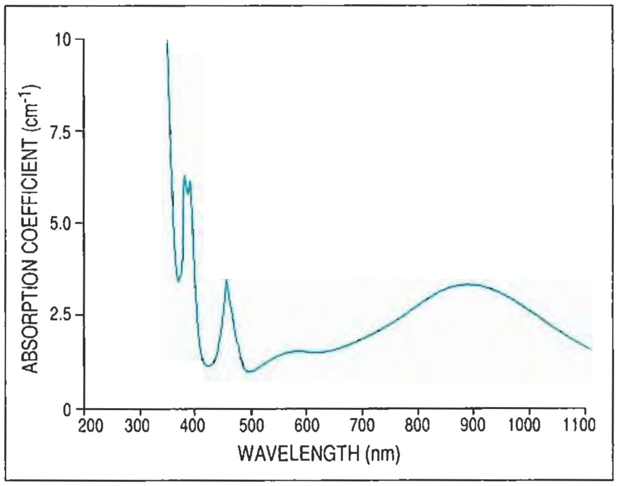
Figure 17. The natural-color stone from which this spectrum was taken is blue because the Fe^{2+}-Ti^{4+} pair absorptions centered at 575 nm (yellow) and 700 nm (deep red; here, overwhelming the weak Fe^{3+} absorption) are much stronger than the absorption at 450 nm. Compare this spectrum with those in figures 9 (yellow sapphire) and 18 (green).

The pale green coloration predominant in Rock Creek sapphire is a combination of Fe^{3+}-Fe^{3+} yellow with a small amount of Fe^{2+}-Ti^{4+} blue. A comparison of the visible-range absorption spectrum of a green sapphire (figure 18) with the spectra of blue (figure 17) and yellow (figure 9) sapphires reveals that the only significant difference in the visible regions of these spectra is the relative ratio of the 450-nm absorption to the 575-nm absorption. Thus, where the 450-nm absorption is much stronger than the 575-nm absorption, the stone appears yellow. As the relative strength of the 575-nm absorption (or concentration of Fe^{2+}-Ti^{4+} pairs) increases, the color goes from yellow to green. With further increases in the relative strength of the 575-nm absorption, the stone appears blue.

With the foregoing information as background, we can interpret the very pale green hue of the majority of Rock Creek sapphires and determine the possibilities for converting these stones to a marketable blue. The low concentration of the Fe^{3+}-Fe^{3+} ion pairs absorbing at 450 nm, combined with a very low concentration of Fe^{2+}-Ti^{4+} pairs absorbing at 575 nm and 700 nm, is consistent with the low concentration of titanium in solution indicated in table 1. Production of a deep blue color in these stones requires the introduction of more titanium into solution in the crystal as Ti^{4+}. It has been suggested that natural sapphire contains titanium as Ti^{3+} (see, e.g., Schmetzer and Bank, 1981) which, thus, could be a potential source of Ti^{4+} by heat treatment. However, this cannot be so. In sapphire, Ti^{3+} is a very strong reducing agent or electron donor and Fe^{3+} is an electron acceptor (Dutt and Kröger, 1975; Mohapatra and Kröger, 1977). Thus, Fe^{3+}+Ti^{3+} would become Fe^{2+}+Ti^{4+} (iron would gain one electron while titanium would lose one) during growth at any reasonable temperature. Other sapphire impurities, such as magnesium, are also electron acceptors (Mohapatra and Kröger, 1977). In sapphire when such electron-acceptor impurities far exceed titanium in concentration, Ti^{3+} will not exist to any significant degree and neither will heat treatment convert Ti^{4+} to Ti^{3+}. Indeed, we have yet to observe the well-known Ti^{3+} absorption spectrum in any natural-color or heat-treated natural sapphire (Ti^{3+} can be produced in very high-purity synthetic sapphire where it is the dominant impurity and is processed under extremely reducing conditions; Lacovara et al., 1985).

The only potential source of Ti^{4+} remaining in these natural sapphires are the microcrystals of rutile. To evaluate this possibility, we had wafers of Rock Creek sapphire cut and polished, perpendicular to the c-axis, as previously described (figure 19). Examination of several hundred of these wafers revealed that more than 90% of the sapphires contain rutile needles, identified by their morphology

Figure 18. The natural-color sapphire (S191AR) from which this spectrum was taken is green because the absorptions in the yellow and red region of the spectrum begin to modify the predominantly yellow coloration produced by the 450-nm absorption. Compare this spectrum with those in figures 9 (yellow sapphire) and 17 (blue).



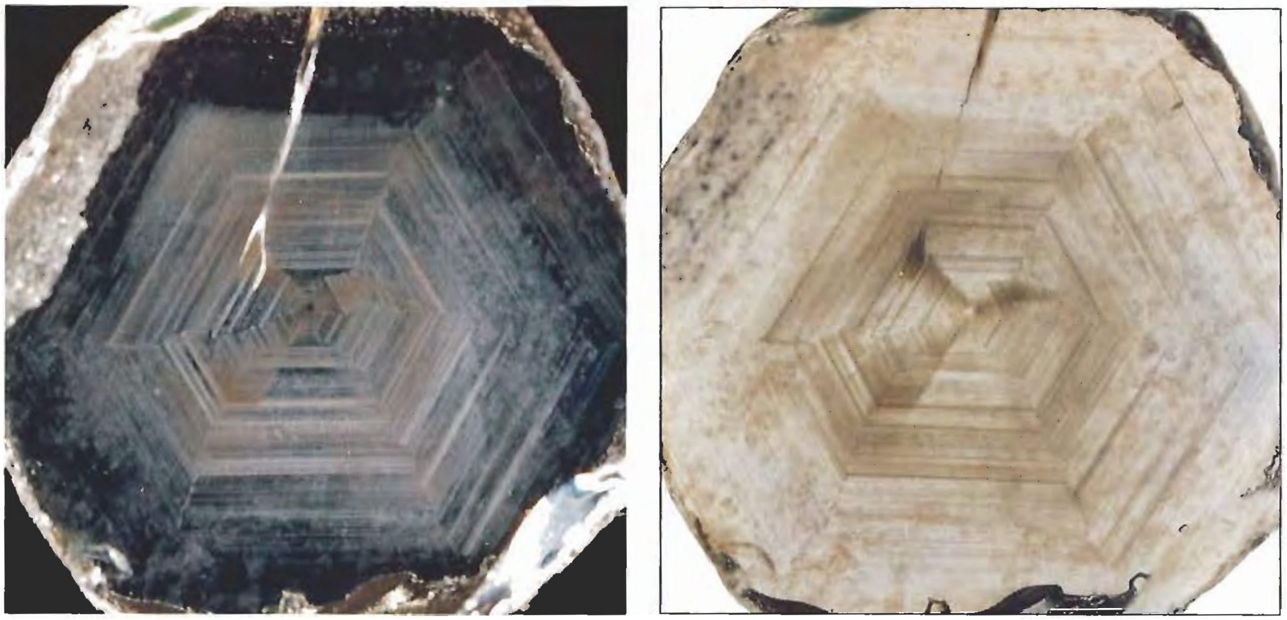


Figure 19. More than 90% of Rock Creek sapphires have been found to contain rutile, as evident in this 1.76-mm-thick wafer viewed with darkfield illumination (left). Only the heaviest rutile concentrations are easily seen without darkfield illumination (right). Photo © John L. Emmett.

and orientation (Phillips et al., 1980), but that the concentration varies widely. Where sufficient concentration exists, the color can be improved by heating the stones first in either an oxidizing or a neutral atmosphere to dissolve the rutile, placing titanium in solid solution as Ti^{4+}, and then continuing to heat them in a reducing atmosphere to reduce some of the Fe^{3+} to Fe^{2+}. The Fe^{2+} reacts with the Ti^{4+}, forming Fe^{2+}-Ti^{4+} pairs, and thus the blue coloration. The actual process is slightly more complex, as the dissolution of rutile in sapphire also forces the reduction of some Fe^{3+} to Fe^{2+} independent of the external oxygen partial pressure, but the basic concept remains the same. Note in figure 20 that the Fe^{2+}-Ti^{4+} pair absorptions are substantially greater in the rutile-containing sapphire heat treated in a strongly reducing atmosphere (spectrum B) than in the natural-color stone (spectrum A). Spectrum B also features a strong, wide absorption band centered at 875 nm—attributed to Fe^{2+}-Fe^{3+} pairs—as a result of reduction. These spectra are very typical for stones that contain substantial quantities of rutile microcrystals. Color coordinates for these spectra are also given in table 2.

As illustrated in figure 21, the blue color induced in the stone by heat treatment is localized to the regions of original rutile deposition. This is because the diffusion of titanium in sapphire is slow compared to the relatively short time (1–10 hours) used for heat treatment. Figure 22 shows a group of the blue stones that resulted from heat treating the near-colorless, pale blue, and pale green Rock Creek material. These stones have been treated by the process described at 1650°C in a reducing atmosphere that contains some hydrogen. The wide range of blue color saturation achieved mirrors the

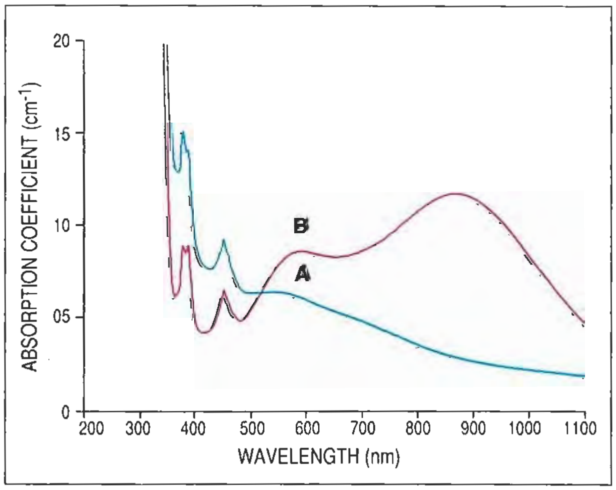


Figure 20. These spectra show the aborption characteristics before (A) and after (B) heat treatment of the sapphire wafer of figures 19 and 21, respectively. The stone became blue because heat treatment substantially increased the absorption in the yellow to red region of the spectrum, while it substantially reduced the absorption in the violet, blue, and green regions. Compare the color coordinates of these spectra in table 2.

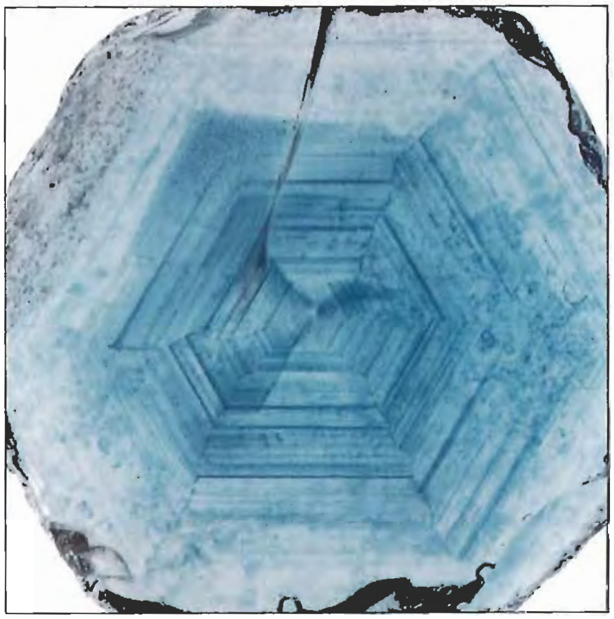


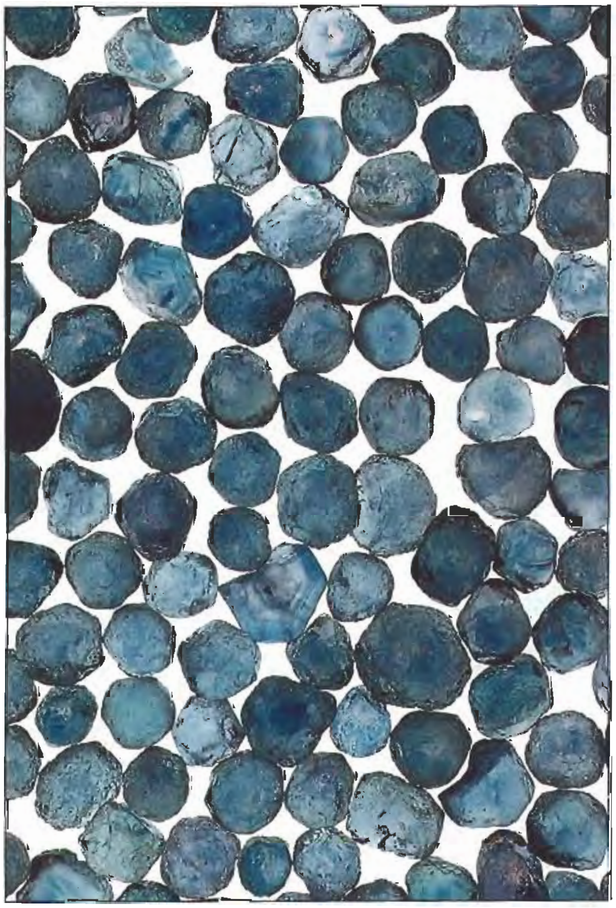
Figure 21. After heat treatment for rutile dissolution and reduction, blue was produced in the sapphire wafer shown in figure 19 by the formation of Fe^{2+}-Ti^{4+} pairs in the sapphire. Although iron is uniformly distributed throughout the crystal, the rutile providing Ti^{4+} is very localized, producing a blue pattern that matches the original rutile deposition pattern. Photo © John L. Emmett.

wide range of rutile concentration in the natural stones. However, the color range shown in figure 22 is 50% of the heat-treated lot. Processing a 400-gram batch of the sample stones yielded about 200 grams, or approximately 1,360 stones similar to those in figure 22. An additional 5-kg lot of the same starting material processed in this fashion gave similar yields. Although the blue coloration produced in the Rock Creek sapphire by this process is not spatially uniform, attractive stones can be faceted (figure 23).

We also investigated whether the color of the lighter blue stones in figure 22 could be deepened by treatment in a more reducing atmosphere. The answer in this case was no. The stones in figure 22 were reduced in an oxygen partial pressure that was found to be optimal for this material. There is an optimum because, while the goal is to create enough Fe^{2+} to form pairs with all of the Ti^{4+}, excess Fe^{2+} (which results when the stone is overreduced) will precipitate out as hercynite microcrystals, adding a gray component to the color. The spectra in figure 24 show the results with optimal processing (A) and slightly deeper reduction (B), with the difference (C) nearly constant across the visible spectrum and thus simply the addition of gray. The color coordinates of the stone for these two processing conditions are given in table 2. Similar spectra have been recorded on 15 wafers, which exhibit a wide range of initial rutile concentrations. It is the relatively high concentration of iron in Rock Creek sapphire, and the associated hercynite precipitation during reduction, that makes optimization of the heat treatment more difficult for this material than for low-iron-concentration material such as the geuda from Sri Lanka.

Since the production by heat treatment of good

Figure 22. These rough blue sapphires were produced by heat treating the pale material shown in figure 7. The wide range of color saturation mirrors the wide range of rutile concentration. The yield of the material shown here from the near-colorless, pale blue, and pale green material of figure 7 is 50%. Photo © John L. Emmett.



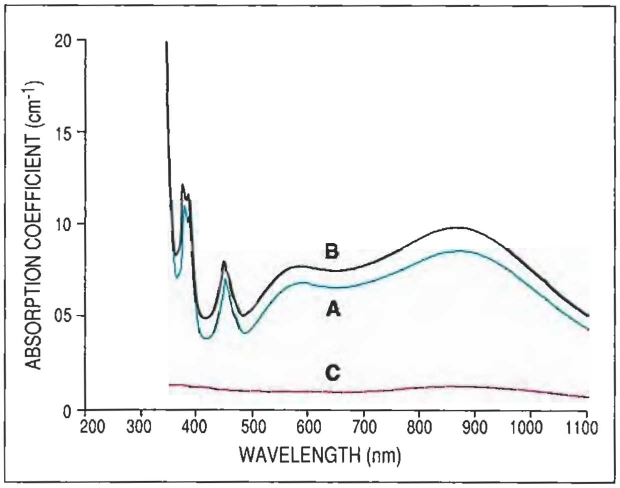
blue stones requires a high titanium concentration, and the production of good yellow stones requires a low titanium concentration, these two groups are produced almost independently from the near-colorless, pale blue, and pale green Rock Creek sapphires. Thus, the total yield of commercially valuable stones from this material is 65%–70%. Note also that the colors produced are stable to both light and heat.

EVIDENCE OF HEAT TREATMENT IN ROCK CREEK SAPPHIRE

TiO_2 occurs in Rock Creek sapphire not only as fine needles, but also as compact euhedral crystals 25 μm to 1 mm in size (but typically 25–250 μm). These inclusions are protogenetic; that is, they formed elsewhere, were transported to the growing surface of the sapphire crystal, and were enclosed by subsequent sapphire crystal growth. Rutile has a higher thermal expansion coefficient than sapphire. Consequently, if an embedded rutile crystal is large enough, it will fracture the sapphire at high temperature. We have observed two types of phenomena related to these inclusions following heat treatment. First, if the crystal is small, fracture does not occur and the inclusion begins to dissolve into the sapphire, creating the familiar blue halo around the inclusion (Koivula and Kammerling, 1988). Second, if the rutile crystal is large, it creates a small plate-like fracture in the sapphire. Titanium oxides rapidly coat the internal surfaces of the fracture and begin diffusing into the bulk of the sapphire. As the titanium diffuses into the sapphire, it reacts with the iron dissolved therein, creating an intense blue coloration. As the sapphire is cooled, the fracture closes almost completely. Thus, it does not reflect light from internal sapphire-air interfaces. What remains in the stone is a deeply colored flat blue disk (figure 25).

Figure 23. The faceted blue sapphires pictured are cut from material like that shown in figure 22. These stones are representative of the color range and clarity that is produced by heat treating the pale green and blue stones shown in figure 7. Photo © GIA and Tino Hammid.

Figure 24. These spectra show what happens if a Rock Creek sapphire is overreduced. Spectrum A is of a stone optimally reduced for its iron concentration. Spectrum B is of the same stone processed to a greater reduction. Subtracting A from B shows the absorption difference, spectrum C, which is almost constant across the visible portion of the spectrum and, thus, only contributes gray to the color of the stone. Compare the color coordinates of these spectra in table 2.



Because the difference in the coefficient of thermal expansion between rutile and sapphire is not large, this fracturing process is quite sensitive to temperature. At 1400°C only large rutile crystals create fractures, but as the temperature is increased, successively smaller crystals create fractures. Fractures around solid inclusions are a common occurrence in natural unheated Rock Creek sap-

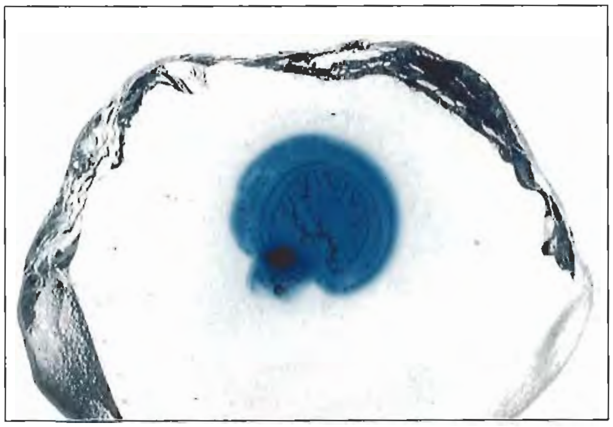


Figure 25. This Rock Creek sapphire shows a compact euhedral rutile crystal that is approximately 300 µm in diameter. When heated, this inclusion expanded more than the sapphire host, resulting in a large plate-like fracture. The titanium oxides then rapidly coated the internal surfaces of the fracture and begun diffusing into the bulk of the sapphire, producing the blue coloration. On cooling, the fracture almost completely closed, eliminating the reflective interfaces usually seen in such fractures surrounding inclusions. Photo © John L. Emmett.

phires, but blue halos around inclusions or blue staining of fracture surfaces are a clear indication of heat treatment.

Two-phase (liquid and gas) inclusions are also observed occasionally in Rock Creek sapphires. During heat treatment, the heated liquid creates enormous pressure, causing a localized "fingerprint" fracture, which can be observed after cool-down to be partially liquid filled.

The incorporation of hydrogen into sapphire is another effect that merits discussion. When sapphire is heated in an atmosphere containing hydrogen, some hydrogen diffuses into the stone and a portion of the H atoms will ionize into an electron and a proton. The proton is a positive point charge that is infinitesimal compared to any other positive ion. As a consequence, it will sink into the electron cloud around an oxygen ion. This creates an OH^- molecular ion in the sapphire crystal that can be detected by infrared spectroscopy at 3310 cm^{-1} (3021 nm; Eigenmann and Günthard, 1971). In the limited set of measurements conducted thus far, we have not seen this absorption feature in any natural unheated sapphire. This subject deserves additional study. If it could be shown that natural sapphire never exhibits this absorption feature, then presence of this feature in blue sapphire would provide additional proof of heat treatment.

While we have not made an exhaustive comparison between natural Rock Creek sapphires of highly saturated coloration, and similar appearing heat-treated stones, we can provide several observations that may be of value to gemologists in the detection of heat treatment.

Blue Sapphires. Observation of the deep blue discs described above, or inclusions with blue halos, is certain evidence of heat treatment. If a blue pattern tied to an original rutile deposition pattern of partial hexagonal structure as shown in figure 21 is observed, it also is almost certain evidence of heat treatment. We have not observed such patterns in any of the several hundred natural wafers we have studied. Finally, we should note that highly saturated blue non-heat-treated Rock Creek stones are quite rare. Thus, the burden of proof should be on the claim that the stone is not heat treated.

Yellow Sapphires. Proof of heat treatment in these stones is far more difficult. The heat-treated point-defect-colored yellow stones without any inclusions are identical in every way we have examined to the natural point-defect-colored yellow stones. Proof of heat treatment comes from effects of heat, such as those that may be observed on inclusions contained within the stone.

We have not studied enough pink and orange stones to make any definitive comments regarding the detection of heat treatment.

CONCLUSION

Heat treatment of Rock Creek sapphire can produce high yields of commercially viable yellow and blue stones. The formation of strong yellow colors in highly oxidizing atmospheres, previously thought to be due to Fe^{3+} absorption, has been shown instead to be the result of a broad absorption band beginning at 600 nm and extending to the shortest visible wavelengths. We suggest that this may be caused by divalent ion-hole pairs or color centers in the crystal. The production of blue proceeds by the well-known mechanism of rutile dissolution in the presence of dissolved iron, followed by reduction of a portion of the iron. However, the relatively high iron content of Rock Creek sapphire constrains the acceptable reduction conditions to a rather narrow range because of hercynite precipitation.

The heat-treatment processes that have been developed for the pale blue, pale green, and near-colorless material yield 65%–70% of marketable yellow and blue sapphires. Excluding the small quantities of orange and "hot pink" sapphire that come from the deposit, the heat-treated material is of substantially higher gem quality in terms of color and clarity than the best of the natural material. The heat-treatment processes have now been tested at batch sizes from 50 grams to 1.5 kg and have proved to be viable, reproducible, commercial processes. Given that the colors studied represent about 75% of the estimated yield of 25 million carats in the assayed portion of the meadow property, the yield of cut stones can be estimated as approximately 3–5 million carats depending on the minimum stone size cut. This estimate excludes any yield from the remaining 25% of other colors in the deposit, significant quantities of which were not available for testing at the time this study was initiated.

Authors' Caution to the Reader. *Reducing gases are, by their very definition, highly explosive when mixed with air or oxygen. Combining this hazard with the high temperatures used during heat treatment poses many substantial risks. We strongly encourage all who would experiment in this field to seek support from people trained in the disciplines of high-temperature chemistry.*

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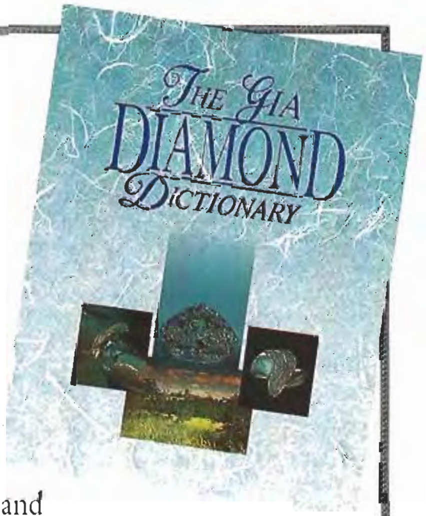

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GARNETS FROM ALTAY, CHINA

By Fuquan Wang and Yan Liu

Gem-quality spessartine garnet and grossular garnet have been discovered in Altay, China. Gemological and mineralogical studies show that their properties are typical for these garnet species. Spessartine and grossular are being mined commercially, but gem-quality grossular with fine color is rare.

The Altay Mountain Range has long been known in China as the "native place of gemstones." For dozens of years, gem-quality varieties of apatite, beryl, spodumene, topaz, and tourmaline have been mined there. Gem-quality spessartine garnet (figure 1) was discovered at the Qibeiling mine in 1950. Since then, it has been recovered as a byproduct of quartz mining. In 1980, gem-quality grossular garnet (figure 2) was discovered about 30 km (18 miles) northwest of the Qibeiling mine at what is now known as the Cocoktau mine. The brown to reddish brown grossular is known by the variety name hessonite; the green variety is referred to in China as "Altay emerald" (Keller and Wang, 1986; Wang, 1986).

This article briefly reviews access to, and geology of, these two relatively new sources of garnets, about which little has been written in the Western literature. The gemological characteristics and chemical composition of both spessartine and grossular garnets from the two mines are described.

ABOUT THE AUTHORS

A gemologist and mineralogist, Dr. Wang recently retired as research professor at the Geological Museum, Beijing, China. His book, Gems and Gem Appraising, has just been published in Chinese. Mr. Liu is a research associate in the Research Department, Gemological Institute of America, Santa Monica, California.

Acknowledgments: The authors thank Mr. Chen Wenao for arranging the visit to the Altay mines, providing samples, and drawing the original geologic map of the Cocoktau deposit. Mr. Guo Jiugao did the ultraviolet-visible spectral measurement of the grossular sample. Dr. James E. Shigley and Dr. Emmanuel Fritsch of GIA Research provided helpful comments.

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LOCATION AND ACCESS

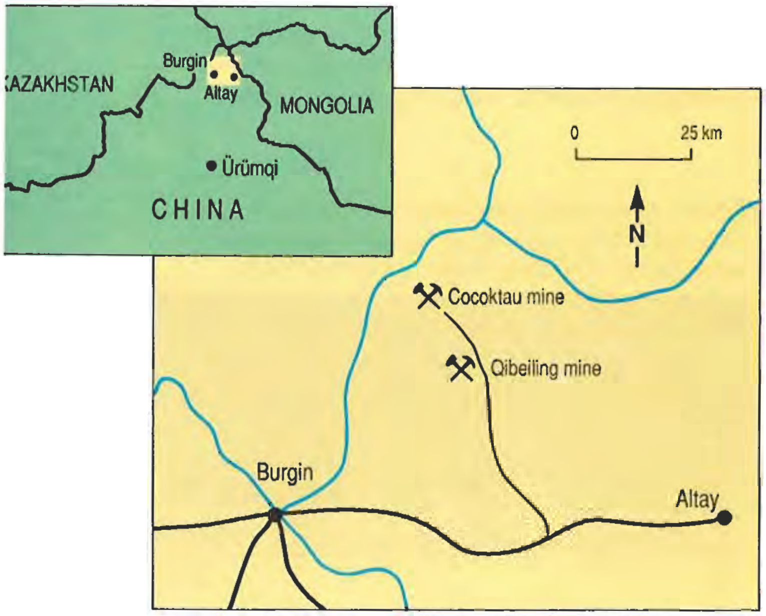
The Altay Mountain Range is north of the Xinjiang Uygur Autonomous Region in remote, sparsely populated northwest China, adjacent to Mongolia and Kazakhstan (figure 3). The Qibeiling and Cocoktau deposits lie, respectively, about 45 km and 70 km (27 and 42 miles) northwest of Altay City (approximate population: 100,000; see again figure 3) in mountainous terrain. Both can be reached via graded dirt roads for only about six months each year, between April and October.

Figure 1. Spessartine garnets recovered from the Qibeiling mine include these faceted stones, which range from 3.5 to 5.5 ct. Photo by Robert Weldon.

Figure 2. Gem-quality grossular garnet from the Cocoktau mine is found in various colors, as illustrated by these faceted stones and pieces of rough ranging from about 0.5 to 6.5 ct. Photo by Robert Weldon.

Heavy snowfall during the cold winters makes access treacherous if not impossible. The Qibeiling deposit covers about 400 m^2, the Cocoktau deposit extends over approximately 560 m^2.

Figure 3. The Qibeiling and Cocoktau deposits lie, respectively, about 45 km and 70 km northwest of Altay City (approximate population: 100,000) in mountainous terrain. Both can be reached via graded dirt roads for only about six months of the year. The inset map shows this sparsely populated region's relationship to neighboring Mongolia and Kazakhstan. Artwork by Carol Silver.



GEOLOGY AND OCCURRENCE

At Qibeiling, a spessartine-bearing pegmatite intruded into schistose biotite-gneiss, the region's country rock. The spessartine occurs in the replacement zones in the inner part of the pegmatite. Associated minerals are albite (variety cleavelandite), quartz (rock crystal), schorl, and muscovite mica. Two different generations of spessartine are found. The first type is smaller, heavily included, and was the source material for the second. The first-generation spessartine, associated with the quartz, was dissolved and redeposited as the second generation, associated with the albite, through recrystallization by hydrothermal growth. This is apparent from specimens studied in various degrees of homogenization. When dissolution and recrystallization of the first generation was complete, the less-included, larger crystals of the second generation resulted. While material of the first generation is of no gemological value, because it is too small and heavily included, specimens of the latter generation are large enough—and of sufficiently high clarity—to be cut as gems.

Although quartz was the primary mineral extracted from the Qibeiling mine during the 1950s, some second-generation spessartine was also recovered. Mining stopped at a depth of about 10 m. Further mining would have necessitated widening the main pit, a task deemed impractical. In the late 1970s, miners found high-quality spessartine—that is, the second type referred to previously—in a pocket within the albite-rich replacement zone of the pegmatite. Over 1,000 kg of spessartine have been recovered since then, about 20% of which is facet grade.

Grossular occurs at Cocoktau in skarns within marble in the form of bands, pockets, and rounded massive bodies, which extend approximately parallel to the general trend of the country rocks. Gem-quality material is mostly found in the middle part of the calcium-rich zones within the skarns (figure 4). Associated minerals were zoisite (early stage), epidote (later stage), albite, diopside, hornblende, and quartz.

Several tons of grossular rough have been recovered from the open-pit Cocoktau mine since grossular was discovered there in the 1980s (figure 5). However, only about 10% is suitable for faceting. Much of the material was either damaged by blasting when the mine was opened or was of low quality to begin with. After faceting, some of this grossular enters the world market through Hong Kong.

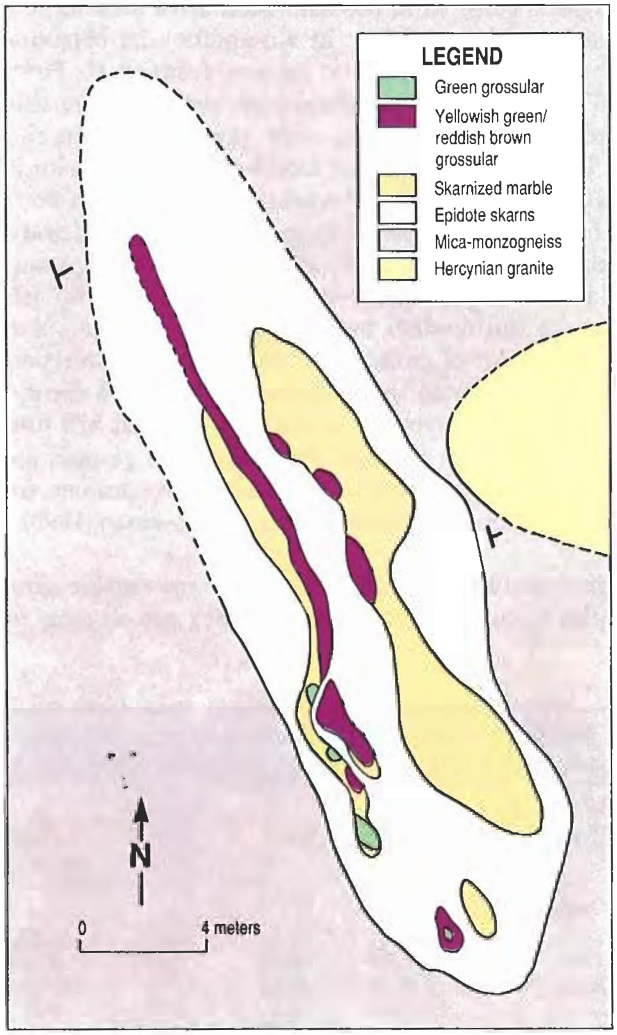


Figure 4. This geologic map of the Cocoktau grossular deposit shows the locations of gem-quality material in linear trends within the skarn zones. From a map by Chen Wenao, artwork by Carol Silver.

MATERIALS AND METHODS

We used standard gemological testing equipment to characterize about 20 polished sections each of grossular and spessartine garnet from the Cocoktau and the Qibeiling mines, respectively. Also examined were rough and faceted stones. Specific gravity was determined hydrostatically. An Hitachi U-4001 spectrophotometer was used to record the absorption spectrum (in the 400- to 650-nm range) of a spessartine sample. Mr. Guo Jiugao recorded the U.V.-visible spectrum of a grossular sample. Chemical composition was determined by wet chemical analysis, using four representative samples—one brown spessartine and three grossular garnets (green, yellowish green, and reddish brown).

THE GARNETS

The spessartine garnets occur as anhedral masses (i.e., lacking crystal form). Translucent to transparent, they range from brown to reddish brown and from 5 to 100 mm (0.2–4 inches) in diameter. The largest gem-quality mass found to date weighed about 1 kg. Most of the gem-quality material is moderately included.

The grossular garnets range from 5 to 20 mm in diameter, and are euhedral to semi-euhedral in crystal form (figure 6). They range from green to yellow-green to greenish yellow to reddish brown. Faceted stones from both localities average 1–3 ct.

Gemological Properties. We recorded refractive indices of 1.805–1.811 for the spessartines and 1.727–1.737 for the grossulars. The specific gravity was 4.20–4.25 for the spessartines and 3.58–3.65 for the grossulars. Neither species reacted to long- or short-wave ultraviolet radiation, and both had a Mohs hardness of about $7\frac{1}{2}$. Gemological properties of both the grossular and spessartine are within known ranges for the respective species, with some almandine (Fe^{2+}) component in the latter (Stockton and Manson, 1985).

Chemistry. Table 1 shows the results of the wet chemical analyses, including end-member compositions as determined by the Rickwood (1968) method. Overall compositions are typical for these garnet species.

Figure 5. The open-pit Cocoktau mine has produced several tons of grossular rough since it began operation in the 1980s; about 10% of the rough is suitable for faceting.

Figure 6. Garnet from the Cocoktau deposit is euhedral to semi-euhedral in crystal form, like these pieces of greenish yellow grossular (about 5 × 5 cm) and hessonite rough (about 8 × 5 × 5 cm). Photo by Fuquan Wang.

These data indicate that Fe^{2+} constitutes a high proportion of the total iron content in the spessartine. The color of spessartine progresses from orange to orange-red as Fe content increases. Refractive index and specific gravity also increase with the Fe concentration, as is often the case with gem silicates (E. Fritsch, pers comm., 1993).

Chemical data for the grossular garnets further confirmed that Fe content was related to color; as Fe content increased, the color progressed from green to yellow-green to reddish brown. Refractive index, specific gravity, and unit-cell parameters all increased as total Fe content rose.

Spectroscopy. Figure 7 illustrates typical visible-range absorption features found in the spessartines: bands at about 409, 422, 430, 460, 482, and 520 nm. All of these absorption bands are related to Mn^{2+} (Manning, 1967). The three major Mn^{2+} absorption bands—at 409, 422, and 430 nm—give spessartine its intrinsic, dominant 586.1–654.5 nm wavelength and orange color. The weak absorptions at 570 nm and 504 nm are related to Fe^{2+}. The overall brown color component of the spessartine is due to an underlying absorption increasing toward the ultraviolet. Such absorption has been attributed to Fe^{2+}-Ti^{4+} charge transfer (Fritsch and Rossman, 1993).

Figure 8 illustrates typical visible-range absorption features found in the grossular garnets; the absorption bands at 366, 408, and 425 have all been related to the presence of Fe^{3+} (Manning, 1967). The 571-nm band has also been attributed to Fe^{3+} in grossular (and Fe^{2+} in almandine); its behavior here suggests that it is not related to Fe^{3+}. Chromium and vanadium both also absorb in this region, although they were not detected in the chemical analyses. The increasingly brown color is also caused by an absorption—attributed to Fe^{2+}-Ti^{4+} charge transfer—rising continuously toward the ultraviolet; virtually absent in the green grossular, it becomes more important in the yellowish green and reddish brown varieties. The greenish component of grossular is due to the transmission window created in the green by the broad absorption with an apparent maximum at about 570 nm. However, the various chromogens in garnets are numerous, and their interrelationships complex; for more information, see Fritsch and Rossman (1993).

Inclusions. The inclusions in the spessartine samples occur in part as bands. They are angular or

TABLE 1. Chemical compositions and properties of one spessartine and three grossular garnets from Altay, China.

Composition/ property	Spessartine	Grossular		
	Brown	Green	Yellowish green	Reddish brown[a]
Oxide (wt.%)[b]				
SiO_2	37.01	39.03	39.40	39.05
TiO_2	0.14	0.02	0.07	0.16
Al_2O_3	19.42	22.65	21.89	20.33
Cr_2O_3	n.d.	n.d.	0.01	0.01
Fe_2O_3	2.15	0.63	1.11	3.12
FeO	11.03	0.02	0.23	0.50
MnO	29.60	0.05	0.05	0.10
MgO	0.17	0.14	0.13	0.30
CaO	0.31	37.04	36.68	36.65
K_2O	n.d.	n.d.	0.02	0.07
Na_2O	n.d.	n.d.	0.01	0.01
P_2O_5	0.17	n.d.	n.d.	n.d.
V_2O_3	n.d.	n.d.	n.d.	n.d.
Total	100.00	99.58	99.60	100.30
Species (wt.%)				
Almandine	26.00	n.d.	n.d.	n.d.
Andradite	0.96	1.79	3.05	8.67
Grossular	n.d.	97.52	96.24	89.67
Pyrope	0.73	0.54	0.49	1.14
Spessartine	72.31	0.12	0.11	0.22
Schorlomite	n.d.	0.03	0.11	0.30
Total	100.00	100.00	100.00	100.00
Gemological property				
Specific gravity	4.23	3.60	3.63	3.65
Refractive index	1.808	1.727	1.737	1.743
Hardness	7$^1/_2$	7$^1/_2$	7$^1/_2$	7$^1/_2$

[a] *Known by the gem varietal name hessonite.*
[b] *As determined by wet chemistry.*

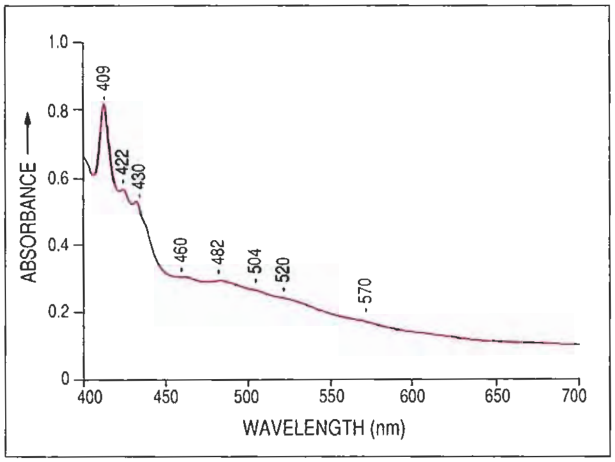


Figure 7. This visible-range optical absorption spectrum illustrates typical absorption features found in spessartine garnet from the Qibeiling mine. The three major Mn^{2+} absorption bands—409, 422, and 430 nm—give spessartine its intrinsic color.

irregular in shape, range from 10 to 52 μm in length, and are typically liquid-containing negative crystals, with about 6%–17% gas. The homogenization temperature of fluid inclusions in spessartine was 200°–290°C.

Inclusions in the grossular samples are angular or irregular in shape, 10 to 40 μm in length, and typically contain both gas and liquid phases (figure 9). The homogenization temperature of inclusions in green grossular was 200°–240°C; that of inclusions in zoisite—the principal associated mineral—was 300°C.

CONCLUSION

Significant quantities of spessartine occur in the pegmatite at Qibeiling and are now being mined commercially; about 20% is facet grade. All of the gem-quality spessartine garnets represent second-generation growth. Several tons of grossular have been recovered from Cocoktau since 1980, but only about 10% is gem quality. Material of fine green color is rare. Production at both localities will continue for many years. Currently, the material is cut in China. It is sold locally and, through Hong Kong, internationally.

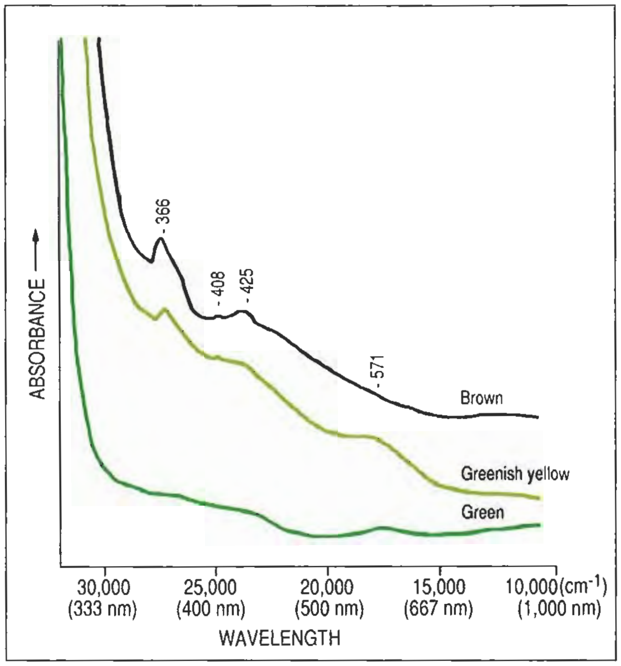
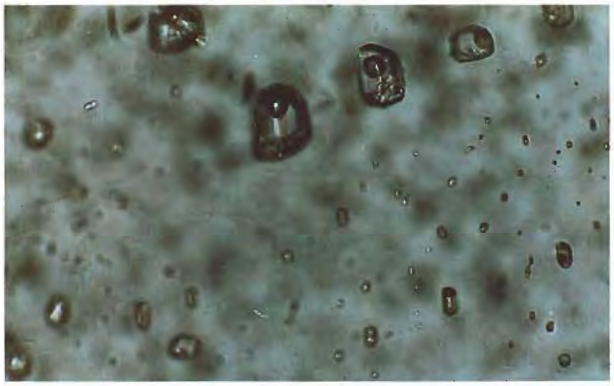


Figure 8. These visible-range optical absorption spectra illustrate typical absorption features found in grossular garnet from the Cocoktau deposit; the absorption bands at 366, 408, and 425 nm have all been related to the presence of Fe^{3+} (Manning, 1967). The 571-nm band has also been attributed to Fe^{3+} in grossular (and Fe^{2+} in almandine); its behavior here suggests that it is not related to Fe^{3+}.

Figure 9. These three-phase—mineral, liquid, and gas—inclusions are typical of those found in grossular garnet from Altay. Photomicrograph by Fuquan Wang; polarized light, magnified 625×.



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GEM TRADE LAB NOTES

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CUBIC ZIRCONIA, Carved to Imitate an Ancient Buddha

A transparent brownish yellow carving of Buddha (figure 1) was submitted to the East Coast laboratory, with the statement that it appeared to be a 16th-century piece. At seemingly random sites on the 30.6-mm-high carving were remnants of a yellow metal gilt. In addition, many incised areas contained a foreign material that appeared to be quite worn, implying considerable age.

Routine refractive-index testing gave only a shadowy over-the-limits refractometer reading. The bright orangy red fluorescence to both long- and short-wave ultraviolet radiation was not of much help either. The similarity in color between the carving and the high-lead-content glass hemicylinder of our refractometer prompted us to check each with a hand spectroscope. The absorption spectra were somewhat similar. When a hardness point was applied in an inconspicuous place, the statuette proved to be slightly harder than synthetic spinel (Mohs 8), thus ruling out glass (Mohs 4–6). However, the specific gravity (determined hydrostatically), which was slightly greater than 6.00, pointed toward cubic zirconia (S.G. of 5.800 ± 0.20).

Figure 1. This 64.19-ct yellow Buddha carving (30.6 mm high) is actually cubic zirconia.

Energy-dispersive X-ray fluorescence analysis (EDXRF) by GIA Research revealed the presence of zirconium, as well as hafnium and yttrium, thus confirming the identification as cubic zirconia. This is the first time we have encountered this common diamond simulant as a carved art object. *GRC*

DIAMOND
Cyclotron-Treated

Although neither cyclotron nor radium treatment is now used commercially to color diamonds, enough diamonds were subjected to these surface treatments in the past that we still see them occasionally in the laboratory. Some have features that are unlike those typically seen in diamonds treated by these methods. For instance, figure 2 shows the usual "umbrella" effect seen at the culet of a green, cyclotron-treated, round brilliant-cut diamond. Note the symmetry of the zone of color that produces the diagnostic umbrella. This contrasts with the lack of symmetry of the umbrella seen in the cyclotron-treated round diamond shown in figure 3.

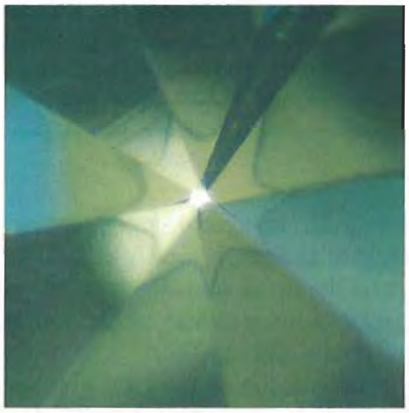

Figure 2. Typically, the umbrella effect seen around the culet of cyclotron-treated round brilliant-cut diamonds is symmetric. Magnified 36×.

An umbrella effect is indicative of the shallow penetration of the green color reaching from the culet to the girdle; typically, the zone of color is uniform around the culet. To try to explain the asymmetric color zone in the diamond in figure 3, we went back to the early literature. In light of the fact that the cyclotron was not

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Editor's note: The initials at the end of each item identify the contributing editor who provided that item.

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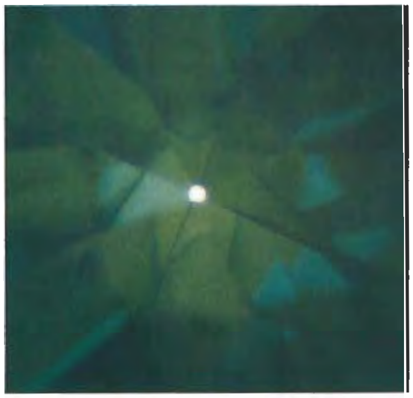
invented until 1931, and there were only three of any size in operation prior to World War II, it was enlightening to learn that the existence of cyclotron coloration of diamond was published as early as 1942, by J. M. Cork (*Physics Review*, Vol. 62: "Induced Color in Crystals by Deuteron Bombardment" [p. 80] and a "Note on Induced Diamonds" [p. 494]). By 1949, such treated stones were appearing in the gem market and the gemological literature. In "Cyclotron Treated Diamonds" (*The Gemmologist*, March 1949), A. E. Alexander observed that the green color appeared to be confined to the crown areas of one stone, an emerald cut, with the pavilion being essentially colorless (evidence of treatment from the top, which was uncommon, rather than from the culet).

Martin L. Ehrmann wrote one of the first good accounts of the history of cyclotron treatment, in the Summer 1950 issue of *Gems & Gemology*. Less than a year later, in the Spring 1951 issue of *Gems & Gemology*, F. H. Pough and A. A. Schulke provided clues to identifying cyclotron treatment in "The Recognition of Surface Irradiated Diamonds." This article gave additional historical background, as well as notes about the different cyclotrons used and methods of holding stones during treatment. Here we find a clue to the possible cause of the asymmetric umbrella seen, in the authors' statement that their first commercial work was with an older cyclotron at Columbia University. This unit did not allow the beam to strike the stones squarely on the culet, so the treater either had to rotate the stone 180° after the first exposure and treat it a second time, or hope for the best with a single exposure. By the time this article was printed, the site for cyclotron treatment had been moved to a much newer and more versatile cyclotron at George Washington University in St. Louis, Missouri.

Figure 3. In this 0.52-ct cyclotron-treated round brilliant-cut diamond, the "umbrella" effect is unusual in its asymmetry. Magnified 29×.



Therefore, the stone with the asymmetric umbrella in figure 3 could be one treated with the old Columbia University cyclotron, if it was not simply misaligned in a more recent procedure. GRC

Fancy-Color Diamond with Unusual Radiation Stains

Natural radiation stains occur on diamonds where they have been in contact with radioactive solutions or solids. On fashioned diamonds, they are most often found on naturals on the girdle, but they also appear in cavities and surface-reaching fractures; less commonly, remnants of such staining have been noted on culets and facets where very little of the skin of the rough diamond has been removed (see, e.g., Spring and Winter 1981 and Fall 1986 Lab Notes).

Recently, the West Coast lab examined a 2.37-ct fancy dark yellowish brown diamond with an unusual internal scene. This included a tapered etch tube, with a hexagonal cross-section, that ran from the pavilion area just below the girdle to the center of the stone. The etch tube had a series of distinct brown radiation stains along its length (figure 4), including one at the very bottom; this created the unusual situation of a surface-related radiation stain in the heart of the stone. Additional radiation stains were noted on the adjacent girdle area and on an upper girdle facet. Another notable inclusion was a cloud of minute white particles throughout the stone that formed a pattern reminiscent of a four-leaf clover. There was also green graining parallel to the "leaves" of this pattern, which is typical of hydrogen-rich diamonds. The absence of any of the absorption features associated with laboratory-induced radiation led us to conclude that the diamond was of natural color. RCK

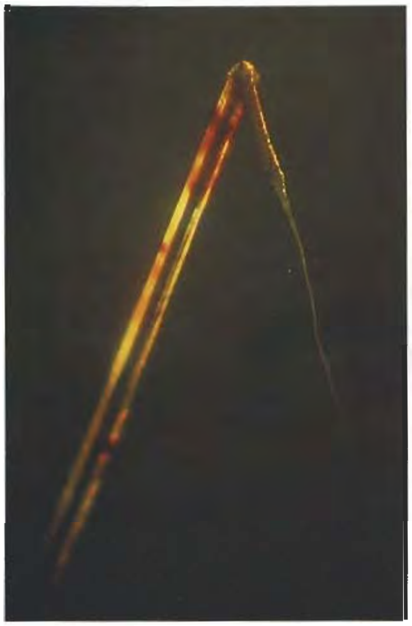


Figure 4. A series of brown radiation stains were noted along the length of this etch tube in a 2.37-ct fancy dark yellowish brown diamond. Magnified 35×.

Unusual "Melted" Cavity in a Diamond

A 0.50-ct slightly grayish green, triangle-shaped, brilliant-cut diamond was submitted to the West Coast lab for a grading report. In addition to numerous brown radiation stains, like those commonly seen on naturals and occasionally in etch channels (as described in the preceding entry), we observed one large brown radiation stain inside a cavity on a crown facet near the faceted girdle.

When we examined the cavity with magnification, we were able to resolve the striated, step-like formation that is characteristic of etch

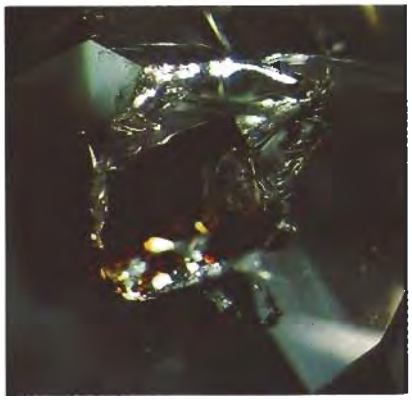


Figure 5. Note the unusual glassy, "melted" appearance on the edge of this cavity in a 0.50-ct diamond. Magnified 30×.

channels. However, we also noted a smooth surface around the edge of the cavity (figure 5) that gave it the appearance of melted glass. Although seen in the Gem Trade Laboratory only rarely, similar features in diamond were described by Yu. L. Orlov in his *Mineralogy of the Diamond* (John Wiley & Sons, New York, 1977 [transl.]). *KH*

Faceted Yellow SYNTHETIC DIAMOND

The Fall 1993 Lab Notes section described a 0.74-ct orangy yellow crystal submitted to the East Coast lab for identification. That specimen exhibited features that clearly identified it as a synthetic diamond and suggested that it might be of Russian origin.

More recently, a 0.34-ct square modified brilliant cut that also had an orangy yellow body color was submitted to the East Coast lab for routine examination. When exposed to an intense beam of white light, the stone luminesced a weak to moderate green. To long-wave U.V. radiation, it fluoresced a zoned, slightly chalky, moderate-to-strong orange; the zones were defined by two narrow, intersecting cross-like "arms" of greenish yellow fluorescence that extended diagonally from the girdle edges. The reaction to short-wave U.V. radiation was similar, but only slightly stronger. Most of the yellow synthetic diamonds we have examined to date have had a significantly stronger reaction to short-wave than to long-wave U.V. radiation. There was no phosphorescence to either wavelength.

Examination with a microscope revealed distinct color zoning. Darker zones set off a lighter yellow central funnel-shaped "core," with these two zones sharply delineated by a very thin rim of an even darker yellow. Table-down, the stone revealed some near-colorless zones near the center and at the corners. Magnification also showed a cloud of reflective pinpoint inclusions throughout the stone, with the heaviest concentration just outside the central, lightest-colored zone. Although we saw drag lines on the table from where these pinpoints broke the surface, we saw no surface graining. We also noted one small crystal and several elongated black inclusions, mostly located at the corners. Remnants of the original crystal surface on two opposing corners indicated that the stone had been cut for maximum size.

We noted weak anomalous birefringence when we examined the stone between crossed polarizers. The stone was attracted by, but did not attach to, a pocket magnet. Infrared spectroscopy showed the diamond to be a mixture of types Ib and IaA.

We subsequently received for examination two crystals and two cut stones, all brownish yellow to brown, that were reportedly obtained from Chatham Created Gems, Inc. Their characteristics indicate that they are from the same source as the synthetic stones described above and the known Russian synthetic diamonds reported in the article by Shigley et al. in this issue.

RCK, TM, and Emmanuel Fritsch

EMERALD, with Large Filled Etch Channels

The GIA Gem Trade Laboratory routinely identifies emeralds that show evidence of clarity enhancement, their surface-reaching fractures filled with transparent, essentially colorless substances. Because these filled fractures are usually very thin, any gas bubbles they contain are generally flat, appearing as highly reflective areas when examined with oblique illumination.

Less frequently, we examine emeralds in which one or more large, cross-sectional areas have been filled. In one such stone—an 8.02-ct round mixed cut—submitted for identification to the West Coast lab, magnification revealed three large, and several smaller, etch channels that had been filled and apparently sealed at the surface. However, they were not completely sealed, as the heat from the microscope's darkfield lamp caused a small amount of the filler to "sweat" out of the larger channels. That the filler below the hardened surface was still a fluid was further confirmed by the presence of large, spherical gas bubbles (see, e.g., figure 6), which moved when the stone was rocked on the microscope stage. These observations, along with the presence of orange "flash effects" from the filled fractures, indicated that the stone had been treated with a synthetic resin and an attempt had been made to polymerize the surface. *RCK*

Figure 6. Note the large gas bubble in the filling material that was used to clarity enhance this 8.02-ct emerald. Magnified 9×.

GARNETS, Fracture Filled

Although much has been written about fracture filling in diamonds and emeralds, the lab periodically sees other stones that have been similarly treated. Just in the past year or so, these have included amethyst, aquamarine, chrysoberyl, sapphire, spinel, tanzanite, and tourmaline.

Twice in about a week this past summer, we found evidence of clarity enhancement in garnets submitted to the West Coast lab for identification. In the first instance, two hessonites contained low-relief fillings that had some flattened gas bubbles. In the second, a pyrope-almandine had a filled break that exhibited very low relief (figure 7). We did not see dispersive flash effects in either case. As is sometimes required with filled breaks, we confirmed the treatment by carefully holding the tip of a thermal reaction tester ("hot point") just above the area where the fractures reached the surface, causing movement within the filling material. (This test should only be performed with extreme caution, as some gem materials are very susceptible to heat damage.)

Readers are encouraged to check all gems for such clarity enhancement. Those with surface-reaching breaks that appear to have lower-than-normal relief are most suspect.

RCK and SFM

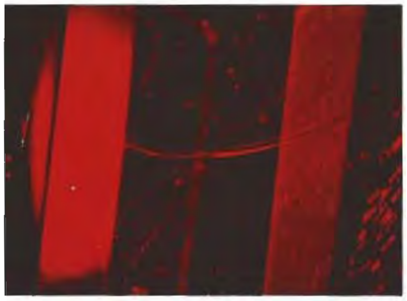


Figure 7. This low-relief filled fracture is in a 17.93-ct pyrope-almandine garnet. Magnified 10×.

Iridescent ORTHOAMPHIBOLE, "Nuummite"

After reading the article describing a new iridescent orthoamphibole from Greenland (*Gems & Gemology*, Spring 1987, pp. 36–42), we wondered how long it would be before examples of this material came through the laboratory. In September 1993, a client brought an attractive necklace of 18.00 × 13.00 mm flattened oval beads (figure 8) into the East Coast lab for examination, saying that the customer to whom they belonged was unsure of the name of the material. She did know that it was from Greenland and that the name sounded like "neumit" or "newmite." We recalled the 1987 article and the fact that the material was being sold under the trade name "Nuummite" (because the deposits were found within about 50 km of the city of Nuuk). The gemological properties listed in the article (average R.I. of 1.64–1.66, average S.G. of 3.24), along with the appearance of the polished stones, made identification fairly easy. We also determined that the beads were attracted to a small magnet, a property not mentioned in the 1987 article.

GRC

Figure 8. The beads (approximately 13 × 18 mm) in this necklace were identified as the iridescent orthoamphibole known in the trade as "Nuummite."

ORTHOPYROXENE, a Carved Mask

Although most of the items submitted to the laboratory are faceted or cabochon cut for jewelry use, we occasionally receive larger items to examine, including carvings. Recently, the opaque, mottled brown-and-white mask of a male face shown in figure 9 was submitted to the West Coast lab for identification. As is often the case with such items, there were limitations on the gemological testing that could be done. The size of the piece, roughly 30.2 × 25.8 × 9.0 cm, prevented determination of specific gravity by normal methods, and the condition of the surface made it impossible to obtain a clear R.I. reading.

Therefore, we performed X-ray powder diffraction analyses on small scrapings taken from three locations on the mask's base. Although the three patterns differed slightly from one another, they all closely resembled those of the orthopyroxenes enstatite and hypersthene. Because none of the patterns was an exact match for any one mineral—and, as the testing indicated, there was some variation in the structure from one area to another—the life-size mask was identified as a rock consisting of one or more minerals in the orthopyroxene group and possibly additional unidentified minerals. Petrographic testing, which is destructive, would be necessary to characterize the material fully.

RCK

Some PEARL Observations

A multi-strand pearl necklace submitted to the East Coast lab was found to be composed of both natural and cultured pearls, a situation that frequently calls for many X-radiographs and tedious examination of every pearl. This necklace was no exception. The surfaces of nearly one-third of the natural pearls on one strand, which consisted mostly of

Figure 9. This life-size carved mask (30.2 × 25.8 × 9.0 cm) is a rock consisting of one or more orthopyroxenes and possibly additional minerals.

natural pearls, had a reticulated appearance that we had never before encountered (figure 10). Many of these pearls were noticeably yellow. Most of the other strands, nine in all, had from one to five natural pearls with the same strange appearance.

At first we thought this unusual surface might be a form of the "hammered" appearance seen often on natural pearls but only very rarely on cultured pearls. However, a typical hammered effect appears to have been done with a flat hammer head (see figure 11), whereas the pearls in question appeared to have been hammered with a ball peen. Since there were several of these "peened" pearls, and almost all were yellower than the bulk of the other pearls, they may all originally have been strung on the same necklace, with some sort of damage responsible for the unusual appearance.

Figure 10. The surface of this 6.5-mm natural pearl has an unusual pattern, as if it had been hammered with a ball peen. Magnified 14×.

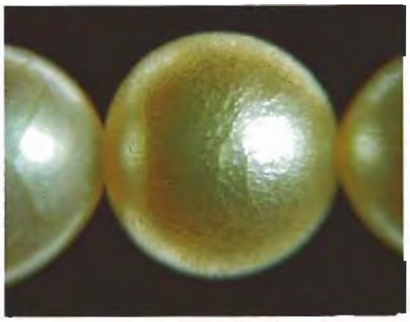
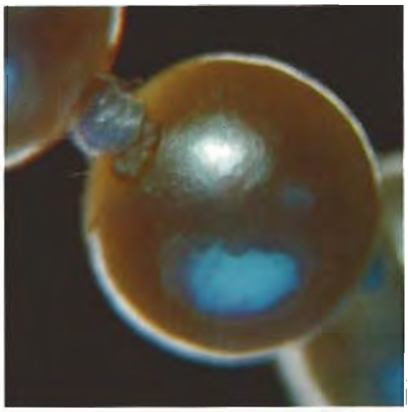


Figure 11. The "hammered" appearance typically found on natural pearls appears to have been done with a flat hammer head. Magnified 17×.



One pearl in the multi-strand necklace had some areas of "normal" hammering (again, see figure 11). In addition, the drill hole was plugged with a small wooden dowel. Such dowels are seen in older natural pearls that have enlarged drill holes, probably due to skin acid on the string.

Our heightened awareness of pearl surfaces led us to note still another surface anomaly, this time on several pearls in a cultured pearl necklace. Here, the surface appeared reticulated, but in a somewhat parallel pattern. As with the dimpled black cultured pearls described in the Summer 1993 Gem Trade Lab Notes (pp. 127–128), these unusual surfaces gave the pearls an added element of charm. *GRC*

SYNTHETIC RUBY, Striae Resolution Technique

The West Coast lab was asked to identify two specimens that had been represented to our client as natural ruby rough from Vietnam. The larger (25.71 ct) of these was relatively easy to identify, inasmuch as curved striae were clearly visible through a "window" that had been polished on one surface.

The second specimen (18.45 ct) presented more of a challenge, since the entire piece exhibited a rough, abraded appearance, with no polished surface. Examination with the microscope—using darkfield illumination (both with and without immersion), brightfield, and shadowing—failed to resolve any growth features. Using a method that is common among European gemologists, we next immersed the specimen in methylene iodide and then examined it with brightfield illumination. Curved striae were easily resolved (figure 12).

Further experimentation with this microscope technique showed that it was often quite helpful in

Figure 12. The curved striae in this 18.45-ct synthetic ruby, which was misrepresented as natural Vietnamese rough, became readily apparent when the stone was examined using combined brightfield illumination and immersion. Magnified 10×.

resolving growth features in melt synthetics. In one test, we examined 10 boule fragments of synthetic ruby and synthetic pink sapphire using a variety of lighting techniques. The brightfield/immersion combination enabled us to see curved striae in six of the 10 specimens; using any other technique, we saw curved striae in only one specimen. Furthermore, the addition of a transparent green plastic filter (for color contrast) between the microscope objectives and the stone increased the relief of the striae. This is comparable to the technique of using a blue filter to resolve striae in yellow-to-orange synthetic corundum. We have since used the brightfield/immersion combination to examine Czochralski-pulled synthetic alexandrites, with some promising results.

Dino DeGhionno and RCK

SAPPHIRE

A Difficult Identification

In the routine identification of blue sapphires, our experience has been that the larger the stone is, the easier the identification will be, with tiny calibre-cut set stones often the most time consuming. Therefore, we were surprised at the problems we encountered identifying a 25+ ct cushion-shaped mixed-cut sapphire that was set in a ring. Initially confident that magnification would quickly establish whether the stone was natural or synthetic, we became concerned when we could not detect any inclusions or color banding. The setting precluded a satisfactory Plato test, which we attempted after exposure to short-wave U.V. radiation revealed a chalky green fluorescence in what appeared to be synthesis-associated curved bands (figure 13). In our experience, however, very large synthetic blue sapphires are almost always watery in appearance, with color stronger in one area than another. This stone was uniformly colored, with no watery appearance. The possibilities were that it was either an unusual synthetic or an early heat-treated natural stone. To no avail, we checked with the hand spectroscope for an iron line, which when present in heat-treated blue sapphires is usually weak. We finally asked the client to remove the stone from the ring.

Figure 13. The fluorescent bands—actually straight parallel growth planes—in this 25+ ct natural sapphire could easily be misconstrued to be curved.

What we saw with the stone loose was diagnostic. Formerly hidden by the setting, but now faintly visible, was a small patch of altered silk. What had appeared under short-wave to be curved fluorescent bands now, with immersion, could be seen to be normal parallel growth planes in a natural sapphire (figure 14).

GRC

Figure 14. When the stone in figure 13 was removed from its mounting, immersion revealed the angular nature of the color zones.

Diffusion Treatment Obscured by Mounting

Recently, the West Coast lab received for identification a 1.14-ct transparent blue, oval mixed cut set in a woman's yellow metal ring. Gemological testing revealed properties consistent with corundum. Although the nature of the mounting severely limited microscopic examination, we did resolve diffused straight color banding and broken "silk" through an exposed area near the culet. All of these observations pointed to an identification of natural sapphire that had been heat treated.

However, because of the possibility of diffusion treatment, we routinely examine all rubies and sapphires with immersion. With the stone in question, immersion revealed a few facets, one row up from the culet, that appeared to lack color. Again, because of the nature of the mounting, this could have been an optical anomaly. We advised the client accordingly, and he agreed to remove the stone from the ring so we could examine it further.

As can be seen in figure 15, the sapphire was, in fact, diffusion treated. This should serve as an excellent

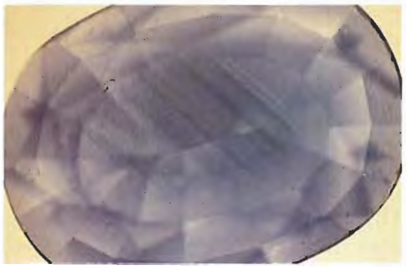


Figure 15. The darker color evident at the facet junctions, and uneven coloration of the different facets, only became apparent when this 1.14-ct diffusion-treated sapphire was removed from its mounting. Magnified 18×.

Figure 16. Prominent, slightly curved parallel graining is evident in this 15.45-ct green YAG. Magnified 17×.

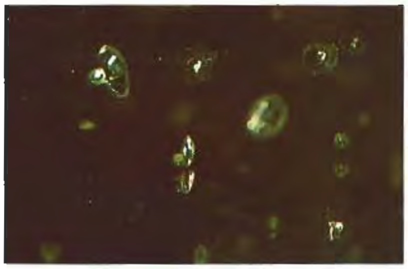


Figure 17. These included crystals, with surrounding disk-like fractures, are unusual in YAG. Magnified 38×.

reminder that the presence of features consistent with high-temperature treatment does not rule out diffusion treatment, as this enhancement technique also employs heating to a high temperature.

RCK and Dino DeGhionno

YAG with Unusual Inclusions

Yttrium aluminum garnet (YAG) debuted in the gem trade in colorless form as a diamond simulant, but it is available today in many colors, including violet, dark blue, greenish blue, green, and yellow. Until recently, most of the YAGs we saw were essentially inclusion-free. Lately, however, we have seen a greater number of included specimens. One such example was a 15.45-ct dark green rectangular emerald cut (13.91 × 12.08 × 7.70 mm) examined in the West Coast lab. Gemological testing identified the specimen as YAG; EDXRF analysis further confirmed both the identity and the presence of chromium as the principal coloring agent. Magnification revealed an unusual inclusion scene: elongated gas bubbles sheathed in fine layers of blue coloration; distinct, slightly curved parallel graining (figure 16); and scattered small, unidentified crystals, each surrounded by stress fractures. The last (figure 17) were reminiscent of the discoid fractures noted in heat-treated corundums.

The colored YAG that first entered the gem industry was most likely material rejected for optical (e.g., laser) applications because of structural defects (for more information, see K. Nassau's *Gems Made by Man*, Chilton Book Co., Radnor, PA, 1980). Now, however, YAG is also produced specifically for gem use. Perhaps lower purity tolerances in the "gem" production process account for the included materials we have been seeing. Or this may be material currently produced in Russia by a floating zone technique referred to as "horizontal crystallization," which we have observed to be fairly heavily included.

RCK and SFM

PHOTO CREDITS

Nicholas DelRe supplied the photos used in figures 1–3, 8, 10, 11, and 13–15. Photomicrographs in figures 4 and 5 are by John I. Koivula. The photos used in figures 6 and 9 were taken by Maha DeMaggio. Shane McClure provided figures 7, 12, 16, and 17.

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The winning articles will be announced in the Spring 1994 issue of *Gems & Gemology*. Cash awards of $1,000, $500, and $300, respectively, will be given to the authors of the articles that place first, second, and third in the balloting. **VOTE TODAY!**

GEMNEWS

JOHN I. KOIVULA, ROBERT C. KAMMERLING, AND EMMANUEL FRITSCH, EDITORS

COLORED STONES

Update on Colombian emerald mining. The Muzo region (Muzo and Coscuez mines) continues to be the major emerald producer in Colombia. Discovery of gem-rich veins at Coscuez early in 1992 yielded large quantities of rich, dark, well saturated emeralds, according to Ron Ringsrud of Constellation Gems, Los Angeles. This heavy production level lasted until about March 1993; production has since returned to pre-1992 levels.

Vietnamese garnets. Collectively, garnets are among the most widely disseminated gem minerals. Those of a predominantly red hue have been found on every continent, including Antarctica. It should, therefore, come as no surprise that red garnets have been found in Vietnam, which has only recently begun commercial gem mining.

Saverio Repetto, of the Gemological Institute of Vietnam, a joint-venture firm located in Hanoi, sent the Gem News editors five faceted garnets for examination. According to Mr. Repetto, these stones were fashioned from rough recovered near the village of Luc Yen in Hoang Lien Son (formerly Yen Bai) Province in the far north of Vietnam, a major ruby-producing area.

The stones, ranging from 1.46 to 2.28 ct, were all very dark in tone, in purplish red to brownish red hues (see, e.g., figure 1). The gemological properties were constant from stone to stone: R.I.—1.799 to 1.800, S.G.—4.14 to 4.15, moderate anomalous double refraction when examined between crossed polarizers, no reaction with the Chelsea color filter, and inert to both long- and short-wave U.V. radiation. Examination with a desk-model prism spectroscope revealed strong bands at about 504, 520, and 573 nm; weak bands at 423, 460, and 610 nm; and weak general absorption below 423 nm. Magnification showed these internal features: abundant rounded-to-subrounded transparent, light yellow monazite crystals; transparent, light yellowish brown euhedral-to-subhedral phlogopite crystals; transparent, near-colorless subhedral-to-euhedral rounded crystals of apatite; zircon crystals (some displaying well-formed tetragonal symmetry) with strain haloes; dark, opaque platelets of ilmenite; and fine, short, parallel acicular rutile crystals. Using the criteria established by C. M. Stockton and D. V. Manson ("A Proposed New Classification for Gem-Quality Garnets," *Gems & Gemology*, Winter 1985, pp. 205–218), we identified all the stones as almandine garnets.

Figure 1. These two almandine garnets (1.46 and 2.06 ct) are typical of material being recovered from Hoang Lien Son Province in northern Vietnam. Photo by Maha DeMaggio.

Mr. Repetto informed us that red garnets have also been found in the Quy Chau District of Nghe Tinh Province, another ruby-producing area of northern Vietnam.

Myanmar mid-year Emporium. In late October 1993, one Gem News editor (RCK) attended two days of the "Mid Year Emporium, Myanma Gems, Jade and Pearl" in Yangon (formerly Rangoon), Myanmar (formerly Burma). The entire event spanned nine days: two days of viewing and inspecting the goods, seven of sales by competitive bidding (four days of jade—614 lots, one of pearls—198 lots, and two of other gem materials—318 lots).

This emporium was the first held in the new Myanma Gems Enterprise (MGE) exhibition hall, built adjacent to MGE headquarters solely for these bi-annual sales. In the ground-floor "Jade Display Room" (primarily one large open room), lots of rough and fashioned jade were displayed. Also offered throughout the entire event were various fashioned items at fixed prices—including all jade-related offerings under US$3,000, the lowest reserve price for jade at auction. Jade was also displayed outside, along the sides and back of the building.

Overseen by MGE officials, the actual auction took place on the second floor of the new exhibition hall.

Figure 2. Dealers examine rough from Monghsu, Myanmar, in the ruby market in Mae Sai, northern Thailand. Photo by Robert C. Kammerling.

Since bidders sat at tables in the large hall, the scene was reminiscent of a banquet. The auctioning was conducted from a raised dais at the front. As each lot was presented for bidding, pertinent information—lot number, category of material, and reserve price—was projected onto one portion of a large screen, with a videotape of the lot itself shown alongside. When a winning bid was announced, the selling price and name of the successful bidder were also projected.

Gems, pearls, and jewelry were displayed in cases on a balcony that overlooked the auction area. Items below a certain reserve price (approximately $1,500 for pearls and $3,000 for other gems) were sold at fixed prices, as was all jewelry. This included jewelry sold on consignment to the MGE, as well as gem-set gold rings produced and marketed by the Myanmar VES Joint Venture Co.

Although rubies and sapphires were the most prevalent gemstones being offered, others were available. These included amethyst, citrine, kyanite, danburite, spinel, topaz, zircon, diopside, scapolite, apatite, aquamarine, and peridot.

Emporium officials reported total sales of $14,533,295 for 506 lots. The breakdown for auction sales was: jade (264 lots) for $5,493,173; pearls (75 lots) for $665,180; and gems (77 lots) for $1,433,531. Additional sales included jewelry (quantity not provided) for $698,024; jade carvings (quantity not provided) for $69,602; fixed-price jade (five lots) for $9,300; fixed-price gems (49 lots) for $5,949,785; special-sale jade (22 lots) for $153,450; and special-sale gems (14 lots) for $61,250. The large figure for fixed-price gems includes a 38.12-ct ruby cabochon, which sold for $5.86 million. According to a report in the October 1993 *Jewellery News Asia* (p. 125), a ruby of this weight and measuring 18.2 × 16 × 12 mm was cut from rough found in Mogok in 1993.

Update on Monghsu ruby. One gem material conspicuously underrepresented at the mid-year emporium was ruby from Monghsu (pronounced "Mong Shoo" by the Shan who live in the area and "Mine Shoo" by the Burmese and Thai). Only four small lots of stones identified as from this area, and described as "heat-treated cut ruby" in the emporium catalog, were offered at auction. All of these stones, which were examined by one of the editors (RCK), exhibited the blue cores that are distinctive of Monghsu material.

However, rubies from Monghsu are readily available in Mae Sai, the northernmost town in Thailand, just across the small Moei Kok River from the town of Tachileik, Myanmar. In Mae Sai, untreated ruby rough from Monghsu is openly traded in shops and at streetside tables along what local merchants call "Soi Tab Teem," or Ruby Lane (figure 2). Here Thai dealers, most from the southeastern city of Chanthaburi, purchase stones from Burmese who cross the bridge daily between Mae Sai and Tachileik.

Informed sources in Myanmar and Thailand described the route from mine to market as follows: Actual mining takes place at a site known as Siahlaing, about 26 km (16 miles) southeast of the town of Monghsu. The rough is then sold at a government (i.e., legal) market about 274 km to the southwest in the city of Taunggyi. Interestingly, when some Burmese in Mae Sai were asked the source of their stones, they replied "Taunggyi," not Monghsu. Instead of going next to Yangon, most of the rough apparently travels east to the town of Keng Tung, from there to Tachileik, and then across the border into Thailand. The first stop there is Chanthaburi for heat treatment—to remove the typically blue-colored core zone—and cutting. Most eventually arrive in Bangkok for marketing throughout the world.

During the editor's visit to Mae Sai, several sources reported that the number of dealers had decreased significantly over the past few months. This was attributed to some controversy surrounding Monghsu rubies and a subsequent drop in price. Fluid inclusions in the material reportedly cause some fracturing during heat treatment. The fractures, in turn, are invaded by the fire-coating substance(s) that are applied to the stones before heat treatment, resulting in inclusions reminiscent of the secondary partial healing planes seen in some flux-grown synthetics. Whereas the dealers generally accept—and expect—heat treatment, they are less forgiving of the presence of such glassy, flux-like fillings deep within fractures, especially in larger stones.

Ruby in kyanite from India. International Colored Gemstone Association (ICA) Laboratory Alert No. 70 (May 17, 1993), from Elisabeth Strack of Hamburg, Germany, reported on rough specimens of ruby in a blue matrix that was offered as ruby in sapphire. X-ray diffraction analysis, however, proved that the blue matrix was kyanite.

Ms. Strack described the rubies as opaque, with an intense pinkish red color. Although she did not know their exact source in southern India, she speculated that they might be from the area around Mysore in Karnataka State or even further south, in Tamil Nadu State. In this regard, it is interesting to note that her description of the rubies is consistent with that of the rubies and pink sapphires described in the Spring 1993 Gem News (pp. 60–61), which also were reportedly from the state of Karnataka, about 160 km (100 miles) south of Mysore.

Rare gemstones from Quebec. During a trip to the Canadian province of Quebec, one of the editors (EF) was loaned a number of rare gemstones from that province by Guy Langelier, a Montreal gemologist. Many pegmatites, some of which contain rare minerals that have been faceted into gemstones, are found in the Kipawa River area in southwestern Quebec. We studied a 0.36-ct orangy pink eudialyte and a 0.27-ct brownish yellow vlasovite (figure 3) from this locality .

The eudialyte had indices of refraction of 1.599–1.602, with a birefringence of 0.003. S.G. could not be determined precisely, because the stone was so small, but it was in the 2.81–3.12 range. The stone was inert to both ultraviolet wavelengths. The spectrum showed two sharp lines at approximately 521 and 572 nm. Magnification revealed a phantom plane that contained numerous groups of minute birefringent platelets (possibly mica); each associated with a dark crystal (possibly hematite) that exhibited a silvery metallic luster. EDXRF analysis confirmed the presence of all chemical elements expected for eudialyte: $Na_4 (Ca,Ce)_2 (Fe^{+2},Mn,Y) ZrSi_8O_{22} (OH,Cl)_2$. Traces of hafnium probably replace part of the zirconium, and traces of ytterbium, part of the yttrium. Potassium, titanium, and strontium were also detected. U.V.-visible absorption spectroscopy, using an Hitachi U4001 spectrophotometer, revealed a broad, iron-related absorption band centered at about 540 nm, which accounts for the pink color. The spectrum also showed weak but sharp peaks at about 453, 461, 519, 523, 570, 579, 584, 594, 734, 740, 750, 800, and 809 nm. A comparison with the energy-level diagram of rare-earth ions proved these to be due to Nd^{3+}. These lines are too weak to influence the color, but some (e.g., at 519, 523, 570, and 579) were easily seen in the handheld spectroscope.

Indices of refraction for the vlasovite were in the range 1.609–1.624, with a birefringence of 0.015. These values are similar to those reported in the literature: 1.607, 1.623, and 1.628 (alpha, beta, gamma, respectively). Again, the small size of the stone prevented a precise S.G. measurement, but we recorded a range of 2.90–3.26. The stone fluoresced a weak, moderately chalky, brownish orange to long-wave U.V. radiation, and a moderate yellow to short-wave U.V. It contained numerous dry fractures (some of which might be cleav-

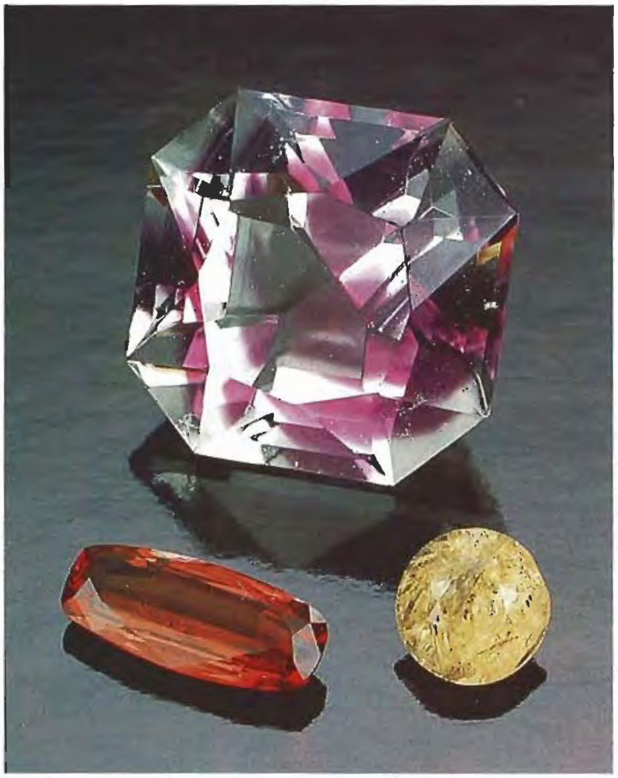


Figure 3. The 6.02-ct color-zoned fluorite (top) is from the Old Chelsea mine; the 0.36-ct orangy pink eudialyte (left) and the 0.27-ct brownish yellow vlasovite are from the Kipawa River area. Both areas are in the province of Quebec, Canada. Photo © GIA and Tino Hammid.

Figure 4. Ornamental marble from Utah, like this 42.20-ct cabochon (31.97 × 25.01 × 6.50 mm), is being promoted as "Picasso marble." Photo by Maha DeMaggio.

ages) and "undulating planes" of internal graining. No spectrum was observed with the handheld spectroscope. EDXRF analysis showed the presence of sodium, silicon, and zirconium—which are the main components of vlasovite according to its formula ($Na_2ZrSi_4O_{11}$)—as well as impurities of iron, potassium, and hafnium (the last probably substituting for zirconium in the structure). Despite the low R.I., there is little doubt that the material is vlasovite, since similar-appearing rough samples from the same find were identified as such by X-ray diffraction analysis.

A color-zoned fluorite from the Old Chelsea mine was faceted to produce a remarkable optical effect: Most of the stone is light greenish blue, except the dark purple culet, which reflects in almost all facets when the stone is viewed faceup (figure 3, top). Optical absorption spectroscopy showed that the light greenish blue color was caused by a weak samarium (Sm^{2+}) absorption at 615 nm.

Attractive ornamental marble. Among the interesting gems seen this year is an ornamental marble (a massive form of calcite) from Utah. The material has a variegated appearance, consisting of a fine-grained gray matrix with randomly oriented black and brown veining. The overall effect of the patterns is reminiscent of some abstract art; in fact, it is being sold under the trade name "Picasso marble" or "Picasso stone."

Gemological testing of a 42.20-ct oval cabochon (figure 4) revealed a spot R.I. of about 1.63 with a weak birefringence blink. The S.G., taken hydrostatically, was 2.74. There was no reaction to long-wave U.V. radiation, and the short-wave reaction was uneven, with some areas inert and others luminescing a weak, chalky yellowish green. The cabochon effervesced strongly to a drop of dilute hydrochloric acid. All these properties are consistent with those reported in the literature for massive calcite, proving marble to be the correct designation. The specimen did not react to an acetone-dipped cotton swab, which indicates that the material was not dyed.

Thai-Myanmar jewelry manufacturing joint venture. As noted in "Status of Ruby and Sapphire Mining in the Mogok Stone Tract" (*Gems & Gemology*, Fall 1992, pp. 154–172), the major legal outlets for Myanmar's gem wealth are the emporia now held twice a year in Yangon. Also noted were sales made through special arrangement with the government.

A newer ingredient in the marketing mix is a joint venture, established in August 1992, between Myanma Gems Enterprise and Thailand's VES Group: Mayanmar VES Joint Venture Company, Ltd. The joint venture cuts and polishes gems, and mounts them in jewelry that it also manufactures.

In addition to marketing at the emporium, Myanmar VES currently shares retail sales space with the MGE in Yangon. According to Marketing Manager Scott Montgomery, the firm anticipates opening at least four of their own retail stores in Yangon in 1994. In late 1993, Myanmar VES had a staff of 130, which they expected to double in early 1994. Local artisans are trained by experienced cutters and goldsmiths brought in from Bangkok.

ENHANCEMENTS

Irradiated phenomenal quartz. One novel gem seen at shows this year is cat's-eye quartz with moderately coarse, eye-visible "needles" and a dark brown, smoky-quartz body color that vendors reported was produced by irradiating a light gray material.

We decided to document the change in color produced in "cat's-eye" quartz (in some specimens, the "eye" is crossed by one or two weaker bands) with a greenish yellow body; this material has been known for years. We subjected one specimen to a nine-hour treatment at 1,490 kw in a nuclear reactor at General Atomics in San Diego, California. Not only did this treatment alter the body color to a very dark brown, but it also produced distinct asterism in the stone. The apparent change in the phenomenon probably resulted from the higher contrast of the reflective bands against the now-dark body color.

SYNTHETICS AND SIMULANTS

Amber simulant from India. An interesting amber look-alike recently brought to our attention is called a "lac" bead (figure 5). According to the vendor, George Darveaux, these beads are produced from a natural resin in Lino Village, approximately a two-hour drive from New Delhi, India.

Figure 5. These "lac" beads (approximately 22 mm in diameter) are an amber simulant manufactured in India. Photo by Maha DeMaggio.

The opaque beads have a swirled texture and a brownish yellow to orangy brown body color. We also noted fine surface cracks like the crazing sometimes seen on fossilized resins. Gemological examination of one sample revealed a spot R.I. of 1.51 and an S.G. of 1.67. This bead was subsequently sawn in half, revealing a medium dark brown interior streaked with a yellow material similar to that seen on the exterior. Magnification revealed that the exterior was actually a bright yellow opaque layer with a brownish orange transparent coating. These two layers have intermixed in places, so that they appear to "swirl" together. Also noted were dark brown specks of color and shallow hemispherical cavities, most likely gas bubbles that broke the surface of the outermost coating.

Artificial glass with high R.I. and S.G. Artificial glass was one of the first fabricated materials used to imitate natural gemstones. It has been produced in virtually every color and diaphaneity. Despite its range of appearances, most glass used today to imitate gems falls within a fairly standard range of R.I. (high 1.40s to 1.60s) and S.G. (2.30 to 4.00) values.

Since the 1950s, a number of crystalline, singly refractive materials with refractive indices over the limits of the conventional refractometer (1.81+) have appeared in the gem trade. Often, these have been seen first in essentially colorless forms and used as diamond simulants; later, colored versions have appeared. Three well-known examples are YAG, GGG, and CZ. Most gemologists confronted with a relatively dense, inclusion-free, colored singly refractive material with an over-the-limits R.I. would suspect that it was one of these three simulants. For loose stones, specific gravity might be used to determine which one it probably was (typical values being YAG—4.55, GGG—7.05, CZ—5.80).

At a recent gem show, however, the editors came across material being marketed under the trade name "Junelite" in a range of colors, including red, blue, green, yellow, brown, and black. What caught our attention was a display card identifying the material as an artificial glass with a 2.0 R.I., a 4.59 S.G., and a hardness of about 6. Subsequent gemological testing on a 20.84-ct sawn section of blue material (figure 6) revealed that the refractive index was indeed above 1.81 and that the S.G. was 4.44. The sample also exhibited anomalous birefringence in the polariscope, which is typical of such high-R.I. materials as YAG, GGG, and CZ. X-ray powder diffraction analysis confirmed that the material was amorphous. Gemologists are cautioned to be on guard for this material to avoid misidentifying it as YAG.

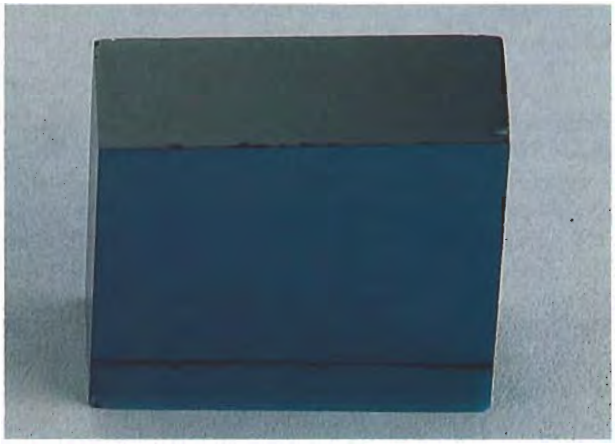


Figure 6. This 20.84-ct piece of artificial glass has an over-the-limits R.I. and an S.G. of 4.44. Photo by Maha DeMaggio.

More on Vietnamese deceptions. In recent years, the Gem Trade Lab Notes and Gem News sections have included several entries concerning the misrepresentation of synthetic rubies and ruby simulants as natural material, both rough and faceted (see, e.g., "Glass Imitating Vietnamese Ruby" in the Fall 1993 *Gems & Gemology*, p. 215). On a recent trip to Southeast Asia, one of the editors (RCK) learned of other such deceptions.

While visiting the town of Yen Bai in northern Vietnam, the editor examined a number of small parcels of what was represented to be natural ruby rough from the nearby Luc Yen mining area. One notable stone—visually estimated to weigh 2–3 ct—had exceptionally good color and, based on inclusions, appeared to be a natural corundum. However, examination with a 10× loupe revealed surface color irregularities. When the stone was scraped with a knife, a red coating was removed, revealing a pale pink body color.

Tony Laughter, manager of the School of Gemological Sciences in Bangkok, recounted why a gem dealer from Thailand, although well aware of ruby decep-

Figure 7. These two synthetic sapphires (19.20 and 29.90 ct) were sold as natural sapphire rough in Vietnam. Photo by Tony Laughter.

tions in Vietnam, believed it was relatively safe to purchase two pieces of "sapphire rough" in Ho Chi Minh City: Both were color zoned, had what appeared to be iron oxide staining in fractures, and had the overall appearance and color of the blue sapphires occasionally seen from Luc Yen (figure 7). When the pieces were subsequently shown to Mr. Laughter, he determined that they were synthetic sapphires containing colorless areas and zones of curved color bands. The bands were especially evident when the specimens were immersed in methylene iodide and examined with magnification (figure 8).

Figure 8. Magnification, used in conjunction with immersion in methylene iodide, clearly reveals the curved color banding in one of the synthetic sapphires shown in figure 7. Photo by Tony Laughter.

Acknowledgments: The editors thank Gustave P. Calderon and Dino DeGhionno, of the GIA Gem Trade Laboratory, for assistance in testing materials described in the previous section.

THE 24th INTERNATIONAL GEMMOLOGICAL CONFERENCE

The first International Gemmological Conference, organized by Professor K. Schlossmacher and Dr. E. J. Gübelin, was held in 1952 in Locarno, Switzerland. Since its inception, the purpose of this invitation-only conference has been the exchange of information among laboratory gemologists and others engaged in the science of gems.

The conference is hosted every two years by a different country. In October 1993, Paris was the site of the 24th International Gemmological Conference, which was organized through the Paris Chamber of Commerce by Jean-Paul Poirot. Official delegates from over 20 different countries presented papers discussing their latest research and gemological observations. Many of these papers described new gem materials, presented new technical information or new ideas about previously known gem materials, or explored new gem localities. It is impossible in the space provided to discuss all of the papers read at this conference. Therefore, the following is an overview of the 24th IGC, with synopses of some of the papers presented.

DIAMONDS

Canada. Canadian delegate Dr. Alfred A. Levinson gave an informative overview of the swiftly evolving diamond-exploration scene in Canada. Currently, at least 150 exploration companies are involved in the search for diamonds. Activity is particularly intense in the Northwest Territories and Alberta. In the province of Alberta alone, the area staked for further exploration is larger than that of the United Kingdom. There is also diamond exploration in eastern Canada, particularly in the Hudson Bay lowlands of Ontario.

Two major kimberlite fields have been discovered so far. The first, at Fort à la Corne in Saskatchewan, contains about 25 confirmed kimberlites, many of which are diamondiferous. The second is in the area of Lac de Gras, Northwest Territories. It contains approximately 20 kimberlites.

Some of the pipes discovered so far in Canada reportedly have yields of 1.25 ct per ton (as compared to the average output for diamond pipes worldwide of 0.25 ct per ton). However, the kimberlite samples to date have not been large enough for definitive economic evaluations of either the number of carats produced or the quality of the diamonds.

India. Dr. Jan Kanis, from Veitsrodt, Germany, gave an update on the current status of gem mining and production in the State of Orissa in India, where he serves as a United Nations expert. Exploration for a possible primary diamond source in western Orissa looks promising. Not only have gem-quality diamond crystals been found by local prospectors, but microprobe analyses of pyrope and chromite recovered in the course of prospecting also show that the chemical compositions of these indicator minerals are characteristic of those found in kimberlites and lamproites.

In addition, Orissa mines are already producing rubies of various qualities. New, commercial primary deposits of good cat's-eye chrysoberyl, cat's-eye sillimanite, and hessonite have been located. As the geologic and gemological knowledge of Orissa's gem fields is expanded, a great similarity to the gem fields of Sri Lanka is increasingly apparent.

Green-to-blue diamonds. George Bosshart, of Lucerne, Switzerland, noted the rarity of a natural green body color—produced by the general radiation (GR) center—in diamonds. He reiterated the sensitivity of such stones to heat produced during cutting, which might induce the H3 band and those at 594 and 637 nm that could be misinterpreted as resulting from natural annealing. He also wondered why no type Ib and type IIb diamonds with GR absorption have been reported so far.

Figure 9. A green "cloud" can be seen in this 0.24-ct natural-color green diamond. Photomicrograph by Nicholas DelRe; magnified 30×.

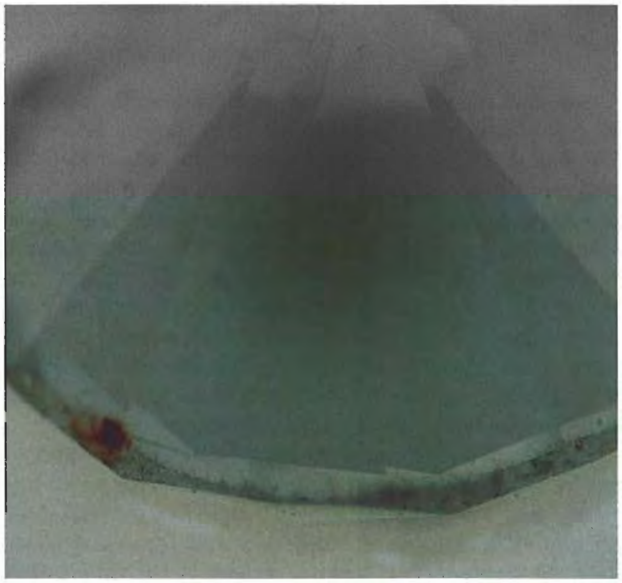


Figure 10. Some blue diamonds, such as this 0.15-ct round brilliant, are colored naturally by irradiation and do not conduct electricity. Photo by Robert Weldon.

Gem News Editor Dr. Emmanuel Fritsch presented new criteria for the separation of green-to-blue diamonds colored by natural irradiation from those colored by artificial irradiation. Clouds of blue or green coloration have been discovered in natural-color blue-to-green diamonds (figure 9). No such features have been observed in treated stones of similar color. Also, a particular type of U.V.-visible absorption spectrum has been found to be typical of one class of type Ia natural green-to-blue diamonds. Another observation is that some natural blue diamonds are colored by radiation, and these stones are not electrically conductive (figure 10).

History of diamond cutting. Finnish delegate Herbert Tillander, from Helsinki, briefly reviewed his comprehensive research into the origin of certain diamond-cutting styles, the subject of his upcoming book. In his presentation, Mr. Tillander focused on the development of the round-brilliant cut. He pointed out that diamond cutting was conducted in great secrecy throughout the 14th century, because religious and mythological beliefs held that diamonds could only be accepted in their natural crystal forms. Fourteenth-century diamond cutters found, however, that they could easily fool even well-educated customers simply by representing the faceted shapes they produced as natural crystal forms. Early diamond cutters had difficulty obtaining gem-quality octahedral rough of any significant size, because the Indian merchants who controlled the supply were reluctant to

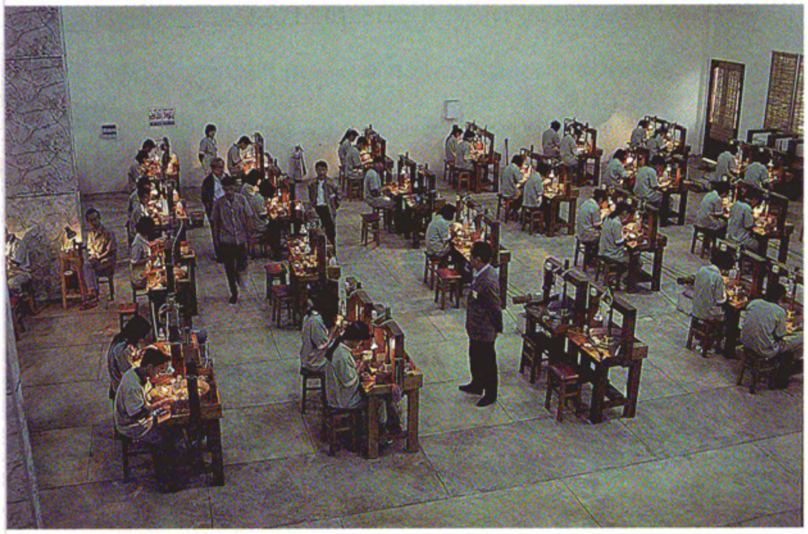
Figure 11. The cutting room of the "Ha Noi — Precious Stone Cutting & Jewelry Factory" had only a few tables in October 1992. Photo by E. Alan Jobbins.

release octahedra. The dodecahedra, macles, and irregular shapes that were more readily available were not ideally suited to produce what today we would call the round brilliant cut.

COLORED STONES AND ORGANIC MATERIALS

Amphiboles. Dr. Hermann Bank, of Idar-Oberstein, Germany, reported on the discovery in East Africa of translucent, emerald-green, chromium-bearing actinolite, which is being called "Smaragdite" in the trade. Transparent greenish brown magnesium pargasite, a member of the amphibole group, has been found in the Embilipitiya gem field in Sri Lanka. Careful studies initiated by Dr. Bank have shown it to be close to the pure end member.

Figure 12. By January of 1993, the cutting room of the Hanoi factory in figure 11 was greatly expanded, with dozens of cutters using contemporary equipment. Photo by E. Alan Jobbins.



Beryl. Recent mining activity for red beryl in the Wah Wah Mountains, Utah, was described by Gerhard Becker, of Idar-Oberstein. A new claim has produced some beautiful hexagonal prisms of gem and mineral-specimen quality. Slices cut from some of these crystals, both parallel and perpendicular to the c-axis, vividly show the strong color zoning that is often present in red beryl.

Dr. Dietmar Schwarz, now of Lucerne, Switzerland, provided an update on emerald-mining activity in the Ural Mountains of Russia, Egypt's eastern desert, the Swat region of Pakistan, the Ndola Rural District of Zambia, and the Sandawana area of Zimbabwe. He also described suites of solid and fluid inclusions that he has identified during his research on emeralds from various localities.

Dr. Jan Kanis also discussed his recent visit to the Machingwe emerald mine in Zimbabwe. At the time of his visit, the open-cast mine was 70-m deep. The emeralds produced are similar in color and quality to those found at the nearby Sandawana mine. He also mentioned reports of new emerald occurrences in Zimbabwe, approximately 40 km northeast of Sandawana.

Charoite. It was pointed out by Eugenia V. Buhtiarova, of Moscow, in the Russian Federation, that the charoite used in the jewelry industry is actually a rock in which the main component is the mineral charoite. She therefore proposed that the name *charoitite* be used for this ornamental material, to signify that it is a rock and not a single mineral. The purple color of charoite is attributed to the coexistence of traces of Mn^{3+} and Fe^{3+} (similar to sugilite). When charoite is iron rich and manganese poor, it is brown.

Corundum. Australia is not generally known as a source of color-change sapphires. In his presentation, however, Dr. E. Ralph Segnit, of East Malvern, Victoria, Australia, reported on a 39-ct color-change sapphire recovered from gravels near the town of Rubyvale in Queensland. Two transparent gems, the largest being 9.17 ct, were faceted from the rough. The color of the stones in sunlight was described as olive green, while in incandescent light they appear dark reddish brown. Electron microprobe analysis carried out at the CSIRO Division of Mineral Products, Port Melbourne, showed an iron content of 1.1 wt.%; no other trace elements were detected with certainty.

Perhaps one of the best examples of how the discovery of an important gem deposit can affect the economy of an area was illustrated by E. Alan Jobbins, of Great Britain, in his lecture updating ruby and sapphire production in Vietnam. Mr. Jobbins photographed the cutting room of the "Ha Noi—Precious Stone Cutting & Jewelry Factory" in Hanoi, Vietnam, first in October 1992 (figure 11) and then in January 1993 (figure 12). The growth of the gem-cutting facility from a small shop to a large, well-equipped factory in just three months is visible proof of the impact that the discovery of rubies and sapphires has had.

Dr. N. R. Barot of Nairobi, Kenya, and Dr. Roger R. Harding of the Gemmological Association of Great Britain, described a new source of pink sapphire from the eastern foothills of Mount Kenya, near Kitui, Kenya. The sapphires are light to medium pink, commonly translucent, and of a quality most suitable for the fashioning of cabochons and beads. Most of the production is sold to the gem-cutting industry in India, although some of the better-quality rough is cut in Kenya or imported to Germany. The sapphires are recovered from gravels by simple open-pit mining techniques. After sieving and washing, about 50 to 100 kg of pink sapphire are recovered each week by 30–50 laborers.

Robert E. Kane, from the U.S. state of Nevada, provided an overview of various commercial and rare gems that have been found in Myanmar, both from the Mogok Stone Tract and more recently from Monghsu. Heat treatment of rubies from the latter locality (to remove or diminish the blue zoning typical of this material) often results in an attractive red, comparable to fine untreated rubies from Mogok. Among the many so-called collectors' gems described were andalusite, kyanite, and chrysoberyl (all of which are rare from Myanmar). Mr. Kane is writing a book on the gems of Myanmar.

Garnet. Namibia is the source of the bright orange, transparent spessartine garnets that are known in the trade as "Hollandine" (illustrated in the Spring 1993 Gem News, p. 61). Israel Z. Eliezri, of Ramat-Gan, Israel, reported that the mine is located in a remote desert region in northwestern Namibia, near the Kunene River (figure 13). It is a nine-hour drive from the nearest settlement, which has limited the use of heavy equipment in the mining operation to only a few pieces. The garnet crystals, which range up to 25 mm in diameter, are recovered from schists. Mining operations at present take place only on the surface.

Meteorites with gems. Dr. Charles Arps, of the Natural History Museum in Leiden, the Netherlands, discussed the need to preserve certain meteorites in museums as they are found, rather than reducing them by lapidary means to pieces and sizes that are suitable for jewelry applications and private collectors. He is particularly concerned about the stony-iron meteorites known as pallasites, which contain yellowish green irregular grains of olivine (see *Gems & Gemology*, Spring 1992, pp. 43–51). When gem quality, some of these peridots have been extracted from pallasite slices and faceted into small gems.

Figure 13. This aerial photo shows the "Hollandine mine" on the southern side of the Kunene River in Namibia (toward the center of the lower portion of the picture). Photo courtesy of Israel Z. Eliezri.

Natural glass. Dr. Frederick H. Pough, of the United States, presented his observations on the increasing popularity among lapidaries of various forms of obsidian. Although the tumble-polished dark brown "Apache tears" from Arizona are still the best-known form of obsidian, also sought are varieties that show colorful phenomena—such as iris or rainbow obsidian (see Gem News, Summer 1993, p. 133) from Mexico, or the iridescent flame or fire obsidian from Glass Buttes in central Oregon. Some lapidary skill is required to bring out the maximum beauty in these gem materials, but the results can be spectacular. Although many of the inclusions that are potentially responsible for the phenomenal effects are difficult to identify because they are so small, inclusions of cristobalite and tridymite are known. Tiny acicular crystals and hexagonal red and brown plates have also been observed but not conclusively identified; possibly they are hematite.

Opal. The Lambina opal field, currently classified as "diggings," is the newest productive opal area in Australia. It was the subject of a paper presented by Australian Grahame Brown, coauthored by I. J. Townsend and K. Endor. This new gem-opal field is located in a remote area of the Lambina Station, in the far north of South Australia, about 1,000 km northeast of Adelaide and 360

Figure 14. This rough opal was recovered from the Lambina "diggings." The largest piece shown is approximately 7.5 cm (3 inches) long. Photo by Jack Townsend.

km south of Alice Springs. There are two separate "diggings" at Lambina Station, 2 km apart, which are administered from Mintabie, a well-established and very productive opal field 90 km to the southwest. The nearest town to the Lambina diggings is Marla, 36 km east of Mintabie.

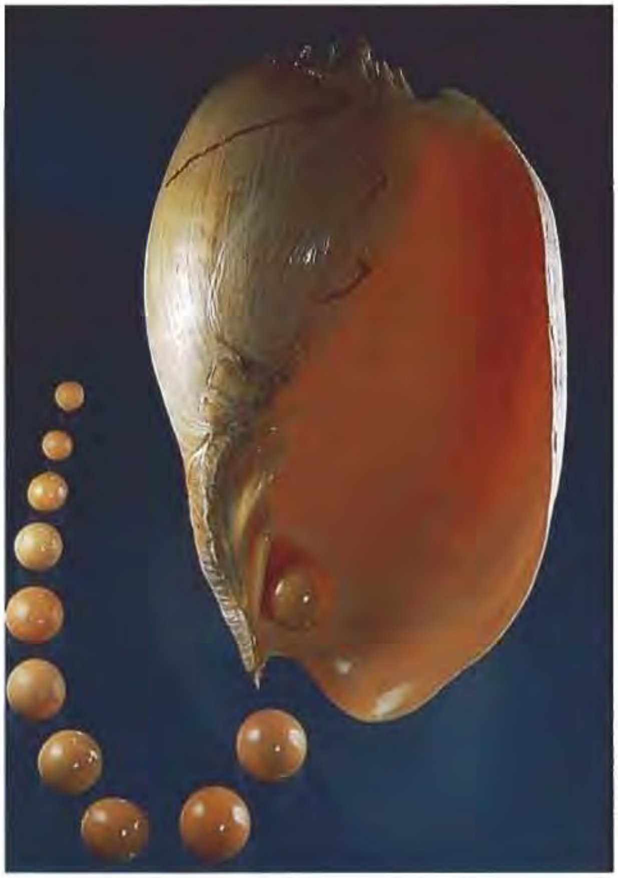
The precious opal from Lambina generally occurs at depths of 10 m or less, in joints and seams in an early Cretaceous claystone unit belonging to the Mesozoic Bulldog Shale. Thin veinlets of opal are also found in overlying jasper breccia of late Tertiary–early Quaternary age belonging to the Russo Beds. Both white and black opal are recovered (figure 14); the material appears to be stable (noncracking).

Certain opals seem to be more susceptible to cracking than others once they are removed from the ground. In a paper coauthored by Michael Duncan, Geoffrey Tombs, of New South Wales, described the results of an ongoing study on the stability against cracking of various types of opal from different Australian localities. Translucent to nearly transparent "misty," milky-looking opal (not to be confused with white opal) with a honey color in transmitted light, and material that shows patches of light gray and dark gray in the matrix, is probably not stable and will eventually crack. The various well-known forms of "precious" Australian opal—such as black opal, white opal, and boulder opal—are considered stable. The authors suggested that water content is one factor in opal cracking, but not the only one.

Porcelaneous "pearls". Kenneth V. G. Scarratt, of Bangkok, Thailand, described his examination of 23 brownish orange, spherical-to-baroque porcelaneous "pearls," which originated from the conch *Melo volutes* (figure 15). The "pearls" examined range from 11.20 to 207.04 ct, and up to 32.09 mm in longest dimension. The results of X-radiography varied. Some samples showed no structure, as is true of most porcelaneous "pearls", while others showed organic concentric structures. All displayed the flame structure typical for nonnacreous "pearls" from *Strombus gigas* and *Tridacna gigas.*

Quartz. Dr. Edward J. Gübelin described and illustrated a variety of interesting inclusions recently observed and identified. Several faceted gems of light pink rose quartz from Sri Lanka hosted a number of eye-visible transparent brownish to pinkish orange almandine garnet crystals; many had an unusual elongated, distorted habit (figure 16). The microscope also revealed small black grains, which proved to be ilmenite. Small monazite crystals and some as-yet-unidentified tiny blue acicular crystals (possibly dumortierite?) were also seen in association with the included garnets. This is a most unusual new suite of mineral inclusions for rose quartz from Sri Lanka.

Figure 15. These spherical porcelaneous "pearls" grew in the Melo volutes. *The largest "pearl" weighs 162.99 ct and has a diameter of about 28 mm. Photo by Nicholas DelRe.*



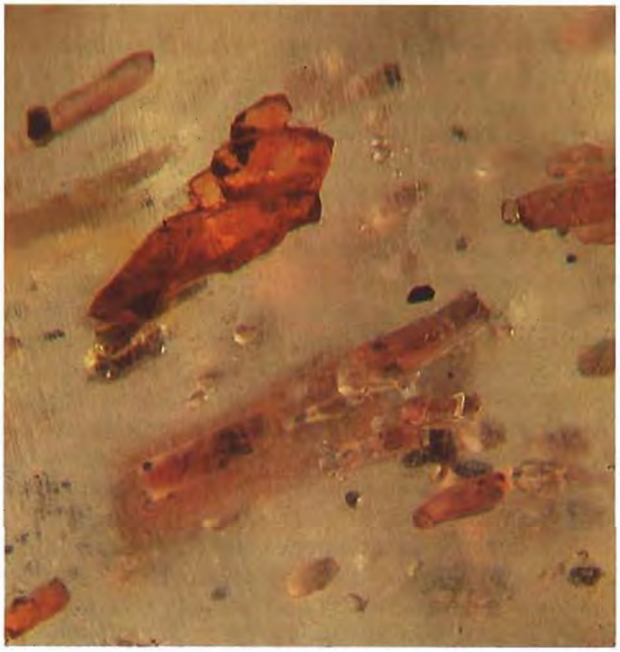


Figure 16. *Almandine garnet crystals, many with an unusual elongated habit, occur with small black grains of ilmenite in rose quartz from Sri Lanka. Photomicrograph by E. J. Gübelin; magnified 15×.*

GEMSTONE ENHANCEMENT

Professor Vladimir S. Balitsky, of Chernogolovka, the Russian Federation, explained that gemologists have been trained in Moscow only since 1978. The enhancement of gem materials is currently being done in Russia both experimentally and commercially. These treatments include irradiation of diamond, common heating of ruby and sapphire (as well as quartz), bleaching of nephrite, fracture filling of emeralds, and high-temperature diffusion of sapphires. Of particular interest is the practice of bleaching rather unattractive brownish nephrite to produce a very pleasing green.

SYNTHETICS

Early synthetics. An interesting report by Dr. Henri-Jean Schubnel, of Paris, described some very unusual early synthetics in the collection of the Museum of Natural History in Paris. Not only does this collection include synthetic ruby, sapphire, and emerald grown before 1888, but it also contains pre-1888 synthetic chrysoberyl, diopside, orthoclase, and zircon.

Russian synthetics. In an overview of the gemological properties of various synthetic gemstones produced in Russia, Dr. Ulrich Henn of Idar-Oberstein addressed those features that are useful to the laboratory gemologist for identifications. In addition to the better-known synthetic amethysts and emeralds, Dr. Henn discussed some important and relatively new Russian synthetics, such as hydrothermally grown synthetic ruby and synthetic diamonds.

Professor Vladimir S. Balitsky also described the hydrothermal growth of phosphorus-doped synthetic rose quartz and displayed a photograph of a 1-m-wide synthetic malachite tabletop.

Dr. Gennadi V. Bukin, of Novosibirsk, Russian Federation, a specialist in both the hydrothermal and flux growth of synthetic gem materials, spoke on the commercial production and marketing of emeralds made by these two techniques. Hydrothermally grown beryls in a variety of colors, flux-grown spinels (primarily red and blue), and synthetic alexandrite produced by both flux and melt techniques are also grown commercially in the Design Technological Institute of Monocrystals in Novosibirsk. Dr. Bukin reported that they have grown synthetic alexandrite by the hydrothermal method, but only experimentally. Using the hydrothermal method, they are also able to heal fractures in natural emeralds.

Douros flux-grown synthetic ruby. Dr. Henry A. Hänni of Zurich, Switzerland, working with Dr. Karl Schmetzer of Germany, presented the results of their preliminary examination of the new Greek flux-grown synthetic ruby being marketed under the trade name Douros. In crystal form and as cut stones, from a gemological standpoint, these new synthetic rubies closely resemble the Ramaura flux-grown synthetic rubies. Chemical analysis showed a variable trace-element composition in the Douros material, with no characteristic chemical profile. The major trace elements found in natural rubies—chromium, gallium, iron, titanium, and vanadium—are also added in variable amounts to the Douros synthetic rubies. Dr. Hänni concluded that, if inclusions and recognizable growth structures are not present, this new synthetic ruby will be extremely difficult to identify.

INSTRUMENTATION

In a paper coauthored by Guerec Quérré and Jean-Paul Poirot, Dr. Anne Bouquillon, from the Laboratoire de Recherche des Musées de France, at the Louvre Museum, described some very interesting work on gem-set gold Egyptian pectorals from the Louvre collections. PIXE (Proton Induced X-ray Emission) analysis with a particle accelerator was used to determine the chemical compositions of the gem materials and metal. In the course of their study, these researchers found a type of manufactured gem material known as "frits," which is composed of a mixture of lapis lazuli and silica powders.

Jean-Marie Dereppe, of Belgium, presented information on the application of nuclear magnetic resonance (NMR) to gemological problems. He discussed the separation of natural from synthetic emeralds using this tech-

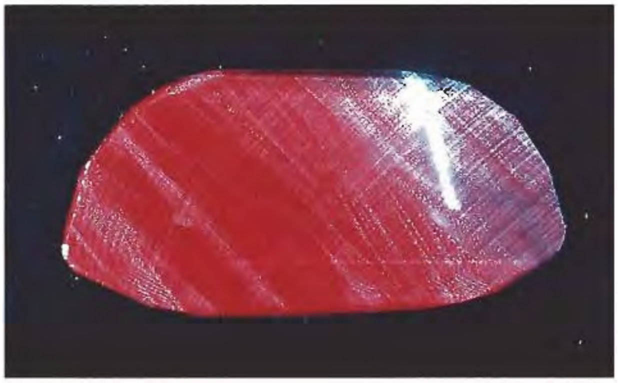


Figure 17. This laser-tomographic image of a 0.68-ct synthetic ruby shows the growth banding characteristic of flame-fusion synthetics as well as the treatment-induced "fingerprints" that result from flux overgrowth. Photo courtesy of Junko Shida.

nique. He speculated that NMR might also be useful in the separation of natural from heat-treated aquamarine, which currently is virtually impossible to do.

Professor Bernard Lasnier, from the University of Nantes, presented two new instruments of interest to gemologists. The first was a desktop Raman spectrometer. While the performance level of such instruments has gone up in recent years, the price has come down considerably, making this type of technology much more affordable. This spectrometer will soon be adapted to a microscope, so it can also be used in nondestructive inclusion identification. Professor Lasnier also showed a small brass "Pearlscope." This combination endoscope-lucidoscope, hand-made by one of Professor Lasnier's students, Har Hatalay, in demonstration worked well in showing the difference between drilled natural and cultured pearls. Mr. Hatalay is investigating the economic feasibility of producing a small number of these instruments for the trade.

Dr. Karl Schmetzer presented his latest observations on the use of immersion microscopy in the examination of microscopic growth structures in rubies to determine natural or synthetic origin. He compared growth features in rubies from Monghsu in Myanmar to those in rubies from Luc Yen in Vietnam. The growth structures of the new Douros flux-grown synthetic rubies, produced in Greece, were found to be very similar to those of the well-known Ramaura flux-grown rubies, produced by Judith Osmer in California.

Observation of rubies and detection of heat treatment by means of laser tomography was the subject of a paper presented by Ms. Junko Shida, of Tokyo, Japan. Using a laser beam as a light source, laser tomography is an optical method to record on film the distribution of scattering centers (such as submicron-size and larger inclusions), as well as features such as growth banding, in crystalline solids like gemstones. One advantage of laser tomography in gem identification is that even submicron scattering centers are visible at low magnification. For example, the laser-tomographic image (shown in figure 17) of a 0.68-ct synthetic ruby clearly illustrates both the curved growth characteristics of a flame-fusion product and the pattern produced by treatment-induced flux fingerprint inclusions resulting from overgrowth. Further studies are planned using this technique to examine and visually document rubies both before and after heat treatment.

Using petrographic analysis and thermobarometric techniques, Dr. John M. Saul and Alain Mercier, both of France, studied the metamorphic primary ruby deposits of the Precambrian Mozambique Belt in southeastern Kenya. They determined that the rubies crystallized at approximately 750°C under a pressure of about 5 kbar. This relatively low pressure indicates that the rubies formed at a depth of approximately 17 km. With this same methodology, other gem deposits could be examined to determine depth of formation and possibly the vertical extent of mineralization.

MISCELLANEOUS

Early collections. Dr. Pieter Zwaan, of the Netherlands, described a collection of 625 gems that King William the First donated to the National Museum of Natural History, Leiden, in 1825. Such collections of known age are of particular gemological interest because the stones reveal what forms of gem treatment were used before a particular point in history. In this collection, the only stones that were treated were chalcedony.

Colored stone cutting. A videotape prepared by Menahem Sevdermish, of Israel, compared the skills and products of Indian and Sri Lankan gem cutters to the production of the sophisticated and highly automated cutting factories in Israel. Mr. Sevdermish concluded that technology has not yet replaced truly skilled hand labor in terms of quantity and quality in the fashioning of gemstones.

BOOK Reviews

SUSAN B. JOHNSON, EDITOR

GEMOLOGY, AN ANNOTATED BIBLIOGRAPHY

By John Sinkankas, 2 vols., 1200 pp., illus., publ. by Scarecrow Press, Metuchen, NJ, and London, 1993. US$179.50, regular edition; $250.00, limited edition**

Eleemosynary, philanthropic, charitable—any one of those characterizations would apply to this monumental undertaking. It is greatly reassuring that a person (actually, a husband-and-wife team), with little hope of more than very modest monetary compensation, would embark on such a long, grueling project. The effort involved defies comparison in the gemological literature, and the quality of the product is equally impressive. Just to list accurately every meaningful publication in the gemological field would be a daunting task, but Dr. Sinkankas has gone a large step further to study and evaluate more than 7,000 books and other publications of importance to gemologists. Not only does he reach back hundreds of years to present the earliest literature in our field (in addition to the more contemporary), but he also includes other languages such as German, French, Italian, Spanish, and Portuguese, as well as some Russian.

The entries vary widely in their size and nature, based on the importance attached to the work and other factors. A full entry on a book by one author usually has a short biographical sketch, followed by the entry number, the date of publication, the title, author, an abbreviated description of all the details of illustrations, binding, publisher, number and size of pages, and many other facts of great interest to a bibliophile. Then the content is described, with some comments as to its potential worth to the reader. The level of detail reflects the meticulousness that Dr. Sinkankas, author of *Gemstones of North America* and many other fine books, has shown in his more than 40 years of research.

There are many fascinating tidbits along the way for a peruser of the *Annotated Bibliography*. For example, under entry 7224—1932, *The Genesis of the Diamond*, by Alpheous F. Williams, is the comment: "A truly monumental work of increasing scientific importance, not so much for its information on diamond and its mining as for its detailed studies of the petrology and mineralogy of kimberlitic pipe fillings. Such treatment of mantle-derived rocks was well ahead of its time in providing clues as to the nature of the mantle and the formation of the crust in general. The significance of Williams' studies escaped even himself, and certainly most others, as evidenced by the niggardly review accorded the work by E. H. Kraus, Amer Min, 18, 4, 1933, 176, who saw it merely as 'supplementing and bringing up to date the monumental and classic work of his father.' Because of the greatly increased interest in mantle problems and plate tectonics, the work now appears to be one of those inadvertently fortunate amassments of accurate data that find applications at a later time."

There are occasional entries about which the author states, "not seen," but these are very few compared to the usual helpful evaluations. Such a comment is usually made only about some obscure early work of little significance.

The appearance in print of *Gemology, An Annotated Bibliography* is one of the very important events in the history of gemological publishing.

RICHARD T. LIDDICOAT
Chairman of the Board
Gemological Institute of America
Santa Monica, California

OPAL ADVENTURES

*By Paul B. Downing, 234 pp., illus., publ. by Majestic Gems & Carvings, Tallahassee, FL, 1990. US$19.95**

Paul B. Downing relates his adventures in opal-mining areas from Andamooka to Virgin Valley. He also describes the adventures of the first hardy miners who braved the Outback—the Never Never—to find glowing opals, and passes on some of the stories that are still told in the opal fields.

Downing makes it clear that modern methods of transportation and mining have not made the search for opal much less trying than it was for the first opal prospectors. There are severe accidents when Land Cruiser meets kangaroo on the dirt roads at night. There are flooded roads, searing temperatures, disappearing water pumps, equipment failures, and sheer back-breaking work. But when a miner finds "color in the wall," all trials are forgotten.

And when that "color" turns out to be a matchless opal, the digger is not only willing but eager to go back and fight all the battles again.

Downing describes the different geology of each of the mining areas, how each site is commonly worked, and the kind of stones each area produces. But first and foremost this is a book about people—not only the full-time opal miners, but those who work other jobs to support their addiction to opal; the retirees who drive their campers over miles of bad road to park in the dust and hunt opal; the amateurs who "noodle" the "mullock heaps" for gems the diggers have missed; and Paul and Bobbi Downing themselves, who climb 75 feet down a shaft "hanging on a ladder swaying back and forth with almost no toe room because it's next to the wall. And I hate ladders."

With more than 27 years of cutting opal behind him, and an appreciation of opals that approaches awe, Paul Downing is the perfect person to write this kind of book. He understands the constant excitement in the hope of discovery that keeps opal miners—Australian or American—pursuing their elusive quarry.

The only chapters that do not seem to fit are those on the cutting and valuation of opal, which appear to be added as an afterthought. These chapters do nothing to diminish the reader's enjoyment of the book, however, which is written in a chatty, personal style and is full of good humor. The color photographs of spectacular opals and the black-and-white photos of the mining operations in the Outback offer a new appreciation of this exceptional gemstone.

SHARON ELAINE THOMPSON
Salem, Oregon

OTHER BOOKS RECEIVED

Diamond Mine, *by Peter Read, 188 pp., publ. by Book Guild, Sussex, England, 1992, US$24.95.** Writers rarely successfully cross the line from nonfiction to fiction. Gemologist Peter Read's mystery is a delightful exception. Set in the diamond fields of South Africa in 1978, scenes are portrayed with a believability that can only be accomplished by someone with an intimate knowledge of the area, a technical understanding of the major diamond mines, and familiarity with the people working at those mines. Scenic descriptions are vivid, colorful, and often majestic. Characters are developed with a rich, cultural, and sometimes earthy dialogue. The tone is idealistic and serious. Although the plot is not complex and is actually quite linear, tension builds quickly and holds the reader's attention throughout.

One of my few criticisms is that the book could have been longer. Also, a few details of the crime are simplistic, especially the method for collecting the ransom. Overall, though, gemology students will find this novel a joy to read and a valuable educational experience.

JOHN D. ROUSE
Carson, California

Practical Uses of Diamond, *by Andrzej Bakon' and Andzej Szyman'ski, translated by Jerzy Tomaszczyk, 248 pp., illus., available from and publ. by Ellis Horwood and Polish Scientific Publishers PWN, West Sussex, England, 1993.* As the title suggests, this book focuses on engineering, not gemology. A well-illustrated and well-documented survey of industrial and scientific applications of diamond, it is written for a limited technical readership, knowledgeable of general chemistry and thermodynamics. Although not recommended for every gemologist's library, it does provide a wealth of valuable information on the physical, chemical, and mechanical properties of natural and synthetic diamond, much of which is not typically included in gemological literature. After two comprehensive chapters on the chemical structure and physical properties of diamond, four chapters delve meticulously into the gemologically arcane uses, design, and manufacture of diamond tools. Another chapter explores scientific applications of diamond's unique mechanical, thermal, and optical properties. Unfortunately, the chapter on diamond jewelry is superficial and, in some cases, misleading. In their concluding section, the authors present their perception that diamond will join stone, bronze, and iron as a pivotal material in the development of technological progress.

SHARON WAKEFIELD
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Mineraux Passion (Mineral Passion [in French]), *by Pierre and Nelly Bariand, 223 pp., illus., publ. by Bordas, Paris, France, 1992.* One cannot help being awestruck by this beautifully illustrated large-format book. The first 95 pages contain a well-written text by Pierre Bariand, curator of the Sorbonne collection in Paris. Mr. Bariand develops some important ideas about minerals and gems, including significant discoveries and "collections and collectors." The text is also rich with anecdotes, interspersed with color photos of crystals and jewelry by world-renowned photographer Nelly Bariand. In the central portion of the book, Nelly Bariand provides large photos of most of the important mineral and gem species in their rough forms. Detailed descriptions are cleverly grouped in the last pages, so the interested reader can learn more about the species shown. Although written in French, this book will be useful to anyone who has—or wants to create—interest in the natural beauty of minerals and gems.

EMMANUEL FRITSCH
GIA Research, Santa Monica

**This book is available for purchase at the GIA Bookstore, 1660 Stewart Street, Santa Monica, California. Telephone (800) 421-7250, ext. 282.*

GEMOLOGICAL ABSTRACTS

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COLORED STONES AND ORGANIC MATERIALS

Check-list for rare gemstones: Sodalite. W. Wight, *Canadian Gemmologist,* Vol. 14, No. 3, 1993, pp. 78–81.

In this month's installment on rare gemstones in the collection of the Canadian Museum of Nature, in Ottawa, information is given for sodalite. Highlighted in both the text and the pencil drawing (the latter by noted gemstone and mineral artist Susan Robinson) is the variety of sodalite known as hackmanite, which is usually white or (in its rare transparent form) light yellow—until it is exposed to ultraviolet radiation, after which it turns pink for some time, fading when left in daylight (see *Gems & Gemology,* Summer 1989, pp. 112–113, for more on this phenomenon). The largest faceted hackmanite weighs 15.33 ct; the museum has a 9.77-ct stone. A checklist gives all information that a gemologist needs to make an identification, including the pertinent properties of gem minerals that might be confused with sodalite. The section ends with a lengthy list of references.

Michael Gray

This section is designed to provide as complete a record as practical of the recent literature on gems and gemology. Articles are selected for abstracting solely at the discretion of the section editor and his reviewers, and space limitations may require that we include only those articles that we feel will be of greatest interest to our readership.

Inquiries for reprints of articles abstracted must be addressed to the author or publisher of the original material.

The reviewer of each article is identified by his or her initials at the end of each abstract. Guest reviewers are identified by their full names. Opinions expressed in an abstract belong to the abstracter and in no way reflect the position of Gems & Gemology *or GIA.*

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Freshwater pearl cultivation in Vietnam. G. Bosshart, H. Ho, E. A. Jobbins, and K. Scarratt, *Journal of Gemmology,* Vol. 23, No. 6, 1993, pp. 326–332.

On a trip to Vietnam in early 1993, the authors learned of a small but growing freshwater cultured-pearl industry, focused primarily at two locations: the estuary of the Red River (Song Hong) and a lake (the Ho Tay) within Hanoi city limits. This article describes the industry and cultured pearls from Ho Tay. The latter was started by a fish-breeding company, assisted by Japanese consultants. Production at Ho Tay increased from 500 cultured pearls in 1990 to 3,000 in 1992. Output is expected to be 8,000 in 1993. Locally manufactured freshwater *Unio* shell beads and local *Cristaria plicata* mollusks (the same used by the Chinese) serve as nuclei and hosts. To date, they have not employed spatting. No more than half of the beads implanted produce nucleated pearls, but the tissue graft of rejected beads usually generates a "non-nucleated" pearl. In a sample of 15 representative cul-

tured pearls, only two were found (by X-radiography) to be bead nucleated. Bead-nucleated pearls are generally 5–7 mm and may be (rarely) as large as 12 mm; non-bead-nucleated pearls are generally smaller. The cultured pearls occur in a broad range of colors, of which orange, brown, and pink are the most common. Spectrophotometry confirmed official claims that the colors are not due to enhancement, but dyeing techniques are being explored. The Ho Tay Fish Development and Investment Company planned to open three additional farms in 1993.
CMS

World of Stones. Nos. 1 and 2, 1993.

A new quarterly magazine for the gemological and mineralogical community has appeared on the scene. *World of Stones,* an English-language periodical, is written and produced in Russia, with fabulous photographs (mostly by famed Russian photographer Alexei Sverdlov). Its layout is similar to the American magazine *Mineralogical Record.*

In the first two issues, topics include new mineralogical finds, profiles of famous Russian mineralogists, Russian museums, and historical localities. There are a few minor problems, which are to be expected in a magazine published in a language foreign to its staff. Sentences do not always make sense. Their structure suggests that the text was translated first into German and then into English. Some scientific words and all the references at the end of the articles use the Cyrillic alphabet. However, these distractions are small when compared to the overall beauty and wealth of information in the issues' glossy pages. Here are some short summaries of articles of gemological interest from the first issue.

"Axinite: New Finds in Russia," by Vyacheslav N. Kalachev, gives the mineralogical description and locality information for this very gemmy material, some of which is making its way into the collectors' market.

"The South Urals: A Brief Mineralogical Guide," by Alexander A. Evseev, gives the sources of many gem materials that have been coming on the market over the past few years, such as pink and blue topaz, grossular var. hessonite garnet, and spinel.

"A Resurrected Museum," by Anna P. Gorbatova et al., describes the collections at the Yershov 'Geological Museum (formerly the Moscow Mining Museum). The article details the history of the museum, and its recent refurbishing, including new well-lit display cases. Described are some huge crystals, such as a forsterite specimen with large crystals up to 9 cm (over 3.5 inches). Special exhibits, one of which is titled "Semi-precious Stones of Moscow's Environs," are being arranged by employees of the Fersman Mineralogical Museum

A profile titled "Alexei V. Sverdlov: One Must Love and Understand Stone," features the photographer's favorite photos, many of which are from the Russian-issued English-language books *Malachite, Selenite,* and *Agate.* One can easily underestimate the quantities of these minerals that have been mined in Russia—until you see the 10-m-high malachite pillars, the carved jasper vase that is 2.6 m across, or the photographs of in-situ satin spar veins. These out-of-print books are prized collectors' items, but at least this magazine is making some of the photos available to a larger audience.

The second issue features a large pink topaz crystal on the cover. Inside is "The Urals (from Middle to Polar): A Brief Mineralogical Guide," by Alexander A. Evseev, a continuation of his article in the first issue. More locality information is given, plus sources and size data for minerals of gemological interest, including alexandrite, amethyst, beryl, demantoid, emerald, malachite, topaz, and tourmaline. Also in this article is a "History of Finds," which provides a chronology of important events in the discovery and processing of Russian minerals, including gem minerals, from 1631 to 1985. The last section details many examples of minerals from the Ural Mountains, now in Russian museums.
Michael Gray

Zircon: A study of material donated by Mr. W. C. Buckingham from various localities (mainly Indo-China). Edinburgh Gemmological Group, *Journal of Gemmology,* Vol. 23, No. 7, 1993, pp. 387–392.

This article reports on the properties of a collection of rough and preformed zircons, which were donated to the Gemmological Association of Great Britain for research purposes. Included are properties determined for 120 representative specimens (10 from each of 12 lots). Among the samples were natural red, gold, and brown—as well as heat-treated colorless, blue, and gold—material from Southeast Asia. (Specific localities are provided.) Average refractive indices, birefringences, specific gravities, pleochroism, and U.V. reactions for the 10 stones in each lot are provided; all were found to be typical of properties previously reported for zircon. Infrared spectra indicated crystalline rather than metamict structure, and minor differences were noted between the spectra of treated and natural stones. X-ray diffraction analysis identified exposed inclusions as goethite and ferrian spinel. Energy-dispersive X-ray spectrometry on a scanning electron microscope (SEM-EDS) revealed that one inclusion may belong to the cordierite-sekaninite series. Note that the levels of analytical confidence reported in table 3 exceed those usually accepted for SEM-EDS analyses. Nevertheless, the empirical data presented is—in this reviewer's opinion—of great value to researchers, as so little such information is available in the gem literature.
CMS

DIAMONDS

All that glitters may be diamonds. L. Sahagun, *Los Angeles Times,* October 3, 1993, pp. d3, d16.

One thousand square miles, straddling the border of Colorado and Wyoming, are "quickening the hearts of investors" with at least 30 kimberlite deposits discovered to date, yielding "thousands" of diamonds. Mr. Sahagun claims that the kimberlite host rock is similar to that found in South Africa.

At least six firms are willing to risk that deposits will pay off. In the forefront are Diamond Co. N. L. (an Australian firm operating out of Fort Collins, Colorado), which is investing $1 million, and Royalstar Resources, Ltd. (of Vancouver, Canada), which is investing about $210,000. Both believe that Americans will favor domestic stones over foreign—from what might be the first commercial diamond mine in the United States. Royalstar has secured 320 acres a few miles south of the Wyoming border; Diamond Co. has a six-year-old stake at a remote Rocky Mountain trout pond, Kelsey Lake, 8,000 feet (2,424 m) above sea level.

Howard Coopersmith, geologist-president of Diamond Co., claims to have culled 600 gem-quality specimens from test samples scraped from his deposit, but admits that it will be a year or more before potential profitability is determined. More than 100,000 carats of small, mostly low-grade diamonds have been recovered throughout the state-line district over the past decade. Indicator minerals—garnet, ilmenite, chromite—are present.

Even if the deposits turn out to be rich, Steve Droullard (past president of a now-defunct joint venture that operated a large sapphire mine in central Montana's Yogo Gulch) predicts that consumer indifference and tax-hungry regulatory agencies will negate profitability.

Irv Dierdorff

Chrome diopside in diamond. J. I. Koivula, *Lapidary Journal,* Vol. 47, No. 8, November 1993, p. 16.

Definitive identification of inclusions in diamond generally requires destructive testing, so methods of gaining knowledge without the sacrifice of material are welcome. In this regular *LJ* feature, "Inclusion of the Month," Mr. Koivula states that no other inclusion in diamond is known to have the "vivid emerald-green" of chrome diopside. Thus, its color alone will suffice to identify this type of inclusion. The article is supplemented by two photomicrographs. *PASG*

Diamonds in dense molecular clouds: A challenge to the standard interstellar medium paradigm. L. J. Allamandola, S. A. Sandford, A. G. G. M. Tielens, and T. M. Herbst, *Science,* Vol. 260, April 2, 1993, pp. 64–66.

Diamonds are everywhere, even in outer space. Evidence is provided by the light emanating from four protostars (stars just forming) located in dense interstellar dust clouds, which was analyzed using infrared spectroscopy. The frequency of the light and the relative strengths of the absorption peaks are characteristic of specific molecules or compounds. One strong peak, found at 2890 cm^{-1} (3460 nm), is attributed to the vibration of three carbon atoms attached to a hydrogen atom. The most likely explanation for this is that the hydrogen atoms are attached to interstellar microdiamonds. The authors present other information to build their case—shock-wave calculations, meteorite microdiamond analysis, and infrared comparisons with diffuse interstellar dust and gas clouds. They conclude that 10%-20% of the carbon in these dense dust clouds is incorporated into microdiamonds. Therefore, microdiamonds may be abundant and stable in interstellar space.

Charles E. Ashbaugh III

Interview Mr. Y. Bychkov [sic]. D. Ringer, *Diamant,* No. 365, 1993, pp. 29–30.

Yevgeny Bychkov is chairman of the State Committee of Precious Metals and Precious Stones, Komdragmet, of Russia. When interviewed at the 26th World Diamond Congress of the World Federation of Diamond Bourses, he revealed that one-sixth of that country's mine production (approximately 12 million carats a year) is facet grade, with 10%–15% of this volume manufactured in Russia by new companies—such as Intertrade, Ruis Diamonds, Kristall Diamonds, and a new venture in Yakutia with an Israeli partner. He also stated that Komdragmet would like a system that lets Russians control prices, allowing them more knowledge of their product's worth on the open market. To accomplish this aim, they might ask to sell directly a larger percentage (20%–25%) of the rough than the 5% currently allowed by their contract with the CSO.

Since January 4, 1993, mine production has gone to Alamazy Rossii-Sakha (a stock company) for all operations, including sorting and sales to De Beers, rather than to Komdragmet. The independently sold percentage still goes through Komdragmet, and local factories buy from Komdragmet, ARS, or Yakutia.

Current government policy is created by Komdragmet (which also controls the entire Russian diamond sector). Komdragmet's policy is to develop Russia's diamond-cutting industry by boosting efficiency and diversifying assortment. Special government permission to buy rough for processing is given to the new joint ventures involved in processing diamonds and marketing polished production. *NDC*

Mineral erosion. B. Jones, *Rock & Gem,* Vol. 23, No. 10, October 1993, pp. 52–56, 82–86.

Mr. Jones concentrates on how erosion affects diamonds and diamond deposits. Beginning with an overview of the chemical composition and structure of diamond, he proceeds to discuss specific diamond sources. In Namibia, huge earthmovers push aside beach sands so that individual workers—armed only with whisk brooms and trowels—can recover the diamonds that were carried down to the coast by Africa's river systems.

Gem-quality diamond is resistant to the forces of erosion and is freed from its more-fragile host rock, rather than being dissolved or destroyed. This makes seaside alluvial deposits, such as those found in Namibia, especially rich. Efforts are also being made to mine diamonds directly from the ocean floor.

Also discussed are the alluvial deposits of China, Brazil, and Russia. According to the article, every major diamond (with the exception of the Cullinan) has been found in alluvial deposits. This underscores the importance of such deposits, and why it is essential for miners to understand how the forces of nature work to move and sort gem rough. *JEM*

GEM LOCALITIES

Aquamarine in the United States. M. I. Jacobson, *Rocks & Minerals,* Vol. 68, No. 5, 1993, pp. 306–319.

Beryl deposits in the U.S. are few and far between; hence, the author maintains, some new aquamarine sites await discovery. In seeking these potential new sources, state and federal geologic survey reports—combined with a knowledge of the geologic environment in which aquamarine occurs—are recommended over gem guidebooks; the latter usually only point to areas already mined out. The article provides an overview of the best-known sites for aquamarine in the U.S., including the Mount Antero–Mount White region of Colorado; the Sawtooth Mountains of Idaho; Oxford and Sagadahoc counties in western Maine; and the Grafton and Keene pegmatite districts of New Hampshire. Probable methods of aquamarine formation are discussed for most localities. Nine areas of minor occurrences are also mentioned, along with descriptions of undeveloped areas of potential interest to the aggressive prospector. The article is heavily illustrated with maps and photos of crystals from the areas cited. *AC*

Emerald mineralization of Barang, Bajaur Agency, Pakistan. S. S. Hussain, M. N. Chaudhry, and H. Dawood, *Journal of Gemmology,* Vol. 23, No. 7, 1993, pp. 402–408.

The authors report the results of their research into emerald mineralization in Barang, including some new information. The emeralds formed in a talc carbonate host rock via late- to post-tectonic pneumatolytic and hydrothermal mineralization. Evidence suggests that the beryllium-bearing fluids responsible for emerald formation originate in the S-type Tertiary minor granites of the region, in contrast to previous proposals of a trench or arc source. Emerald quality is highly variable, but good gem material is available. The refractive indices are high (n_e = 1.576 to 1.593 and n_o = 1.586 to 1.604) due to high Cr and Fe content, both of which result in typical spectroscopic features. X-ray diffraction revealed cell dimensions of a = 9.2548 ± 0.0036 and c = 9.1905 ± 0.0075. Maps and tables support the text. *CMS*

An examination of garnets from the Sinai Peninsula, Egypt. R. C. Kammerling, J. I. Koivula, and G. P. Calderon, *Journal of Gemmology,* Vol. 23, No. 7, 1993, pp. 412–414.

The authors describe a strand of 36 garnet beads, reportedly from the Sinai Peninsula of Egypt. Garnets have been known from this region since ancient times, but they have been neglected since the advent of modern gemology. The exact source of the beads could not be determined, but they are of recent origin. Although actually very dark brownish red and transparent, they appear almost opaque black in reflected light. Properties are consistent with members of the Mn-Fe continuous series (R.I. > 1.81, inert to U.V. radiation, and spectral absorption bands at 410, 430, 460, 500, 525, and 575 nm); EDXRF analysis revealed a composition typical of almandine-spessartine garnets, with Fe > Mn. *CMS*

Gem scapolite from the Eastern Pamirs and some general constitutional features of scapolites (in Russian). A. A. Zolotarev, *Proceedings of the Russian Mineralogical Society,* Vol. 122, No. 2, 1993, pp. 90–102.

Gem scapolite from the Kukurt deposit, Eastern Pamirs, can be distinguished from other scapolites by its chemical composition, cell parameters, and other properties. Chemical analyses and cell parameters are given for eight scapolites with 5.4–34.0% meionite. IR, optical absorption, and EPR spectra are presented. The data suggest the existence of a hitherto unrecognized solid solution between marialite and Ca-marialite. The nature and cause of the lilac color of the Kukurt scapolite is of particular interest, but additional investigations are needed. *RAH*

The location, geology, mineralogy and gem deposits of alexandrite, cat's-eye and chrysoberyl in Brazil. J. Cassedanne and M. Roditi, *Journal of Gemmology,* Vol. 23, No. 6, 1993, pp. 333–355.

Alexandrite, cat's-eye, and transparent chrysoberyl are all found in Brazil. An overview is provided of the various localities, their geology, methods of extraction, and the gems produced.

Chrysoberyl is mined primarily in the states of Minas Gerais, Bahia, and Espírito Santo. Pegmatite deposits include those at Triunfo, Santa Leopoldina, Antônio Coelho, and Castelinho in Espírito Santo; the Córrego Faisca area of Minas Gerais; and Carnaiba and Socotó in Bahia. These primary deposits have produced fine crystal specimens, including single crystals, V-twins, and trilling twins. Detrital (secondary) deposits—eluvial, colluvial, and alluvial—occur extensively, and the nature of these is discussed in some detail, assisted by illustrations of stratigraphic sections from various alluvial deposits. Prospecting is haphazard and, except for dredging, extraction is by manual labor, involving small groups of independent *garimpeiros.* Detrital deposits occur in Minas Gerais in the regions of Padre Paraiso—Americanas, Malacacheta, and Itabira. Of these, the Hematita or Nova Era deposit, discovered in 1986, is the best known, having perhaps the richest concentration of alexandrite in the world. Other secondary deposits occur in Bahia and Espírito Santo, of which Córrego Alegre (in the latter state) is the most important, having the greatest deposits of transparent and cat's-eye chrysoberyl in the country.

The article finishes with a review of the gems' known properties, including a thorough summary of inclusions. Thirty black-and-white and color illustrations (maps, drawings, and photos) accompany the text. Figures 29 and 30 have been reversed. *CMS*

Observations of red beryl crystals from the Wah Wah Mountains, Utah. M. Hosaka, K. Tubokawa, T. Hatushika, and H. Yamashita, *Journal of Gemmology,* Vol. 23, No. 7, 1993, pp. 409–411.

New data on red beryl from the Wah Wah Mountains essentially support previous research. The authors report, for an unknown number of specimens, n_e = 1.561 to 1.565 and n_o = 1.567 to 1.571; birefringence = 0.004; SG (by heavy liquids) = 2.63 to 2.72; orange-red and purplish red pleochroic colors; inert to long- and short-wave ultraviolet radiation and to the Chelsea filter; and contents of Mn = 0.23 wt.% and Fe = 1.3 wt.% (by atomic absorption analysis). More extensive studies of spectroscopy and electron-spin resonance (ESR) expand the available data on this unusual material. Optical and infrared spectroscopy reveal spectra similar to those of Colombian emerald, which contains both type I and type II H_2O as previously reported, although the latter is relatively weak. ESR revealed the presence of Fe^{3+}, as indicated by the optical spectrum. It was found that the ESR spectrum of Mn^{2+}, the known chromogen in red beryl, is masked by interference from Fe^{3+}. A solid black inclusion, analyzed by electron microprobe, was found to be bixbyite. *CMS*

JEWELRY HISTORY

The Forties—when stones were king! E. Blauer, *Lapidary Journal,* Vol. 47, No. 8, November 1993, pp. 20–25.

In this continuing section on jewelry history, Ettagale Blauer deals with jewelry of the 1940s. Although the late Dutchess of Windsor's "flamingo" brooch is pictured, it is said to be an anomaly for the period. More indicative is the 18K gold bib necklace (also illustrated) that the Duchess of Windsor commissioned from Cartier in 1945.

The "Forties" style actually began in the mid-1930s, reaching its height during the dark days of World War II. Also referred to as "Retro," it relied on large designs and stones. Because platinum was reserved for military use, gold became the jewelry metal of choice. Also—since the war cut off the supply of Asian rubies, sapphires, and emeralds—gems usually either came from the breaking up of other jewelry or from South America. Citrine, aquamarine, amethyst, and natural blue topaz were used in profusion and in enormous sizes. Catering mainly to Hollywood, the jewelry had the flamboyance associated with the movie makers of the era. Spectacular jewelry of the time is shown, although, tellingly, all the photos are credited to auction houses. *PASG*

JEWELRY MANUFACTURING

Cuttlefish casting. P. Minturn, *Jewellery Time,* No. 7, February 1993, pp. 22–23.

The author briefly describes an ancient casting method—using the calcified internal shell of the cuttlefish, a squid-like marine mollusk—that he occasionally employs in jewelry fabrication. Mr. Minturn presents step-by-step instructions for this unusual method of casting, which he claims is a time-saving method for jewelers in a pinch for proper materials. However, he warns that the smell produced by cuttlefish casting is "evil beyond description." *Juli Cook-Golden*

JEWELRY RETAILING

Appraising vintage wristwatches. S. Oltulski, *Canadian Gemmologist,* Vol. 14, No. 3, pp. 71–77, 82–84.

This article begins with a short history of the wristwatch market, as seen by this author from Toronto. It then covers the appraiser's job and the attributes to look for when appraising and "Analysing the Wristwatch." This is followed by a complete checklist of information necessary for such an appraisal. An appendix provides a sampling of reference materials needed to help determine the final valuation. *Michael Gray*

China's appetite for jewellery grows. *Jewellery International,* June/July 1993, pp. 7–8.

According to Gold 93, the annual survey from Gold Fields Mineral Services, China has become the world's largest gold consumer, and exports of jewelry and watches are making a major contribution to its emergence as an international economic power. China's jewelry exports totaled US$600 million in 1992, while domestic jewelry consumption rose to $3.5 billion. Exports of finished jewelry to China from neighboring countries helped boost the West's jewelry fabrication by 15% to a record 2,461 metric tons. The country's first industry trade fair—the Beijing International Jewelry, Watch, Spectacles and Technical Equipment Fair, to be held November 3–7, 1994—is being hailed as a landmark event in China's shift to a market economy.

A phenomenal projected minimum 12% growth rate in China's GNP has caused concern that the country's new State Economic and Trade Commission may impose austerity measures to control inflation, which in turn could cause the present skyrocketing consumption to fall. Nevertheless, manufacturers and retailers are targeting China's huge and increasingly prosperous 1.1-billion population as the world's most lucrative new market.

AC

PRECIOUS METALS

Gold fabrication demand falls by 5%. *Retail Jeweller,* Vol. 30, No. 805, September 9, 1993, p. 6.

According to Gold Field Mineral Services (GFMS), a commodities research company, world gold-fabrication demand fell by 5% during the first half of 1993, compared to the same period in 1992. The decline was mainly caused by weaker levels of jewelry manufacturing in parts of Europe and Asia, contrasting with a modest recovery in both North and South America. Italy and Germany both experienced a decline in jewelry-fabrication demand. Demand also fell in the United Kingdom, but GFMS feels the "underlying situation" is starting to improve. Meanwhile, global mine supply of gold increased by 2% in the last year, while the amount of official-sector gold coming onto the market fell sharply. GFMS states that the price of gold could move further upward if a stronger physical demand occurs as the market moves out of the period of seasonal weakness.

MD

SYNTHETICS AND SIMULANTS

Hi-tech synthetic gemstones. S. Voynick, *Rock & Gem,* Vol. 23, No. 9, September 1993, pp. 36, 78–81.

Many in the jewelry trade do not realize that most synthetic gems are used in industry and science. Only a small fraction are actually used by the jewelry industry. Author Steve Voynick takes a fascinating look at synthetics by presenting their history, starting in 1885 when the first synthetic gems were created by the flame-fusion method. Scientists next perfected the flux and hydrothermal methods of gem synthesis. The first "luxury" synthetics were created in the 1930s. In the 1950s and '60s, synthetics were greatly advanced by industry for technological uses. Synthetic ruby was essential to the development of lasers; later, YAG, GGG, and CZ were created in the quest for new high-tech industrial material. Also discussed in the article are some of the most common uses for synthetic gem materials and the methods of manufacture. *JEM*

A preliminary spectroscopic study of the Biron synthetic pink titanium-beryl. E. Fritsch, S. Muhlmeister, and A. Birkner, *Australian Gemmologist,* Vol. 18, No. 3, 1992, pp. 81–82.

This report covers the testing and characterization of a crystallographically oriented sample of synthetic beryl, using energy-dispersive X-ray fluorescence plus ultraviolet-visible and infrared absorption spectroscopy. The EDXRF analysis revealed silicon and aluminum as major elements (beryllium not being detectable on the instrument used), with minor amounts of iron and titanium and traces of calcium, potassium, and chlorine. These data are consistent with the literature in terms of the coloring agent (titanium) and the general growth process used for Biron synthetic beryls.

Mid-infrared absorptions were also consistent with features observed in Biron synthetic emeralds. Near-I.R. absorption features revealed the presence of "type I water" but no "type II water," which was interpreted as diagnostic of hydrothermal synthesis. In the visible range, a broad absorption band, with apparent maxima at about 495 and 550 nm (in the blue and orange, respectively), explains the material's pink color. The visible-range spectrum is quite different from that of natural pink beryl, and would thus further serve to separate this hydrothermal synthetic. The shape of this absorption pattern is also noted to be typical of Ti^{3+} in octahedral coordination. The authors close by reminding readers that this synthetic can also be distinguished from natural pink beryl by traditional gemological testing.

RCK

TREATMENTS

Gemstone enhancement—detection of polymer-treated jadeite. A. Hodgkinson, *Journal of Gemmology,* Vol. 23, No. 7, 1993, pp. 415–417.

Mr. Hodgkinson relates discrepancies in results encountered by researchers using a test that he proposes for the identification of bleached, polymer-impregnated jadeite. The test uses concentrated HCl and depends on the permeability of the sample. Details of the procedure are provided; its advantage (over infrared spectroscopy) is that it can be performed by the "basically supplied" gemologist. Investigations showed that different results were due to regional differences in temperature and humidity. This can be counteracted by placing the sample, along with a container of water, under a glass cover, immediately following application of the acid. The technique appears promising, but caution must be exercised. This method should be used only on jadeite, as some simulants could be damaged by the acid. In addition, nothing is said about what effect the acid might have on jadeite dyed by other methods; the color could be affected. *CMS*

Russians reveal enhancement techniques. *New York Diamonds,* Summer 1993 (reprinted from *Diamond World Review,* June–July 1993), pp. 64–66.

It should come as no surprise that the Russians—leading producers of fine-quality rough diamonds—are also leaders in testing color stability and clarity enhancements of diamonds. This article reports on several treatments being performed (with varying degrees of success) in Russia to enhance gem-quality rough and raise the grade of near-gem-quality stones.

In one annealing procedure, diamonds are being heated at atmospheric pressure in an inert environment to remove green or yellow spots caused by natural irradiation. Decolorization of light green diamonds reportedly occurred after 15 to 30 minutes of heating at 600° to 700°C.

Decolorization of cape-series and brown diamonds has been attempted with moderate success (in stones up to 1 mm in diameter) by thermobaric (high temperature/high pressure) treatment. Although the procedure is now very expensive, it seems likely that testing will continue to produce one that is more successful and cost effective.

Another enhancement, called laser irradiation, is being tested in an attempt to heal "micro-fractures" and relax the strain in rough crystals. The article mentions other, more exotic enhancements—surface dissolution to enhance frosted or coated diamonds, thermodiffusion of inclusions—as well as the deposition of a synthetic diamond thin film on diamonds. Senior diamond-industry officials in Russia maintain that to date no diamonds enhanced by these methods have been released into the trade. They add that they will not market any enhanced diamonds without an accompanying certificate detailing the procedure used.

This article makes for interesting reading and will keep you asking "what's next?" from the science of gemology. *GAR*

MISCELLANEOUS

Collecting smart—The hottest collectibles for the 1990s. *Cigar Aficionado*, Vol. 1, No. 2, 1992/1993, pp. 81–91.

This wide-ranging article, actually a compilation of short reports by the president and seven experts from the auction house of Butterfield & Butterfield, focuses on what they predict will be the seven "hottest" categories of investment collecting in the '90s—20th-century art, Art Nouveau and Art Deco European glass, fine silver, fine photographs, fine jewelry, Asian art, and antique firearms.

The jewelry section, written by JoAnna Scandiffio, Butterfield's director of fine jewelry and timepieces, suggests that signed pieces of unusual design and from a specific time period are the most desirable in the collectors' market today. Pieces by top-notch designers—such as Tiffany, Cartier, Van Cleef and Arpels, and Harry Winston—command excellent prices at auction. Conversely, a small delicate piece with a whimsical design might also command a price significantly above original estimates because its unique craftsmanship cannot be duplicated. *JEC*

Continued from p. 227

this wording is not in the actual published FTC guidelines.

Actually, the obligation of disclosing gemstone enhancement and instability in sales and appraising exists in U.S. law. Can a vendor, gemologist, or appraiser be sued for not disclosing enhancement or instability? In a word, yes!

The FTC guidelines for the jewelry industry do list as an "unfair trade practice" the sale or offering for sale of any industry product "having the capacity . . . of deceiving purchasers or prospective purchasers . . . as to the type, kind, grade, quality, [and] . . . durability . . . of such industry product, ..." Although for this section to be interpreted as encompassing enhancement of gemstones, the ruling has to be interpreted broadly, use of the word durability does seem to cover the disclosure-of-instability issue.

More often than not, it is at the state level that an action is initiated. My research has shown that some states have adopted parts of the various FTC rulings and guidelines as their own. An obvious advantage is that when the FTC does not have jurisdiction to pursue a problem, the state does.

The laws in most jurisdictions recognize as fraud the omission of "facts that materially affect the desirability of property and which facts he knows and are unknown to the buyer." (34 Cal. Jur. 3d, § 24) If the court believes that gemstone enhancement or instability is something that a buyer needs to know as part of the decision-making process, omission of that information is fraud. There are advocates of "if we cannot test to prove it, we need not disclose it." Yet the courts often hold responsible those who may have had reason to know, or even just have had access to such information. A professional's ignorance of information available in his or her trade is no excuse.

The law is complicated and inscrutable to the average jeweler, appraiser, or gemologist. Laws can vary from region to region, and are continually changing. Before taking or responding to any legal action, talk to an attorney—one who is versed in the law that is applicable in the proper jurisdiction. The best advice, however, is not to chance being the target of legal action. Always disclose.

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SUBJECT INDEX

This index gives the first author (in parentheses) and first page of the article in which the indexed subject occurs. For Gem News (GN), Gem Trade Lab Notes (GTLN), and Letters (Let) sections, inclusive pages are given for the subject item. The reader is referred to the Author Index at the end of this section for the full title and the coauthors, where appropriate, of the articles cited. The pages covered by each issue are as follows: Spring (1–78), Summer (79–148), Fall (149–226), Winter (227–305).

AUTHOR INDEX

This index lists, in alphabetical order, the names of authors of all articles that appeared in the four issues of Volume 29 of *Gems & Gemology,* together with the inclusive page numbers and the specific issue (in parentheses). Full citation is provided under the first author only, with reference made from joint authors.

Indexes prepared by Dona Dirlam