



DIAMOND IDENTIFICATION

LENGTH-TO-WIDTH RATIOS AMONG FANCY SHAPE DIAMONDS

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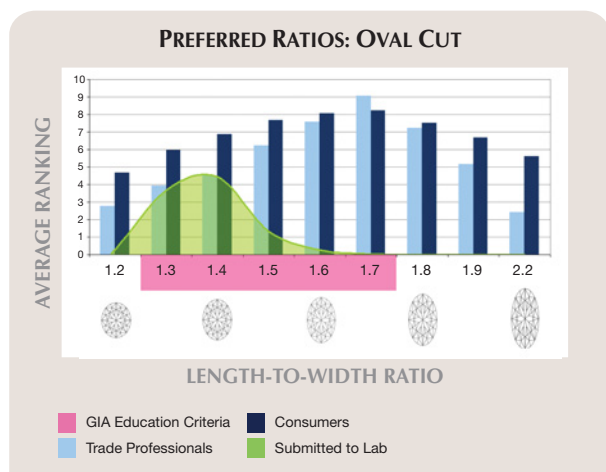
Evaluating cut in diamonds with fancy shapes is inherently more challenging than evaluating round brilliants because of the great diversity of cutting styles. Some parameters are unique to certain shapes, such as the degree of incision in a heart cleft, while others, such as length-to-width ratio, are common to most fancy shapes.

The length-to-width ratio is derived by dividing the diamond's length by its width. This ratio is an indicator of whether the outline is narrow (a higher ratio) or wide (a lower ratio). Fancy shape diamonds are commonly cut with certain ratios that primarily reflect the shape of the original rough, durability considerations, and occasionally perceived consumer preferences.

GIA conducted a survey in 2009 to assess personal preferences in the length-to-width ratios of fancy shapes. Images of four shapes—emerald, pear, marquise, and oval—with various lengths and widths were presented to 19 trade professionals and 25 consumers. The opinion results were compared to the “best” ratios taught by GIA educators and the distribution of length-to-width ratios of diamonds submitted to the GIA's laboratory. Overall, consumers and trade professionals preferred narrower shapes than those being submitted to the lab.

Increasing length-to-width ratios for brilliant styles (oval, marquise, and pear) can limit the combinations of angles that

This histogram of length-to-width ratios for oval cuts compares opinions of trade professionals and consumers with the distribution of diamonds submitted to GIA's laboratory. The range of recommended ratios taught by GIA Education is highlighted in pink for comparison.



produce pleasing light return. Some jewelry manufacturers also believe that narrower stones are more likely to incur damage during the manufacturing process or normal wear—especially susceptible are the points of thin-girdled pear or marquise shapes. The cutter, meanwhile, must consider the original shape of the rough and what it can economically yield. These concerns could skew the distribution of diamonds (as seen in the lab) toward shapes that are wider than those actually preferred by consumers or trade professionals.

We conclude that the trade should not be discouraged from cutting narrower stones when the opportunity exists, as long as these ratios are not combined with thin girdles.

HYDROGEN-RICH DIAMONDS FROM ZIMBABWE WITH NATURAL RADIATION FEATURES

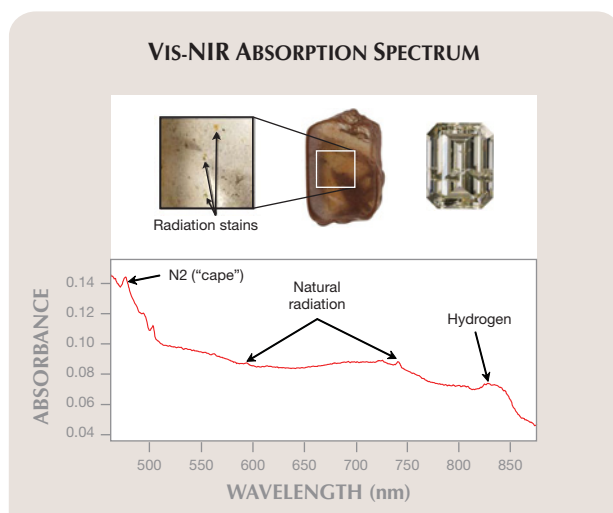
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Over the last five years, diamonds originating from eastern Zimbabwe have sparked considerable controversy. Concerns over the potential “conflict” status of stones from the large Marange alluvial deposits in particular have resulted in export bans, smuggling, and limited disclosure of such diamonds in the marketplace. Some diamond samples from eastern Zimbabwe recently became available for study, and their properties are very interesting.

Gemological observations and spectroscopic data were collected from 26 diamonds (17 rough and nine faceted) from eastern Zimbabwe to characterize their identification features. The stones weighed 0.96–19.40 ct and were colorless, light yellow, or greenish yellow. All the rough diamonds and some of the faceted stones also showed greenish or brownish hue modifiers resulting from radiation damage, observed as green and brown stains on natural surfaces. UV-Vis-NIR absorption spectroscopy indicated that the yellow color was caused by “cape” diamond defects (N3 and N2), with the greenish and brownish overtones resulting from a combination of radiation-related (GR1, 595 nm, H3, and H4) and hydrogen (563 and ~834 nm) defects. Infrared absorption spectra further revealed that all of the Zimbabwean diamonds were type Ia with abundant B-aggregated nitrogen defects, except for one colorless stone that was type IIa. Most samples showed somewhat variable but significant IR absorption at 3107 cm⁻¹ caused by high concentrations of hydrogen-related defects. This combination of hydrogen- and radiation-related defects in cape yellow diamonds is uncommon, and could prove to be a useful identification feature for Zimbabwean diamonds.

Color-origin determination for diamonds with greenish hues produced by radiation has always been difficult for gemologists because of similarities in lattice defects between naturally and artificially irradiated samples. Since the eastern Zimbabwe deposits became prominent a few years ago, GIA has seen a



This 5.82 ct rough diamond crystal from eastern Zimbabwe is covered in brown and green radiation stains. It was cut into a 2.67 ct Fancy Light brownish greenish yellow diamond that showed a combination of cape-, hydrogen-, and radiation-related spectral features.

noticeable increase in the number of hydrogen-rich yellow and greenish yellow diamonds with radiation-related features submitted for identification reports. Consequently, it is critical that laboratories be able to separate natural-color from artificially irradiated diamonds. Comparing naturally irradiated Zimbabwean diamonds to similarly colored samples known to have been artificially irradiated reveals many similarities, but also a few important differences that make their separation possible in most cases.

RECENT STUDIES OF COLORED DIAMONDS FROM ARGYLE

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The color in pink and brown diamonds tends to lie along lamellae, which has long been taken to suggest that the colors result from plastic deformation of the crystal lattice. But how do the characteristics of the two colors differ, and what do they reveal about the cause of the colors?

This study involved an examination of four rough pink and brown-pink diamonds from the Argyle mine in Australia. Combinations of both pink and brown parallel lamellae occurred together in some stones, and commonly multiple sets of crystallographically aligned slip planes were present. These slip planes were especially prominent as fluorescence features seen with a confocal microscope when the diamonds were excited by 488 nm light.

Visually, though, in all the diamonds examined the color

banding appeared angled to these slip planes. This “illusion” was caused by the progressive weakening and strengthening of color along parallel planes. In some instances, curved banding was produced. Nitrogen concentrations appeared to affect the susceptibility of slip or the defects produced, as evidenced by a specimen containing two sets of colored lamellae corresponding to growth horizons. The pink diamonds generally had low concentrations of nitrogen (less than 100 ppm in mixed A and B forms), whereas the brown-pink stones typically had higher nitrogen concentrations with dominant B forms.

Birefringence strain analysis using a Metripol instrument indicated that pink and brown regions were generally associated with less strain than colorless zones.

Photoluminescence spectroscopy with 633 nm laser excitation revealed an emission line at 661 nm for the pink diamonds and one at 710 nm for the brown-pink stones. These emissions were polarized on one plane, presumably perpendicular to the direction of slip: very strongly for browns and weakly for pinks.

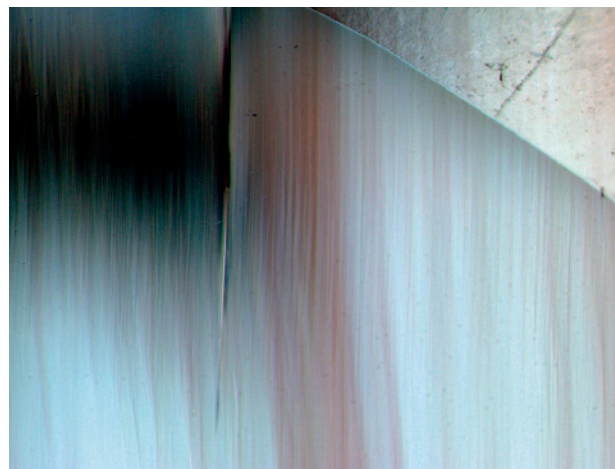
Brown color in type II diamonds has been reported to be associated with vacancy clusters (Avalos and Dannefaer, 2003), and this correlation has also been found in type I browns from the Argyle mine.

An interpretation of the above observations is that a sequence of two or more slip events is necessary to produce the pink defects, whereas a single event is sufficient to produce brown. It is these defects, most likely incorporating an impurity atom, that interact with vacancy clusters to produce the electronic energy levels required for the absorptions that cause the colors.

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Pink and brown graining is seen here in the polished face of a 0.6 ct rough Argyle diamond. Photomicrograph by J. G. Chapman.



EVIDENCE OF AN INTERSTITIAL 3H-RELATED OPTICAL CENTER AT 540.7 NM IN NATURAL DIAMOND

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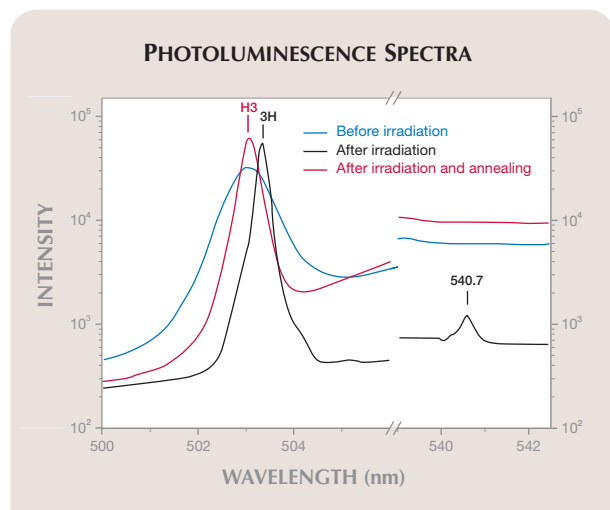
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Features resulting from radiation damage are important to the fundamental study of point defects in diamond. The primary products of radiation damage are vacancies and interstitials. Vacancies in both their neutral and negative charge states have been extensively investigated, but only relatively recently have detailed experimental studies been carried out on interstitials. The 3H and H3 defects have zero-phonon lines (ZPLs) that are very close to each other: 503.5 and 503.2 nm, respectively. While there has been some confusion among gem testing laboratories in the reading of these ZPLs in photoluminescence (PL) spectra, the two defects have very different vibronic structures.

The 3H defect consists of an interstitial carbon atom, while the H3 defect is formed by two next-nearest-neighbor substitutional nitrogen atoms separated by a vacancy. Because the 3H defect requires relatively little energy to relax into a normal diamond bond, it is much less stable than the H3 defect at high temperature. The 3H defect has often been observed in natural diamonds. We detected the 3H defect in 69 of 100 tested natural diamonds (Choi et al., 2009); all 69 also showed a line at 540.7 nm. Interestingly, when the H3 center was present without the 3H center, the 540.7 nm line could not be detected. This suggested there was a relationship between the 3H center and the 540.7 nm defect.

These PL spectra were taken from a diamond before and after irradiation and subsequent annealing at 600°C.



To establish whether the 540.7 nm peak belongs to the 3H center, we measured PL spectra taken with 488 nm laser excitation at liquid helium temperature on five type Ia diamonds that initially did not have the 3H defect, and the spectra were collected again after the stones were irradiated in an electron beam (10 MeV , $5 \times 10^{16} \text{ electrons/cm}^2$) and then after annealing at 600°C . Following are the results:

1. Before irradiation, none of the diamonds had a 3H center and no PL emission was detected at 540.7 nm.
2. After irradiation, 540.7 nm luminescence appeared along with 3H luminescence in all samples.
3. After heating, the 3H defect and 540.7 nm feature disappeared, and there was some loss of GRI luminescence.

On the basis of these observations, we suggest that the emission line at 540.7 nm belongs to the 3H center and an interstitial carbon atom.

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OPTICAL PROPERTIES OF SILICON-RELATED DEFECTS IN CVD SYNTHETIC DIAMOND

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The presence of silicon in diamond is routinely established by detecting the 737 nm zero-phonon line (ZPL) using photoluminescence or optical absorption spectroscopy. The 737 nm ZPL is attributed to the negatively charged Si split-vacancy center (Si-V^-). Unless preventive measures are taken, Si impurities may be introduced into chemical vapor deposition (CVD)–grown synthetic diamond by etching of the Si-containing reactor components. Intentional Si-doping has been achieved for both CVD and high-pressure, high-temperature (HPHT) synthetics. The occurrence of (Si-V^-) in natural diamond is rare, with only about 10 gem-quality examples reported thus far. Consequently, observation of (Si-V^-) frequently helps distinguish between natural, CVD synthetic, and treated diamond.

However, the (Si-V^-) signal can be diminished by exposure to UV radiation. Thus, the absence of the 737 nm ZPL does not necessarily rule out Si-related impurities in diamond, which emphasizes the importance of determining optical analogs of other Si-related defects to detect the presence of silicon. Electron

paramagnetic resonance (EPR) and computational studies have shown the existence of the neutral charge state of the Si split-vacancy center (Si-V)⁰, though past studies have not conclusively ascribed a ZPL to it.

In this study, we characterize and attribute a ZPL at 946 nm, visible in both PL and absorption spectra of some CVD synthetic diamonds, to (Si-V)⁰ by combining the results of optical and EPR measurements. The intensity of the 946 nm feature was found to increase in Si-doped material after successive electron irradiation and annealing treatments, showing similar behavior to the 737 nm line and suggesting the involvement of vacancies. It was associated with Si by its shift to a longer wavelength when the dominant Si isotope was changed from ²⁸Si to ²⁹Si, consistent with a shift of the 737 nm band. Charge transfer was induced between the neutral and negative charge states by illumination or heating in the dark, allowing calibration factors relating the integrated optical absorption coefficient of their respective ZPLs to the defect concentration to be determined at 77 K. With these coefficients, concentrations for both (Si-V)⁻ and (Si-V)⁰ can be calculated using optical absorption techniques that are readily available in industrial laboratories.

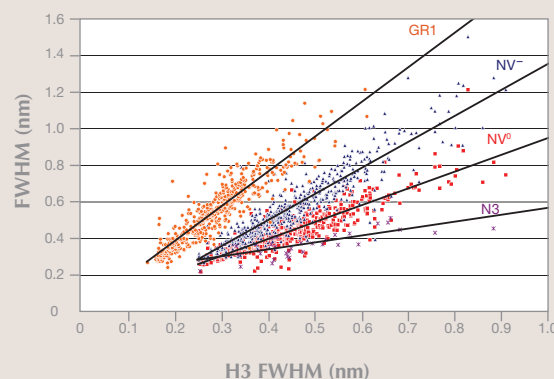
OBSERVATION OF STRAIN THROUGH PHOTOLUMINESCENCE PEAKS IN DIAMONDS

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Brown color in type IIa diamonds is believed to be caused by vacancy clusters (Fisher, 2009), and the depth of color corresponds to the degree of strain (Fisher et al., 2006). Since HPHT treatment can remove brown color from type IIa diamonds but results in only a limited reduction of strain, the ability to qualitatively assess the level of strain in diamonds is of important gemological significance.

An indirect but relatively consistent indication of strain can be obtained from the peak widths of defects commonly observed in photoluminescence (PL) spectra. We took PL spectra (liquid nitrogen temperature) of 600+ type IIa diamonds and 100 type IIb diamonds. In the type IIa diamonds, the peak widths for the GR1, NV⁰, NV⁻, H3, and N3 defects all showed a linear relationship. When these data were plotted in units of meV, they displayed significant overlap in both position and slope. These defects are known to involve different numbers of nitrogen atoms (none, one, one, two, and three, respectively) and various electronic charges, but all contain a single vacancy. Other known defects, including the H4 (nitrogen B aggregate with a vacancy) and the Si-V also showed a linear relationship. However, the 3H defect (ascribed to the carbon interstitial and not directly related to a vacancy) had peak widths that fluctuated within a narrow range and showed minimal to no correlation with either strain or

PEAK WIDTHS OF COMMON DEFECTS IN TYPE IIa DIAMOND VS. PEAK WIDTH OF H3 DEFECT



Peak widths for over 600 type IIa diamonds were calculated for some of the commonly observed defects in their PL spectra. The width of the H3 defect was chosen as the abscissa due to its near-universal detection in PL spectra. Although the peak widths are more appropriately compared in units of meV, they are shown here in nanometers so the data are better separated and distinguished. The N3 peak was detected with 325 nm laser excitation, the H3 defect with 488 nm excitation, and the NV centers and GR1 defect with 514.5 nm excitation.

the peak widths of the vacancy-related defects.

We also analyzed 20 grayish green natural diamonds. Their PL spectra typically contained peaks at 701, 787, and 794 nm, which are ascribed to a nickel-nitrogen vacancy complex (Tretiakova, 2009). The widths of these PL peaks also showed a linear relationship with the GR1 defect.

Several peaks that are commonly observed in the PL spectra of natural diamonds, but which have unknown configuration, displayed a tendency similar to those of the defects shown in the figure; these include peaks at 505, 612.4, and 776.5 nm. Other peaks of unknown origin, such as those at 535.8 and 648.2 nm, do not show corresponding changes in peak width, which suggests they are not affected by strain. By analogy with the known defects, we postulate that configurations for the defects causing the peaks at 505, 612.4, and 776.5 nm may include a vacancy, while those for the defects with peaks at 535.8 and 648.2 nm do not.

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CHARACTERIZATION OF SOME NATURAL AND TREATED COLORLESS AND COLORED DIAMONDS

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Methods for altering color in diamonds are constantly improving, so determining the origin of a diamond's color poses a tremendous ongoing challenge for gemological laboratories. The origin of color in most natural diamonds can be unambiguously established through absorption and photoluminescence (PL) spectroscopy, and polarized light and fluorescence microscopy.

EGL USA performed comprehensive testing to characterize the origin of color of 50 diamonds, known to be treated or untreated, ranging from colorless to near-colorless, yellowish green, orange, brown, pink, and black. The samples were characterized with a Thermo FTIR spectrometer to specify diamond type, an SAS-2000 for visible-range absorption spectroscopy, and a Horiba Jobin LabRam instrument (514 and 632 nm excitation) for PL spectroscopy. This study confirmed several spectroscopic peculiarities in treated and untreated diamonds.

In the PL spectra of the natural black diamonds, the zero-phonon lines (ZPLs) of vacancy-related optical centers were very broad (e.g., the ZPL of the GR1 center could not be resolved). These same lines were considerably narrower in the artificially irradiated black diamonds.

The PL spectra of almost all the untreated type IIa and IaB diamonds revealed a weak GR1 center with a sharp doublet at 741/744 nm. In contrast, the GR1 center was never observed in the HPHT-treated diamonds, unless it had been reintroduced by subsequent low-dose irradiation.

The PL spectra of many of the untreated type IIa diamonds exhibited at least traces of the ZPL of the 576 nm center, which may overlap with the ZPL of the 575 nm (NV⁰) center. The 576 nm center was rarely observed in the HPHT-treated diamonds.

At liquid-nitrogen temperature, the 637 nm (NV⁻) center of most of the HPHT-treated diamonds had a full width at half maximum (FWHM) greater than 0.6 nm. In the untreated diamonds, this line was usually less than 0.5 nm wide. In the PL spectra of the untreated type IIa diamonds, several weak lines were invariably detected between 550 and 580 nm (e.g., 566, 575, 576, and 578 nm). Within this range, the HPHT-treated type IIa diamonds usually revealed only the ZPL of the 575 nm (NV⁰) center.

PINK HPHT SYNTHETIC DIAMONDS— A NEW COLORATION TECHNIQUE

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New high-pressure, high-temperature (HPHT) growth techniques and post-growth color treatments applied to synthetic diamonds present new identification challenges. Recently observed in the GIA Laboratory were three pink HPHT-grown synthetic diamonds that had been treated by a combination of irradiation and HPHT annealing to achieve their desirable colors. These were grown with controlled amounts of nitrogen, enabling better results with post-growth color treatments.

The three synthetics (0.14, 0.20, and 0.53 ct) were studied using standard gemological testing, infrared spectroscopy, visible spectroscopy, photoluminescence (Raman) analysis, and observation of luminescence with the DiamondView instrument. The three gems were quite clean, with few inclusions and a very even distribution of color. The latter feature is particularly important, as HPHT synthetic diamonds usually have very well-defined growth structure and color zoning. In the strong short-wave UV



These three synthetic diamonds (0.14, 0.20, and 0.53 ct) owe their coloration to a combination of carefully controlled growth and treatment. Subtle growth structures are visible in their corresponding DiamondView images. Photos by Jian Xin (Jae) Liao (top), K. S. Moe (bottom left and right), and P. Johnson (bottom center).

radiation of the DiamondView, however, the samples displayed a subtle growth structure that is characteristic of synthetic diamonds; in some cases, this structure was more obvious in the pavilion facets.

Mid-infrared absorption spectra showed that all three synthetic diamonds had very low concentrations of aggregated nitrogen. It is believed that the aggregated nitrogen content is intentionally controlled during the growth process, enabling nitrogen-vacancy (NV) centers to be induced during post-growth treatment. Absorption features due to these NV centers, evidenced in the visible spectra, are responsible for the desirable purplish pink and pink colors of these synthetic diamonds. They received color grades of Fancy pink, Fancy Intense purplish pink, and Fancy Vivid purplish pink.

CHARACTERIZATION OF DISTINCTIVE COLOR ZONING AND VARIOUS INCLUSIONS IN LOW-GRADE DIAMONDS

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With the exception of colored diamonds, the value of most natural diamonds is directly related to their lack of color, and their clarity. However, bort and other heavily included diamonds typically used for industrial purposes may still present interesting study samples because of their internal features. These inclusions may affect the color of diamonds depending on how they are polished. The environment of diamond crystallization influences the occurrence of such inclusions, which also are manifested in various complex forms by epigenetic causes.

We investigated unusual inclusions in low-grade natural diamond crystals. Each sample was classified by the forms and colors of its inclusions. The chemical composition and structure of each inclusion were analyzed with scanning electron microscopy–energy dispersive spectroscopy, X-ray fluorescence, high-resolution transmission electron microscopy–selected area electron diffraction, and confocal micro-Raman spectroscopy. The growth directions and properties of the inclusions were observed through their cathodoluminescence patterns. We also used normal and focused FTIR spectroscopy to characterize the host diamonds.

Normal FTIR analysis did not reveal a correlation between inclusions and diamond type; most of the diamonds were classified as type IaAB. However, in samples with triangular-shaped color zoning, focused FTIR spectroscopy showed the nitrogen content inside and outside color zones was correlated with diamond type. Analysis of the structures and chemical composition proved that most of the inclusions were oxides of iron with various trace elements. Graphite inclusions are often found in natural diamonds; these inclusions typically appear dark gray and have

dendritic structure, hexagonal form, or fibrous elements. However, in the samples examined in this study, the shape and color of the inclusions varied, and graphite inclusions were not identified in the inclusion analysis using Raman spectroscopy. Our observations demonstrated a correlation between chemical composition and the resultant structure and color of various inclusions present in these low-quality diamonds.

MINERALOGICAL CHARACTERISTICS OF DIAMONDS FROM THE NURBINSKAYA PIPE, YAKUTIAN DIAMOND-BEARING PROVINCE, RUSSIA

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Discovered in 1996 in the eastern part of the Yakutian diamond-bearing province, in the Nakynsky area, the Nurbinskaya kimberlite pipe has a high diamond content. This study was conducted to identify the diamonds' typomorphic features. More than 6,000 samples from the current production were grouped into the varieties classified by Orlov (1977) according to crystal morphology, internal structure, physical properties, and impurities. The following percentages for different size classes were tabulated:

Variety I:	75.0–81.9%
Variety III:	0–1.3%
Variety IV:	8.5–12.1%
Variety V:	0.8–3.9%
Varieties VIII–IX:	6.3–11.6%

Although variety I prevailed in this pipe, its percentage was lower than that recorded for other Yakutian deposits. Most variety I diamonds had flat faces that were stepped and polycentric. Crystals with rounded faces were less common. The variety I diamonds were mainly light yellow, with some dark browns among the smaller crystals. When exposed to UV radiation, they displayed a noticeable blue and violet fluorescence in different crystals.

Variety IV diamonds from this pipe contained two subgroups of crystals: (1) samples with a thin or barely noticeable fibrous coating, and (2) samples with a thick or very thick fibrous coating. In some samples, the surface was not fully coated. We have not found such crystals in other Russian diamond deposits. Samples with a thick coating had a fibrous component that significantly dominated over the core. As many as three color zones could be seen on broken areas of the thickly coated crystals. Polycrystalline aggregates of variety VIII occasionally had coatings. Variety V was represented mainly by crystals of complex shape with octahedral faces and rounded dodecahedral surfaces.

The most common inclusions were those of ultramafic paragenesis: olivine and sulfides. Chromite, purple Cr-bearing pyrope,

and diamond inclusions were observed less frequently.

IR spectroscopy revealed the presence of A, B1, B2, and H defects in the diamonds. The A defect featured a complex distribution (with two maxima, 5–20 and 30–40 cm^{-1}) that appears to be characteristic of this material. Other defects were consistent with those in other diamonds, and Raman spectroscopy did not reveal any peculiarities.

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THE NATURE OF BLACK COLORATION IN GEM-QUALITY DIAMONDS FROM BRAZIL

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This study investigated the black coloration in diamonds from alluvial placers of the Macaubas River basin in Minas Gerais, Brazil. The samples consisted of three rounded octahedrons and two tabular dodecahedrons, with an adamantine luster. From each of these crystals, a 0.5-mm-thick plate was sawn. The octahedrons were sawed then polished, while the dodecahedrons were only strongly polished. The plates showed uniform, very saturated brown (dodecahedrons) or green (octahedrons) coloration, and they contained no color-causing inclusions. However, we did not know whether the brown samples were naturally colored or if they turned brown as a result of heating during polishing of the plates.

In all crystals before polishing, visible-range absorption spec-

tra (at room temperature) showed transmission starting at 700 nm, with a GR1 line at 740 nm and a band at 1076 nm. The infrared spectra of all crystals showed the nitrogen absorption systems A, B1, and B2, and a band with a maximum at 1530 cm^{-1} (absorption coefficient 0.6–0.7 cm^{-1}). This band is due to irradiation and proves there was no subsequent heating to temperatures above 200°C. In the polished plates, the GR1 system was detected in the absorption spectra of all samples. The H3 system was only detected in the absorption spectra of the brown plates. The spectra of all the plates also featured a system with the main band at 1078 nm (absorption coefficient 0.8 cm^{-1}).

The plates had a heterogeneous distribution of the main nitrogen defects A and B1, with some weak color variations in one green plate. Annealing of all plates was performed for 5 minutes at temperatures up to 600°C at 50° intervals and FTIR and visible-range spectra were recorded at each interval. Thermal behavior of the 1450 cm^{-1} band showed that the brown samples had been heated during polishing to temperatures above 600°C, while the green samples were heated during polishing to temperatures of 400–500°C. After annealing at 600°C, the green plates became greenish brown, and the GR1 band was reduced in intensity by 50%.

Testing of these plates revealed that all of the “black” diamond crystals were originally dark green, and that plates sliced from two of them turned brown because of heating during the polishing process.

This study was supported by the Russian Federal Purpose Program “Scientific and scientific-educational cadres of innovative Russia” for 2009–2013.

DONOR NITROGEN AGGREGATION IN SYNTHETIC DIAMONDS ANNEALED IN THE GRAPHITE STABILITY FIELD

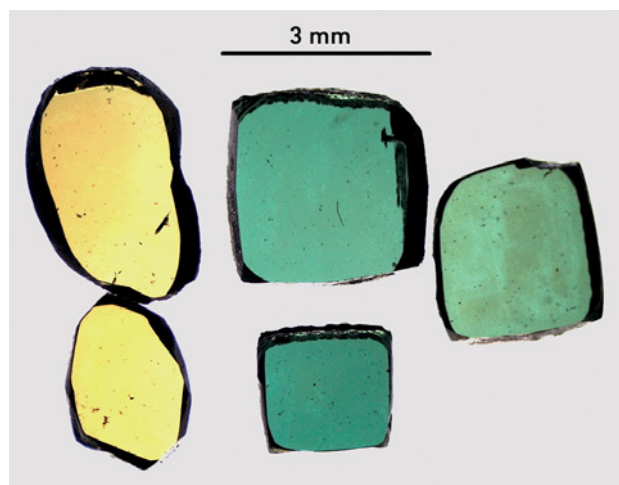
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This study focused on the C→A nitrogen aggregation that occurs during high-temperature annealing of high-pressure, high-temperature (HPHT) synthetic type Ib diamonds grown in nickel- and cobalt-containing systems. In the first series of experiments, the synthetic diamonds were subjected to high-temperature treatment in the presence of argon gas under atmospheric pressure. The samples were annealed at increasing temperatures (from 1400 to 1700°C) at 50°C intervals. At an annealing temperature of 1700°C, the nickel-containing diamonds showed an absorption increase at 1282 cm^{-1} due to A centers and a simultaneous decrease in absorption at 1344 cm^{-1} associated with C cen-

These 0.5-mm-thick plates were cut from “black” diamonds and studied for this report. Photo by E. Vasilyev.



ters. The cobalt-containing samples revealed no aggregation even at higher temperatures (1800°C).

The activation energy of aggregation (E_A) was 6.6 ± 0.6 eV in the nickel-containing samples. After the synthetic diamonds had been electron irradiated ($3 \text{ MeV per } 2 \times 10^{18} \text{ cm}^{-2}$) and annealed at 900°C for 120 minutes, however, nitrogen aggregation was observed at 1400°C. This was due to the formation of NV⁻ and N_I radiation-induced defects. The E_A value decreased to 0.5–1.5 eV in the nickel-containing samples, and to ~2.9 eV in the cobalt-containing synthetics.

The lower activation energy (and, in turn, the higher aggregation rate) can be attributed to two additional mechanisms involved in the aggregation process:

1. A vacancy mechanism (according to Collins, 1980): $N_S + N_V \rightarrow N_S - N_S (A) + V$
2. A donor-interstitial mechanism: $N_S + N_I \rightarrow N_S N_I \rightarrow A + C_I$

The C→A nitrogen aggregation caused a change in color (from brownish yellow to greenish yellow) and diamond type (from Ib to IaA).

In the second series of experiments, the samples were subjected to low-pressure, high-temperature (LPHT) treatment. They were treated in hydrogen plasma at 1600 and 1700°C. No C→A nitrogen aggregation was observed, and the samples remained type Ib. The IR absorption intensity at 1130 cm^{-1} decreased by 5–10%, and the μ_{1130}/μ_{1344} ratio increased by 8–12%. These effects could be due to proton thermal diffusion from the hydrogen plasma. The protons are localized at diamond structural defects, with some donor electrons from C centers being compensated. As a result, the samples became more colorless. The protons block the C→A aggregation, creating additional crystallographic strain that is reflected in a higher μ_{1130}/μ_{1344} ratio.

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NEW ULTRA-DEEP DIAMOND CLEANING TECHNOLOGY

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Clarity is one of the most important characteristics in determining the value of natural diamonds. Yet the efficiency of existing technologies for surface and fracture cleaning leaves much to be desired. The reagents in these technologies can only be used between 220 and 240°C, under a pressure no greater than 40 atm. And even if the process is repeated several times, the diamonds are not completely clean.

A new ultra-deep diamond cleaning technology is now available that surpasses existing methods in quality and speed. The innovative aspect of this technology is its capacity for temperatures above 300°C and acid vapor pressures of 200–400 atm. Under such conditions, the reagent activity is so high that only one mixture of reagents (rather than two or three) is needed. Cleaning becomes a faster, more efficient one-step process. Even large contaminant inclusions that reach the surface through tiny fractures are cleaned out completely. The new ultra-deep cleaning technology is not a natural diamond enhancement technology because the diamond is neither changed at the atomic level as during color enhancement nor laser-drilled and fracture-filled as during clarity enhancement. The diamond is simply cleaned from surface contaminants and inclusions. This technology increases the value of the diamond 30–100% and can be used by large diamond mining and selling companies.

GEM LOCALITIES AND FORMATION

BLUE AND PINK SAPPHIRES FROM MULING, NORTHEASTERN CHINA

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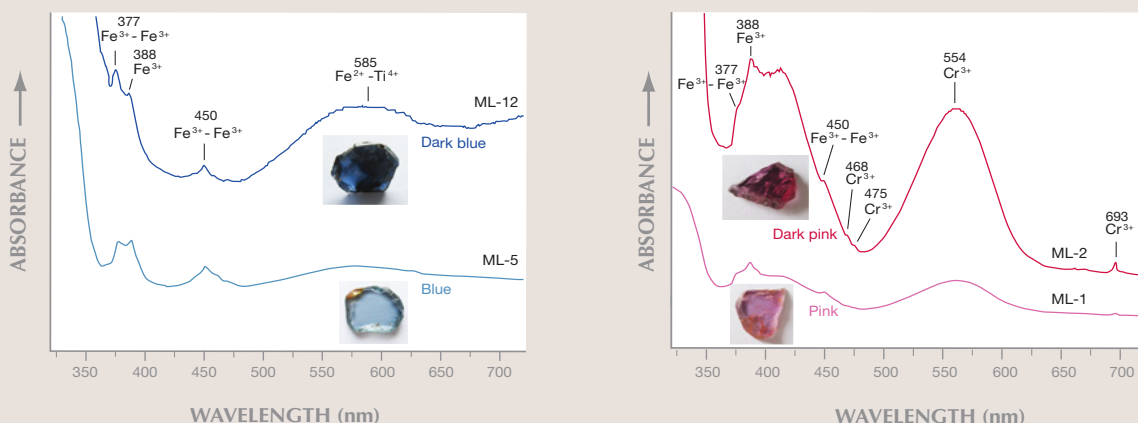
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Pink and blue sapphires occur in alluvium derived from Tertiary alkali basalts at Muling, in the northeastern Chinese province of Heilongjiang. Associated heavy minerals in the alluvium include zircon (Chen et al., 2011), garnet, spinel, enstatite, and olivine; some are gem quality. The Muling deposits were discovered in 1985, but exploitation for gem production is still limited.

Twenty-five blue and pink sapphires from Muling were characterized using standard gemological methods including infrared and UV-Vis spectroscopy. The samples consisted of 13 polished blue sapphire plates (0.10–1.14 g), five polished pink sapphire plates (0.16–0.51 g), and seven rough blue and pink sapphires (1.12–10.36 g). The rough blue sapphires mostly formed six-sided barrel-shapes. SG values were 3.98–4.09 (rough), 3.94–4.08 (blue plates), and 4.02–4.05 (pink plates). RIs were $n_o = 1.768$ – 1.770 and $n_e = 1.760$ – 1.762 , with a birefringence of 0.008–0.009. The blue sapphires were inert to both long- and short-wave UV radiation, while the pinks showed moderate to faint red in long-wave and were inert to short-wave UV. The sapphires' internal features consisted of two-phase, fluid, and various crystal inclusions (colorless zircon, apatite, and short rutile needles), as well as hexagonal color zones.

UV-Vis ABSORPTION SPECTRA



UV-Vis spectra of sapphires from Muling show absorption features related to Fe and Ti (blue samples, left), or Cr and Fe (pink samples, right).



This map shows the major rock types and associated mineral localities in southern Brazil.

No absorption bands resulting from O-H (at $\sim 3400\text{--}3200\text{ cm}^{-1}$) were visible in the pink samples; three blue samples showed small absorptions at 3307 and 3231 cm^{-1} . UV-Vis spectra of the pink sapphires showed Cr^{3+} features (i.e., two large absorption bands centered at ~ 400 and 550 nm). A diagnostic narrow band at 693 nm was also attributed to Cr^{3+} . Small bands at 388 nm (attributed to Fe^{3+}) and at 377 and 450 nm (attributed to $\text{Fe}^{3+}\text{-Fe}^{3+}$ pairs) also were observed in the pink sapphires. The blue sapphires had narrow peaks at 377 , 388 , and 450 nm that were weaker than the $\text{Fe}^{2+}\text{-Ti}^{4+}$ absorption band at 585 nm .

Although these sapphires have yet to be mined commercially, the Muling deposit is a promising source of gem corundum.

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GEM MATERIALS IN THE SOUTH OF BRAZIL

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The southern Brazilian states of Paraná, Santa Catarina, and Rio Grande do Sul contain various gem deposits in several geologic units.

These minerals are used as faceted gems for the jewelry trade, and also as ornamental and collector stones.

Most important are the huge agate and amethyst geode deposits in Paraná Basin, hosted by volcanic rocks of the Serra Geral Formation. The Salto do Jacuí region of Rio Grande do Sul is the main producer of agate, which occurs in a variety of colors and exotic patterns. The region also contains deposits of onyx and carnelian, as well as gem-quality opal. The opal exhibits a range of crystallinity (opal-C and opal-CT) but no play-of-color. It is typically translucent to transparent and can exhibit various attractive bodycolors, including yellow, blue, and red (fire opal).

The main amethyst producer is the Ametista do Sul region of Rio Grande do Sul, where rock crystal, rose quartz, jasper, calcite, gypsum (selenite), and barite can occur in association. Important amethyst deposits are found also in western Santa Catarina and southwestern Paraná States. Natural citrine has not been recovered from these deposits, but significant amounts of amethyst are heat treated to produce this quartz variety.

A number of zeolites, associated with apophyllite, have yielded superb mineral aggregates in geode deposits in Rio Grande do Sul and Santa Catarina States. In northern Santa Catarina, ruby and sapphire (pink, colorless, brown, gray, and black) are found in large colluvial deposits, associated with granulitic rocks. Most of the rough material is opaque to translucent, but it may exhibit special features such as color zoning, chatoyancy, and asterism. Alluvial deposits in the Tibagi River valley of Paraná are known for small but high-quality diamonds. Blue and green sapphire, agate, jasper, rock crystal quartz, and black tourmaline may occur together in the gravel. Rio Grande do Sul contains serpentinite deposits that originated from Precambrian gabbros and peridotites. These specimens are light yellowish green to dark green, with patches, veins, and bands. In the central region of the state, a large deposit of petrified wood is hosted by Gondwana-associated sedimentary rocks. Considered one of the most important earth-silicified fossil wood records, it has become a conservation site where commercial mining is prohibited.

RUBY FROM LIBERIA

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One of these authors recently found rubies and smaller amounts of sapphires while prospecting for alluvial diamonds in two areas of Liberia (Douman, 2011). The sediments consisted of quartz grains and smaller black grains, some of which could be identified as tourmaline and staurolite. One prospecting area lies on the Mano River (along the border with Sierra Leone), while the other



These rubies (and two sapphires) were found in Liberia. The larger crystals with well-defined shapes come from Nimba Province close to the border with Guinea, while most of the smaller waterworn rubies are from the Mano River along the border with Sierra Leone. The smaller of the two sapphire crystals weighs 1.52 g and is 11.6 mm long. Photo by L. Kiefert.

is located in Nimba Province close to the Guinean border. At the latter locality, yellow to green chrysoberyl and orange spessartine also were found.

The Mano River rubies consisted of small waterworn pebbles weighing less than 0.2 g, while those from Nimba Province constituted well-formed crystals larger than 1 g with prism, basal, and rhombohedral faces.

The rubies ranged from near-opaque and purplish red for the larger crystals to transparent and pinkish red to red for the smaller ones. The larger purplish red crystals were heavily twinned in three directions following the rhombohedral faces. The smaller crystals from the Mano River were not quite as heavily twinned, but showed iron oxide staining in the fissures more frequently than the larger crystals. In addition, networks of partially healed fissures were observed in some samples from the Mano River. Initial microscopic examination of samples from both deposits showed inclusions of black rounded and elongated crystals, as well as clusters of small rounded transparent crystals (most likely zircon). One well-formed zircon crystal was identified by Raman spectroscopy in one of the samples from Nimba Province.

The twinning pattern and chemical data for the Liberian samples from both localities fit well with other African rubies such as those from Malawi, Tanzania, and Mozambique, while they were distinctly different from Burmese, Nepalese, Tajik, Afghan, Sri Lankan, and Vietnamese rubies. Cr contents from both localities varied between 0.3 and 0.7 wt.%, while Fe values ranged from approximately 0.6 to 1.2 wt.%.

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SYSTEMATIC DIAMOND DESCRIPTIONS FOR USE IN GEOLOGY AND EXPLORATION

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Diamond crystal descriptions are used by dealers, cutters, physicists, and geologists. Yet each discipline has different needs and applications, and no coherent classification scheme exists. Researchers such as Orlov, Harris, Gurney, Robinson, Afanasiev, and Spetsius have published valuable works that describe diamond crystals, but objective comparison between terminologies is often elusive. For the purpose of geologic study, exploration, and resource evaluation, an industry-wide classification scheme is proposed.

As one of the few commercial diamond recovery laboratories in the world, the Saskatchewan Research Council Geoanalytical Laboratories Diamond Services (SRC-GLDS) has worked with various sectors of the industry. SRC-GLDS has implemented the proposed scheme into its diamond analysis and received substantial positive feedback. A trained geologist, gemologist, or mineralogist can use this system to generate a complete description of diamond crystals, thereby producing consistent and objective raw data.

The diamond classification scheme calls for observation and qualitative determination of the following criteria: color, clarity, inclusions, crystal shape, surface features, and descriptors. Color is broken down into seven groups based on saturation. Clarity is represented by three degrees of light transmission. Inclusions are divided into five categories, ranging from absent to heavily included. Diamond morphology has been narrowed down to eight primary and secondary crystal shapes for easy reference. Resorption of the octahedron is compared to the visual standards devised by Robinson (1979). Surface characteristics that affect the stone's overall appearance are placed into nine categories. Last, six descriptors are provided for other common features, such as twinning and breakage.

This systematic diamond crystal description scheme is supported by qualitative standards referenced through the use of photographs and charts; it also incorporates detailed discussion to aid classification. Analysis of the data produced can be used to aid geologic study and resource evaluation of diamond deposits. SRC-GLDS's goal is to create international consensus for this classification scheme within an enigmatic industry.

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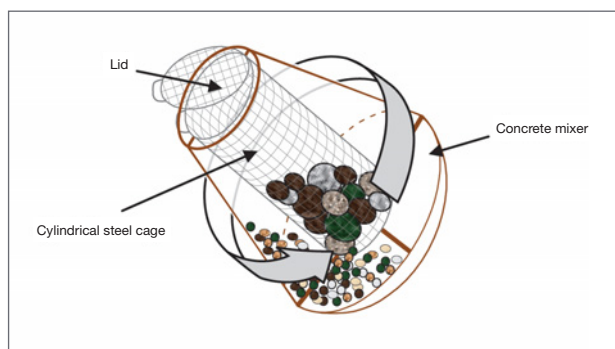
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USING A CONCRETE MIXER TO SORT GEM-BEARING GRAVELS FOR ARTISANAL AND SMALL-SCALE MINING

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An inexpensive concrete mixer can easily be converted into a washing and sorting machine for gem-bearing gravels. The inside of the mixer is fitted with a cylindrical steel cage (40 cm in diameter and 80 cm long) that functions as a trommel. The cage can have a mesh size of 1 inch (2.5 cm) or any other desired size. This changeable steel cage is installed inside the concrete mixer body by connecting it with bolts to the base and side walls. Around the curved area toward the bottom of the mixer, openings of suitable size are cut and covered with sieves that are bolted to the surface. Therefore, sieves of various sizes can be changed quickly as needed.

To operate the machine, the trommel is filled with gem-bearing gravels and the mixer is spun at an angle of $\sim 20\text{--}45^\circ$. The angle and



This diagram shows a concrete mixer fitted with a cylindrical steel cage that functions as a trommel.

rotational speed are adjusted for maximum efficiency. A small water pump sends high-pressure spray through a $\frac{1}{2}$ inch nozzle into the rotating trommel. After a few minutes, once the water flowing out of the mixer is clean, the washing and sorting is complete. The coarse-grained materials are trapped inside the trommel, while the medium-grained pebbles and gravels are left in the bottom of the mixer. The fine-grained sand, silt, and clay are eliminated with the washing slurry through sieves. The coarse and medium-sized material can then be easily collected and processed by hand-picking.

The thick body of the mixer is sturdy enough to handle the hard work of sizing stream sediments, and the machine can be conveniently moved between various mining sites. With this device, artisanal and small-scale miners can bring more product to market.

PETROGENESIS OF THE LI-BEARING STEWART PEGMATITE, PALA, CALIFORNIA

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A study is underway to unravel the petrogenesis of the gem- and lithium-bearing Stewart pegmatite in Pala, California, which is a source of pink tourmaline and other gems. Prevailing concerns include: (1) the relationship between the host gabbro and the pegmatite, (2) the age of the gabbro and the pegmatite, (3) the source and nature of the pegmatite-forming material, (4) the temperature and pressure of pegmatite crystallization, and (5) the duration of pegmatite formation.

The host gabbro and the Stewart pegmatite have initial ⁸⁷Sr/⁸⁶Sr ratios of 0.7037 and 0.7040, respectively, consistent with a common origin. The Sycamore Flats olivine gabbro, a small-scale analog of the Pala gabbro, contains 48% SiO₂ and minor micropegmatitic stringers in its center with 77% SiO₂. The micropegmatites' setting indicates they were derived from the gabbro magma as immiscible components. Findings show that the micropegmatites formed from a gaseous fluid, not a silicate melt.

We interpret that the Stewart pegmatite was derived from an immiscible gaseous fluid derived from the crystallizing gabbro. The U/Pb age of zircon from the Pala gabbro is 103 Ma, while the ⁴⁰Ar/³⁹Ar age of Stewart muscovite is 100 Ma; adjusting for the temperature of Ar retention in muscovite, the gabbro and pegmatite are the same age.

After pegmatite emplacement, volatiles rose within the pegmatite, making the footwall cooler than the solidus and forming the aplitic-textured footwall. After most of the pegmatite had crystallized, pegmatite formation continued as gaseous fluids moved up from the core zone, autometasomatically replacing the earlier-formed pegmatite. The metasomatic pegmatite formed upward-tapering "chimneys." The outer portions of the chimneys consist of albite, quartz, muscovite, and perthite, while their cores are largely albite-containing, gem-bearing miarolitic cavities.

Tourmaline in the chimneys systematically crystallized as schorl in the uppermost part of the chimney, followed by green/blue elbaite in upper miarolitic cavities, pink elbaite and morganite in intermediate cavities, and finally pink elbaite and kunzite in the lowest cavities. The Li-rich core zone, which is devoid of miarolitic cavities, consists of albite, petalite, heulandite, lepidolite, frozen elbaite, amblygonite, and frozen laths composed of petalite, spodumene, heulandite, stilbite, and tridymite.

A STUDY OF RUBY ON PAINITE FROM THE MOGOK STONE TRACT

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Rubies from the Mogok Stone Tract in Myanmar are among the finest on Earth. Although the marble source in the Mogok metamorphic belt is well established, the process of ruby formation has been a subject of much debate. Iyer (1953) attributed this process, and that of spinel, to metamorphism of the aluminous component in the carbonate sediment. Gübelin (1965) proposed a pneumatolytic interaction of granitic liquids with the marble. Garnier (2003) and Giuliani et al. (2007) hypothesized that ultra-saline hydrous fluids from evaporitic components of the sediments scavenged the silica to leave corundum through a metasomatic reaction. On the basis of mineral associations (scapolite, cancrinite-group, moonstone, etc.) in some ruby specimens, Harlow (2001) argued that they formed similarly to a skarn.

Our observations of ruby overgrowths on painite, CaZrBAl₃O₁₈, have defined the mineral assemblages and relative timing of crystallization in the Mogok Stone Tract. At Wetloo, an abundance of painite was found at the contact of a pegmatite with marble. Two painite specimens with overgrowths of ruby were sectioned to permit textural and mineral examination with X-ray diffraction, electron microprobe, backscattered-electron imaging, and microscopic study. The painite crystals are actually clusters of parallel hexagonal prisms (rods), with an interstitial mixture of zircon + ruby and foitite + zircon. Coronal overgrowths on painite and vermicular intergrowths indicate a second generation of foitite, plus new margarite, zircon, and srilankite. Corundum is in intimate contact with foitite and some zircon.

We propose that painite formed from a skarn reaction of a Zr-rich pegmatitic fluid with marble. A subsequent fluid led to a reaction of painite to zircon ± foitite ± margarite ± srilankite, though perhaps not in a single stage, as evidenced by the differences in silica activity observed in the concurrent phases. The intergrowths and overgrowths of corundum suggest a coeval to late fluid-carbonate reaction; alumina and Cr are at least partially sourced from painite. Clearly, both textures and phase assemblages indicate reaction relationships for the formation of corundum with painite. U-Pb dating of Wetloo zircon yielded 16 ± 0.5 Ma (Thu, 2007), indicating they are younger than the 18.7–17.1 Ma (both ± 0.2 Ma) age of other Mogok ruby associations reported by Garnier et al. (2006). For Mogok ruby, multiple ages and mechanisms of formation must be considered.

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GEMSTONES FROM MEXICO—A REVIEW

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Nature endowed Mexico with enormous metallic and nonmetallic mineral resources. But despite extensive research, scientists still have not properly explored the Mexican territory from a mineralogic or especially a gemological point of view (Victoria, 1998; Ostrooumov, 2001). Moreover, some gemologists have considered it an insignificant source of gem materials. Unfortunately, there have been relatively few publications dedicated to the evaluation and characterization of Mexican gem deposits, while those reports that have been published are often confusing and even contradictory.

The most economically important gems produced in Mexico today are volcanic opals, with or without play-of-color, from the states of Jalisco and Querétaro. The color and crystal chemistry of these volcanic opals were investigated recently (Ostrooumov, 2007a,b). Other traditional gems and collector's stones—such as moonstone, topaz, danburite, amethyst, fire agate, amber, turquoise, malachite, obsidian, “onyx” marble, pearl, and coral—are exploited on a limited scale. Tourmaline, sphene, peridot, and grossular and almandine are rare. Recently, the first Mexican amazonite was discovered in Chihuahua State, and the first jadeite-bearing pebbles were found in secondary deposits in the Vizcaino Peninsula of Baja California Sur. These finds demonstrate the importance of systematic research of the Mexican subsoil, which could lead to the discovery of other gem localities.

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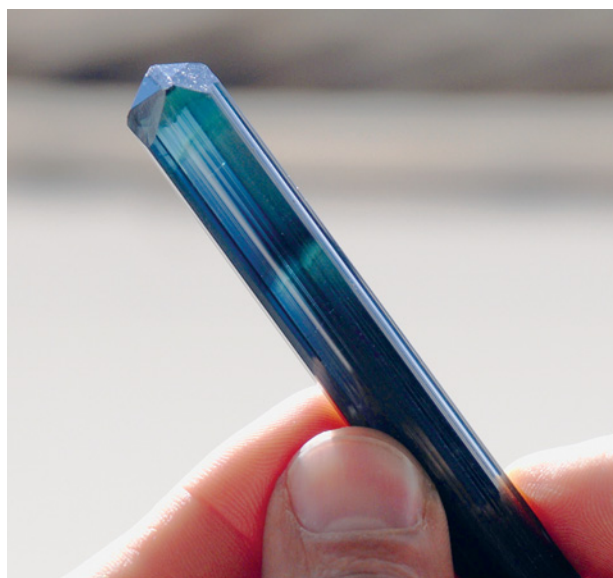
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THE PEDERNEIRA PEGMATITE, MINAS GERAIS, BRAZIL: GEOLOGY AND GEM TOURMALINE

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The Pederneira mine, located a few kilometers north of the famous Cruzeiro mine in the São José de Safira area of Minas Gerais, Brazil, produced an extraordinary quantity of gem tourmaline crystals from 1980 to 2006. In 2010, U.S.-based Fine Minerals International began a geologic prospecting and under-

This gem-quality tourmaline crystal was recently produced from the Pederneira mine in Minas Gerais, Brazil. Photo by Marco Lorenzoni.



ground mining project to evaluate the deposit's remaining potential. The lead author has been involved in the geologic study of Pederneira and collected new data and representative samples of pegmatitic rocks, minerals in pockets, and tourmaline gem material. A complete gemological characterization of tourmaline from this locality was conducted in collaboration with the University of Milan and the National Council of Research in Milan.

The Pederneira tourmaline deposit is characterized by two major pegmatitic bodies: a lower one miners call *Dilo*, and an upper one known as *Dada*. These two masses are roughly prismatic in shape and dip steeply to the southwest. They are interconnected, and bounded at the top and bottom by subhorizontal barren pegmatitic dikes. The host rock is composed of biotite- and muscovite-bearing paragneiss, with quartz and plagioclase, and accessory garnet and tourmaline (dravite). Both pegmatites exceed 30 m in width. The Dilo pegmatite contains large enclaves of host rock. Large, spectacular gem-bearing pockets are distributed along the core zone of both the Dilo and Dada pegmatites.

Pederneira's gem tourmaline is characterized by a wide variety of red-to-purple and green colors. Bicolored and "watermelon" crystals are common. Blue-green to grayish blue and blue colors are rarer, as is cat's-eye material (red or green). The high-quality gem crystals in the pockets largely consist of second-generation "pencils" that grew into the cavity in the crystallographic direction of the analogous pole (mostly pedial terminations) or the antilogous pole (mostly pyramidal terminations). Microprobe analyses of the gem material revealed compositions in the elbaite field, with variable contents of fluorine and a high rossmanite component in some pink samples. Foitite was confined to dark green to black portions of the crystals. The only significant minor elements were iron and manganese. At present, the potential for future production is uncertain, and a significant investment in the mining of new exploration tunnels is in progress.

BLUE "OPAL" (OR CRISTOBALITE?) FROM RIO GRANDE DO SUL, BRAZIL

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Rio Grande do Sul is well known for its huge agate and amethyst geode deposits in volcanic rocks. Various colors of opal are also associated with these deposits, especially in areas near the main agate production center of Salto do Jacu . The opal is usually found within geodes in alternating layers with chalcedony, cementing breccias, or irregularly deposited along fractures and ancient lava flow structures. The degree of crystallinity varies considerably,

from highly disordered opal-CT to well-ordered opal-C.

This work focused on some blue "opals" that occur in the region. They have greater refractive index (1.475) and specific gravity (2.25) values than those reported for pure Brazilian opal and other opal occurrences worldwide. Their X-ray diffraction pattern presents all the characteristics of a pure cristobalite spectrum, with a very intense and narrow peak at 4.04   with a full width at half maximum (FWHM) of only 0.036  . The Raman spectrum also shows the typical features of pure cristobalite, with peaks at 419, 232, and 114 cm⁻¹. The main Raman peak has a FWHM as low as 23 cm⁻¹. Furthermore, thermogravimetric studies revealed a transition from α - to β -cristobalite at 266 C. This transition was confirmed by recording X-ray spectra while slowly heating the material from room temperature to 300  C. The final result of heating true opal should always be α -cristobalite.

We therefore consider this gem material cristobalite. Thermogravimetric analysis can be used as an additional tool to distinguish it from opal-C samples with very high RIs and SGs. Although the material's values still lie below those listed for cristobalite, lower values are to be expected for a porous aggregate that contains water and/or air in its voids. Indeed, this cristobalite contains nearly 2% water that is released from the pores at very low temperatures (39 C), causing it to destabilize and whiten if exposed to heat or dry air for extended durations. We also had the opportunity to analyze a very similar blue "opal" from Oregon. Our results suggest it is identical to the cristobalite material described in this work.

RECENT TRENDS IN WORLD COLORED GEM PRODUCTION

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The U.S. Geological Survey publishes world production figures for more than 80 mineral commodities annually. Colored stone production, unlike that of diamond, is inherently difficult to estimate because of the fragmentary and commonly informal nature of the industry, the lack of government oversight in many of the source countries, and the wide quality variations for each gem material. For these reasons, world production figures for colored stones were not published by the USGS until 2008. Concerns over the misuse of diamonds and possibly other gems to fund civil wars and terrorism have led the USGS to reexamine colored stone production in detail. Based on government data, company reports, and a review of the colored stone mining literature, the agency has estimated global production of amethyst, emerald, ruby, sapphire, and tanzanite for the years 1995 to 2008, and for alexandrite from 2001 to 2008.

From 1995 to 2005, Colombia was the world's leading emerald supplier, accounting for about half of global production by volume.

TABLE 1. World emerald production (1996–2008).^a

Country	1996	1999	2002	2005	2008
Brazil ^b	1,300	460	700	1,500	2,500
Colombia ^b	2,300	2,100	1,800	1,700	570
Russia	—	—	800	618	270
Zambia	570 ^b	445	1,860	1,100 ^b	1,800
Zimbabwe	108	21	33	20 ^b	—
Other ^b	25	29	118	135	111
Total ^b	4,300	3,100	5,300	5,100	5,300

^a Values in kg. Sources: U.S. Geological Survey Minerals Yearbook, company reports, and unpublished data.

^b Estimated; data are rounded to no more than three significant digits.

By 2008, Colombia ranked third in volume, behind Brazil and Zambia. Russia resumed emerald mining in 2001 with the reopening of the Malysheva mine, which shut down again in 2008.

Ruby production in Madagascar and Myanmar appears to have declined in recent years. Tanzania's output likely rose in 2008 with the discovery of the Winza deposits. Ruby mining also seems to have increased in Pakistan and Tajikistan, and to have resumed in Malawi. Greenland and Mozambique, meanwhile, have emerged as new ruby sources.

World sapphire production likely declined in recent years, with diminished output from Afghanistan, Australia, China, Madagascar, Myanmar, Nepal, and Sri Lanka. In Australia, large-scale mining operations either shut down or scaled back because of high production costs. Madagascar's output declined with the depletion of near-surface deposits at Ilakaka and Sakaraha, as well as the 2008–2009 ban on rough gem exports.

Bolivia, Brazil, Uruguay, and Zambia appear to be the world's leading amethyst producers. Uruguayan production has increased in recent years. In Zambia, output from the Kariba mine peaked in 2007.

India's alexandrite production climbed in 2008 after the Vishakhapatnam mines reopened. Russian alexandrite enjoyed a resurgence from 2001 to 2008, with the reopening of the Malysheva mine.

COLORED STONE AND PEARL IDENTIFICATION

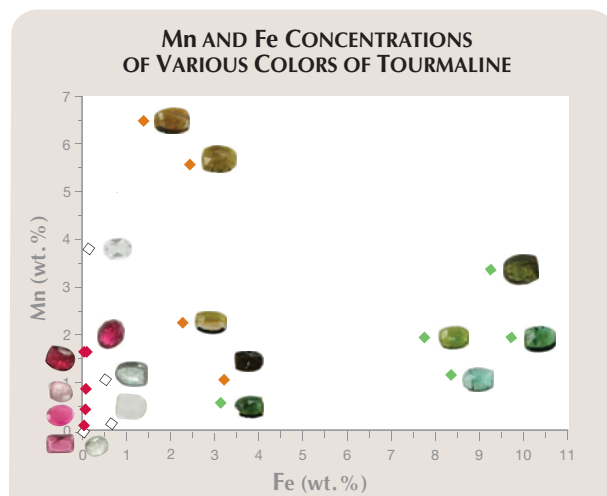
SPECTRAL CORRELATION OF MANGANESE AND IRON IN TOURMALINES FROM MADAGASCAR

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Eighteen colored tourmalines (colorless, pink to yellow, green to blue, and brown) from Madagascar were studied using UV-Vis, FTIR, and wavelength-dispersive X-ray fluorescence spectroscopy. The samples had been irradiated and/or heat-treated. Most had prominent amounts of Mn and/or Fe, which were responsible for the different colors. The green to blue samples contained distinctly higher Fe contents, while the lowest Mn contents were detected in the pink to yellow samples. The brown samples had significant Mn and ~3 wt.% Fe.

UV-Vis spectroscopy of the pink tourmalines showed broad absorptions in the vicinity of 510 and 530 nm due to Mn³⁺, but these bands were absent from the colorless tourmaline. After the pale pink and colorless tourmalines were irradiated with an energy of 10 MeV and a dose of 2×10^{17} electrons/cm² for one hour, they changed to red and yellow, respectively. Greenish blue tourmalines exhibited absorption maxima in the 710–740 nm region attributed to Fe²⁺ (no Cu²⁺ absorptions were detected). Brown tourmalines showed absorption bands at 410 and 710 nm that resulted from Mn²⁺ and Fe²⁺, respectively. Thus, the brown color was produced by a combination of the two absorption bands.



This plot shows the Mn and Fe contents of tourmalines of various colors.

If Mn occurs as Mn²⁺, the tourmaline will appear very pale pink or colorless because the d⁵ configuration does not have spin-allowed transitions. Therefore, Mn²⁺ is not a significant chromophore in tourmaline. When the pale pink tourmaline was irradiated by electrons, a strong absorption band, apparently due to Mn³⁺, appeared in the vicinity of 510 nm. The d⁴ configuration of Mn³⁺ has been assigned to absorption bands at 390 and 510 nm as 'd-d' transitions of ⁵E → ⁵A₁ and ⁵B₂ → ⁵A₁, respectively (Marly and Sandao, 1988). In the FTIR spectra, a combination of stretching and bending modes of cationic units (MOH, where M may be Al, Mg, Fe, Mn, etc.) was observed in the 4600–4300 cm⁻¹ range (Reddy et al., 2007).

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CHINESE FRESHWATER CULTURED PEARLS WITH EXOTIC METALLIC COLORS

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¹Designs by Blaire, San Diego; ²PearlParadise.com Inc., Los Angeles

First seen occasionally in multicolored strands, metallic cultured pearls have steadily become more common over the last five years. Entire strands of these exotic cultured pearls are now readily available in lower grades in 6–12 mm sizes. Exceptionally high-grade goods are more difficult to come by, but they are available through special collaboration with producers.

Exotic-colored metallic cultured pearls initially aroused suspicion that their color and mirror-like surface was the product of human intervention. Upon investigation, this has not been the case. There are only a small number of these cultured pearls available, but they have been selling for the same price as standard-color tissue-nucleated products. They are regarded by processors as a nuisance in strand matching.

Compared to the standard Chinese freshwater cultured pearl colors—white to “ivory,” “peach” to “apricot,” and pink to lavender—the metallic ones are easily recognized on close inspection.

Pink sapphires and diamonds complement the exotic color in this metallic cultured pearl ring by Takayas Mizuno. The cultured pearls in this photo are 8–10 mm. Photo by B. Beavers.



They may glisten on the surface as if coated in “aurora borealis” (a commercial coating intended to mimic the natural phenomenon of colorful lights displayed in the polar sky), or they may have a purely metallic look.

Called *strange-color* by the Chinese, the pink-green-“bronze” color is the rarest of the exotic colors of these metallic cultured pearls. Other unusual colors, such as green, purple, and rarely, blue may be seen. Many of the better baroque cultured pearls have a strong orient that appears to float on the surface. As more of these beautiful cultured pearls are used by designers and consumer awareness grows, producers are sure to hand-select them as premium goods.

NATURAL NON-NACREOUS PEARLS FROM THE GIANT CLAM *TRIDACNA GIGAS*

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Non-nacreous pearls from the giant clam *Tridacna gigas* are an often overlooked curiosity in the mollusk realm. Although these specimens are natural, their typically baroque shape keeps them in the shadows of their more attractive nacreous and non-nacreous counterparts.

Known in folklore as the “giant killer clam,” these mollusks have been documented to measure more than four feet across and weigh more than 200 kg. Inhabiting the Indo-Pacific waters, these living jewels display a variety of colors. In death, they become jewels of a different sort. Demand for the giant clam’s meat and ornamental shell has led to overharvesting, and they are now one of the most endangered clam species. This has prompted conservationists to protect the mollusk through nurseries, aquaculture programs, and import restrictions on giant clam products. Noted guidelines have been formalized by CITES (Convention on International Trade in Endangered Species of wild flora and fauna). These restrictions have also made it more difficult for gemologists to obtain specimens for in-depth documentation. Particularly rare are the large blister and loose pearls produced by some giant clams. Of historical note are the Pearl of Allah, the Pearl of Elias, and the Palawan Princess.

The authors recently examined the 2.27 kg Palawan Princess, as well as more than 40 smaller pearls from *Tridacna gigas* and other species from the same genus. The weights ranged from <1 to 72 ct, and sizes ranged from 5.95–5.97 × 3.04 mm to 26.10 × 22.84 × 16.63 mm. Shapes were variable, from symmetrical to baroque, with some being worked. Colors ranged from white to off-white, some being brownish and yellowish; two were an unusual orange color. Physical, chemical, and optical properties were obtained from standard gemological testing (RI, SG, surface

textures, etc.) and from UV-Vis, Raman, FTIR, and EDXRF spectroscopy. Surface luster was porcelainous, waxy, or matte, and the silky flame-like structure observed was variable (none to quite strong). RI and SG were standard for *Tridacna*. One worked specimen turned out to be crafted from *Tridacna* shell. UV-Vis, Raman, FTIR, and EDXRF spectroscopic features were consistent with the coloration and carbonate material of the non-nacreous pearls tested.

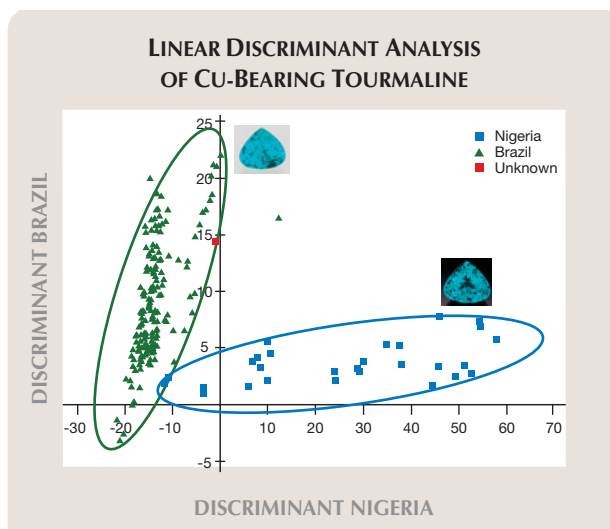
APPLICATION OF DISCRIMINANT ANALYSIS IN GEMOLOGY: COUNTRY-OF-ORIGIN SEPARATION IN COLORED STONES AND DISTINGUISHING HPHT-TREATED DIAMONDS

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Country-of-origin determination for corundum and Cu-bearing tourmaline is a service often sought by the trade. Inclusions and other features are unique to some localities, and microscopy can narrow down the geographic origin considerably. Trace-element chemistry is an integral part of this determination process and becomes critical when samples lack distinctive microscopic features.

LA-ICP-MS analyses of the trace elements in ruby, sapphire, and Cu-bearing tourmaline samples from several deposits were used to measure subtle differences in the geologic environments represented, providing “fingerprints” of the source locality. Linear discriminant analysis is a statistical method related to both multivariate analysis of variance and multiple regression. It considers all elements provided and uses Fisher’s linear model (Fisher, 1936) to place unknown samples into the most likely category of known groups. In addition to selecting the country of origin based on the highest discriminant score, we also superimposed each unknown sample’s scores for the two locations with the highest likelihood of occurrence onto a plot of previous scores for known samples. The plot provides a visual assessment of how closely an unknown sample fits a particular known group relative to another known group. Below is a list of samples and localities analyzed.

- Ruby (522 samples): six elements (Mg, Ti, V, Cr, Fe, and Ga) and nine localities—Mong Hsu and Mogok (Myanmar), Tajikistan, Lake Baringo (Kenya), Songea (Tanzania), Thailand, and undifferentiated deposits in Madagascar, Pakistan, and Vietnam.
- Sapphire (407 samples): six elements (Mg, Ti, V, Cr, Fe, and Ga) and seven localities—Mogok, Kashmir, Andranondambo and Ilakaka (Madagascar), Sri Lanka, Songea (Tanzania), and Lam Dong (Vietnam).
- Cu-bearing tourmaline (336 samples): six elements (V, Cu, Zn, Ga, Sr, and Pb) and three localities—Brazil (including



This plot illustrates how linear discriminant analysis can be used to determine the country of origin for Cu-bearing tourmaline. Here, an unknown sample falls within the discriminant field corresponding to Brazil; it will then be plotted in a diagram comparing Brazil and Mozambique.

Paraíba and Rio Grande del Norte States), Nigeria, and Mozambique.

In addition, we have begun applying the technique to peridot for the purpose of identifying the source of particular gems of archaeological significance.

Discriminant analysis has also been useful in separating HPHT-treated from natural-color diamonds with photoluminescence spectroscopy. Numerous peak heights, full width at half maximum (FWHM) measurements, and peak areas were analyzed. The absorption centers most useful for identifying HPHT-treated diamonds were at 503.2, 575, and 637 nm.

REFERENCE

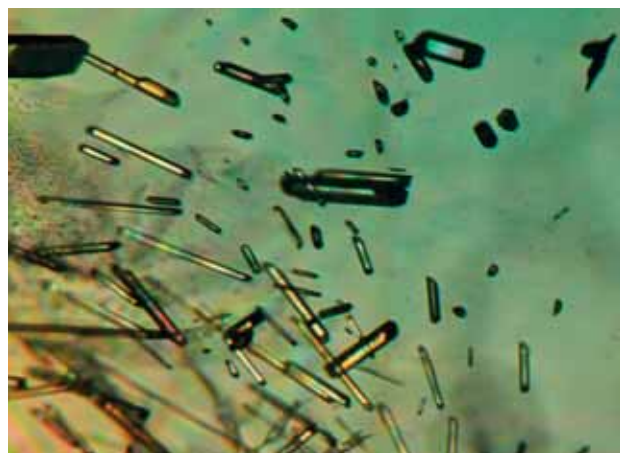
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REMARKABLE GEMS ENCOUNTERED AT THE GEM TESTING LABORATORY, JAIPUR, INDIA

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Since June 2010, several remarkable gems have passed through the Gem Testing Laboratory in Jaipur, India.

Oriented needle-like inclusions were found in a flux-grown synthetic emerald. The needles appeared to be oriented along the prism faces; however, they intersected one another at approximately 60°. This synthetic emerald also contained numerous birefringent and elongated colorless crystals showing a hexagonal pro-



These elongated birefringent colorless crystals with a hexagonal profile were seen in a flux-grown synthetic emerald. Photomicrograph by G. Choudhary; crossed polarizers, magnified 60 $\times$.

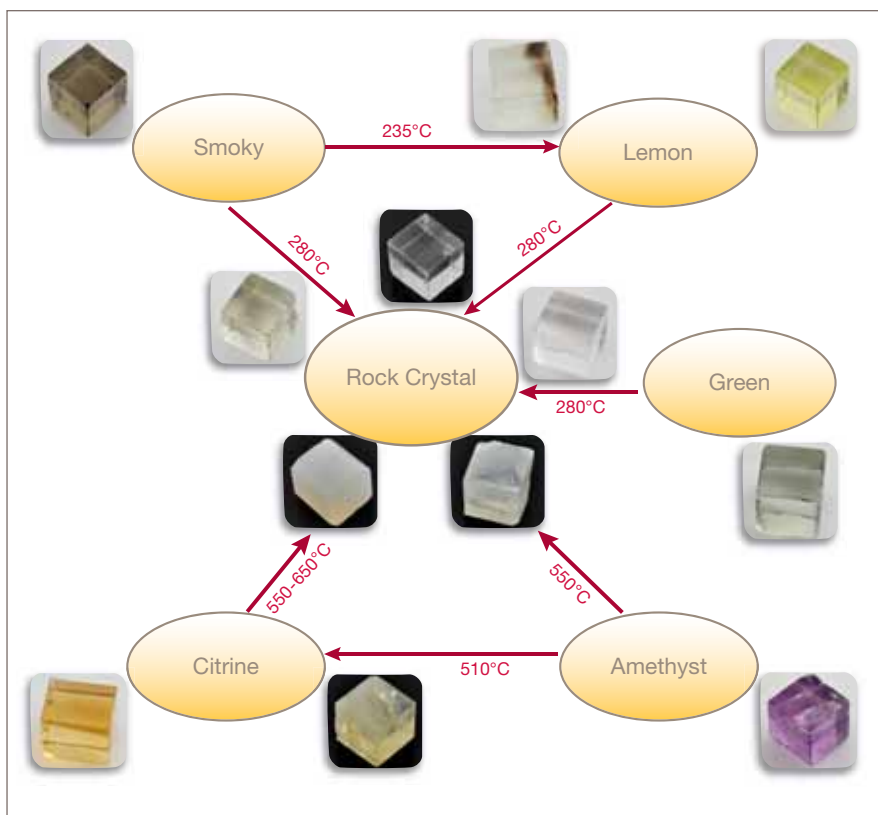
file. In the absence of flux “fingerprints,” it could easily have been mistaken as natural. The specimen was conclusively identified as synthetic by its infrared spectrum, which did not display any water-related features.

A green quartz contained “lily pad”-like inclusions. The presence of color zones/planes perpendicular to the optic axis indicated synthetic origin, which was confirmed by FTIR analysis.

A dark bluish green serpentine was remarkable for its purple transmission in fiber-optic light. The exact cause of the purple transmission could not be determined, but it appeared to be the presence of minute particles arranged in planes. The specimen also displayed a strong absorption in the yellow-to-green region of the desk-model spectroscope.

Other interesting materials included a synthetic sapphire with natural-appearing milky zones, a fluorite with corundum-like color zones, and glass specimens with transparent included crystals.

Changes in color are produced by heating various colors of natural or synthetic quartz, as shown here for natural samples.



SPECTROSCOPIC EXAMINATION OF COMMERCIALY AVAILABLE QUARTZ VARIETIES: A GEMOLOGICAL PERSPECTIVE

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The lack of inclusions and visible growth features (color zoning) makes the separation of colorless natural and synthetic quartz quite challenging. Colorless quartz (rock crystal) can also be produced by heating other natural or synthetic quartz varieties, such as amethyst, citrine, smoky, green (prasiolite), and greenish yellow (lemon). Rock crystal is the purest variety of quartz, but it often contains Al³⁺ impurities for which the charge imbalance is compensated by a nearby interstitial alkali ion; this is a precursor for smoky quartz, which is produced by natural or artificial irradiation. Iron impurities result in green (Fe²⁺), yellow (Fe³⁺), or violet (Fe⁴⁺) colors.

Infrared spectroscopy provides useful data for differentiating between natural and synthetic quartz, while also identifying the original color variety. In our study, the OH, Al-OH/Li, Al-OH, Si-O/Al-OH, and Si-O related bands at ~3593, 3480, 3379, 3305, and 3198 cm⁻¹ consistently appeared in natural rock crystal, while the 3584, 3421, 3297, and 3198 cm⁻¹ absorptions were pre-

sent in synthetic rock crystal; the most important band for distinguishing natural from synthetic material was at 3480 cm^{-1} . IR data also help differentiate between natural and synthetic versions of other colored varieties and whether the color is natural or produced by heating.

IR AND UV-VIS SPECTROSCOPY OF GEM EMERALDS—A TOOL TO DIFFERENTIATE NATURAL AND SYNTHETIC STONES, AS WELL AS GEOGRAPHIC ORIGIN?

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Research on emerald's characteristics and origins is of great importance to the gem industry. We tested the usefulness of two spectroscopic methods to (1) distinguish synthetic from natural emeralds, (2) discriminate between the different provenances of natural emeralds, and (3) identify the various types of synthetic emeralds. Using UV-visible and Fourier-transform infrared spectroscopy, we investigated 133 emeralds of natural or synthetic origin and, for the natural stones, known provenance. Based on our spectroscopic observations, we were able to assign 78% of the emeralds to their proper origin. We identified every synthetic emerald and recognized all natural Colombian emeralds as well as all flux and hydrothermal synthetics. We also observed characteristic features in 86% of the Zambian emeralds.

EXTREME CONOSCOPY

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Conoscopy is an important yet sometimes challenging gemological technique for locating and identifying interference figures in gem materials. Using fixed polarizing filters, combined with mini- and micro-sized transparent, colorless spheres singly and in multiple arrays, demonstrates: (1) typical uniaxial, uniaxial quartz "bull's-eye," and biaxial conoscope images and their crystallographic relationships; and (2) uniaxial versus bull's-eye figures in Brazil law-twinned amethyst or ametrine.

Preparation—Uniaxial: Stack two sticky-backed polarizing filter sheets in crossed-polar orientation with the glue sides facing each other. Place polished quartz and tourmaline slabs (looking down the optic axis) on the stacked filters and trace their outlines. Cut the traced shapes from the marked filters and peel the protective plastic from the glue and non-glue sides. Next, fit and adhere the filters to opposite sides of each mineral slab, maintaining crossed-polar orientation. Each slab is now fixed with its own polariscope.

Preparation—Biaxial: Locate one optic axis in a danburite

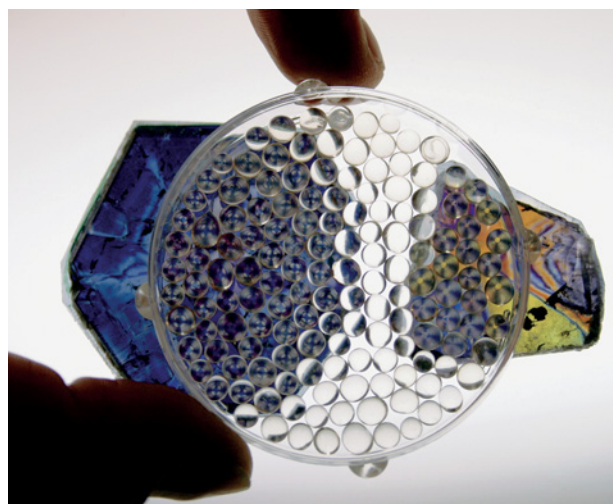
crystal by positioning it horizontally between crossed polars and rolling the horizontal crystal until a prism face exhibits interference colors. Adhere the fitted crossed-polarizing filters on this prism face and its opposite face. The danburite crystal is now also bound within a polariscope.

Sphere Array: Line the bottom of a plastic Petri dish with mini- or micro-sized spheres. This is now a single-plane, multi-conoscope unit for unaided or magnified viewing.

Process: Place the filter-bound specimens over a diffused white light source such as a pocket torch or light table. Interference colors will be evident. Alternately place larger individual spheres and the multi-sphere arrays over each specimen. Compare the various figures that appear in the spheres. This method is recommended as an adjunct to conventional conoscopy.

The many advantages of fixing specimens in a polariscope include: (1) easy specimen manipulation for better observation; (2) connection of crystal orientation and optic axes; (3) simple determination of optic figures; (4) observation of Brazil-law twinning; (5) the potential to demonstrate right- or left-handed twinning in quartz (with the use of retardation plates); and (6) relative ease of capturing photographic and video images of interference figures. Larger sizes of strained spheres (glass, plastic, or Biogel) that would normally exhibit notable strain within a polariscope show minimal strain outside the polariscope when used over the filter-bound specimens.

An array of mini-sized spheres shows multiple uniaxial interference figures across the entire surface of the twinned amethyst slab on the left. The ametrine slab on the right exhibits typical uniaxial figures in Brazil law-twinned zones as well as uniaxial bull's-eye figures in untwinned areas. Both types of figures are visible in the amethyst, showing that it can exhibit twinned and untwinned zones in the same crystal. Photo by S. M. Gumpesberger; specimens courtesy of the Royal Ontario Museum, Toronto, Canada.



DETERMINING THE CHEMICAL COMPOSITION OF GARNETS USING RAMAN SPECTROSCOPY

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Garnets are a group of minerals with diverse chemical compositions and a multifaceted impact on the geological and gemological sciences. Chemical composition is critical to the identity of a garnet's species, such as andradite (demantoid), grossular (tsavorite), almandine, pyrope, or spessartine. Garnet composition is typically determined using an electron microprobe or mass spectrometer. In recent decades nondestructive Raman spectroscopy has been used to identify crystalline materials by observing their vibrational modes. Forty garnets, representing all six major species, taken from RRUFF project samples (<http://rruff.info>), were analyzed to develop a technique that correlates the Raman modes of a garnet with its chemical composition. Chemistry was determined by electron microprobe, and Raman spectra were measured using a Thermo Nicolet Almega microRaman system or an open-access, custom-built Raman instrument. A correlation matrix was created to correlate the shifts in Raman peak position with changes in chemical composition.

This approach can characterize garnet samples with 15 chemical compositional variations using six Raman modes. The method was accurate to within 3% of the electron microprobe calculation of bulk chemical composition, and it correctly identified all species of garnet. This technique makes it possible to determine the chemical composition of garnets nondestructively and relatively inexpensively, and made the identification of garnet group species much faster and easier than with the use of microprobe analysis.

CIRCLE AND SPOT FORMATION MECHANISMS AND CHANGES IN LUSTER, COLOR, AND ROUNDNESS OF CULTURED PEARLS BY GRAFTING METHODS IN *PINCTADA MARGARITIFERA*

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This study investigated factors affecting the quality of cultured pearls, such as circles, spots, and irregular shape, luster, and color. Some pearl mollusks show phenomena similar to circle and spot marks on the nacreous part of their inner shell, and changes in shape, luster, and color have been reported by pearl-grafting technicians and farmers. Between 2006 and 2009, a total of 4,011 cultured pearls were examined for their quality, of which 828 with

circle marks were chosen for the experiments. As the pearl industry does not have a unified grading standard, the author adopted the GIA grading system. A GIA-educated pearl grading expert was employed to assess quality, and grafting operations were conducted by a highly regarded retired master technician.

The results indicated that circles most likely form during the first, or "virgin," cultivation. The harvest from regrafted *P. margaritifera* mollusks ("seconds") showed fewer instances of circling, and circles were less prominent.

It is widely speculated that circles form because of rotation or movement of the cultured pearl inside the pearl sac, and that circled products are found more often in younger, more muscular mollusks. According to this theory, the rotation or movement of the cultured pearl should produce non-linear or sinuous marks. This study found no such sinuous patterns among the several thousand samples examined, with only a few showing circles that crossed or overlapped. Virtually all had perfectly "ringed" or linear forms. The circle marks were directional, perpendicular to the axis of rotation, and parallel to one another. This suggests that an implanted piece of mantle tissue propagated directionally, and that the newly formed pearl sac could represent groups of directionally formed epithelial cells.

Thus, the author proposes that aligned groups of cells have similar or identical functions in nacre secretion capability, which develops into circle marks. This hypothesis would shed light on a century-old myth about circled pearl formation and possibly unite current theories on the mechanisms of mantle epithelium cell proliferation and gene-controlled nacre crystallization processes.

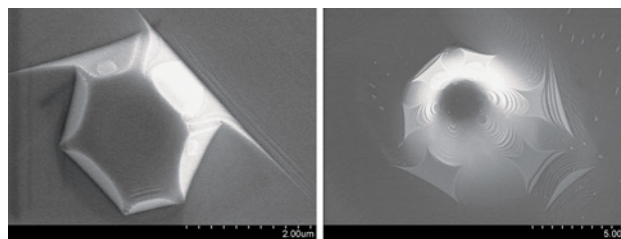
Another finding of this research concerns differences in formation between circles and spots: While most of the circles appeared to have originated during the virgin pearl formation, spots tended to occur in pearls cultured from mollusks that had been regrafted. The results from three years of consecutive grafting experiments further revealed that roundness increased in the "seconds" and "thirds" compared to the virgin cultured pearls, while luster and color tended to fade.

THE OBSERVATION OF DEFECTS AFTER THE PRETREATMENT AND SIMPLE HEAT TREATMENT OF RUBY

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Ruby is commonly pretreated to remove unnecessary impurities before heating. We have developed a hydrothermal pretreatment method, using a mixed-acid solution (10HF-3HCl-2H₂SO₄) at 200°C for 72 hours, that eliminated impurities faster than the process commonly used. The technique affected not only color and



After heat treatment, alumina particles with hexagonal or pyramidal shapes were visible on the surface of this ruby that had undergone pretreatment.

clarity, but also the weight of the stones after treatment.

We examined the surface features of rubies of various origins (Mozambique, Madagascar, Myanmar, Vietnam, Sri Lanka, and Cambodia, as well as a Verneuil synthetic ruby for comparison) before and after the pretreatment process, and then after heat treatment. After pretreatment, we observed several differences in visible surface defects and solubility according to sample origin and quality (i.e., the amount of inclusions and of hydrated alumina minerals such as diaspore, boehmite, and bauxite). The natural rubies showed various surface defects (etch pits, pores, and cracks) when viewed with high-magnification (SEM-EDS); the pores were formed by the dissolution of hydrated alumina impurities. FTIR analysis prior to pretreatment indicated that the higher-quality rubies contained less alumina impurities.

During hydrothermal pretreatment, the alumina was dissolved and precipitated on the surface as a visible white powder. After simple heat treatment at 1600°C, the alumina particles showed hexagonal or pyramidal shapes, depending on the quantity of Fe. For rubies with a higher Fe content, the particles took a pyramidal shape; low-Fe samples exhibited hexagonal pillars. We observed that, in addition to the formation of alumina particles, heating helped heal some of the etch pits, pores, and micro-cracks.

OPERATIONAL CONSIDERATIONS OF EDXRF, LA-ICP-MS, AND PHOTOLUMINESCENCE TECHNIQUES IN THE ANALYSIS OF PEARLS

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The gemological characterization of pearls requires knowledge of their internal structures (microradiography and/or computed microtomography) and chemical composition (in particular, Mn and Sr) to help differentiate between freshwater and saltwater environments. This information also plays a role in identifying the producing mollusks. Modern analytical techniques such as EDXRF spectroscopy, LA-ICP-MS, and photoluminescence (PL) are used to detect Mn and other trace elements at various sensitivities and sampling depths.

EDXRF spectroscopy, a nondestructive technique, typically provides semiquantitative or quantitative results for Mn and Sr

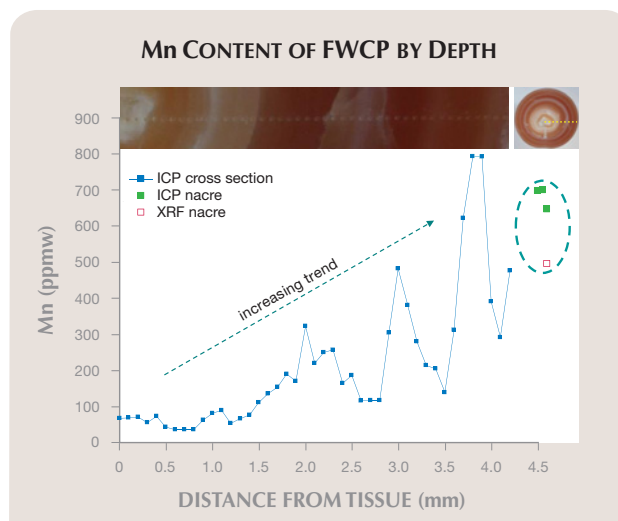
over a circular sampling area of 1–3 mm in diameter. The conventional technique of X-ray fluorescence imaging is capable of sampling through the whole pearl at elevated X-ray energy. However, the technique does not directly provide quantitative information on chemical makeup to differentiate pearls in the way that EDXRF permits.

LA-ICP-MS, which leaves tiny, submillimeter pits in the sample's surface, offers high sensitivity and covers a greater range of elemental concentrations. Yet it only samples the outermost layers of the pearl.

PL spectroscopy is known to be highly sensitive to trace amounts of elements down to the parts per billion (ppb) level. Laser-induced PL spectroscopy is a convenient extension of Raman spectroscopy during pearl analysis.

In this study, the detection depth of EDXRF was examined initially by placing a piece of lead (impenetrable to the X-ray beam) on sections of cultured pearls of various thicknesses. The results suggested a maximum penetration depth of about 1 mm. However, further tests on Akoya bead-cultured pearls proved that the actual detection depth for Mn was much shallower, at well below 500 µm. To illustrate the potential problems of this limited sampling depth, three freshwater non-bead cultured pearls were cut in half and elemental analysis was performed throughout their cross sections by LA-ICP-MS. The results showed unequal distribution of Mn concentration from the center to the surface of these cultured pearls. Moreover, the amount of Mn coincided with the samples' growth rings and color variations at regular intervals. This kind of information cannot be obtained if only the surface nacre is analyzed by EDXRF and

Natural variations in the amount of trace elements present within the internal growth structures of pearls are shown in this LA-ICP-MS data for Mn content taken from a cross-section of a freshwater cultured pearl.



LA-ICP-MS. Finally, a preliminary study was performed on the sampling depth of PL by placing a piece of ruby beneath the cultured pearl samples. The presence of ruby's characteristic luminescence peaks for thicker cultured pearl samples indicates that laser PL analysis occurs throughout the nacreous layers deep into the samples, unlike EDXRF and LA-ICP-MS techniques. The potential for laser PL to be a more useful technique in pearl analysis therefore exists.

In conclusion, these studies provide comparative findings on cultured pearls examined using the methods mentioned above, and show that some operational considerations should be taken into account particularly during quantitative data collection.

EXPERIMENTS ON ANCIENT GEM TREATMENT TECHNIQUES

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Gemworld International, Glenview, Illinois

Many gem treatments commonly encountered today have been known, practiced, and documented since ancient times. In fact, some techniques for altering and improving the natural appearance of low-quality gems predate the gemological literature. These procedures, recorded as recipes, describe both treatments as well as methods to imitate valuable gems using ordinary materials.

Some recipes recorded in the early literature include very unusual ingredients that would not be considered as part of a scientific study today. There is a point in history where science had an unclear distinction from alchemy—between, roughly, the 13th and 20th centuries, “magical” and medicinal use of gems was more common than ornamental use. But contrary to general interpretation of ancients by our modern society, this approach was rarely seen before medieval times.

The ancient treatment techniques include heating, dyeing, oiling, and quench crackling. This study reviews some modern experiments using these recipes. Ancient gem-related texts such as Theophrastus' *On Stones* and Pliny the Elder's 37th volume of *Natural History* are the most notable documents. However, significant yet lesser-known ancient writings such as the Stockholm Papyrus from 400 AD and Al-Biruni's 11th century *In Knowledge of Precious Stones* contain gem treatment recipes that were the focus of this study.

Stockholm Papyrus and Pliny's *Natural History* give details of heat treatment of agates in honey to darken their color. As an early example of a gem treatment, this was widely practiced in Hellenistic and Roman eras to provide suitable carving material for engraving cameos. Schmidt (2009) demonstrated the steps of this procedure and proved that a combination of honey and controlled heating darkened the color and enhanced the layered appearance of agates. This particular experiment also verifies the

capability of ancient lapidaries in using locally available material rather than relying on imported agates, as otherwise suggested by many historians based on Pliny's writings.

Similarly, Al-Biruni gives a recipe for removing dark coloration in rubies. In order to test the recipe, J. Emmett (Crystal Chemistry, Brush Prairie, Washington; pers. comm., 2011) heat treated Mong Hsu rubies at 1100°C for 10 hours in air, precisely as described by the ancient text. The result was lighter and uniformly colored rubies.

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A GEMOLOGICAL COMPARISON OF THE TWO MAJOR OREGON SUNSTONE DEPOSITS

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Gem feldspar naturally colored by copper has been mined for many years in the state of Oregon and has come to be known as “Oregon sunstone.” Two areas produce almost all of this material. The first lies in the southern part of the state, near the small town of Plush. This is a large area in which there are many mines, the largest of which is the Dust Devil. The second site, located to the north, is a single mine known as the Ponderosa. The gem labradorite from these two sources is similar in many respects. Oregon miners, however, have long maintained there are significant differences. This study investigates what differences, if any, there are from a gemological viewpoint.

Physical Appearance: At both sites, the rough material occurs mostly as broken fragments. Many pieces have some unbroken surfaces that show evidence of dissolution. But whereas the Dust Devil feldspar is largely free of matrix, the Ponderosa rough often has a thin coating of opaque reddish brown material adhering to the surface.

Most of the samples recovered from the two deposits are light yellow with no schiller. The Dust Devil material is a deeper yellow and mostly transparent. The Ponderosa material is typically pale yellow—almost colorless—and semitransparent. Both sites also produce yellow stones with copper schiller, as well as red, green, and bicolored material (with and without schiller), but the Ponderosa mine yields a rare deep red feldspar that this author has not seen from the Dust Devil.

Inclusions: Aside from the persistent cloudiness of many Ponderosa specimens, there is no apparent difference in the inclusion suites of stones from the two areas.

Chemistry: Samples from both mines fall within the labradorite compositional range for plagioclase. Yet the Ponderosa material plots closer to bytownite, sometimes even

crossing the border into that species, while the Dust Devil stones plot closer to the middle of the labradorite range. These groupings are distinct but do show a small amount of overlap.

Conclusion: From these and other observations, we know there are clear differences in the gem feldspar from these two locations. These differences may help in understanding the complex formation of these stones, and in detecting and anticipating feldspar treatments.

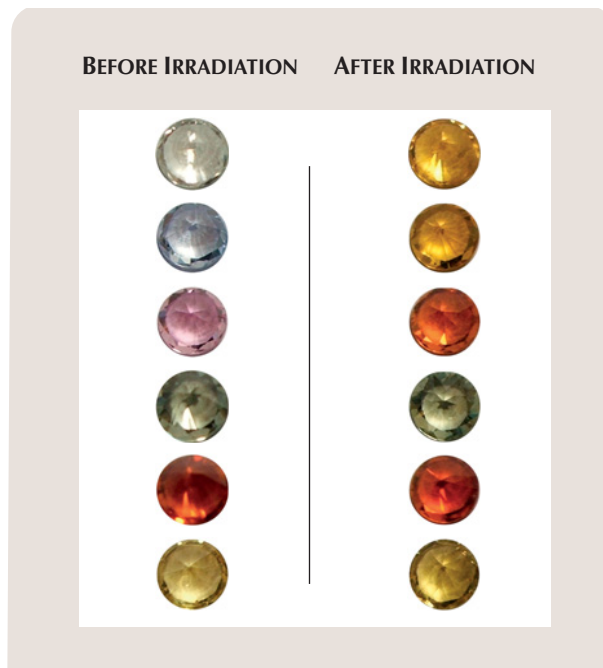
CHANGES IN COLOR AND OPTICAL PROPERTIES OF VARIOUS SAPPHIRES BY ELECTRON-BEAM IRRADIATION

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Sapphire may occur in various colors as a result of intervalence charge transfer (IVCT) depending on the type and combination of transition metals (e.g., Fe, Ti, and Mg) that substitute for Al. Iron may exist in a ferrous (Fe^{2+}) or ferric (Fe^{3+}) state in sapphire. Yellow is caused by Fe^{3+} existing singly or as a pair; charge transfer between Mg^{2+} and a trapped hole can also cause yellow color. Titanium alone cannot produce color, but if iron and titanium atoms are present, a sapphire will be blue. In general, the origin of the blue color is thought to be generated by IVCT between Ti^{4+} and Fe^{2+} , while pink, orange, and green colors are believed to originate through the interaction of the blue color from the IVCT of Ti^{4+} and Fe^{2+} , and the yellow produced by the IVCT of Fe^{3+} - Fe^{3+} (Burns, 1981).

In this study, we investigated changes of color and spectral characteristics in six colors of sapphire (colorless, blue, orange, yellow, pink, and green) after electron-beam irradiation. The irradiation was performed with an energy of 10 MeV and a dose of 3×10^{17} electrons/cm². After irradiation, the colorless, blue, and pink groups (which had somewhat lower Fe content by wavelength-dispersive XRF analysis) changed from their initial color to dark yellow; the green, orange, and yellow groups did not. Interestingly, Ti was not detected in any of the samples by XRF, but Si^{4+} (a donor ion) was detected in all samples. The Si content of the colorless, blue, and pink groups was very low compared to the green, orange, and yellow groups. The important factor is the total amount of Si and Fe within the sapphires of each group. In the case of the colorless, blue, and pink groups, IVCT takes place between the Fe^{2+} and Si^{4+} ions, but since there are fewer Si^{4+} ions to consume than in the green, orange, and yellow groups, it is likely that many extra Fe^{2+} ions remain even after interacting with Si^{4+} ions. The remaining Fe^{2+} ions could not influence the color of the sapphire until electron-beam irradiation transformed them to Fe^{3+} , producing dark yellow coloration.



Shown here are the effects of electron beam irradiation on various colors of sapphire.

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THE GIA GEM PROJECT—AN ONLINE RESOURCE OF INFORMATION ON GEMSTONES

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In 2005, GIA acquired the gem collection of the eminent Swiss gemologist Dr. Edward J. Gübelin (1913–2005). The collection consists of more than 2,800 samples representing 225 different minerals and other gem materials. Dr. Gübelin assembled it over a span of six decades (from ~1940 to 2000) by purchases from knowledgeable dealers and during trips to major gem-producing localities. The items in the collection are now being systematically documented to expand GIA's gem information database.

To help fulfill its mission as a public-benefit organization, and to support its students and staff, GIA is making the contents of the Edward J. Gübelin collection database available on its website (www.gia.edu/gia-gem-project). At present, data on 330 gemstones—including beryl, garnet, spinel, tourmaline, and zircon, among others—can be viewed, and additional groups will contin-

ue to be posted. Each listing, also available as a downloadable PDF document, contains a photo of the gem, standard gemological properties, a photomicrograph of an interesting internal feature, and several types of spectra (visible, infrared, photoluminescence, and Raman, along with EDXRF qualitative chemical analysis). Also provided is an explanation of the data collection procedures used for this project.

This is the first publicly available online database that includes gemological, spectroscopic, chemical, and photographic data gathered on a wide variety of natural gemstones. Although valuable mineral databases do exist, they often do not provide essential information needed by gemologists, and the books published on minerals and gems generally represent compilations of information. By presenting entire sets of data collected from each gem sample, obtained using consistent collection procedures and analytical instrumentation, this database will allow a better correlation of gemological properties. With the preservation of the Edward J. Gübelin gem collection at GIA, samples will be available for characterization as new analytical instrumentation or techniques are introduced, or as new gemological studies are needed.

SPECTROSCOPIC CHARACTERISTICS OF SOME GEM TOURMALINES

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In the gem trade, jewelry-quality tourmalines are usually defined by color rather than by chemical composition or mineral species. Five species of tourmaline are commonly used for gems and jewelry: elbaite, dravite, liddicoatite, schorl, and uvite. In this study, yellowish green, greenish blue, and green to dark green tourmalines were separated into elbaite and dravite using photoluminescence (PL), EDXRF, and in some cases UV-Vis-NIR spectroscopy. The PL spectra of dravite displayed dominant peaks from about 680 to 690 nm (Cr^{3+} and Fe^{3+}), while the elbaite showed main peaks at about 627–633 nm (V^{3+}). The PL data were consistent with the EDXRF chemical data, in that dravite always had a higher Mg content than elbaite. With UV-Vis-NIR spectroscopy, dravite showed strong absorption peaks at ~437 and 606 nm (V^{3+}), whereas elbaite displayed strong absorption from ~715 to 730 nm (Fe^{2+}). For gemologists, these spectroscopic data can be used as preliminary diagnostic tools for differentiating elbaite and dravite.

NEW ARTIFICIALLY ASTERIATED GEMSTONES

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About 40 different gems are known to display asterism (and several trapiche varieties can show fixed stars). The minute, oriented

inclusions of these gems are able to create stars with four, six, eight, 12, 18, or even 24 rays. In addition to the well-known stones with four- and six-rayed stars, this author has encountered some rare new varieties of asteriated gems (color-change garnet, chrysoberyl, and rutile).

Synthetic star corundum has been known since about 1947, and diffusion-treated blue star sapphires first appeared on the market during the early 1980s (Nassau, 1981). The use of artificially etched crystal faces or scratched metal plates (at the base of the cabochon) to create asterism was documented as early as the first half of the 19th century. A relatively new imitation of asterism—stones with stars created by scratching fine lines on the upper dome of the cabochon—appeared about 10 years ago. Such artificially asteriated gems mentioned in the literature include cassiterite, chrysoberyl, garnet, rutile, samarskite (scheelite?), and sinhalite (McClure and Koivula, 2001); black tourmaline (Schmetzer and Steinbach, 2002); and sphalerite (Hyršl and Steinbach, 2009). Artificially asteriated examples of pyrite, iolite, green garnet, chrome diopside, green tourmaline, and sapphire are described here for the first time.

Features used to identify the scratching include:

- Unnatural appearance of the star.
- Lack of oriented, acicular inclusions in the stone.
- Oriented scratches on the surface of the cabochon.
- Incomplete, crooked, or asymmetrical rays of the star.
- So-called “satellite beams” on the stone.
- Extra rays incompatible with the crystal symmetry.
- The star appears sharpest when the camera is focused *above* the surface of the cabochon.

The star in this 4.57 ct iolite was created by scratching fine oriented lines on the dome of the cabochon. Photo by M. P. Steinbach.



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EXPERIMENTS ON HEATING OF BLUE SAPPHIRES WITH BERYLLIUM

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The Gem and Jewelry Institute of Thailand has conducted experiments on the beryllium-diffusion treatment of blue sapphires. Rough corundum samples from both metamorphic and basaltic deposits were collected; they ranged from light to medium blue. Eight to 10 samples were used in each experimental batch. The stones were analyzed specifically for their trace-element chemistry using LA-ICP-MS and other spectroscopic methods such as UV-Vis and FTIR. These properties, as well as visual characteristics (color, zoning, and internal features), were recorded before and after each step of the treatment.

The sapphires were first heated in the presence of beryllium oxide to 1650°C in an electric furnace for 50–80 hours. Almost all the metamorphic samples turned yellow, greenish yellow, or yellow with blue patches; the latter could be further heated to achieve a greenish yellow color. For the most part, the basaltic sapphires showed mild reactions to the experiment, but some of the medium blue samples turned very dark blue.

The sapphires then underwent further heating without beryllium in a reducing environment at 1200–1500°C for 12–24 hours, and were left to cool in the furnace. Their resulting colors were blue, greenish blue, and (especially in the basaltic stones) dark blue. These experiments showed that not all sapphires turn blue with beryllium-assisted heating under these experimental conditions, though longer heating might be needed.

The origin of the corundum was critical to the outcomes, as metamorphic sources yielded better results. Several of the samples showed internal features resembling those seen in Be-diffused blue sapphires in the marketplace.

It is likely that heating with the assistance of beryllium better dissolves mineral inclusions in the samples, especially Ti-bearing phases such as rutile. Such heating also appears to promote a better distribution of blue color-causing elements such as Ti and Fe. Subsequent lower-temperature heating in a reducing atmosphere helps produce blue coloration, and LA-ICP-MS analyses showed that some of the beryllium is driven out of the samples during that step.

NEW TECHNOLOGIES AND INSTRUMENTATION

INCLUSION MAPPING IN DIAMONDS

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Inclusions are part of the life cycle of diamond cutting and evaluation, from the marker's decision on how to cut the stone through the polishing process and clarity grading after the diamond is fully polished. In the rough stage, a frosted surface may obscure the inclusions or conceal their true location. To view the inclusions, the marker polishes flat “windows” on the surface. However, the polisher cannot judge the penetration depth and the final weight of the diamond if he were to polish it out. With regard to polished diamonds, the current method of documenting the structure and location of inclusions relies on an experienced gemologist using a quality microscope or loupe, and the results are often mixed.

Sarin has systems for accurate 3D mapping of the diamond surfaces (rough and polished) and has introduced a new system, Galaxy, to map their inclusions. It covers all types of inclusions: cracks, clouds, crystals, etc., both transparent and opaque. It scans most types of diamonds, from clean to heavily included, as well as transparent, frosted, and even slightly coated. It detects inclusions down to VS size, and even VVS in many cases. As a result, the planner can maximize the value of the polished diamonds to be cut from the rough, while the polisher can better evaluate the option of polishing out inclusions to improve clarity. It also greatly speeds up the clarity grading process by detecting all significant inclusions and generating a 3D model of their distribution in the diamond, allowing the gemologist to focus on assigning a grade.

SYMMETRY: FROM ASSESSMENTS TO METRICS

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The symmetry grading of polished diamonds is based on roundness, variation in angles and alignments, and other parameters. Non-contact measuring systems such as the Sarin DiaMension

allow calculated 3D modeling of the data required to evaluate symmetry with regard to these manufacturing parameters. However, current systems for 3D modeling are not accurate enough to provide reliable, repeatable values. The recently introduced Sarin DiaMension HD uses a high-resolution camera, advanced optics, improved calibration, and a sophisticated algorithm to generate a 3D model of a diamond's shape. It enables the automatic symmetry grading of a diamond in the same manner a proportion scope was once used to evaluate cut.

There are two challenges in assessing symmetry. One is evaluating how well the facets meet (their "pointing"). A standard round brilliant has five types of pointing and a total of 40 corners where facets meet. The asymmetry of the pointing is defined by the diameter of the circle that encloses the meeting point. Once the values for each pointing are known, a grading laboratory can set the upper and lower limits for each grade and pointing type. With these limits, a symmetry grade can be assigned to the 40 individual meeting points. The second challenge is to assign an overall symmetry grade. This is determined by the lowest grade of the various parameters (roundness, table off-center percentage, culet off-center percentage, table/culet alignment, table size variation, crown height variation, pavilion depth variation, girdle thickness variation, crown angle variation, and pavilion angle variation) or a combination of grades. The Sarin device provides both the means and metrics to measure the symmetry features, and a tool to automatically determine the overall symmetry within a grading laboratory's defined parameters.

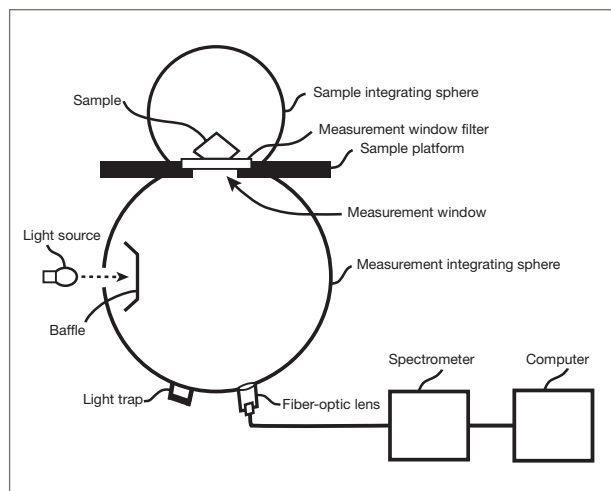
INSTRUMENTAL COLOR MEASUREMENT AND GRADING OF FACETED GEMSTONES

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A dual integrating sphere spectrometer with artificial intelligence (including neural network and fuzzy logic algorithm software) has been developed for the color measurement and color grading of faceted gemstones using the Universal Color Grading System. The spectrometer can also accurately grade fancy-colored diamonds using a modified GIA grading system, as well as green jadeite according to Chinese grading standards.

The dual integrating sphere optic arrangement includes measurement and sample integrating spheres, and a sample platform with a measurement window. CIE Standard Illuminant D65 and the CIE 1931 2° Standard Observer are used. The illuminating/viewing geometry is diffuse/0 degree (d/0) to simulate the geometry of human visual color grading. The measurement integrating sphere provides diffused light to illuminate a gemstone face-down on the sample platform, and the sample integrating sphere serves as a white background. The light reflected from the table plus the transmittance light reflected back through



This dual integrating sphere spectrometer was developed for color measurement and color grading of faceted gemstones.

the stone by the sample integrating sphere is collected by a lens at the bottom of the measurement integrating sphere. The collected light is sent to the spectrometer to measure the spectral reflectance.

The color grading software includes a neural network, a color calculation routine, a CIELAB-to-color-nomenclature look-up table, and a fuzzy logic algorithm. The trained neural network collects physical and optical properties, and outputs parameters for the spectrometer to measure the spectral reflectance. The color calculation routine determines the average color from the measured spectral reflectance. The software then checks the look-up table to determine its average color grade within the Universal Color Grading System. Based on the parameters from the neural network and the average color, the fuzzy logic algorithm determines the true color grade. The Universal Color Grading System optimizes the arrangements of color grades in CIELAB color space. The System has a minimum number of boundaries with a maximum color grade in three color dimensions. Importantly, all color grades are also optimized so that the largest possible color difference of each color grade is minimized. The spectrometer can directly measure visible fluorescence, since the illuminating light is in the whole visible wavelength range. The spectrometer can also accurately measure the color of gemstones that have visible fluorescence, such as the red color of ruby.

AUTOMATED REAL-TIME SPECTRAL ANALYSIS FOR GEMSTONES

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Spectra are now routinely collected in gemological laboratories as nondestructive analytical measurements. They can be vital to revealing the geographic source, color origin, and identity of gem

materials. As treatments and gem synthesis techniques become more sophisticated, gemologists are required to search for increasingly subtle clues that can distinguish natural from synthetic and treated gem materials. Therefore, gems are often subjected to several types of spectroscopy to reveal the histories hidden in their defect configurations and chemical compositions. The most effective testing method is to gather sets of known samples, collect their spectra, and then analyze the peaks in those spectra using advanced chemometric techniques. The confluence of data extracted from the spectra of unknown samples can then be analyzed, and the conclusion will have a quantifiable confidence.

To aid in that analysis, we have developed an innovative peak-finding/fitting computer program called Spectralysis, which can process spectra on an industrial scale. The program can also handle complex spectra, which we define as those having more than 60 peaks, including numerous convoluted peaks, a combination of broad and sharp peaks, and background fluorescence. The analysis extracts quantitative results, enabling users to draw substantiated conclusions regarding origin identification (e.g., natural, synthetic, or treated).

The program performs batch processing so human interaction for each spectrum is unnecessary. This algorithm thus allows researchers to spend less time and resources on data mining and processing, while opening new avenues of research by highlighting previously unknown relationships between peaks.

The variation in peak width and height between Spectralysis and a manual peak-fitting program such as Grams is generally less than 5%. Our experience has shown that an error of up to 10% can be introduced by human variation in calculating the full width at half maximum (FWHM) in Grams. Most importantly, Spectralysis automatically retains peak parameters such as height and area for searching, categorizing, and correlating with other spectra using chemometric methods.

The functionality described here should not be confused with that of library-matching programs—Spectralysis is compatible with them nonetheless—that can distinguish ruby from garnet, for example, but generally not natural from treated gemstones, which is the intended scope of our software. We have demonstrated the program's effectiveness using nonproprietary spectra culled from the RRUFF database (<http://rruff.info>).

DETERMINING THE PROVENANCE OF GEMSTONES USING THE MATERIALYTICS SEQUENCING SYSTEM (M2S)

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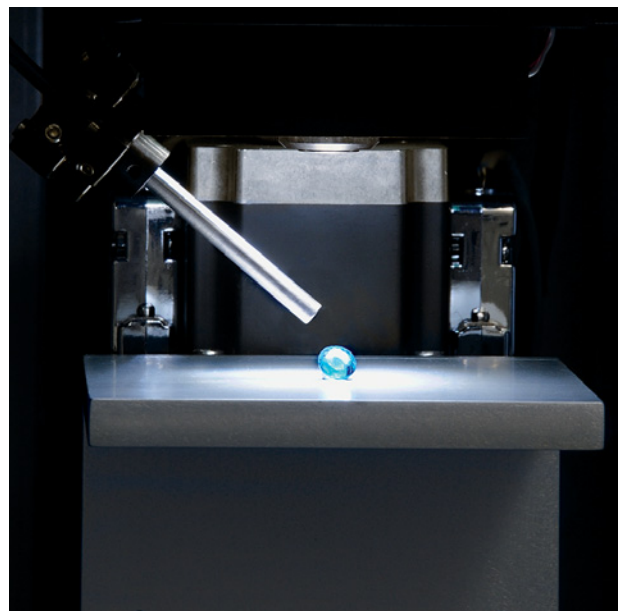
A new quantitative process, the Materialytics Sequencing System (M2S), increases accuracy in identifying the provenance of certain geomaterials, including (but not limited to) beryl, corundum, gold, and tourmaline. Using laser-induced breakdown spectroscopy (LIBS) and unique pattern-recognition software, this system can match these geomaterials to their country of origin with greater than 95% accuracy.

An extensive inventory of specimens—more than 42,000 and growing—has been collected and maintained; the integrity of this sample set is crucial to provenance identification. The Materialytics inventory contains samples from six continents, more than 60 countries, and 225 localities in all.

The M2S system consists of dual Nd:YAG lasers (266 and 1064 nm), an intensified CCD camera, an Echelle spectrometer, and computer software designed to maximize the signal obtained from a sample while minimizing the traces of testing. The laser ablates a small area of the sample, producing a microplasma that emits light in the 200–900 nm range. This light is collected by more than 40,000 channels of the spectrometer. These 40,000 dimensions are then analyzed using pattern recognition software that compares the signature of an unknown specimen to a large database of signatures from thoroughly documented specimens.

The interplay between the variability and commonality of the data from crystal to crystal, mine to mine, mining region to

This blue topaz is shown inside the LIBS chamber of the Materialytics Sequencing System (M2S). Photo © Materialytics.



mining region, and country to country requires a combination of statistical pattern recognition methods (principal components analysis, maximum redundancy analysis, partial least squares, and Bayesian networks) to achieve consistent results over a wide range of samples. M2S integrates these various methods into a single computer program that adapts to each sample, based on the nature of the data, and does not require any human intervention.

RECENT ADVANCES IN SYNTHETIC SAPPHIRE GROWTH

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Hundreds of tons of synthetic corundum are produced annually. This demand is fueled in part by high-technology applications and has driven innovations in sapphire crystal growth techniques. These improvements have resulted in the production of larger, higher-purity, and more defect-free synthetic sapphire material. Traditional crystal-growth methods employed for the production of gem-quality synthetic sapphire and ruby are now being joined by several other techniques—including edge-defined film-fed growth (EFG), heat exchanger method (HEM), Kyropoulos, vertical horizontal gradient freezing (VHGF), and controlled heat extraction system (CHES)—in the quest for larger, more perfect colorless synthetic sapphire.

EFG works by pulling melt through a shaped die in an evacuated furnace. The die is placed at the top of the melt, the melt wets the die through capillary action, a seed is dipped into the melt at the top of the die, and a shaped crystal is drawn upwards (Harris, 2004).

The HEM involves no movement. The seed is placed in the bottom of a crucible, and the filled crucible is evacuated and resistively heated. A low flow of helium is used to keep the seed from melting. The furnace temperature is held constant through the entire growth cycle. When growth is complete, the furnace is slowly cooled and the crystal is annealed *in situ*. The lack of motion and long growth time contribute to low dislocation density (Harris, 2004).

Kyropoulos growth involves seeding an inductively heated melt from the top, rotating the seed and crystal during growth, and crystallizing the melt in the crucible by decreasing the temperature (Dobrovinskaya et al., 2009).

The VHGF method, a variation of vertical Bridgeman growth, also involves no motion of the melt or crucible. The resistively heated melt is seeded from the bottom and has its extremely small vertical and horizontal temperature gradients tightly controlled, resulting in very low dislocation densities (Ahn, 2011).



Rubicon's first synthetic sapphire grown by the Kyropoulos method at their new plant in Batavia, Illinois, measured ~30 cm in diameter. Courtesy of Business Wire.

The CHES technique maximizes large-diameter cylindrical synthetic sapphire. The melt is produced and homogenized over a significant period under vacuum, is seeded from the bottom, and the crucible is vertically translatable. Also movable are the gradient control device and seed-cooling component. To induce crystallization, the melt is cooled from the bottom and the seed is cooled with He, Ne, or H (Gupta et al., 2010).

Most of these new techniques employ conditions that are not ideally suited to the growth of synthetic ruby and colored sapphire. But with the availability of increasing amounts of synthetic sapphire from these continuously improving techniques, it is helpful to have some basic familiarity with these methods and the material produced from them.

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PROVENANCE OF RUBIES AND SAPPHIRES: AN APPLICATION OF LASER-INDUCED BREAKDOWN SPECTROSCOPY (LIBS) AND ADVANCED CHEMOMETRICS FOR THE GEM INDUSTRY

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Rubies and sapphires totaling 572 samples of known origin from 24 deposits in 12 countries (Afghanistan, Australia, Greenland, India, Kenya, Madagascar, Myanmar, Pakistan, Sri Lanka, Tanzania, the United States, and Vietnam) were analyzed using an Ocean Optics 2500+ LIBS system. A 1064 nm Nd:YAG nanosecond laser was focused on a small area of each stone and pulsed at 120 mJ to ablate the sample, forming a short-lived, high-temperature plasma. As excited electrons decayed back to their stable configurations, photons were emitted and transmitted via an optic fiber to a spectrometer that separated the light into its constituent wavelengths, each of which corresponds to a specific element. Analyses were performed in an argon atmosphere to enhance the signal and minimize traces of testing. Average ablation craters were approximately 200 μm diameter; LIBS systems can be customized to minimize damage. Each stone was analyzed 30 times. Raw spectra were processed with a pair of advanced chemometric techniques: principal component analysis (PCA) and partial least squares (PLS) regression using Unscrambler software. PCA was used to simplify the dataset from 13,700 dimensions (each wavelength measured) to two to four dimensions by



These sapphire crystals (0.08–0.40 g) from Ratnapura, Sri Lanka, were analyzed by LIBS. Courtesy of Materialytics.

generating meaningful combinations of wavelengths (elements).

PLS regression models were calculated to characterize half the sample set (trainers). The trainers defined chemofacies, or chemically distinct datasets, which could be separated using the algorithm developed in this study. Because each deposit defines a unique chemofacies, it is possible to predict the provenance of the samples not used in the calculations (verification samples). Using the algorithms developed, tests of 122 verification sapphires and 164 verification rubies yielded correct identification rates of 93% and 90%, respectively. Misidentified samples were the result of poorly characterized chemofacies due to small sample sets. This work demonstrates that the provenance of rubies and sapphires can be determined through chemometric analysis of LIBS spectra.

BUSINESS TRACK

“PIGEON’S BLOOD” RUBY AND “ROYAL BLUE” SAPPHIRE: COLOR STANDARDS FOR THE GEM TRADE

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The Gem and Jewelry Institute of Thailand (GIT), with the cooperation of the Thai Gem and Jewelry Traders Association and the Chanthaburi Gem and Jewelry Traders Association, has

developed a quality assessment system for colored stones, specifically gem corundum. This system considers three major factors: color, clarity, and cut. Research has been conducted since 1999, and the assessment system has been continually refined through input from gem traders and gemologists. The GIT has established colored stone master standards for eight varieties of corundum, including ruby and blue, padparadscha, yellow, pink, purple, orange, and green sapphires. These master stones are oval shaped and at least 0.50 ct each.

The GIT’s standards are based on the Munsell system. The locally-used common color names were converted to the Munsell color codes, which were then modified so that they can be better understood by relying on the color code chart of the ISCC-NBS (Inter-Society Color Council—National Bureau of Standards) system. Moreover, the Munsell color codes can be converted into color notations in two CIE (Commission Internationale de l’Éclairage) systems, CIE L*U*V and CIE L*a*b, that are widely

used in spectrophotometer and other colorimetric equipment.

In addition, the historic terms *pigeon's blood* ruby and *royal blue* sapphire are still ambiguous to a number of traders and certainly unclear to most consumers. Such confusion has impeded potential buyers. Therefore, the GIT's comprehensive research has also focused on standardizing these color descriptors. A color master set of pigeon's blood rubies was established, consisting of 10 master stones in the vivid red range with intense color and medium tone. The color master set of royal blue sapphires contains 10 master stones in the vivid blue range with intense color and medium-dark tone.

These standards for pigeon's blood ruby and royal blue sapphire have been successfully implemented to promote the sale of Thai gemstones both domestically and internationally since 2008.

"TOO PRECIOUS TO WEAR": THE ROLE OF THE JEWELRY INDUSTRY IN CORAL CONSERVATION

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Coral reefs are the most diverse marine ecosystems, second only to tropical rainforests in terms of biological diversity, supporting more than 5,000 known species. Historically, an estimated nine million marine species, or a third of all marine life, lived on the shallow-water coral reefs. But corals and coral reefs throughout the world are being threatened by climate change, ocean acidification, pollution, overfishing, and consumer demand for this attractive material in jewelry and home décor items. Red and pink corals are among the most valuable and widely traded of these species. With the loss of habitat and the disappearance of precious coral from shallow-water reefs, extraction of red and pink corals from deep-water sources for jewelry use poses one of the greatest threats to deep-water reefs. But it can be remedied through changes in the marketplace and consumer behavior. Leaders in the jewelry and home décor industries can help reduce

demand for precious corals by refusing to incorporate them into their designs. Tiffany & Co. and other jewelers are participating in an initiative led by SeaWeb, a nonprofit ocean conservation organization.

SeaWeb's "Too Precious to Wear" campaign seeks to reduce the use of coral as a gem material by:

1. Highlighting the threats posed by consumer demand and an unregulated international coral trade.
2. Working with influential jewelers and designers to bring together leading voices for coral conservation.
3. Raising awareness of coral alternatives that celebrate the ocean without harming it.

The jewelry industry is in a unique position to help prevent further loss to red and pink coral. By simply becoming aware of the issue and looking to corals as an inspiration in jewelry designs, but not as part of the jewelry—leaving vital corals where they belong—designers and retailers can make a difference.

MARKET TRENDS IN A CHANGING GLOBAL ECONOMY

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Emerging markets worldwide have had a significant impact on gemstone prices. The United States has historically been the number one consumer of gemstones, driving prices up or down. This has changed, and we are now seeing countries such as China and India influence prices. The U.S. recently experienced its worst recession in 80 years, and demand for fine gems practically halted there over the past two years. One would have expected gem prices to plummet due to the serious lack of demand. Yet we saw increases, in some cases quite dramatic. The U.S. was no longer dictating the market.

Another key factor that has kept prices for colored stones high is the significant reduction in mining activity. While mining costs increased, overall global demand slowed, thus there was little incentive to keep mines operating. As shortages arose for some gems, the

Red coral (left) is being unsustainably harvested and worked into products such as coral beads (right, 1.3 cm long each) for the international jewelry trade. Alternatives to real coral should be utilized to reduce pressure on this species. Photos by Juan Cuetos/Oceana (left) and Ernie Cooper/World Wildlife Fund (right).



demand from emerging markets continued to push prices up.

Top-quality ruby has always been scarce, and prices have historically been strong and rising. With increased treatments of commercial material and global demand for finer goods, prices have surged even higher in recent years. Premiums for unheated rubies over heat-treated material continue to rise. Although unheated rubies can come from multiple locations, the main source of interest is Myanmar. Despite the U.S. embargo, prices increased dramatically in the past five years mostly due to emerging markets and demand from countries such as China and India.

Prices for blue sapphire dropped in the mid- to late-1990s due mainly to the large production from Madagascar. With the strong worldwide demand and the same economic factors, we are seeing recent price increases for blue sapphire, especially in finer qualities.

Prices for emeralds are rising with better demand in Europe and Asian markets and the weakness of the U.S. dollar against Colombian and other currencies. Also, the maturing attitude toward treatments of emeralds has reduced fears and increased the appetite to buy them.

While we are seeing a gradual return to buying in the U.S., the long-term projection is that cyclical changes will result in at least a partial return to a stronger U.S. economy and more prominent influence on the global gem markets. There is a spreading of wealth globally, with emerging and transitioning economies that did not exist a decade ago. At the same time, we are seeing a demographic shift toward younger consumers outside the U.S. While the U.S. will still have an influence on world gem prices, it will not be as strong as in the past.

Changing premiums on 1 ct Burmese rubies, unheated.

	Commercial	Good	Fine	Extra Fine
2006	0% to +75%	+50% to +75%	+50% to +75%	+50% to +75%
2010	0% to +125%	+75% to +125%	+75% to +150%	+150% to +250%
2011	0% to +150%	+125% to +175%	+125% to +200%	+200% to +300%

GEMSTONE COLOR AS NATURE'S PALETTE: VAN GOGH'S COMMENTARY ON A 111 CT STAR SAPPHIRE AND OTHER GEM-QUALITY CORUNDUM

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The shimmering beauty of blues, yellows, reds, and pinks in gemstones is reminiscent of masterpiece paintings. Vincent Van Gogh's remarkably vivid blues in *The Starry Night* have captivated



The application of color in the visual arts and in nature shows many interesting parallels. Both the Starry Night Sapphire, a 111.96 ct unheated Burmese gem shown here (and recent recipient of a GIA Monograph) and its namesake Van Gogh painting evoke a celestial feel rendered through variations of blue coloration. Although expressed through entirely different media, the messages conveyed by these works of art are remarkably similar. Photo by Robert Weldon.

viewers for the past century. We examined a 111.96 ct Burmese star sapphire with a similar color.

Sapphire owes its color to traces of titanium and iron. The depth of color often varies according to the viewing angle and the inclusions in the stone. For example, the nature and orientation of color banding in sapphire greatly influence the face-up color. The same intense parallel banding of color can be seen as a painting by Mother Nature. Van Gogh's brush often painted feverish, nearly parallel swatches of color, as also illustrated in the 111 ct Burmese sapphire.

Ruby is colored by trace amounts of chromium. The color of a classic Burmese ruby can evoke the shade of red seen in Van Gogh's *The Night Café*. Chromium present in lesser concentrations uses softer brushstrokes, imparting the delicate pink prized in padparadscha sapphires, which can also be seen in the vase of flowers in *The Night Café*.

AN ANALYSIS OF THE DEVELOPMENT AND TAX POLICY OF CHINA'S GEM INDUSTRY

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Over the past three decades, China's decision to open itself to trade with other nations has led to rapid economic growth and a rise in the number of Chinese families with high net worth. With this prosperity, China has become the world's third-largest consumer of luxury goods, according to Goldman Sachs,

accounting for 12% of global consumption. By 2015, that figure is expected to rise to 29%, with China surpassing the United States and Japan as the most important luxury player. China is already estimated to be the world's largest jewelry market, and the expansion of its gold market has attracted more and more high-end brands from overseas. As a result, it is playing an increasingly significant role in the international jewelry trade.

Within this context, it is important to study the impact of the Chinese government's policies with respect to the country's gem market and its future. A newly imposed domestic tax on the gem market, 5% for gold, silver, platinum, and diamond jewelry or diamonds, and 10% for other expensive jewelry or jade, will be a huge challenge in the coming years. Although the initial aim of levying a tax on the gem market is to limit luxury consumption by the wealthy and reduce the income gap between rich and poor, in practice the taxation on these gem products has already had a larger effect on average consumers than wealthy ones. The tax may bring changes in consumption by middle-class consumers, leading to lost tax revenue and reduced financial support for fair income allotment by the government. It may also shrink the gem market and limit the growth and development of China's gem industry.

MINERAL COLLECTORS—AN OVERLOOKED GEM MARKET

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Although numbers are not readily available, mineral specimens are a multi-million-dollar-per-year business. Fine mineral specimens often sell for tens of thousands of dollars. Gem minerals sell for a premium over non-gem minerals, with some specimens offered for millions of dollars. Most dealers in gem rough fail to take advantage of this market. To do so, they must understand which factors mineral collectors care about, and which gem qualities are less important.

Ideally, a mineral specimen should have sharp crystal faces, including a well-formed termination. It should appear complete from at least one viewing direction. Crystal faces should be lustrous and the edges undamaged. Attached matrix is desirable. Color and internal clarity are secondary factors. The most common undesirable feature in a specimen is visible damage, though sawn or polished crystal surfaces are considered worse than broken ones.

Although a mineral specimen should appear completely natural, most undergo cleaning. Treatments such as repair and oiling should be disclosed. Drastic treatments (e.g., dyeing, applying colored oils, and irradiation) detract from a specimen's value. Mineral specimens can be "faked" by artificial assemblage and synthetic overgrowths; fakes have value mainly

as curiosities.

A mineral specimen should have accurate locality information, at the county/state/country level. In general, the more specific the information is (such as mine, stope, or pocket, and date of collection), the better.

Collectors prefer to acquire specimens they can examine in person. For this reason, many specimens are sold during regional, national, or international mineral shows, through private transactions, or at natural history auctions. Mineral dealers also have physical stores, catalogs, and internet sites.

How can a gem dealer tap into this often-overlooked market?

1. Learn about mineral aesthetics. Visit museums and mineral shows, and consider subscribing to mineral magazines such as *Mineralogical Record*, *Rocks & Minerals*, and *Lapis*.
2. Look through your stock. High-quality rough that makes an attractive specimen could be sold to mineral collectors at your usual gem price or higher.
3. Use a different marketing channel for your minerals than you use for your gems, such as a separate website, show, booth, or display case. Or partner with a mineral dealer. Consider selling minerals in a retail venue.

HALLMARKING: A POWERFUL BENEFIT TO THE CONSUMER, RETAILER, AND INTERNATIONAL TRADE

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Since the Middle Ages, many countries have adopted assaying and hallmarking as a means of providing consumer protection and

These examples show the types of information that can be contained in a hallmark. Top left: Czechoslovakia, 1921–1929, 800 silver; top right: France, 1912–1994, 750 gold and 950 platinum minimum standards, tested by touchstone, up to 69% is gold with balance in platinum; bottom: Scotland, 1861–62, 925 sterling silver, assayed in Glasgow, duty was paid, maker's mark on left.



quality assurance with regard to the fineness of precious metal items. Today, assaying and hallmarking are universally recognized as essential to upholding such fineness standards. Just as a diamond grading report or a colored stone identification report provides the consumer with an independent confirmation of a stone's quality analysis, a hallmark is a permanent universally recognized stamp that guarantees that a precious metal item has been assayed and meets or exceeds the indicated standard of fineness.

With gold, silver, platinum, and palladium presently trading at record prices, the practice of under-karating has plagued countries without mandatory hallmarking laws. Austria, during hundreds of years of hallmarking, once had less than 1.5% of its precious metal items declared as under-karated. The country discontinued mandatory hallmarking in 2001, and by 2006 under-karating had increased to 14.9%. The government of India and their Bureau of Indian Standards, recognizing the ever persistent problem of manufactured substandard articles of precious metal, spent over 10 years implementing mandatory hallmarking, effective as of 2011.

Today with globally linked economic and social interaction, the practice of hallmarking will continue to instill consumer confidence in both the domestic and international trade of precious metal items. The Hallmark Research Institute (HRI) is dedicated to the study, education, and publication of reference materials on hallmarks of the world. HRI is a firm advocate for hallmarking and believes that, for the benefit of the consumer and for international trade acceptance, global hallmarking is a feasible goal.

A CASE STUDY IN THE PERCEPTION OF RARITY—RUBY

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Developments from the late 20th century and into the new millennium have had a profound influence on the fundamental perception of rarity in the global gem trade. The concept of rarity as it pertains to ruby, which was once regarded as the king of all gems, has been so distorted as to relegate many of these stones to costume jewelry status.

Methods for enhancing ruby have evolved dramatically during the past 25 years. At no point in history have treatments altered a gem to the extent that is routinely achieved today. The prevalence of treatments has unlocked the potential to market a vast quantity of previously unsalable natural corundum. The implications of this for the perception of rarity and the very definition of a "gem" material should be apparent.

Gemology dictates that a mineral must be *beautiful*, *durable*, and *rare* to qualify as a gem. However, current practices are navigating the international gem trade away from this standard. In recent years a proliferation of treated corundum has been marketed to consumers as "rare" and "valuable." Yet these products are

unsalable without the often substantial alteration achieved from treatment.

Historically, treated stones were not considered natural stones in commerce. This attitude appears consistent until the early- to mid-20th century, when the concept of *natural (but treated)* was promulgated among dealers. The reality is that the ability to own fine gems would not extend beyond the wealthiest members of society if not for treated gems. However, the increasing reliance on treatments has contributed to formation of a bifurcated market in which natural (unenhanced) gem-quality ruby shares few if any characteristics with the vast majority of "ruby" sold as its precious namesake.

The extent to which the global market relies on treatments would suggest that it is no longer the mineral's beauty, but often instead its *potential beauty* to be achieved through treatments that joins durability and "rarity" as a defining trait.

Additional challenges regarding nomenclature have caused confusion in the ruby market. It is not uncommon to encounter a gem that is sold as "unheated" yet has some superficial enhancement (e.g., oiling) that goes undisclosed. Inconsistencies in nomenclature are also seen in the area of provenance testing. Terms such as *Classic Burma*, *Burma*, and *Burma-like* are designed to associate ordinary material with a high-value provenance. Yet it was the historic *rarity* of fine ruby from Burma that led to its recognition as the pricing benchmark by which all other origins were measured. With an abundance of corundum that can be vastly improved by treatments, what image will the term *ruby* create in the minds of consumers in the future?

ABBREVIATED JEWELRY DESCRIPTIONS—A UNIFORM STANDARD

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Shorthand notations are widely used for appraisal and auction jewelry descriptions, yet they are not employed consistently or in a systematic fashion. Standardizing these abbreviations would advance the science of gemology, and the jewelry industry at its most basic level, increasing productivity for all users.

Contract work for the U.S. Department of Justice as administered through the U.S. Marshals Service in the past five years has developed a standardized system of written abbreviations for jewelry descriptions. The system is effective in quickly and concisely communicating levels of quality between professionals, resulting in increased efficiency in appraisals, note taking, inventory, and auction cataloging. Adopting these standards throughout the gem and jewelry industry would foster improved communication within the trade, and would bridge the communication gap between jeweler and consumer.

Here is an example of an auction description of a jewelry item: RING: Lady's 14kt diamond engagement ring; 1 (ctr) rb dia, 5.68mm × 5.72mm × 3.42mm = est 0.76ct, V.Good/G/VS₂; 4 tap bag dias, 4.0mm × 2.0mm-1.5mm = est 0.40cttw, Good/G-I/VS; Size 6.5; * tdmk; 6.84 grams.

Partial listing of jewelry description abbreviations.

Karat	kt	Equals	=
Center	ctr	Estimated	est
Round Brilliant	rb	Carat	ct
Diamond	dia	Very Good (cut)	V.Good
Millimeter	mm	Carat Total Weight	cttw
By	x	Trademark	tdmk

LECTURES—AN INSPIRATIONAL WAY FOR ARTISTS TO COMMUNICATE

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Gem and jewelry artists should explore every path that can lead them to new customers, including telemarketing, email, the Internet, and social media. Another very successful approach is through lecture presentations: events where you can showcase and describe your artwork, while demonstrating your expertise. Giving a well-organized presentation that features distinctive photos, along with exhibiting some characteristic pieces for participants to examine, is an engaging form of communication. Whether it is a highly specialized trade audience at a national event, or your local gem and mineral society, arts group, or civic club, you have an audience that came to listen to you. Face-to-face personal interaction is one of the best ways to find new customers. Potential customers become engaged when they hear your personal story. They want to know when and how you got started, who influenced you, sources of inspiration, and the process of creation. These are the main questions asked time and time again. Your audience is looking for an understanding of the value of your work, an inspiration to start creating their own jewelry and cut stones, a reason to own one of your pieces, or maybe all of the above. They are looking for encouragement and knowledge.

In giving your talk:

- Share your journey, elaborate on your artwork, and disclose techniques.
- Discuss the costs behind the artwork.
- Give a virtual tour of your workshop. Show your tools.
- Describe labor-intensive lapidary and jewelry procedures.



This necklace Marine Ray, featuring a detachable pendant and pin, is composed of carved Larimar (205.0 ct), two faceted chrysoberyls (1.12 carats total) and freshwater cultured pearls, set in 18K yellow gold. Photo by A. Herman and H. Serras-Herman.

- Know the origin and properties of your gem materials.
- Feature new or rare gem materials (e.g., Larimar), and share stories about their discovery, or your personal mining adventures.
- Invite them to visit your website to look at your artwork and calendar of upcoming events for shows and lectures.
- Invite them to your next open studio, show, or exhibit.

Benefits:

- The value of your artwork will be better understood.
- Those previously unfamiliar with your work may become your new customers, while your existing clientele may see a new piece that they would like to have.
- There may be people in the audience from another group or organization who may in turn invite you to make a presentation.
- The host group, the local newspaper, or a national magazine may write an article about the event and your work.

Give an inspirational talk, and your artwork will become memorable. Connect with your lecture audiences and you will find loyal new customers.

POLISHED DIAMOND SUPPLIES FROM SECONDARY MARKET SOURCES

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The supply of polished diamonds from secondary market sources—that is, sales from consumers and estates back into the trade—has increased nearly threefold during the past five years because of two major factors: (1) record prices for gold and platinum have provided an economic incentive for consumers to sell their jewelry items for their metal value, and (2) the difficult economy of the past three years has made the sale of jewelry items necessary for many people. The path of these diamonds can be traced through a number of channels, including retail jewelers, pawn shops, special trade shows, liquidators, a brokers' network and back to the New York and Indian diamond industries. While no exact figures are available, the estimated quantity of diamonds sold through such channels in 2010 ranged between two and three million carats—an output comparable to a major diamond mine.

The potential for recovering diamonds from previously sold jewelry is vast. Surveys of the U.S. diamond jewelry industry conducted between 1976 and 1999 found that more than 400 million pieces were sold on the secondary market during that period.

RECOMMENDATIONS FOR ADVANCING THE COLOR SCIENCE OF GEMOLOGY

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A simple nomenclature change for diamond master stones, from E, F, G, and so forth to D-E, E-F, F-G, etc., along with a tightening of tolerances and the elimination of the mid-grade master, would improve the system of color grading. It would enable industry professionals to determine more precisely which color grade a diamond will receive on a grading report.

Face-up color descriptions of diamonds such as *top white*, *white*, *near white*, and *yellowish white* are more meaningful than the table-down descriptions of *colorless*, *near colorless*, and *faint yellow*. When transparent, colorless diamonds are viewed face-up, the light that is reflected appears white, just as it does when reflected from crushed ice or fallen snow.

The fancy-color diamond system rates the amount of color in a stone, rather than describing its face-up color appearance. The terms *Fancy Yellow* or *Fancy Pink* are incomplete, lacking adjectives to better define their place in color space. The *Fancy Intense Pink* grade is given to diamonds with less color saturation than comparably described colored gemstones. I propose that fancy-color diamonds be described and graded using the same system

that is used for colored gemstones.

In the real world of color, as tone is increased in certain hues, the color we perceive changes. Pink turns red, yellowish pink turns orange, and yellow turns brown. The Munsell Color-Order System, developed in 1905, accurately describes the visual color space on three axes, each scaled with equal visual steps representing hue, tone, and saturation. I recommend that the industry adopt its use.

The Verilux lamps used in the GIA DiamondLite and DiamondDock emit a significant amount of UV radiation. A very strong blue fluorescent diamond will have its true bodycolor appearance and grade improved by three to four letter grades when viewed under Verilux lamps. LED lighting is UV free. Because approximately 15% of the diamonds have fluorescent strengths great enough to be affected, I propose that two different color grades be given on a diamond grading report. One grade would be assigned while being viewed under Verilux lamps, and one while under LED lamps.

When a lab uses a faint blue fluorescent diamond master standard to determine fluorescence strength, it is inaccurate to note a stone having slightly less fluorescence as *None*. I suggest that *None* be replaced with *Negligible*.

Because fluorescence is noted on diamond grading reports for identification purposes, it is important to include a hue with the term *Faint*. I suggest that labs using *Faint* to describe fluorescence change their policies to include a hue in their description.

THE ANAHÍ AMETRINE MINE: A MODEL FOR GEMSTONE SUSTAINABILITY

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In southeastern Bolivia, close to the Brazilian border, lies the world's principal source of ametrine. Once under the control of the Bolivian military, the Anahí mine reverted to private ownership in the late 1980s. Since acquiring the mine, Ramiro Rivero has transformed the custodianship of the mine's resources, its product marketing, and environmental impact.

Anahí is managed by a group of companies, the Minerales y Metales del Oriente Group (M&M), that includes the mining camp concession and sorting facilities. In Santa Cruz de la Sierra, M&M oversees Anahí Jewelry Manufacturing, which includes factories for preforming and cutting as well as jewelry design and manufacturing. M&M also administers retail outlets and franchises across Bolivia under a division known as Joyerías Anahí, SRL.

Rivero's mine-to-market approach is guided by the safety and well-being of the group's 300 employees. Working hours are regulated at the mine, where the miners receive three daily meals,

and leisure time is promoted for greater creativity and better morale. Because of the area's remoteness, telephone service is provided to keep miners in touch with families far away. In addition to a nurse and emergency medical facilities, a local airstrip is available for the rapid transport of injured or sick workers to hospitals in larger cities. Gender equality at M&M's sorting, cutting, and jewelry design plants is also evident. "I want anyone to feel comfortable coming into my office with an idea," Rivero says. "We are a family."

M&M is conscious of the mine's environmental footprint. One illustration of this is the handling of silt from the water canons used to wash the mined material. The silt is systematically separated, dried, and used for brick making or remixed with larger particulates. Also strict prohibition on hunting and fishing on the mine's property is enforced.

The socially and environmentally responsible practices implemented at Anahí serve as a model for other gem localities.



Minerales y Metales del Oriente controls the supply chain of amethyst, citrine, and ametrine from the mine to the market in a sustainable fashion. Here, a worker sorts rough ametrine crystals. Photo by R. Weldon.

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G&G eBrief



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