

DIAMOND IDENTIFICATION

A CASE STUDY OF NATURALLY IRRADIATED DIAMONDS FROM ZIMBABWE

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The identification of artificially irradiated diamonds remains a challenge for gem laboratories. To better distinguish the treated material, it is important to study naturally irradiated diamonds from different geographic origins. In December 2008, the Kimberley Process published its first profile of rough diamonds from the Marange diamond fields in Zimbabwe (www.diamonds.net/cms/Zimbabwe/docs/Recognize_Rough.pdf). The occurrence of greenish colors suggests that some of the diamonds were naturally irradiated.

The Research Department at HRD Antwerp examined a set of seven rough diamonds from Marange. The samples were analyzed using standard gemological methods and more advanced imaging and spectroscopic techniques, such as examination with the D-Scope gemological microscope and DiamondView imaging, as well as IR, UV-Vis, and photoluminescence spectroscopy. Three of these rough samples were polished and re-examined using the same characterization methods.

All the samples showed typical irradiation features, such as an absorption band at 741 nm, which were easily detected with UV-Vis absorption spectroscopy. Some also showed features due to subsequent annealing. Microscopic investigation revealed green and orange radiation stains, a common occurrence in natural diamonds that have been irradiated or irradiated and heat-treated.

RADIO-COLORATION OF DIAMOND

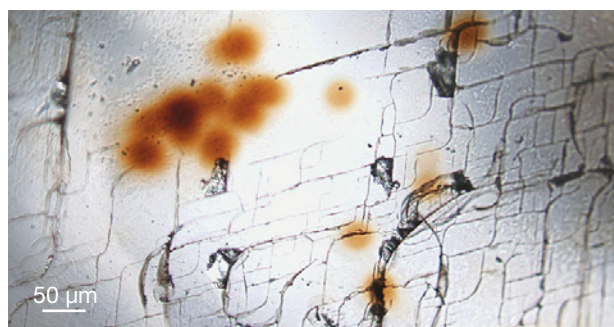
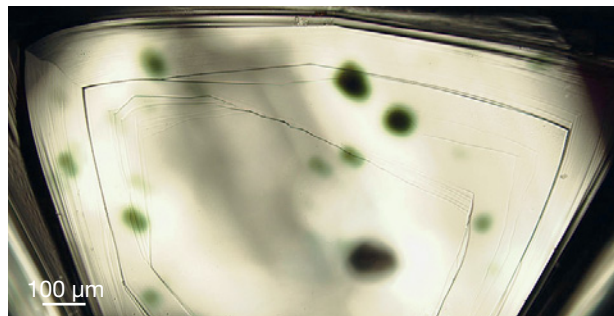
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This study investigated the green and orangy brown spots that commonly occur on the surface of rough diamonds and which are caused by external irradiation by helium ions in the form of alpha particles. These ions are believed to be generated by the decay of radionuclides in radioactive minerals that were located close to a diamond in its geologic past. Helium ions generated in



These radiation-induced surface spots occurred on a diamond crystal from Quebrada Grande, Venezuela (top), and an alluvial diamond from Namaqualand, South Africa (bottom). Photomicrographs by L. Nasdala.

the U- and Th-decay chains have energies in the 4.0–8.8 MeV range; their travel distances in diamond are up to 29 μm . Depending on the sizes (mostly unknown) of the radiation sources and their proximity to the diamond's surface, helium irradiation typically results in blurred round spots with green color. These spots are usually deformed semi-spheres with fuzzy boundaries. With moderate-temperature heating, the green radio-coloration turns orange-brown.

Raman measurements revealed that these richly colored green and brown spots represent elevated levels of radiation damage. The same observation was made on spots produced by the irradiation of diamond plates with 8.8 MeV He ions in a tandem accelerator, followed by annealing experiments. The transformation from green to brown was accompanied by relatively low degrees of structural reconstitution.

Our experiments showed that irradiation with about 1×10^{16} He ions per cm^2 is needed to produce strong radio-coloration. This in turn leads us to conclude that radio-coloration on the surface of natural stones must be a long-term process: A typical spot has a size on the order of $1,000 \mu\text{m}^2$, requiring about 1×10^{11} helium ions. If the helium irradiation emanated, for instance, from a 5 μm uraninite crystal (>80 wt.% U), it would take more than 10 million years to accumulate 1×10^{11} helium ions in the neighboring diamond. In the case of a 10 μm zircon crystal containing 1,000 ppm of uranium, that same alpha dose would require more than 2 billion years,

Editor's note: Underlined author signifies presenter; asterisk indicates keynote speaker.



Significant color changes are produced by HPHT treatment of natural type IIa diamond. The brown diamond is 0.82 ct and the HPHT-treated colorless stone is 0.84 ct. Courtesy of the DTC Research Centre.

which seems implausible. Therefore, radio-coloration is likely due to the action of small grains of strongly radioactive phases that lay adjacent to the diamond for at least several million years.

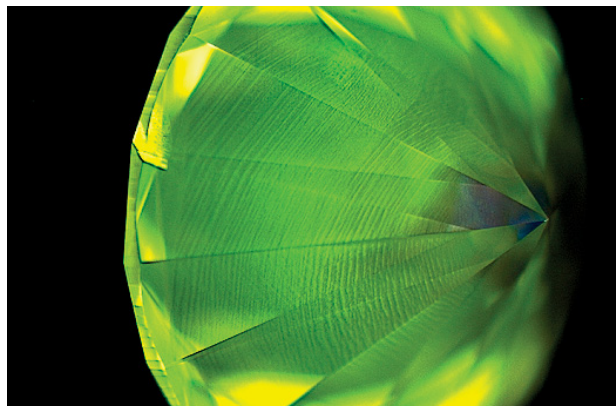
TREATED DIAMOND IDENTIFICATION

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Extrinsic properties of materials are determined by the presence of impurities and defects, and these can be more important than the intrinsic properties. The entire semiconductor industry, for example, is dependent on the ability to add impurities that control a material's electrical properties and remove defects that would degrade the carefully engineered functions. For gem materials that are intrinsically colorless, such as diamond, the presence of impurities and defects can dramatically alter the color and value of the stone.

Many natural diamonds have an undesirable brown hue. Recent research has shown that the brown color is caused by the presence of vacancy clusters, which in natural diamond are created as a result of plastic deformation. For synthetic diamonds grown by the high-pressure, high-temperature (HPHT) process,

Treatments cannot remove some features that reveal that a diamond is laboratory grown. In this 0.56 ct CVD synthetic diamond, the differential uptake of impurity-related defects during growth results in striations that are observable with the DiamondView, even after HPHT treatment. Courtesy of the DTC Research Centre.



the color of the as-grown material is usually determined by the presence of substitutional nitrogen and boron impurities. A range of colors can be produced, including nitrogen-doped yellow-brown, low-nitrogen near-colorless, and boron-doped blue material. Unless rigorous steps are taken to remove nitrogen from the chemical vapor deposition (CVD) growth process, the synthetic diamonds produced will appear brown. There is a strong correlation between the saturation of the brown color and the nitrogen concentration in the process gases. It has been proposed that the brown hue again originates from vacancy clusters, but that the vacancy clusters in the CVD material are different from those in natural diamond. Near-colorless CVD synthetics can be produced by carefully tailoring the growth conditions and excluding unwanted impurities such as nitrogen. Furthermore, adding boron-containing species to the CVD source gas can produce blue CVD synthetic diamonds.

It has been widely reported that the color of both natural and synthetic diamonds can be altered by different treatments. Annealing and irradiation, or combinations thereof, are by far the most common treatments in use today. For more than a decade we have known that HPHT treatment can effectively reduce the coloration of some type IIa brown diamonds, or produce green diamonds from suitable type I brown natural diamond. We have also known that irradiation and annealing can be used to introduce defects that alter the color of a diamond. The types and concentrations of those defects depend on the impurities present in the starting material, the radiation dose, and the annealing conditions. In recent years, there have been numerous reports of diamonds that have undergone multiple treatments to engineer their color.

Although the technological advances in treatments pose some challenges to the identification of genuine natural diamonds, the vast majority of treated diamonds can be rapidly identified by a combination of gemological features, spectroscopic techniques, and the ever-improving knowledge of defect physics in diamond. Annealing under conditions not encountered by natural diamonds and the introduction of large nonequilibrium concentrations of vacancies and interstitials by irradiation damage provide characteristic combinations of color centers that not only indicate treatment but also allow the investigator to infer the nature of the treatment(s). Furthermore, it should be remembered that some telltale features of synthesis or treatment are very difficult, if not impossible, to remove. For example, HPHT treatment of brown nitrogen-doped CVD synthetic diamond can dramatically reduce the absorption in the visible region of the spectrum and change the luminescence characteristics. However, the differential uptake of impurity-related defects during growth on the risers and terraces of surface steps produces striations that are readily observed in DiamondView images of both as-grown and HPHT-treated material, exposing it as CVD synthetic diamond. As the physicist Sir Frederick Charles Frank noted, "Crystals are like people: It is the defects in them that make them interesting."

A REVIEW OF DIAMOND COLOR TREATMENT AND ITS IDENTIFICATION

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The color of diamond is attributed to optical centers, which have selective absorption in the visible light region of the electromagnetic spectrum. Various treatment techniques have been developed to improve the color appearance of natural diamonds by either removing unwanted centers or introducing optimal ones.

Irradiation with or without subsequent annealing has been applied to diamond since the 1950s. Depending on the defect configuration in the starting material, optical centers (including the H2, GR1, NV, 595 nm, H3, and H4) can be introduced, creating a wide range of colors, such as green, blue, yellow, orange, pink, and red. This treatment technique adds color to a diamond, but it cannot remove preexisting colors.

Annealing at high pressure and high temperature (HPHT), a process introduced in the 1990s, is a more dramatic color enhancement. This technique not only removes preexisting colors, but can also produce fancy colors. The major effects of this treatment include the removal of brown color related to vacancy clusters, the release of optically inactive boron, and the formation of other optical centers such as isolated nitrogen, H2, and H3. In addition to decolorizing type IIa and IaB diamonds, HPHT treatment can enhance the blue color in type IIb diamonds and the pink color in type IIa diamonds, or create green, yellow, and orange coloration.

Although irradiation and HPHT treatment have been used separately in the past, recently they have been combined to create colors that cannot be achieved with any single process. While



This 0.24 ct diamond was treated by multiple processes, including HPHT annealing and irradiation, to achieve its attractive Fancy Intense yellowish green color. Photo by C. D. Mengason.

most diamonds in the market that have been subjected to multiple treatments are pink to red, many other colors can also be introduced.

Identification of diamond color treatment has been a challenge in gem laboratories for decades. It has been accomplished mainly by finding the differences in optical defect configurations between known natural-color and treated-color diamonds. These include differences in defect type as well as their concentration, combination, and distribution. Advanced testing methods are required to detect the subtle differences in defect configurations.

GEM LOCALITIES AND FORMATION

THE FUNDAMENTALS IN MINING FOR COLORED GEMSTONES AND MINERAL SPECIMENS

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Mining for colored gemstones and mineral specimens presents unique challenges. Each of the four phases—prospecting, exploration, development, and exploitation—is different from almost every other type of mining. In fact, prospecting is the only phase that shares some characteristics with other commodities. In gem mining, the exploration, development, and exploitation phases usually take place simultaneously: One explores the deposit while developing the structure to find something to exploit. Blasting

could be considered part of the crushing process in most metal mining operations and in sand and gravel quarries. But in gem and mineral specimen mining, one must carefully take the rock apart using a minimal amount of the proper explosive, drill the right pattern for the rock type and the desired outcome, and then detonate the holes in the correct sequence to achieve the proper breakage with minimal damage.

Each gem deposit has its own idiosyncrasies that must be addressed individually; chemical composition and texture can change constantly as mining proceeds, so the owner/operator must be able to read the signs to follow the enriched zone. This usually requires that one person (or a small crew) assume the roles of geologist, driller, blaster, and mucker (i.e., the person who removes the blasted rock). That person will decide on the drilling

direction based on the visual geology, know what they are drilling through by observing the drill cuttings, load the holes far from any enrichment with the proper type and amount of explosives, and detonate them so the main wave front moves away from the enriched area. While mucking, this individual can see if the projection was correct and find any gems that may have been blasted out. Another reason for consolidating the various roles into one person (usually the owner/operator) is that one stone could represent a substantial portion of the entire value of a single pocket. If that stone is stolen, accidentally destroyed, or goes unobserved, significant revenue will be lost.

Each piece must be cleaned, sorted, trimmed, and evaluated before it can be priced. Pricing depends on a combination of size, shape, color (both intensity and purity), and rarity.



Author Jim Clanin excavates a pocket of tourmaline and smoky quartz at the Cryo-Genie mine, near Warner Springs, San Diego County, California. Photo by Brendan M. Laurs.

THE MAKING OF A DIAMOND MINE: WHY EVERYONE CANNOT HAVE ONE

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Diamond deposits are rare occurrences that require specialized geologic and engineering expertise to discover and especially to develop into mines. They take the forms of primary kimberlite/lamproite deposits and secondary concentrations in alluvial deposits. These can be mined as open pits, underground operations, or even undersea. Diamond deposits are generally small to medium in size and may occur in remote and/or difficult-to-access locations. They are defined by the concentration, size, and quality of the diamonds, and whether they are in an environment where extraction costs are less than ore revenue. Many natural and technical considerations affect the balance of revenue and



Shown here is a kimberlite bulk sampling operation (large diameter drilling) at the DO-27 kimberlite, Northwest Territories, Canada, in March 2006. Photo by H. G. Coopersmith.

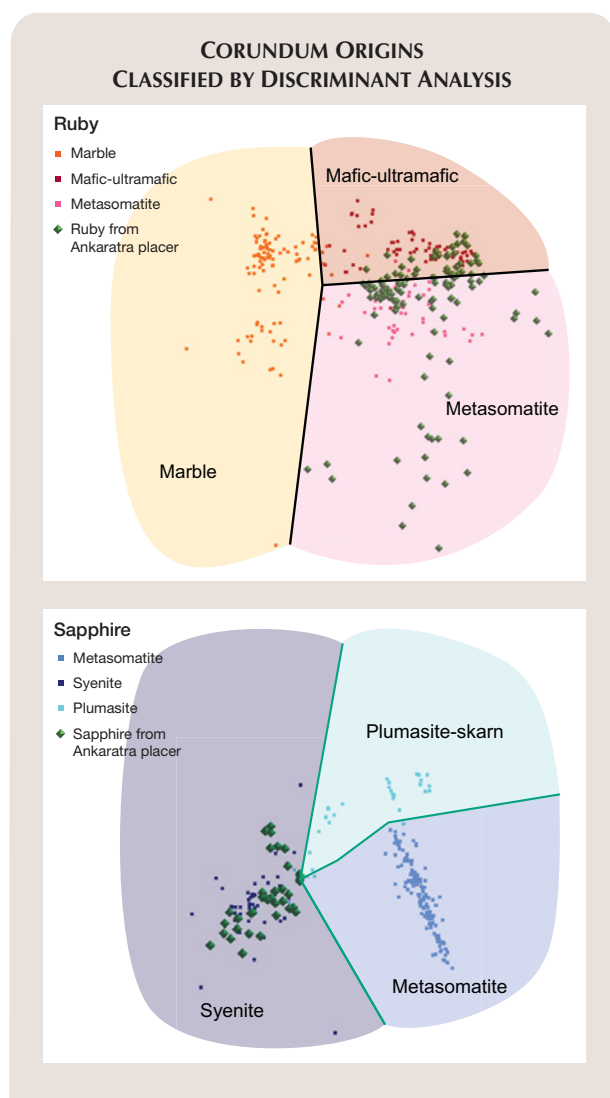
costs. Diamond distribution and size frequency distribution are highly dependent on the nature of the kimberlite and its primary emplacement and secondary distribution processes. A thorough and detailed understanding of the geology produces accurate modeling, which is essential in exploration through feasibility analysis, production, and eventually resource reconciliation. Diamonds are a purely accidental product of several unique geologic processes that form the first part of the puzzle. Mine discovery and feasibility include many factors that form the second part of the puzzle, and only rarely do all the factors align.

STATE OF THE ART IN THE FORMATION OF HIGH-VALUE COLORED STONES

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Whereas diamonds are mined by large international companies and cut and marketed through a well-established distribution network, most high-value colored stones are extracted by independent miners or small companies and sold through less-organized channels. Exploration and grading protocols for ruby, sapphire, emerald, tsavorite, tanzanite, and alexandrite are virtually nonexistent due to the lack of intense research efforts or standardized values on the international exchange. Grading the quality of diamonds on the basis of the 4Cs (color, clarity, cut, and carat weight) is universally accepted and there are virtually no provenance-dependent variations in commodity value. With colored stones, though, geographic origin is an important factor for determining price.

The trace-element (e.g., Cr, V, Ti, Mn, and Fe) and oxygen-isotopic composition of gems depend directly on the geological, physical, and chemical conditions of their formation. These



Discriminant analysis, based on oxide concentrations (Cr_2O_3 , FeO , Ga_2O_3 , MgO , TiO_2 , and V_2O_5) for the main types of gem corundum deposits worldwide, deciphers the origin of rubies (top) and sapphires (bottom) in placers associated with the Ankaratra alkali basalt field in central Madagascar.

include temperature, pressure, fluid composition, redox conditions, and the source of these minor elements. There are still many questions regarding the geology of high-value colored stone deposits, and further research on their genesis is necessary, as has been done on ruby in marbles, corundum in basalts, and Colombian emeralds. Although colored stones may occur in both metamorphic and igneous rocks, the most important primary sources are metamorphic. Deposits of Colombian emerald, marble-hosted ruby, tsavorite, and tanzanite are all evaporite-related, linked to metasedimentary platform carbonates at different geological periods. The association of evaporite-organic matter with black shale and carbonates plays a key role in the formation of

highly saline fluids in open hydrothermal systems such as those that formed Colombian emeralds (basinal and highly saline fluids). High-temperature fluids of appropriate composition in closed metamorphic systems can significantly mobilize the chemical elements required to produce gems, such as marble-hosted ruby in Asia (CO_2 -salty and sulfate-rich metamorphic fluids and molten salts) and tsavorite and tanzanite in the Neoproterozoic Mozambique Belt (sulfur-rich metamorphic fluids).

Rubies form in various types of metamorphic-metasomatic deposits: mafic-ultramafic rocks (M-UMR), desilicated pegmatites hosted by marble or M-UMR, and M-UMR dikes in marbles. The metamorphic origin of the marble-hosted ruby deposits of Tanzania is different from those of Central and Southeast Asia. Most of the Tanzanian deposits are linked to metasomatism of mafic dikes (amphibolite) injected into marbles (the Lukande, Greyson, and Kitwalo ruby deposits in the Mahenge district). The mafic dikes and the marbles were previously altered metasomatically by fluid percolation. The final product is the formation of a Mg-rich phlogopite reaction zone at the contact of both formations. Rubies are concentrated in this zone or in the neighboring marble, or both. Sapphires occur in desilicated pegmatites in M-UMR as well as in magmatic environments such as alkali basalts, syenites, and skarns. Chemical classification of corundum using discriminant analysis of oxide concentrations (Cr_2O_3 , FeO , Ga_2O_3 , MgO , TiO_2 , and V_2O_5) of ruby and sapphire from primary deposits worldwide allows us to determine the most probable origin of corundum in placers. Rubies from alkali basalt placers in the Ankaratra plateau of central Madagascar have two main sources, M-UMR and metasomatites, while the sapphires are of magmatic origin (syenitic source).

Unlike Colombian emeralds, other types of emerald deposits are directly linked to:

1. The presence of pegmatites, aplites, or quartz veins intruding M-UMR or Cr-V-bearing sediments.
2. Pegmatitic pods in anorogenic granites such as at the Kaduna plateau in Nigeria, where the source of Cr is still debated.
3. Shear zones characterized by the absence of pegmatites where emerald is contained in phlogopite or talc-carbonate host rocks (i.e., the Santa Terezinha de Goiás deposit in Brazil and the Swat deposit in Pakistan, respectively).
4. Regional metamorphic rocks, such as those in Austria (Habachtal), Egypt (Jebel Sikait, Jebel Sakara, and Umm Kabo), and South Africa (Leydsdorp), despite the presence of pegmatites (transformed to albitites).

The first of these genetic pathways is the most common. It is characterized by emeralds contained in Mg-rich micaceous rocks known as biotite or phlogopite schists. Generally the pegmatite and the adjacent M-UMR suffer intense fluid percolation and

metasomatism, which dissolves quartz in the pegmatite (which is transformed into a plagioclase of generally albite-oligoclase composition). The M-UMR is converted into the micaceous host rock to the emeralds. Yet the metasomatic processes are highly variable and depend on the P-T conditions, the timing and intensity of the regional deformation, and the extent of fluid infiltration. At Canada's Tsa da Gliza deposit, Be-bearing magmatic fluids from the neighboring granite continuously reacted with the Cr- and V-bearing UMR. Emeralds formed in aplite, pegmatite, and quartz veins surrounded by phlogopites. At the Sandawana deposit in Zimbabwe, the intrusion of pegmatites into the M-UMR, their shearing and boudinage, and their Na-K-Mg metasomatism were all coeval with regional deformation, and emerald formation was syntectonic. At the Ianapera deposit in Madagascar, two coeval emerald deposits are notable: (1) proximal, formed classically at the contact between the pegmatite and the UMR; and (2) distal, formed far from the pegmatite, in shear fractures developed in the M-UMR and filled by emerald-bearing phlogopites.

The genesis of alexandrite is directly linked to that of emerald. Alexandrite is found in placers (the Hematita deposit in Brazil, for instance) but also in primary deposits such as those in the Urals and Spain. The Cr-bearing chrysoberyl is generally associated with phenakite (Be_2SiO_4), which is stable at high Al_2O_3 activity and a rather low SiO_2 activity. A transformation of alexandrite and phenakite to emerald results from an increase in SiO_2 activity, expressed by the equation:



The stability fields of alexandrite and emerald correspond to those required for the formation of desilicated pegmatites (i.e., transformed by dissolution of quartz and crystallization of Na-rich feldspar). In this chemical domain, high Al_2O_3 activity would permit the formation of either alexandrite or corundum if the fluids were saturated with respect to corundum. The Poona deposit in Australia is the only known locality with a ruby, alexandrite, and emerald association.

MYSTERY DIAMONDS—FROM ALLUVIAL DEPOSITS

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Diamond deposits occur in three main types: alluvial, primary (or pipe), and coastal (marine). Before the discovery of kimberlite pipes as the primary source of diamonds, the origin of alluvial diamonds was not known. One theory held that diamonds grew in gravels and were biogenic in nature, since diamond is composed of carbon; some inclusions in diamond were interpreted as being composed of vegetable matter. After the discovery of kimberlite pipes, many alluvial deposits could be traced directly to these rocks, but many others could not, and their precise origin is still a mystery.

The major localities of alluvial deposits are:

1. *Southern Africa*, where the large Vaal-Orange (South Africa), Lunda–Western Kasai (Angola and Democratic Republic of the Congo), and Eastern Kasai (DRC) alluvial deposits can be traced to kimberlite pipes, but the Lichtenburg (South Africa) and Marange (Zimbabwe) deposits cannot.
2. *Equatorial Africa*, where the origin of alluvial deposits in the Central African Republic, northern DRC, Republic of the Congo, Cameroon, and Gabon remains a mystery.
3. *West Africa*, where most of the alluvial deposits in Sierra Leone, Guinea, and Liberia can be traced to kimberlite pipes and dikes, but the origin of diamonds in the Birim River alluvials of Ghana is still unknown.
4. *South America*, where some alluvial diamonds in Rondônia and Mato Grosso (both in Brazil) can be traced to kimberlite pipes, but the origin of most other alluvial deposits in Brazil, Guyana, and Venezuela has not been identified.
5. *India*, where the origin of most alluvial deposits, especially the Golconda deposits, cannot be traced.
6. *Borneo*, with alluvial deposits that cannot be traced to a primary rock and have an unfavorable geologic setting.
7. *Eastern Australia* (same comments as for Borneo).
8. *Canada*, where the origin of the Archean alluvial deposits at Wawa (Ontario) is still unexplained.
9. *The United States*, where alluvial diamond occurrences in California and the Appalachian Mountains remain a mystery.

Explanation of the sources of these mysterious deposits include (1) reversal of drainage, (2) primary rock not yet found, (3) primary rock not kimberlite and thus overlooked, and (4) a different theory of formation (e.g., subduction in eastern Australia and Borneo). None of these explanations is completely satisfactory, and the origin of many alluvial deposits is still unknown.

GEOLOGY, EXPLORATION, MINING, AND PROCESSING OF GEMS AND GOLD FROM PLACER DEPOSITS ON THE MUHUWESI RIVER, TUNDURU, TANZANIA

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Diamond, gold, and various colored stones are found in placer deposits within a delta-shaped basin at the junction of the Muhuwesi and Nampungu rivers near the southern Tanzanian

village of Muhuwesi. Granitic gneiss and granulite of the Usagaran Formation are the primary source rocks of the gold and colored stones, while the diamonds originated from Tertiary–Quaternary volcanic rocks that erupted through the Karoo Formation. The colored stones range from less than 0.2 g to more than 20 g, and good-quality diamonds weighing more than 50 ct have been found. The gold varies from fine dust to nuggets larger than 0.5 cm. Garnet and chrysoberyl are the most abundant gems, and they are used as pathfinder minerals during exploration.

In this swampy basin, trenching exploration using a backhoe is limited to depths of 3–4 m. The Dutch Banka drill is unsuitable because the core samples are too small. Mechanized bore-pile drilling can be used instead to penetrate through large gravel beds, and bulk samples of coarse material can easily be obtained from the large-diameter bailers. The drilling costs are half those of the Banka drill, while the results are much more efficient and accurate. The bore pile drill can be conveniently used as an exploration as well as semiproduction drilling machine for this type of operation.

Mechanized open-pit mining to expose the gem-bearing gravel beds that lie beneath the groundwater table (4–10 m) is too costly and inefficient because of the need to remove the sliding overburden and drain the groundwater. The problem can be solved by using a suction dredge to excavate waste tailings directly into the previously excavated open pit, in combination with a fully equipped mineral processing machine for recovering the final concentrate.

Gravity concentration processing uses a sorting jig to separate coarse-grained gems and gold from associated minerals. The coarse-grained minerals are concentrated on the jig floor, whereas the fine-grained products are discarded as undersized tailings.

This series of jigs is being used in the Tunduru area of Tanzania to separate coarse-grained minerals—including gems and gold—from the fine-grained material. Photo by R. Limsuwan.



Fine-grained gold and small gems can be recovered from these tailings with many practical processing methods.

Entrepreneurs should have a clear understanding of an area's geologic details to insure that mining and processing methods match the scale of the deposit.

GEM POCKETS IN PEGMATITES—A WORLDWIDE STUDY AND COMPARISON

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To locate gem pockets, we must consider the morphology of pegmatite systems with their individual veins and structures. Gem-bearing pegmatite and greisen systems also deserve comparison with other ore deposits. Many of their pocket formation mechanisms and structural features are similar. An igneous rock contains a series of structures and vein types, such as miarolitic pockets in granite; pegmatites in the form of pods; chamber pegmatites (Ukraine, Finland); ascending “drops” of pegmatite (South Platte, Colorado); chimneys, mushroom formations, and stoves (“baking ovens”); fracture fillings in granite or pegmatite; and brittle to ductile wallrock relations. The content and quality of gem species in pockets varies considerably, adding to the unpredictability.

Delicate, undisturbed, relatively thin pegmatite veins (around 1 m thick), such as those at Stak Nala and Biensapi in Pakistan and the Himalaya–San Diego dike system in California, formed in conditions that led to a large number of pockets, with an abundance of high-quality gem crystals 3–20 cm long in the first and second pocket generation. Commonly there are 2–4 generations of gem species in a pocket, and many individual pegmatites have several generations of pockets (e.g., the Karelia beryl mine). Thicker veins with similar characteristics may have pockets localized along thin fracture lines: Virgem da Lapa, Brazil; Darra-i-Pech, Afghanistan; and Alabashka, Russia. Much larger veins—such as at the Stewart mine (California) and Mount Mica (Maine) in the United States, Mawi in Afghanistan, Urucum and Morro Redondo in Brazil, Mokrusha in the Russian Urals, and some pegmatites in the Haramosh/Shigar/Braldu areas of Pakistan—may have significant amounts of very high-quality gem material in sections or single cavities. Adjacent cavities may have a completely different mineralogy. Large pegmatites, due to their scale and mining exposures, may have a less visible and longer multistage complex formation of pockets, ovens, and chimney structures.

Namibia's Erongo Mountains host large pegmatite veins containing gem tourmaline-rich pockets on the Davib Ost farm. Nearby, in the Erongo granite, is a completely different type of mineralization: thin fissures may open into pegmatite veins or pockets/chimneys up to dozens of meters long and a few decimeters wide, with a vertical segregation of gem aquamarine, black tourmaline, quartz, hyalite opal, fluorite, jeremejevite, and other minerals. More hydrothermal-like veins are found at Chumar

Bakhoor in Pakistan and Mount Xuebaoding in China, yielding aquamarine. A detailed study of the Malmberget iron mine in Sweden revealed that many of its structures, fractures, pockets, and crystallizations are similar to those of pegmatites.

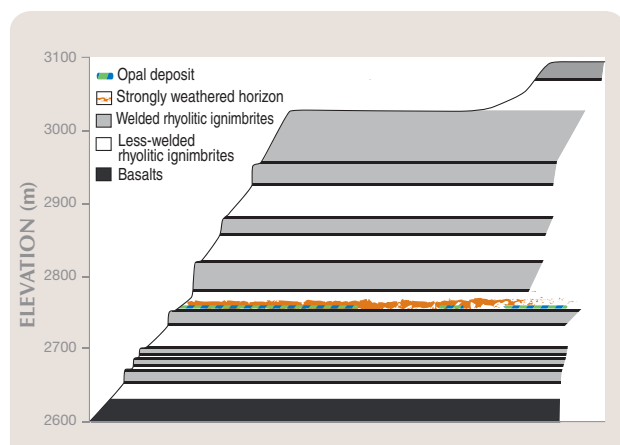
AMAZING PLAY-OF-COLOR OPALS FROM WOLLO, ETHIOPIA—TOWARD A GENETIC MODEL

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The area around Wegel Tena in Ethiopia's Wollo Province is becoming a major producer of opal. Some specimens are very large and display amazing play-of-color. A November 2010 field trip confirmed at least 10 distinct deposits, with many more likely to be discovered in the future. All the deposits occur at the same strongly weathered stratigraphic level in a thick Oligocene volcano-sedimentary series. Each deposit consists of a flat lens about 10–100 m long and about one meter thick, where opal occurs as irregular masses cementing clay gravels or filling in cavities. Many biological features have been observed, such as plant fossils within specimens and opal filling in root-like cavities. We also observed many sedimentary characteristics within the volcanoclastic strata, such as desiccation features, rounded clay-gravels, and conglomerates. This evidence suggests that the opal formed during an episode of weathering in the Oligocene period, in between volcanic emissions.

Opal deposits in Ethiopia's Wollo Province formed within a strongly weathered horizon of ignimbrite (partially fused volcanic ash).



DIAMONDS AND CRATONS—DOES THE RELATIONSHIP HOLD FOR THE CANADIAN DEPOSITS?

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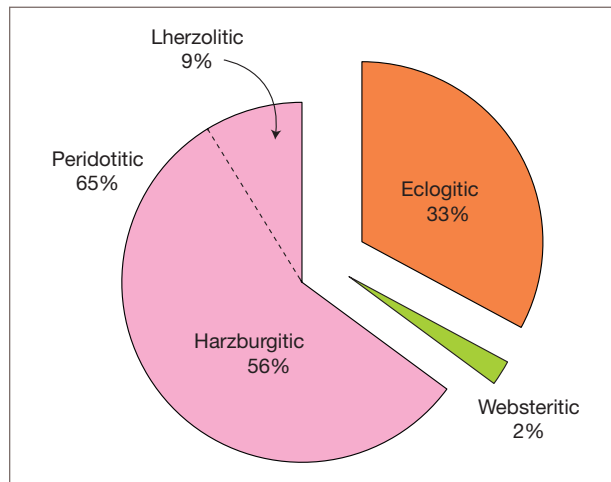
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Diamonds and Cratons. The exclusive association of primary (kimberlite- or lamproite-hosted) diamond deposits with long-term stable continental cores, termed *cratons*, was established empirically in the 1960s and became known as Clifford's Rule. In its original version (Clifford, 1966), Clifford's Rule defined cratons as those cores that have remained stable for at least 1.5 billion years; later revisions pushed this age standard back to the end of the Archean eon, 2.5 billion years ago. Through a combination of geophysical data and geochemical studies—employing mantle xenoliths (mantle-derived rock fragments) and inclusions in diamonds—it was recognized in the 1980s that the ultimate cause for this link between diamonds and cratons lies in unusually deep-reaching lithospheric keels beneath cratons, extending about 200 km into the convecting mantle.

The lithosphere, or rock-sphere, is the nonconvecting outermost shell of our planet, and includes the crust and top portion of the upper mantle. Formed during intense extraction of partial melts in an Archean mantle much hotter than the present one, the residual rocks that make up these lithospheric mantle keels are buoyant, making them stable over time and almost devoid of heat-producing radioactive elements. Consequently, the relatively cool and deep-reaching mantle roots beneath cratons are the only areas on Earth where the lithosphere reaches into the diamond stability field. Today we know that more than 99% of the world's diamond production ultimately derives from subcratonic lithospheric mantle, with only very rare diamonds coming from even greater depth. The role of kimberlite and lamproite magma is to provide a transport vehicle, picking up diamonds during their passage through the deep lithospheric mantle and rapidly conveying them to the earth's surface.

From the study of inclusions in diamonds, three suites of rocks have been identified that may act as a substrate for diamond formation in the lithospheric mantle: peridotite, eclogite, and websterite. Peridotite, named for its high olivine (peridot) content, constitutes the bulk of the upper mantle. Eclogite is the high-pressure equivalent of basalt, the volcanic rock that covers about two-thirds of the earth's surface beneath the oceans. The presence of eclogite in the lithospheric mantle appears related to the closure of ocean basins during past plate tectonic cycles and the associated process of subduction. The websteritic inclusion suite is loosely defined as being compositionally intermediate between peridotite and eclogite. Websteritic diamond sources may have multiple origins.

Silicate and oxide mineral inclusions recovered from more



This chart shows the proportion of diamonds of peridotitic, eclogitic, and websteritic suites, based on the study of some 3,000 inclusion-bearing diamonds from mines worldwide. The subdivision of peridotitic diamonds into a harzburgitic and a lherzolitic (including 1% websteritic diamonds) paragenesis is based on garnet inclusions only.

than 3,000 diamonds derived from worldwide sources demonstrate that peridotite is the most important source rock of diamond. Peridotite accounts for 65% of inclusion-bearing diamonds, followed by eclogite (33%) and websterite (2%). Based on garnet inclusion chemistry, Gurney (1984) established that the vast majority of peridotitic diamonds belong to the harzburgitic paragenesis, a subclass of peridotite characterized by strong depletion through melt extraction (a process in which easily fusible components are removed, leading to low concentrations of elements such as Al, Ca, and Na). Despite being the most important diamond source, harzburgite is a rare rock type in the earth's mantle. It is almost exclusively restricted to Archean lithospheric mantle, where on average about 10% of peridotitic garnets sampled are harzburgite derived.

Analyses of diamond's carbon isotopic composition and nitrogen content have yielded new insights into the actual processes surrounding diamond formation. Diamond appears to form during redox reactions where either carbonate is reduced or methane is oxidized to elemental carbon. Both processes are documented to be widespread, but preliminary data suggest a shift from methane oxidation to carbonate reduction as the preferred mode of diamond formation over geologic time.

Diamonds in Canada. Following the 1991 announcement of the discovery of diamonds at Point Lake and the subsequent exploration and mining rush, Canada emerged as an important producer in 1998 with the opening of the Ekati mine. As of 2011, approximately 700 kimberlites have been discovered across the Canadian Shield. Four mines are operational, and several mining projects are in advanced stages.

Among Canada's cratons, the Slave Province has remained the most important diamond source economically. Its three currently



This map (after Kjarsgaard, 2007) shows kimberlite fields and clusters in Canada. Current mines are located in the Slave Province—in the Lac de Gras area (Diavik and Ekati) and at Snap Lake—and in the Superior Province (Victor mine in the Attawapiskat Field).

operational mines—Diavik, Ekati, and Snap Lake—will produce about US\$23 billion in diamonds over their life spans of typically around 20 years. Based on isotopic studies, diamond formation in the Slave Province occurred in two main phases: between about 3.5 and 3.3 billion years ago for peridotitic diamonds, and about 2 billion years ago for eclogitic diamonds. Peridotitic diamonds account for most of the production of the three current mines, which are located in the Central and Southern Slave; eclogitic diamonds predominate in the currently defunct Jericho mine (Northern Slave). Comparative studies of the Slave and Kaapvaal (South Africa) cratons show that the central and southern portion of the Slave lithospheric mantle has experienced less-obvious secondary modification (“mantle metasomatism”). This observation likely explains the overall less-resorbed nature of Diavik, Ekati, and Snap Lake diamonds (compared to, for instance, the typical De Beers Pool production from South Africa).

Canada’s largest craton, the Superior Province, is host to the Victor mine at Attawapiskat and the advanced Renard project in the Otish Mountains of Quebec. Victor produces diamonds of spectacular quality, and its spatial association with the 1.1-billion-year-old midcontinent rift suggests parallels to the Cullinan mine (formerly known as the Premier) in South Africa, where younger generations of lherzolitic and eclogitic diamonds formed in association with and subsequent to the major Bushveld magmatic event. Preliminary studies on diamonds from the Otish Mountains indicate a “normal” cratonic suite of predominantly peridotitic origin.

Over the last few years, an abundance of diamondiferous kimberlites have been discovered in the northern and western

parts of Canada’s third major craton, the Churchill Province. In addition, Saskatchewan’s Fort à la Corne kimberlite field, located on the small Sask Craton, is approaching economic feasibility thanks to a detailed understanding of its geologically complex diamond distribution. Kimberlites in the Buffalo Hills of Alberta pose a challenge to the rigorous interpretation of Clifford’s Rule that specifies Archean lithosphere as the precondition for primary diamond deposits. At Buffalo Hills, several of the approximately 50 known kimberlites carry significant quantities (up to 0.5 ct/tonne) of overall very high quality diamonds. Yet this area, the Buffalo Head Terrane, does not constitute a craton in the strict sense, due to its intense reworking about 1.9 billion years ago. Similarly unconventional diamond deposits have recently been identified, including the Amazon Shield in Brazil, where the diamondiferous Pimenta Bueno and Carolina kimberlites are emplaced in an area stabilized only 1.8 to 1.2 billion years ago.

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COLORED STONE AND PEARL IDENTIFICATION

GEOGRAPHIC ORIGIN DETERMINATION OF COLORED GEMSTONES

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Colored gemstones such as ruby, sapphire, emerald, and Paraíba-type tourmaline may achieve higher prices when associated with a specific geographic pedigree. Therefore, dealers and collectors increasingly turn to gemological laboratories for country-of-origin analysis. To determine provenance, a laboratory must be knowledgeable about the gems’ geologic formation conditions and types of host rock, crystal growth features, and mineralogical and gemological properties. When the geologic conditions of the primary rock are very similar among several different localities, however, the gemstones’ properties may overlap, rendering origin determination difficult or impossible. Laboratories must meet

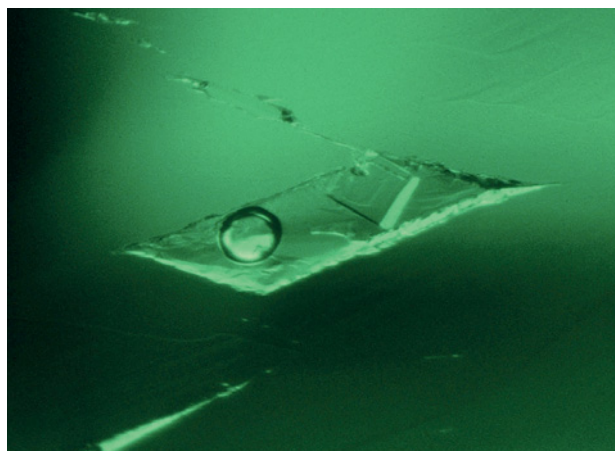
The author collects reference samples in situ from a sapphire mine in Australia (Rubynvale, Queensland). Photo by Terry Coldham.



this complex challenge by extending their observations and analytical capabilities to identify multiple features that yield diagnostic patterns to distinguish between similar sources.

Studies of gemstones from known deposits have been carried out for decades. Inclusions, spectra, trace-element chemical composition, and oxygen-isotope tracers are used to constrain source parameters. But which techniques are most effective for each type of stone? In conducting origin determination, laboratories must characterize gems by nondestructive (or micro-destructive) testing methods, and must also consider the following:

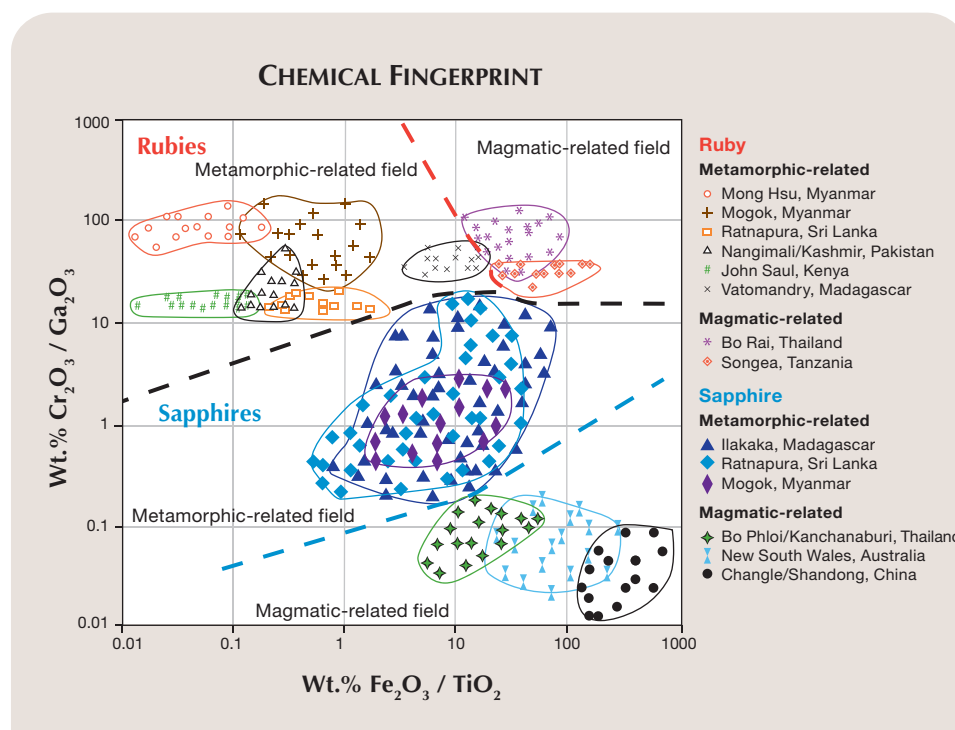
1. A database of properties from samples of known origin requires a reference collection containing numerous representative stones, including those from the newest sources. To ensure authenticity, the samples should ideally be collected from the host rock and/or directly from the producing mine.
2. Internal features (inclusions and growth structures) may help determine a gem's geologic environment, and may provide enough evidence to clearly separate different sources. For example, zircon clusters indicate the host corundum may be from Madagascar, and three-phase inclusions in emerald are characteristic of a Colombian source.
3. UV-Vis-NIR absorption spectra may directly or indirectly reveal the geologic environment (i.e., metamorphic, metasomatic, or magmatic origin of corundum) by their Fe-related features. Some features related to mineral inclusions or molecular vibration due to water can be detected by infrared



Inclusions can help distinguish the geologic environment in which a gem was formed. This three-phase (solid, liquid, gas) inclusion is characteristic of emeralds from Colombia. Photomicrograph by John I. Koivula; magnified 40x.

spectroscopy, making it useful for determining provenance. For example, unheated Mong Hsu (Myanmar) ruby may show dominant absorption in the mid-infrared region that is related to diasporite inclusions. Also, unheated magmatic-type sapphires tend to show strong bands related to Ti-Fe-OH vibrations; these are absent from metamorphic-type sapphires.

4. From a chemical standpoint, patterns of major, minor, and trace elements can reveal a sample's geographic origin.



This diagram shows the chemical fingerprinting of ruby and blue sapphire from a variety of sources.

Certain elements (e.g., Fe and Cr in ruby, and Fe and Ga in sapphire) can be used to establish chemical “fingerprints” of different geologic environments. EDXRF spectroscopy is a rapid technique that is readily available in most gemological laboratories, but it provides limited data compared to more advanced (and expensive) methods such as LA-ICP-MS. Accurately measuring a wider range of characteristic trace elements increases the possibility of reliably identifying geographic origin using two-dimensional trace-element chemical fingerprinting and multivariate statistical analysis. Metamorphic- and magmatic-related corundum can be separated on the basis of $\text{Cr}_2\text{O}_3/\text{Ga}_2\text{O}_3$ versus $\text{Fe}_2\text{O}_3/\text{TiO}_2$. The origin of emeralds can be narrowed down by plotting $\text{Cs}_2\text{O}+\text{K}_2\text{O}$ versus $\text{FeO}+\text{MgO}$ to separate Santa Terezinha (Brazil), Kafubu (Zambia), and Sandawana (Zimbabwe) sources from Panjshir (Afghanistan), Itabira–Nova Era (Brazil), Cordillera Oriental (Colombia), Kaduna (Nigeria), and Swat (Pakistan) deposits. Paraíba-type tourmaline from Brazil, Mozambique, and Nigeria can be differentiated by plotting $\text{Ga}+\text{Pb}$ versus $\text{Cu}+\text{Mn}$ and also $\text{Cu}+\text{Mn}$ versus Pb/Be .

A combination of internal characteristics, absorption spectra, and chemical data obtained by LA-ICP-MS is effective for separating gems from different geographic origins.

AUSTRALIAN OPAL NOMENCLATURE AND ASSESSMENT

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Precious opal (i.e., opal that shows play-of-color) has long been considered one of the most difficult gems to describe, categorize, and appraise. Work on a suitable nomenclature system began at the Gemmological Association of Australia (GAA) in 1995, and the system was published in *Australian Gemmologist* two years later (Smallwood, 1997). At the time of its publication, the nomenclature was supported by all the Australian opal and jewelry industry associations. While CIBJO adopted the system and other overseas associations entered into initial discussions on it, further international acceptance was limited by a lack of effective promotion.

The GAA's standardized nomenclature is based on the different genetic types of precious opal. The present authors propose a new approach to grading precious opal that is based on components of the accepted nomenclature. A simplified terminology clarifies existing industry standards while adhering to both industry practice and the established nomenclature.

The aim of this new approach is to introduce three easily understood categories by which precious opal from any source can be graded, evaluated, and marketed. The 3 C's—*Category*, *Color*, and *Cut*—determine the quality grade. Each category is

evaluated using a point system that quantifies the various quality features of precious opal. *Category* defines the type of precious opal: *Natural type 1—opal*, *Natural type 2—boulder opal*, and *Natural type 3—matrix opal*. *Color* describes the range of quality color features. *Cut* describes the style and quality of cut. Based on this evaluation system, each precious opal can be assigned one of five quality classifications: *Exceptional gem*, *fine gem*, *gem*, *commercial gem*, and *promotional gem opal*. This will promote confidence and understanding of precious opal at all levels, from wholesale to retail and on to the consumer. This combination of opal nomenclature and grading systems provides a complete and universal system of terminology for use in applications such as appraisals and certifications. Myths and mistakes will be eliminated, fostering global appreciation of Australia's national gem.

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AN LA-ICP-MS STUDY OF LAVENDER JADEITE FROM MYANMAR, GUATEMALA, AND JAPAN

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Jadeite jade with colors variously termed *lavender*, *mauve*, or *purple* is among the most prized for jewelry and decorative arts. Studies on the mineralogy of these jades and the source of their lavender color have ascribed the color variously to Mn, Fe, and Ti (Chen, 1999; Ouyang, 2001), and more specifically to Fe^{2+} -O- Fe^{3+} (Rossman, 1974) and to Mn^{3+} in synthetic samples (Nassau and Shigley, 1987). Samples in the American Museum of Natural History collections were studied by electron microprobe and LA-ICP-MS to assess their geochemistry and potential compositional correlations with lavender color and source.

In a sample from the Myanmar's central Jade Tract, relatively intense lavender-colored growth zones showed clear highs in MnO_T (up to 0.15 wt.%; T = total) and low FeO_T (<0.03 wt.%) in nearly pure jadeite (Jd). Jadeite without lavender color, verging on gray or green, typically had <0.02 wt.% MnO_T and 0.01–0.7 wt.% FeO_T in crystals with Jd_{99-88} . Nepheline was a trace phase.

A pale lavender cabochon from Nansibon, Myanmar, proved to be a mix of jadeite and omphacite, with low MnO_T and FeO_T (both ≤ 0.1 wt.%) in Jd_{99-85} ; FeO_T also was low (≤ 1.2 wt.%) in (and for) omphacite. Cymrite was a trace phase.

A lavender jadeite from La Ensenada, Guatemala, occurred in pumpellyite-jadeite and contained ≤ 0.06 wt.% MnO_T and <0.02 wt.% FeO_T in crystals with Jd_{100-98} . “Colorless” jadeite from this locality generally had ≤ 0.01 wt.% MnO_T and comparable FeO_T . Mn was partitioned into the gray pumpellyite in amounts at least three times that of the jadeite in these jadeites. Grossular and albite also were present.

Pale lavender jadeite from Kotakigawa in Japan was Jd_{100-90} with ≤ 0.05 wt.% MnO_T and $0.1\text{--}0.5$ wt.% FeO_T , whereas the “colorless” crystals contained <0.01 wt.% MnO_T and <0.1 wt.% FeO_T . Pectolite inclusions were common.

A comparison of some trace-element concentrations in the jadeite samples is shown in the table.

This study confirms Mn as the lavender chromophore in nearly pure jadeite with relatively low Fe. Although the valence has not been determined, Mn^{3+} is a likely candidate. Mineralogy and trace elements can be used to distinguish lavender jadeites from these sources.

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Trace-element composition (in ppm) of lavender jadeite from various localities.

Element	Jade Tract, Myanmar	Nansibon, Myanmar	La Ensenada, Guatemala	Kotakigawa, Japan
Li ^a	27–60	60–90	50–80	11–34
B	<2	10–20	0.1–4	30–60
Sr	~3 (lavender) 60–150 (other)	10–50	1–6	80–160
Zr	27–60	60–90	50–80	11–34

^a All with no portioning with color.

SPECTRAL DIFFERENTIATION OF NATURAL-COLOR SALTWATER CULTURED PEARLS FROM *Pinctada margaritifera* AND *Pteria sterna*

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The popularity of colored cultured pearls has grown dramatically over the last 30 years. Saltwater cultured pearls (SWCPs) from *Pinctada margaritifera* and *Pteria sterna* are among the most intensely colored in the market today. Their various combinations of body-color and overtone result in a wide variety of color appearances.

New research into their spectral characteristics has led to proposed criteria for identifying which of the two mollusks is the source of a cultured pearl as well as for separating natural- from treated-color specimens. We performed photoluminescence (PL) spectroscopy with green laser excitation in the UV-Vis-NIR region (0.7 nm resolution) on 40 natural-color SWCPs from both mollusks, covering a wide range of colors.

Six color-inducing absorption features were observed in natural-color SWCPs from *P. sterna*:

- A continuous absorption that gradually cut through the visible region with a maximum in the near-infrared (at about 820 nm).
- An absorption from the UV-to-blue portion (330–460 nm, consisting of two bands at 330–385 nm and 385–460 nm).
- Three absorption features at ~405, 460, and 495 nm, and one in the red at ~745 nm.

These same absorptions were also found in natural-color SWCPs from *P. margaritifera*, with an additional band at ~700 nm. Small absorptions at 530, 585, 625, and 680 nm were recorded in natural-color SWCPs from both mollusks, but they had little impact on their coloration.

To our knowledge, only the cause of the 405 nm band is known to date: it is a type of uroporphyrin. The exact color of these cultured pearls is due not to a single absorption, but to the relative intensity of several absorptions. The vast majority of natural-color SWCPs from *P. margaritifera* show an absorption at ~700 nm that has not been observed to date in *P. sterna* natural-color SWCPs. Samples of the latter—even white ones—show a very pronounced PL peak at 620 nm (often accompanied by two others at 650 and 680 nm) that is faint or absent from the spectra of *P. margaritifera* samples. PL bands at ~475 and 530 nm were observed in all colors of SWCPs from both mollusks.

Acknowledgments: The authors thank Perlas del Mar de Cortez, Guaymas, Mexico—as well as Ecole de Greffe (school of pearl farming techniques), Rangiroa, French Polynesia, and the ADEQUA program (Service de la Periculture) and IFREMER (French Research Institute for Exploration of the Sea), French Polynesia—and Centre de Recherche Gemmologique for providing the study samples.

PEARL IDENTIFICATION—A PRACTITIONER'S PERSPECTIVE

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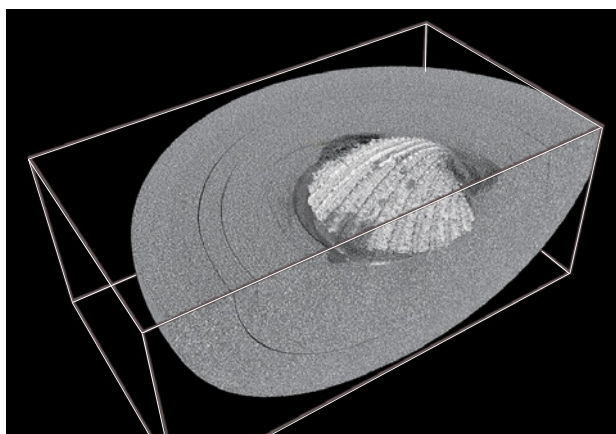
Due to the highly specialized nature of pearl identification, most gemologists do not readily recognize the ongoing challenges in areas such as detecting certain natural and cultured varieties, treatments, and mollusk species. While these issues have long been

compounded by the secrecy that has generally been endemic within the pearl industry, the trend toward greater openness has led to numerous breakthroughs. At the same time, embracing the increasingly expensive identification technologies has placed financial pressure on laboratories.

The current battery of testing methods includes everything from macro and microscopic observations to spectroscopy, chemical analysis, fluorescence, and various forms of X-ray imaging.

1. Visual observation distinguishes nacreous and non-nacreous pearls, reveals the condition of the surface, and determines whether a sample has been subjected to polishing, heavy or light working, or dyeing. Viewing into drill holes may reveal a shell bead or the characteristic warm centers of a natural pearl from *Pinctada radiata*. The non-nacreous surface structures of some pearls may also help determine their source (e.g., scallop, clam, pen, or Melo).
2. Raman spectroscopy can determine whether the surface layers are composed of calcite or aragonite, the nature of the coloring elements, and the presence of some dyes. UV-Vis spectroscopy may help establish whether the color is natural or due to a treatment process, and if luster enhancement has recently taken place.
3. Chemical analyses provide particularly useful information in distinguishing between saltwater and freshwater origin, and in some instances they can identify specific localities within those origins. Chemical data also assist in the detection of dyes and coatings.
4. X-ray fluorescence observations may help separate saltwater from freshwater origins, while UV fluorescence is often useful in determining the type of mollusk.
5. X-ray imaging, still the bedrock of pearl testing techniques, is used to detect the presence of a shell bead and show growth characteristics.

Separating Natural and Cultured Pearls. As growth techniques continue to improve, the separation of natural from non-bead cultured pearls, both saltwater and freshwater, becomes particularly challenging. Traditionally, this identification has involved the interpretation of microradiographic images. For more than eight decades, these images have been recorded on fine-grained industrial X-ray film and examined with magnification (using a 10x loupe, microscope, and custom-built apparatuses). With the need for finer detail and higher-resolution images, combined with the trade's demand for speed and digitized data, laboratories have moved toward high-resolution real-time microradiography and, more recently (when necessary), micro-CT X-ray imaging. Even with these advances, though, other forms of data collection are often necessary.



*This 3D-constructed image (from a micro-CT X-ray scan) shows a scallop shell in the center of a 19.06 grain natural pearl produced by *P. maxima* in Australian waters. Image by Nick Hadland, Nikon Metrology.*

A case in point is the separation of U.S. freshwater natural pearls from Chinese freshwater cultured pearls. Their microradiographic structures are sometimes similar, requiring detailed chemical analyses to assist in the separation. A new problem is the separation of natural from cultured conch pearls, a situation made more difficult by the color instability of conch pearls to X-rays.

Treatment Issues. Pearls may be treated in a variety of ways. The best-known method, though still something of a mystery, is the bleaching of akoya cultured pearls. The pretreatment to this bleaching, known as Maeshori treatment, has become popular with other cultured pearl varieties as a stand-alone process to temporarily enhance luster. UV-Vis spectroscopic techniques have

Chinese non-beaded freshwater cultured pearls (here, 8–12 mm) and U.S. freshwater natural pearls often have similar microradiographic structures, and detailed chemical analyses are required for this separation. Photo by K. Scarratt.



been developed to detect this treatment.

Most dyes can be readily spotted through visual observation, with Raman and chemical analyses providing confirmation. More difficult to uncover are subtle coatings, and UV imaging has proved particularly useful in this regard.

The working of natural pearls has been around for hundreds of years, particularly with natural blister pearls. But with the high prices being paid for exotic natural pearls from the Melo volutes, the practice of working a baroque Melo pearl into a perfectly round specimen has become endemic.

Mollusk Identification. Apart from rare cases, mollusk identification was not a concern as recently as 10 years ago. Today it is an important aspect in determining whether the pearl is cultured or has been treated in some way. An example of this importance is in the identification of natural or cultured pearls from *P. margaritifera* through its unique reflectance spectra when compared with other pearls that have been treated to a similar appearance, or identifying various *Pteria* species and their sometimes unique natural microradiographic structures.

NATURAL-COLOR TANZANITE

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The violet to blue variety of the mineral zoisite took the gem industry by storm after its discovery in 1967. Since then, tanzanite has become one of the four most popular gemstones sold at retail. It is well known that the vast majority of tanzanite in the market owes its color to a relatively low-temperature heating process that transforms the original brown zoisite into tanzanite.

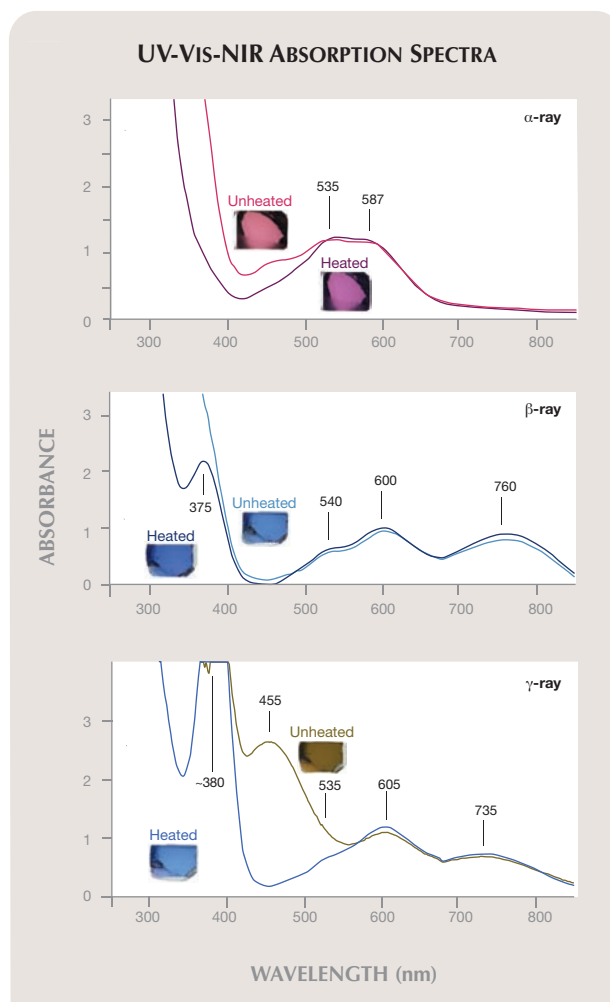
It is also known that a small amount of zoisite comes out of the ground already blue. It was generally thought that this was an extremely small percentage (<1%), but the author's trip to the tanzanite mines in October 2009 revealed a higher proportion, estimated at more than 10%. In all, nearly 300 natural-color tanzanite samples were collected directly from the mine-run at the TanzaniteOne facility and from the group's sightholders. All samples were tested using standard gemological instruments, and advanced analytical tests were performed on a core subset that were fashioned into crystallographically oriented cubes for oriented and polarized UV, visible, near-IR, mid-IR, and Raman spectroscopy. Controlled heating experiments were conducted on oriented cubes and rough, and all data were collected again to record the changes that took place.

The brown color of zoisite correlated to two specific absorption features: an increasing general absorption continuum toward the UV and a broad band centered at approximately 455 nm. The intensity of these absorptions determined whether the zoisite had an overall brown appearance or a brown coloration along only one of the three pleochroic directions. The violet to blue coloration is attributed to V^{3+} in an octahedral coordina-

tion. The elimination of both browning absorptions during heating creates a transmission window at approximately 450–480 nm, which changes the observed color along the gamma pleochroic direction from brown-yellow or brownish greenish yellow to slightly greenish blue. Little to no change was recorded in the absorptions attributed to vanadium.

The change in color of brown zoisite to tanzanite has been attributed by past researchers as a conversion of V^{4+} to V^{3+} . The

Heating of zoisite produced little to no change in V^{3+} absorptions. Along the alpha pleochroic direction a shift in the absorption edge was recorded, while additionally along the beta direction a band at 375 nm became apparent. The most significant change took place along the gamma direction where the shift in the absorption edge revealed another band at ~380 nm and the combined removal of the 455 nm band created a transmission window in the blue region of the spectrum, causing this pleochroic hue to change dramatically from a brown-yellow or brownish greenish yellow to slightly greenish blue.



observed character and annealing behavior of the two browning absorptions in the present study has sparked further investigations into other potential causes, involving lattice defects and color centers. In addition, the data recorded during this study expands that previously documented for natural-color tanzanite.

EXPERIMENTAL TREATMENTS INVOLVING DYE AND HEAT FOR CHINESE FRESHWATER CULTURED PEARLS, AND THEIR DETECTION WITH RAMAN SPECTROSCOPY

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Ten nonbeaded Chinese freshwater cultured pearls (button shapes, 4.11 × 2.71 mm to 4.41 × 2.88 mm) were subjected to five different treatments (i.e., two samples for each process). The effects on appearance and durability were observed, and the samples were also analyzed by Raman spectroscopy. Their original color was white, and the presence of Newton rings (visible with a gemological microscope) suggested they had been previously bleached.

The treatment processes involved:

1. Heating in an electric oven at 250°C for 15 minutes.
2. Dyeing with a hair toner (Redken 03B) for 30 minutes.
3. The same process as in (2), plus heating as described in (1).
4. Dyeing with a hair colorant (Wella Koleston 5/77) for 30 minutes.
5. The same process as in (4), plus heating as described in (1).

The color changes and their effects on UV fluorescence are listed in the table.

Viewed with a microscope, the heated cultured pearls from process (1) showed cracks and brownish color spots around the drill hole. The toner (2) caused a brown rim at the drill hole and “splash” effects beneath the surface. Additional heating (3) led to cracking and surface peelings. The colorant (4) caused a brown rim at the drill hole, and subsequent heating (5) produced cracks with color residues.

Raman analyses were obtained for five of the cultured pearls at the SSEF laboratory using 514 nm laser excitation. All spectra were corrected by a square or cubic baseline subtraction, to eliminate the increasing luminescence and make the pigment peaks visible. Apart from the dominant calcium carbonate vibrational peaks, the samples dyed with toner and colorant revealed distinct Raman peaks between 1800 and 1100 cm⁻¹ that were smoothed out in the dyed

and heated cultured pearls. The untreated cultured pearl showed very weak peaks at approximately 1525 and 1130 cm⁻¹ due to natural color pigments (Karampelas et al., 2007).

Photoluminescence testing with 514 nm laser excitation revealed a general luminescence in all the samples, with a maximum at ~4000 cm⁻¹ (or 648 nm). The untreated cultured pearl showed weak luminescence, ~3–5 times lower than in the treated samples. The luminescence of the heated-only sample was so strong that the aragonite peaks nearly disappeared, and the signals could only be measured by lowering the laser beam's intensity.

Readily available toners and dyes can be used to alter the color of cultured pearls, either alone or in combination with heating. Heating by itself is also effective. Each of the treatments caused damage and changed UV fluorescence reactions. Raman spectroscopy revealed distinct spectral differences between the treated and untreated cultured pearls.

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Effects of treatments on Chinese freshwater cultured pearls.

Treatment		Color	UV fluorescence (long-/short-wave)
Untreated		White	Strong blue/ weaker blue
(1) Heat		Bronze	Pinkish/yellowish in parts
(2) Toner		Brownish gray	Blue in parts/ weaker reaction
(3) Toner + heat		Brownish bronze	Inert to pink in parts/same reaction
(4) Colorant		Brownish gray	Blue in parts/ weaker reaction
(5) Colorant + heat		Grayish brown	Pink in parts/ weaker reaction

DURABILITY AND SAFETY TESTING OF LEAD GLASS-TREATED RUBY AND BERYLLIUM-TREATED SAPPHIRE, AND ENVIRONMENTAL IMPACT ASSESSMENTS

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Tens of thousands of carats of ruby and sapphire recently sold in the world market appear to have been treated using complicated techniques that may involve chemical additives. Many parties have raised concerns about the stability and safety of these treated stones with normal wear, as well as the environmental impact of the treatment processes involved. Researchers from the Gem and Jewelry Institute of Thailand, a public organization, have collaborated with experts to conduct environmental impact monitoring of Pb-glass and Be-diffusion treatments, as well as standard testing on the stability and safety of the products of both. The three-stage sequential extraction procedure suggested by the European Standards, Measurements and Testing Program (formerly the Community Bureau of Reference, or BCR) was selected for this study.

Three forms of metals (acid-extractable, reducible, and oxidizable) were tested. Chemical analyses of the leached solutions and observations of alterations within the samples were carried out at each stage of the experiment by ICP-MS. Lead concentrations in the solution extracted from rubies treated with Pb-glass were much lower than the maximum allowable concentration. Be concentrations in the solution extracted from Be-treated sap-

phires were below the detection limit (~ 0.01 ppm). Thus, we concluded that these treated stones are safe for normal wear. In the durability testing, the gemological properties of both treated groups remained unchanged, though the treated rubies appeared to have lower transparency after prolonged testing.

We conducted further analyses of Pb and Be concentrations in the form of respirable particulates at several home-based factories in Chanthaburi Province. The results showed that lead particulates were only emitted when the furnace gate was opened, with the highest concentrations recorded within the first 10 minutes. The amount of Be particulates was much lower than the maximum allowable concentration in air.

While our studies have shown very little or no impact from these treatment processes, we recommend an efficient ventilation system to help separate the treatment areas from living areas in a home factory.

ARCHAEOGEMOLOGY OF PERIDOT

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The Red Sea island of Zabargad, also called St. John's Island, is perhaps the world's oldest and most famous source of gem olivine, or peridot. Although early accounts attest to knowledge of its existence, and much has been written about Zabargad's geology and modern mine workings, the ancient site was not located until recently. In June 2010, archaeological evidence of occupa-



At left is a biconvex oval peridot ringstone (18.0 × 16.0 × 5.0 mm, Greek, 2nd century BC), engraved with the head of a maenad and mounted in a modern metal setting. At right is a convex oval peridot ringstone (8.5 × 7.4 × 3.1 mm, Hellenistic, mid-1st century BC), possibly depicting Ptolemy XII. Both intaglios are heavily abraded. Courtesy of the Ashmolean Museum, University of Oxford (left), and the Michael C. Carlos Museum, Emory University, Atlanta, Michael J. Shubin collection (right).

tion associated with mining activity was identified by author JAH, including about 150 surface pits, peridot fragments, ruins of dwellings, a well, and pottery sherds dating from the Hellenistic era (323–31/30 BCE) into the Roman Imperial period (after 30 BCE). The archaeological finds correlate with those excavated from the ancient trading center of Berenike, which is situated near Ras Banas on Egypt's southern Red Sea coast, the nearest port to Zabargad Island. Both Zabargad's peridot mine and Berenike were founded by Ptolemy II Philadelphus, who ruled Egypt from 285 to 246 BCE. Under Roman occupation, Berenike rose to prominence as an international entrepôt, exporting peridot and other gems from local Egyptian mines while importing gems from distant sources, including India, Sri Lanka, and possibly points farther east, through the mid-6th century.

A survey of ancient carved peridots in private and museum collections reflects the rising fortunes of Zabargad and Berenike through the 1st century CE. The survey reveals a narrower timeframe of production and fewer surviving examples than previously supposed. Most peridots of this period were cut from relatively large crystals, and all exhibit exceptional clarity and a saturated yellowish green color without any trace of a brownish cast. Although archaeological and textual evidence of Graeco-Roman peridots originating from Zabargad appears compelling, other sources cannot be excluded summarily. In *Natural History* (77 CE), Pliny the Elder describes different sources for several other gems with varietal names that may be peridot, and the gems examined by the author LT are strikingly similar to specimens from other sources, especially Pakistan and Myanmar (Burma).

A provenance study on peridot is in progress at GIA. Samples collected from the ancient mine site on Zabargad and from other sources—including Saudi Arabia, Pakistan, Sri Lanka, Myanmar, and China—may reveal salient data points for future comparison against ancient carved peridots. A definitive determination might also shed light on the mysteries concerning the origins, circulation, and use of peridot in the ancient world.

RESEARCH AND IDENTIFICATION OF NATURAL AND TREATED NEPHRITE IN CHINA

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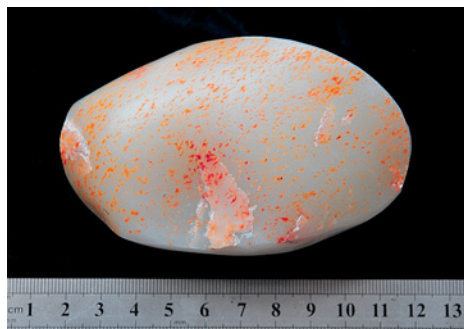
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Nephrite (particularly Hetian jade) is a treasured gem material in China. Its use extends back 7,000 years and is closely connected to Asian culture. Primary deposits are distributed mainly in the Kunlun Mountains in Qinghai Province and the Xinjiang Uygur Autonomous Region. Secondary deposits are found nearby in alluvial settings or desert areas.

With China's rapid economic development, nephrite has become even more popular, and this has been accompanied by sharply rising prices. In addition to the material from Qinghai and Xinjiang, various white and colored nephrite jades from other countries, as well as treated and imitation nephrites, are appearing in Chinese markets. Due to the rarity and value of white nephrite pebbles that display a surface coloration, various imitations and treated-color products (dyed, heated, or otherwise enhanced) are also appearing.

To both guide and support the nephrite jade market, the NGTC has organized a research team to perform a systematic investigation of this material. This involves both field studies of the nephrite sources and laboratory examination of samples using a variety of techniques. The samples are characterized on the basis of their morphology, surface microstructure, spectroscopic features (visible, infrared, and Raman), and chemical composition. The surface microstructures of thousands of samples have been analyzed using high-resolution digital imaging techniques. We have found that natural nephrite pebbles can be recognized by their surface microstructures, which are apparently caused by geologic processes such as glacial or water transport and weathering. For example, chatter marks caused by glacial abrasion and plucking processes occurred on the surfaces of the pebbles. The natural coloration on the pebbles' surface is formed mainly by iron-containing secondary minerals that occur along grain boundaries. Surface-treated samples can be distinguished by differences in surface microstructures, as well as by spectroscopic and chemical data.

The natural nephrite pebble on the left (95 × 78 × 38 mm) shows typical surface microstructures and orange-yellow spot-like coloration. The artificial nephrite pebbles on the right (8–35 g) were manufactured from low-quality nephrite; some have been treated to add surface coloration.
Photos by Yong Zhang



NEW TECHNOLOGIES AND INSTRUMENTATION

THE IMPACT OF THE CHOICE OF ILLUMINATION IN THE WHOLESALE BUYING, SELLING, AND GRADING OF GEMSTONES

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Members of the gem community often demand very specific types of illumination, depending on the gem material they are dealing with and whether the application is related to buying, selling, or grading. This study examines what a trade person at the wholesale level expects from a light source, in terms of color/hue and overall appearance, when illuminating a gemstone. The testing involved 43 individuals and was conducted on-site at offices, trade fairs, and auctions. The illumination consisted of a tabletop lamp with four different compact 18-watt fluorescent lamps and a 35-watt incandescent halogen lamp. The fluorescent lamps varied from 6500 to 3000 K in correlated color temperature (CCT), while the halogen lamps with enhanced CCT covered a range of 4700–3500 K. The color rendering index (CRI) of the light sources was between 90 and 98. The traders were asked to view their own gems in each of the five light sources and give their preferences.

While the main focus was on colored stones, cultured pearls and fancy-color diamonds were evaluated as well. Fluorescent lamps of 6500 K are uncommon today, and even fancy-color diamonds are typically illuminated by 5800–5400 K light. Only blue sapphires are presented in the 6500 K light traditionally used for diamonds, but very often in combination with 5800 K lamps. Rubies, on the other side of the color spectrum, are typically displayed with incandescent lamps of 3200–2800 K or fluorescent lighting of 5400–3200 K.

The results supported a well-known axiom of the colored stone trade: “The best light source is the one that gives you the best selling results.” This often differs from the official recommendations of the CIE International Commission on Illumination, which specifies a color temperature for gem materials in the 6500–5500 K range. It also appears that the practical illumination of the trading environment is very different from the standardized grading used at gem laboratories. Now that LED and OLED technologies—with their specific characteristics, spectrum, color of light, and CRI—have added to the available options, the evaluation of gem colors must be considered “in a new light.”

ADVANCING THE UNDERSTANDING OF LUMINESCENCE IN GEM MATERIALS

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The luminescence of gem materials is used to address an array of identification problems in gemology. In fact, luminescence spectroscopy was the technology that made it possible to identify HPHT-treated near-colorless diamonds. However, the cause of this visible-light emission in many gems often remains a mystery to gemologists.

Luminescence must be preceded by an excitation, which in gemology is usually ultraviolet or visible-light absorption. Hence, interpreting this phenomenon is even less straightforward than interpreting absorption itself (which is the cause of color in most gems), as it represents only the first step in the emission process. Some causes of luminescence are well known, such as Cr³⁺ in a variety of gems or some common color centers in diamond. For the most part, though, the causes of luminescence have not been explored systematically. Nevertheless, they can usually be determined by analyzing the emission and excitation spectra generated by luminescence spectroscopy, often combined with trace-element analysis.

The better-known (but not necessarily most common) causes of luminescence in gems include Cr³⁺, Mn²⁺, and other isolated transition metal ions, as well as molecular groups, color centers (extended and point-defect), and organic materials. Recent studies we conducted have demonstrated the complex nature of the luminescence in some gems. We investigated samples of these materials with several varieties of luminescence spectroscopy. We first used emission and excitation spectra on a traditional permanent-regime spectrometer (the Jobin Yvon Fluorolog). Some clues as to the time behavior were obtained with a far more complex custom-built transient-regime spectrometer using femtosecond laser excitation to observe emissions lasting only a few nanoseconds. In diamonds, in particular natural type Ib crystals, the luminescence can be dominated by unidentified broad bands, whereas more common, easier-to-identify emissions (e.g., H3, NV⁻) remain a minority component. In opals, the classic green luminescence is due to uranyl (UO₂²⁺) but its transient behavior is somewhat surprising. The blue component in opal luminescence is intrinsic, due to two surface-related defects.

The origin of orange luminescence in sapphire has never been systematically investigated. It appears in all colors of corundum, natural or synthetic. It is almost always present in Be-diffused corundum, and therefore probably related to a hole center. It is very short-lived (5 ns on average), in contrast with the long-lived Cr³⁺ emission.

ADVANCED GEM CHARACTERIZATION

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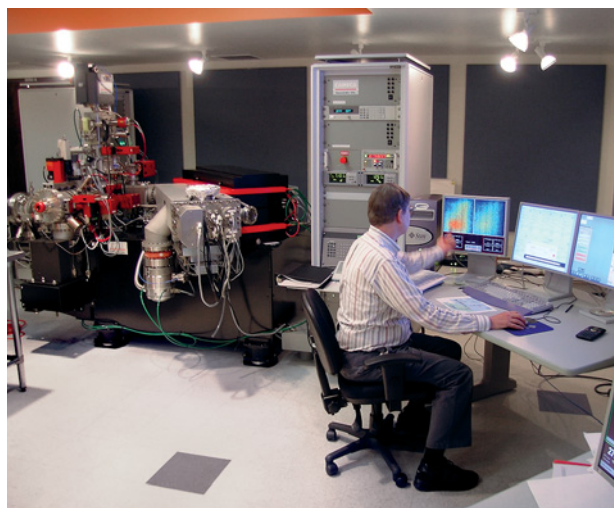
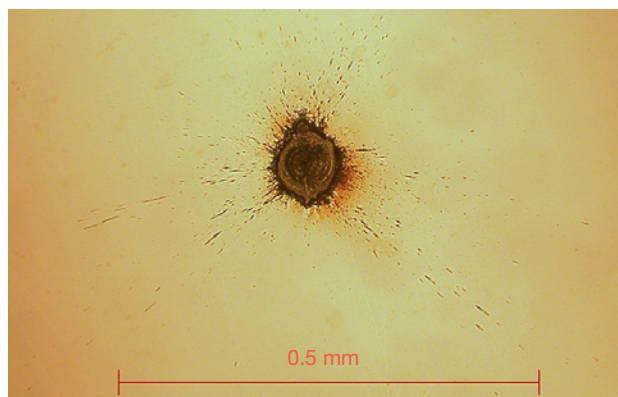
As clever minds combine an ever-increasing menu of high-tech methods in the quest to enhance the properties of both natural and synthetic gems, the challenges of gem characterization continue to grow rapidly. Gemology has adopted new methods to keep pace.

Techniques considered advanced a decade ago—such as infrared, Raman, X-ray fluorescence, and photoluminescence spectroscopy, as well as LA-ICP-MS—are now routine analytical tools in well-equipped gemological laboratories. Trace-element analyses at the parts per million level are now at the forefront of determining locality of origin and treatments. New methods now being used in academic and industrial laboratories will become increasingly important in gemological labs as the technology applied to gem treatments rapidly advances.

Established tools remain important, though. Infrared spectra can be used to identify phases (including X-ray amorphous phases), detect the presence of organic oils and resins in stones, classify diamond type, and identify certain minor and trace constituents of minerals that may reveal clues to their origin or treatments. Raman spectra are also used for phase identification. Because the beam can be focused as small as a micrometer in diameter in laboratory-grade instruments, Raman spectroscopy has become the method of choice to identify small inclusions in stones. The availability of large libraries of spectra makes this a powerful technique for nondestructive phase identification (even of organic components).

Visible-range spectroscopy remains a primary tool for studying color in minerals. Combined with chemical analysis, it can determine which metals cause color, in which oxidation states the metals occur, and even the site in the crystal where they

This minute crater on the surface of a pink sapphire was produced by LIBS analysis. Photo by G. R. Rossman.



A nanoSIMS is a powerful analytical instrument that can detect both trace elements such as beryllium diffused into corundum and the isotopic compositions of the stone. Photo by Brendan M. Laurs.

occur. Such information can assist in geographic origin studies.

Luminescence reveals much about the growth history of minerals, and several of these methods have found important gemological applications as well. Luminescence helps identify certain treatments and is of particular use in separating natural and synthetic diamonds. Thermoluminescence testing responds to radiation damage induced either by nature or by laboratory treatment. Unfortunately, this test is destructive and will remove color from most samples.

Laser-ablation methods (LA-ICP-MS and LIBS) have opened up a whole new range of quantitative analyses of most elements in the periodic table. In addition to providing basic information about the chemical composition of a gem, these analyses are often of great use in establishing geographic origin, while leaving only a tiny crater on the gem's surface. Secondary-ion mass spectrometry (SIMS and nanoSIMS), an ion-beam method, provides highly sensitive chemical analysis of selected elements and also gives isotopic compositions (leaving craters of just 20 to 0.1 μm in diameter). This technique is also well-suited for obtaining chemical depth profiles of coatings.

X-ray methods have evolved from a primary method for phase identification to a tool for nondestructively detecting and analyzing a number of minor components, and now digital X-ray methods are used to obtain images of the internal structure of pearls.

This author anticipates that other new tools will become commonplace in the years ahead. Electron paramagnetic resonance (EPR) is a particularly sensitive analytical tool for detecting certain metals, color centers, and radiation damage centers at low concentrations. This could be particularly useful in the examination of color centers in diamond and the changes these centers undergo with heat and other treatments. Unlike ther-

moluminescence, EPR does not destroy radiation-induced color. Analysis of specific isotopes is now frequently applied in academic research, but has seen comparatively little use in gemology. Oxygen isotopes show a wide range of variation in geologic systems. Analysis of oxygen isotopes has already been established as a powerful method to distinguish emeralds and corundum from different geographic origins. Argon isotopes, meanwhile, have played a major role in proving that some samples of red andesine from Asia have been treated.

APPLICATIONS OF FLUORESCENCE IN GEMOLOGY

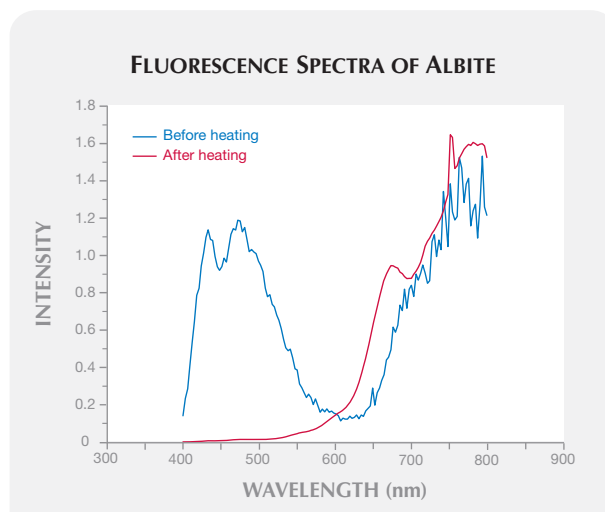
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Fluorescence, or luminescence, is used extensively in mineralogy to investigate both intrinsic and extrinsic atomic crystalline defects, including their nature and relative concentrations (Finch and Klein, 1999). Although the technique has seen limited use in gemology, it provides insights into genesis, paleochemistry, and paleotemperature that can potentially differentiate natural, treated, and synthetic gems (Pagel et al., 2000). Following are applications of both continuous-wave and time-resolved luminescence as we have applied them to gemology.

Data were obtained through imaging and wavelength spectroscopy, and by studying luminescence as a function of both wavelength and luminescence lifetime time-resolved photoluminescence. We are investigating the utility of X-ray excited optical luminescence (XEOL), which uses X-ray luminescence from a synchrotron source, both as a function of the lifetime and the energy of the incident X-rays. We are also using time-resolved fluorescence in the form of fluorescence lifetime imaging microscopy (FLIM) to study fluorescence structures within gems and minerals. A mature methodology in biochemistry and cell biology (Becker, 2005), FLIM shows exciting potential for mineralogy and gemology.

These methodologies have applications in determining gem provenance and detecting treatments and synthetics. Defect patterns in the form of color centers and luminescence centers in gems can be used to identify, for example, characteristic growth and chemical signatures. Differentiating between natural and treated color continues to challenge gemologists. Luminescence offers a powerful nondestructive methodology with great potential to assist in this endeavor.



Wavelength resolved emission spectroscopy shows distinct differences in a sample of albite before and after heat treatment.

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