2008 LAB NOTES

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AQUAMARINE with Kelp-Like Inclusions

At GIA's inaugural Show Service Laboratory in Tucson, Arizona, this past February, we examined a 15.80 ct light greenish blue aquamarine submitted by Lisa Elser of Custom Cut Gems Co., Port Moody, British Columbia. This pear-shaped checkerboard cut, said to be from Pakistan, contained interesting thin bladed inclusions arrayed in patterns reminiscent of kelp. The inclusions were transparent and formed fans with distinctive branches (figure 1, left) that were large enough to be seen with the unaided eye.

Standard gemological testing easily identified the gem as a natural aquamarine. When examined with magnification and polarized light (figure 1, right), the inclusions proved to be birefringent and displayed dramatic interference colors that shifted as the analyzer on the microscope was rotated. Becke line testing indicated that the inclusions had a refractive index somewhat higher than the surrounding beryl host. Because we had never before encountered such inclusions in beryl, we asked the owner for permission to bring the stone back to the Carlsbad laboratory for further analysis to conclusively identify them.

Figure 1. Discovered in an aquamarine that reportedly came from Pakistan, these transparent blades (left) in a distinctive fan-like arrangement were identified as triploidite. The interference colors seen with polarized light (right) proved that the inclusions were birefringent. Field of view 3.0 mm.

In Carlsbad, we used Raman microspectroscopy on one of the inclusion blades, which had been polished through and exposed at the surface of the pavilion. The results indicated triploidite, a monoclinic manganese-iron phosphate that is known to occur in granitic pegmatites. We have encountered triploidite inclusions only once before, in quartz. Since aquamarine is also a known product of granitic pegmatites, however, the inclusion of triploidite in Pakistani aquamarine is geologically reasonable.

We in the laboratory thought it very appropriate to have inclusions of a rare mineral that resembles fans of kelp in a gem variety known as *aquamarine*.

John I. Koivula and Alethea Inns

Editors' note: All items are written by staff members of the GIA Laboratory.

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DIAMOND with Repeating Growth/Dissolution Features

Diamond crystallization is a complex process. Natural diamonds typically experience multiple stages of growth; it is believed that many also experience episodes of dissolution from one stage to the next (A. R. Lang, "Internal structure," in J. E. Field, Ed., *The Properties of Diamond*, Academic Press, London, 1979, pp. 425–469). Yet whereas the multiple growth stages may be seen

Figure 2. This square-cut 5.20 ct Fancy brownish greenish yellow diamond experienced multiple growth/dissolution stages during its formation.

with fluorescence or cathodoluminescence imaging as banded structures in the same growth sector, features clearly related to dissolution are less frequently observed and reported. In the New York laboratory, however, we recently examined an unusual diamond with distinctive growth/dissolution features.

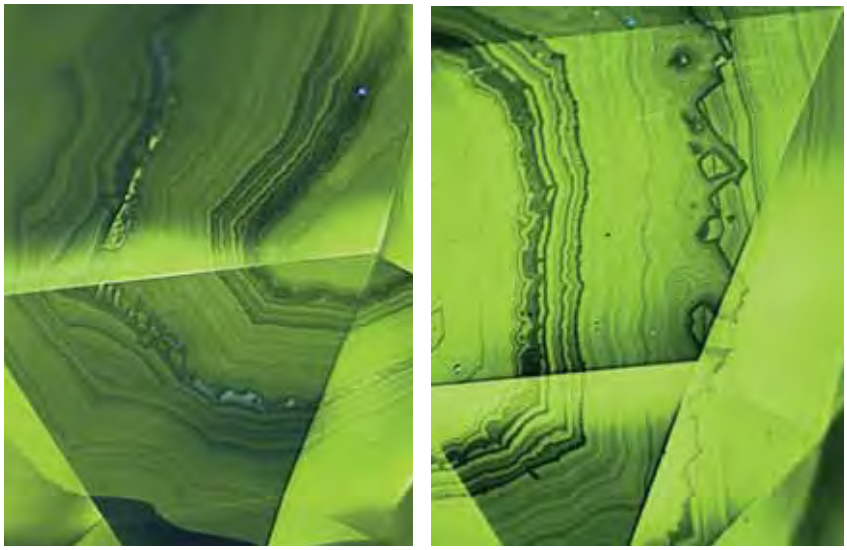
The square-cut 5.20 ct diamond in figure 2 was color graded Fancy brownish greenish yellow. Infrared spectroscopy showed that it was a type Ia diamond with a high concentration of nitrogen and structurally bonded hydrogen. Observation with an optical microscope revealed clear octahedral {111} and cubic {100} growth sectors. Clouds of submicron-sized inclusions were spread throughout the cubic growth sector, and the yellow color was more concentrated in the octahedral sector. As a result, this stone displayed patchy color distribution and clear internal graining at the boundaries of the two types of growth sectors.

DiamondView fluorescence imaging revealed multiple growth zones (figure 3). Each fine zone, representing a specific growth stage, either fluoresced greenish yellow or was inert (dark), due to variations in lattice defect configurations. Most of the narrow growth zones were perfectly parallel to one another, with sharp and straight boundaries indicating a repetitive growth process. This process was interrupted at least twice, however, as evidenced by the two areas in figure 3 where several of the greenish yellow and inert bands are discontinuous. These "zigzag" areas were caused by dissolution of the previously formed diamond and subsequent additional diamond growth, again with continuous growth zones and curved boundaries following the morphology after dissolution. Faceting produced the "islands" seen in figure 3 (right), remnants of the original growth zone that remained after dissolution, now surrounded by newly precipitated diamond.

The occurrence of dissolution in this diamond strongly indicates that it was subjected to repeated transformation from thermodynamically stable conditions to unstable ones, which may have involved changes in pressure, temperature, system chemistry, or various combinations of these factors. Rarely have we seen such a clear illustration of growth/dissolution features in a diamond.

Wuyi Wang

Figure 3. These DiamondView fluorescence images clearly illustrate two episodes of growth and dissolution (the jagged, zigzag-shaped zones) in the diamond in figure 2.



First CVD SYNTHETIC DIAMOND Submitted for Dossier Grading

Synthetic diamonds grown by the chemical vapor deposition (CVD) technique have been discussed in several recent *Gems & Gemology* articles (W. Wang et al., "Gem-quality synthetic diamonds grown by a chemical vapor deposition [CVD] Method," Winter 2003, pp. 268–283; P. M. Martineau et al., "Identification of synthetic diamond grown using chemical vapor deposition [CVD]," Spring 2004, pp. 2–25; and W. Wang et al., "Latest-generation CVD-grown synthetic diamonds from Apollo Diamond Inc.," Winter 2007, pp. 294–312). They have rarely, however, been encountered in the day-to-day grading operations of the lab.

Recently, the Carlsbad laboratory identified a near-colorless CVD synthetic diamond weighing approximately one third of a carat that had been submitted for the standard GIA Diamond Dossier grading report. This is the first CVD product submitted to the Carlsbad lab for a grading service. Previously, all of the CVD samples we examined were received directly from the manufacturer for research purposes (see above references).

Figure 4. Examination between crossed polarizers revealed an irregular strain pattern in this CVD synthetic diamond, which was submitted to the Carlsbad lab for a grading report. Field of view 3.7 mm.

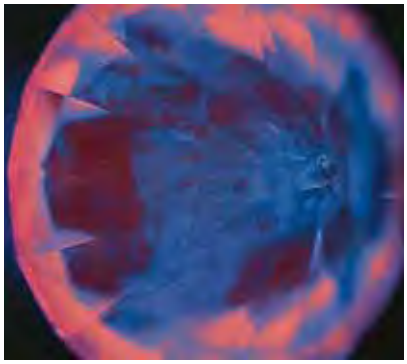


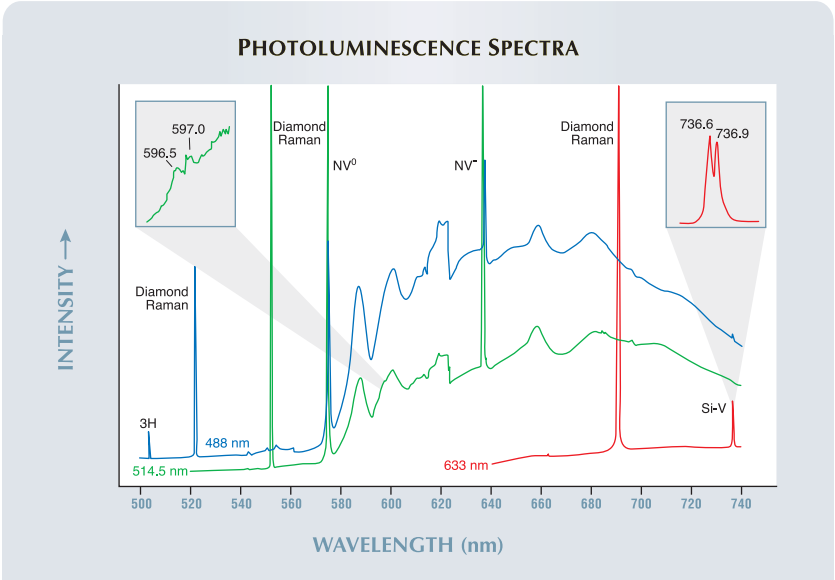
Figure 5. DiamondView imaging of the round brilliant in figure 4 showed an orangy pink fluorescence color with irregular blue zones, similar to the pattern reported previously for CVD synthetic diamonds.

Growth of synthetic diamonds via the CVD method can be accomplished at relatively low pressures, in contrast to the more extreme requirements for growth of high-pressure, high-temperature (HPHT) synthetics. During CVD growth, gaseous interactions result in deposition of synthetic diamond onto a suitable substrate; single-crystal synthetic diamond is the substrate typically used for production of gem-quality material (Wang et al., 2003; Martineau et al., 2004). Element Six of the United Kingdom and Apollo Diamond Inc. of Boston are two well-known producers of gem-quality CVD materials, though only Apollo has produced facetable material for sale to the jewelry trade.

Microscopic examination of the sample submitted for grading revealed numerous feathers and related cavities on the pavilion, which resulted in a clarity grade that fell into the Slightly Included (SI) range. We also observed pinpoints. Between crossed polarizers, the synthetic diamond showed unevenly distributed, high-order interference colors (figure 4)—the first of many similarities we encountered between this sample and those discussed by Wang et al. (2007). It exhibited no visible fluorescence to either long- or short-wave ultraviolet (UV) radiation emitted by a desk-model UV lamp; however, when subjected to the stronger ultra short-wave UV emissions of the Diamond-View instrument, it showed an overall strong orangy pink to pinkish orange fluorescence (typical of CVD synthetic diamonds), interspersed with patches of blue (figure 5). When viewed through the pavilion, the fluorescence details became significantly clearer—including red striations that were most prominent in the pink/orange region and concentration of the irregular blue patches toward the culet. These latter features were both described by Wang et al. (2007). The weak blue phosphorescence noted in the DiamondView was also similar to the Wang et al. findings.

FTIR analysis indicated that the synthetic diamond was type IIa, and low-temperature photoluminescence (PL) spectroscopy revealed a classic CVD signature consisting of peak doublets at 736.6/736.9 nm (due to the silicon-vacancy [Si-V] defect) and at 596.5/597.0 nm. PL spectra were collected using four different laser excitations to confirm the presence of these features (for ease of reproduction, only the results for three of these are shown in figure 6). While the 596.5/597.0 nm doublet is still considered unique to CVD synthetic diamonds, the Si-V doublet has been reported in some rare colorless and near-colorless natural diamonds (see C. M. Breeding and W. Wang, "Occurrence of the Si-V defect center in natural colorless gem diamonds," *Diamonds and Related*

Figure 6. Photoluminescence spectra collected from the near-colorless synthetic diamond at 488, 514.5, and 633 nm laser excitations showed distinctive CVD-related features.



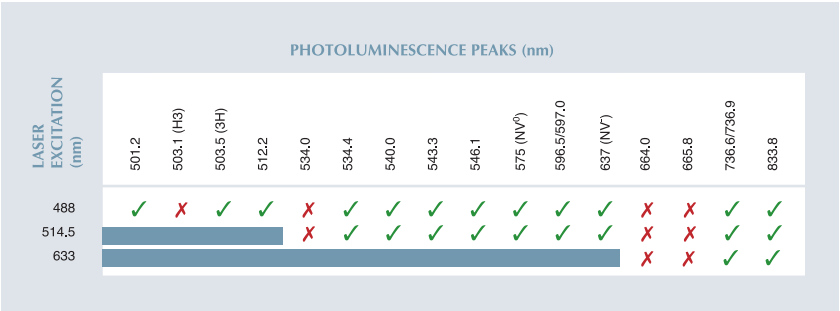


Figure 7. A comparison of PL peaks from analysis of the CVD synthetic diamond in figure 4 and those presented by Wang et al. (2007), using laser excitations at 488, 514.5, and 633 nm, reveals many similarities. A check (√) indicates that the peak was observed in both studies, whereas an x *indicates a lack of correlation; gray portions are regions outside the working range of the specific laser.*

Materials, in press). We also observed most of the other peaks presented by Wang et al. (2007), including the 3H (503.5 nm) defect; a comparison of our photoluminescence results with those PL features is shown in figure 7. The results for the fourth laser excitation, at 830 nm, were also generally consistent with those reported by Wang et al. (2007).

Given the many similarities between this synthetic diamond and the Apollo CVD material produced during 2006–2007 (Wang et al., 2007), it is likely that this sample is from a similar generation. Its submission to the lab for Diamond Dossier grading confirms that at least some CVD-grown synthetic diamonds are currently present in the marketplace. Examination by a gemological laboratory remains the most effective way to confidently identify synthetic diamonds.

The sample was returned to the client with a Synthetic Diamond grading report and the words "LABORATORY GROWN" laser inscribed on the girdle, as is GIA's standard practice.

Karen M. Chadwick and Christopher M. Breeding

Interesting FILLED VOIDS

Carbonate minerals such as calcite, dolomite, and magnesite are occasionally encountered in emeralds, rubies, and other gems. As inclusions, the carbonates can provide valuable evidence that the host gem has not been treated.

For gem treatments involving filling with epoxy resins and solder (high lead content) glasses, it is generally believed that lower-quality starting material is first immersed in hydrochloric or oxalic acid to remove foreign matter from surface-reaching cracks and pits to "clean" the gem and make the treatment more effective. If surface-reaching cracks extend to solid mineral inclusions, then those inclusions will also be attacked by the acid—or, in the case of hydrochloric acid and carbonate minerals, totally dissolved so that only a void remains. While most such voids do not show any recognizable form, occasionally we encounter examples with obvious carbonate habits. Recently we examined two gems with such voids. One was a ring-mounted emerald that was reportedly mined at Chivor, near Somondoco, Colombia. It was submitted for gemological examination by Manuel J. Marcial of Emeralds International, Key West, Florida. The other was a 2.58 ct ruby, thought to be from Madagascar, that was provided by E. Gamini Zoysa of Mincraft Co., Mount Lavinia, Sri Lanka.

The emerald hosted two large filled voids as well as a very distinctive light brown translucent mineral with the visual appearance of the very rare carbonate parisite (figure 8). Parisite is known to occur in Colombian emeralds, although it is generally thought to indicate emeralds mined at Muzo (see Winter 1982 Lab Notes, p. 230). The voids next to the mineral inclusion were of very low relief, and each contained a single large, spherical gas bubble. They also had the same general shape as the apparent parisite.

Figure 8. The single gas bubble and the flash-effect colors in each of these two voids prove that the host emerald has been filled. The light brown well-formed crystal has the appearance of the rare carbonate mineral parisite, which is known to occur in Colombian emeralds. Field of view ~5.6 mm.

Figure 9. These bright flash-effect colors provide clear evidence that the host ruby has been filled with a glass that closely matches it in RI. Field of view ~3.5 mm.

With shadowed illumination, flash-effect colors at the edges of the filled voids readily delineated them.

On first inspection, the ruby clearly showed extensive evidence of solder glass filling in the form of bright flash-effect colors (figure 9). More detailed microscopic examination revealed a rhomb-shaped void in the pavilion that contained a single spherical gas bubble, visible just below the girdle (figure 10). As with the void in the emerald, shadowed illumination enhanced the visibility of this feature. Although no actual carbonate inclusions were present in this ruby, the habit of this filled cavity and the well-known vulnerability of carbonate minerals to acid attack made us suspect that the original mineral occupying this void was a carbonate.

John I. Koivula, Shane F. McClure, and Dino DeGhionno

GLASS with Devitrified Inclusions

Glass is a very common gem simulant, and the lab regularly encounters glass specimens—most of them unexciting—in the course of its work. In fall 2007, however, the New York laboratory received an 11.17 ct (12.26 × 12.09 × 8.66 mm) round modified brilliant cut that immediately piqued our interest because of the striking asterisk-like arrangements of long fibrous inclusions it contained (figure 11).

Figure 10. Measuring approximately 0.56 mm in length and containing a single gas bubble, this rhomb-shaped glass-filled cavity in the 2.58 ct ruby probably once contained a carbonate mineral such as calcite.

Microscopic examination revealed the presence of several gas bubbles, consistent with a glass. This identification was confirmed by its singly refractive optic character (with slight anomalous double refraction) and Raman and Fourier-transform infrared (FTIR) spectroscopy.

With the sample's over-the-limit refractometer reading and a specific gravity of 4.44, we were able to exclude natural glasses such as obsidian and moldavite, as well as less common natural materials such as Libyan desert glass and tektites. Based on the high clarity and the unusually pure light yellowish green color, we determined that the glass was manufactured. This was supported by energy-dispersive X-ray fluorescence (EDXRF) results indicating an expected strong signal for silicon, as well as zirconium and barium (and moderate strontium), a signature that would be very unusual for natural glass but is

Figure 11. This 11.17 ct specimen of manufactured glass contains several unusual clusters of inclusions.

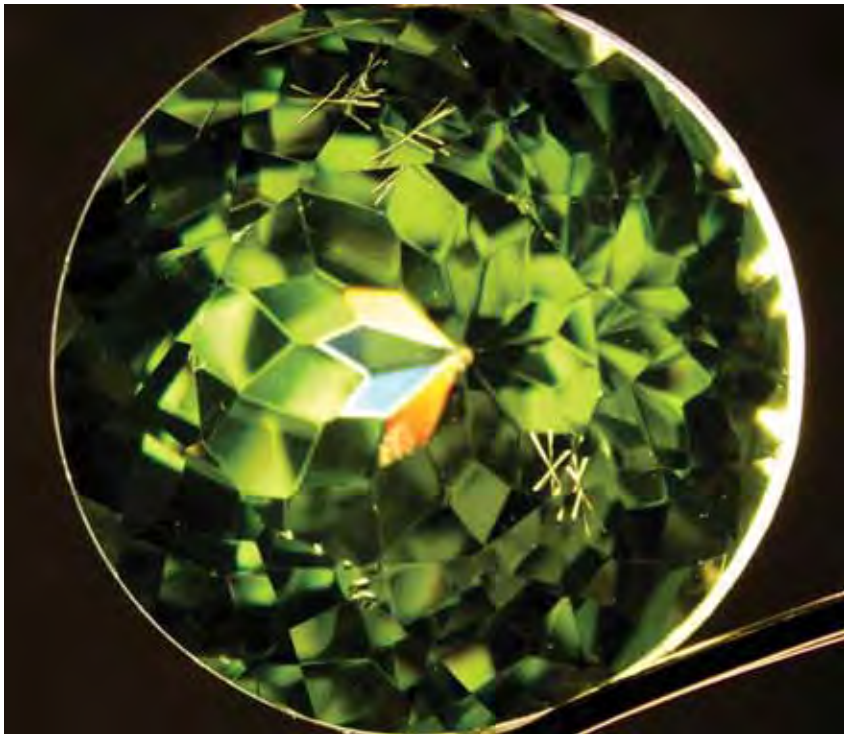


Figure 12. These long, fibrous inclusions were likely formed by devitrification of the glass host. Field of view ~3.1 mm.

not uncommon for some manufactured glasses. The presence of these heavy elements also explained the high RI and SG values.

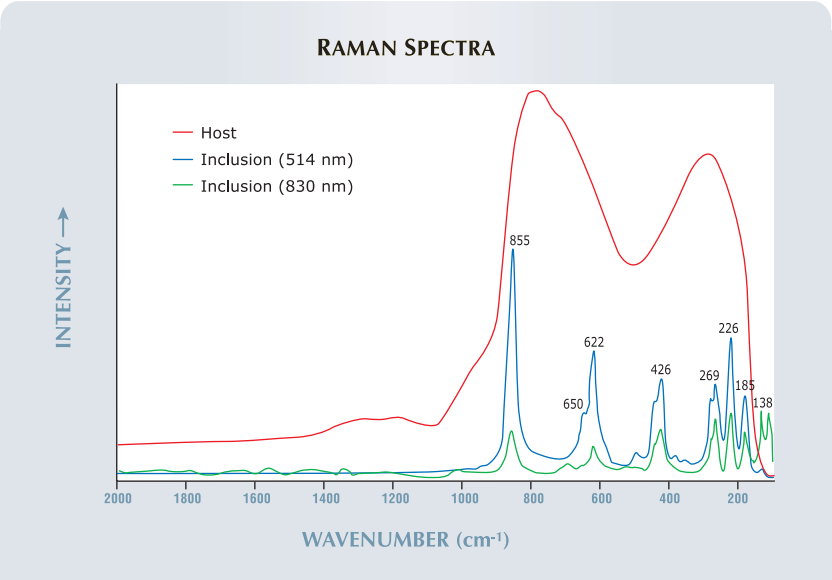
As the fibrous inclusions had a discernable crystalline character (figure 12), we concluded that they were exsolved from the glass host. Faint growth lines were present at the tips of the fibrous bundles, and crossed polarizing filters showed low-order interference colors. Examination with a calibrated camera microscope indicated that the inclusions had an approximate average length of 1.2 mm and a cross section of about 60 µm.

In our experience, the crystalline inclusions were best explained as the result of partial devitrification (i.e., regions where the glass's amorphous state has locally changed to a crystalline material). Many examples of devitrified inclusions in manufactured glasses have been published in *G&G* (e.g., Lab Notes—Fall 1993, p. 201; Summer 1995, p. 137; Summer 1996, p. 123—and G. Bosshart, "Cobalt glass as a lapis lazuli imitation," Winter 1983 *Gems & Gemology*, pp. 228–231). Excellent examples may also be found in the *Photoatlas of Inclusions in Gemstones* (E. J. Gübelin and J. I. Koivula, Vol. 1, Opinio Verlag, Basel, Switzerland, 1986, pp. 437–439).

In an attempt to identify these particular inclusions, we used confocal Raman spectroscopy on one fibrous bundle that broke the surface of a bezel facet. With both 514 and 830 nm laser excitation, the spectra showed peaks at the same positions, indicating that they were due to Raman scattering from a crystalline substance as opposed to photoluminescence (figure 13). Unfortunately, although we acquired an excellent Raman spectrum, we were unable to match it to any known materials in our mineral reference database.

David M. Kondo and Donna F. Beaton

Figure 13. Raman analysis of one of the devitrified inclusions gave clear results (with major peaks at 855, 650, 622, 426, 269, 226, 185, and 138 cm^{-1}), but they could not be matched to a reference spectrum. The spectrum taken with 830 nm laser excitation is baseline corrected.



PEARL

White Clam Pearl with Original Shell

The New York laboratory recently received a 9.13 ct white non-nacreous pearl (figure 14) for identification. According to the client, it was recovered from Peconic Bay, off the North Fork of Long Island, New York. The client, who has clammed in the area for more than 30 years and has a degree in oceanography, estimated the clam to be about eight years old (based on its growth rings). He submitted the shell to the lab along with the pearl (figure 15). The button-shaped pearl (12.26 × 8.40 mm) had a clean surface

Figure 14. This fine example of a white clam pearl (12.26 × 8.40 mm) was reportedly recovered from a clam found off the coast of Long Island, New York.

Figure 15. The color of the pearl in figure 14 closely matches that of the shell in which it was found.

with a soft porcelaneous luster, as well as a pure white color that matched the interior of the shell. The X-radiograph showed very subtle growth features, as is typical of clam pearls.

In addition to the opportunity to examine the original shell from which the pearl came, the excellent condition, size, pure white color, and local origin made this an interesting and unusual submission.

Akira Hyatt

Figure 16. This baroque conch pearl (39.45 × 24.55 × 19.15 mm) is unusual for its size and shape, as well as the patches of different colors seen on its surface.

Large Baroque Multicolored Conch Pearl

The New York laboratory recently received a large (125.26 ct) baroque non-nacreous pearl for identification (figure 16). Standard gemological testing established that it was of natural origin and from the *Strombus gigas* mollusk, commonly referred to as the queen conch. The pearl displayed variegated color, with prominent patches of orangy pink, white, orange, orange-brown, and even a small patch of purple. Many of these colors are characteristic of various parts of the conch shell. Additionally, the shape of the pearl suggests that it may have grown in or near one of the folds of the shell. The pearl was chipped at its narrowest edge, but otherwise it showed an intact surface with a porcelaneous luster and a subtle flame structure typical of conch pearls (see, e.g., E. Fritsch and E. Misiorowski, "The history and gemology of Queen conch 'pearls,'" Winter 1987 *Gems & Gemology*, pp. 208–221). The shape and multicolored nature of this pearl, as well as its large size, made it an unusual specimen.

Akira Hyatt

Green SYNTHETIC SAPPHIRE with Vibrant Blue Inclusions

In today's gemological world, synthetic colored stones seldom garner the attention that is bestowed on treated gems. The latter are now available in much greater numbers than ever before and are enhanced using increasingly sophisticated technology, whereas it is not often that a new form of synthetic gem is encountered. Thus, we were intrigued when Leon M. Agee of Agee Lapidary in Deer Park, Washington, sent us a 44.66 ct polished section from a flame-fusion synthetic sapphire boule and a 0.91 ct octagonal step cut fashioned from the same material (figure 17). Both displayed a dull green color that we had never encountered before, as well as numerous vibrant blue solid inclusions (figure 18). Because of their deep blue color (similar to cobalt glass), we suspected that these inclusions contained cobalt.

The standard gemological properties were consistent with synthetic corundum. The material fluoresced moderate chalky orangy red to long-wave UV radiation and was inert to short-wave UV. We observed a very weak cobalt spectrum with the desk-model spectroscope. In addition to the expected elements for corundum, trace elements detected through laser ablative–inductively coupled plasma–mass spectrometry (LA-ICP-MS) analysis included vanadium (~200 ppm), cobalt (150 ppm), and chromium (60 ppm).

Figure 17. This 0.91 ct octagonal step cut represents an unusual color for flame-fusion synthetic sapphire.

Raman analysis could not precisely identify the blue inclusions even though clear target sites were exposed on the surface of the boule section in dramatic dendritic form (figure 19). The closest Raman library match suggested that the blue substance was related to spinel, and polarized light microscopy demonstrated that the inclusions were isotropic.

This is the first time we have encountered a synthetic sapphire with this unusual green color and such vibrant blue solid inclusions. Perhaps this material was the result of an "accident" that occurred during crystallization.

John I. Koivula, Alethea Inns, and Andy Hsi-Tien Shen

High-Temperature Heat-Treated ZIRCON

Although zircons are routinely heat treated, the temperatures typically used are considerably lower (near or well below 1000°C) than those used to alter the color in corundum (which may exceed 1500°C). The temperatures used on corundum are capable of doing serious damage to almost any mineral inclusions that might be present. So while it is common to encounter obviously altered solid inclusions in rubies and sapphires, they are oddities in zircons.

When rubies and sapphires are heat treated, however, it is not unusual for non-corundum gem materials such as chrysoberyl, spinel, or zircon to be accidentally mixed in. This can result in some rather interesting changes in the appearance of these stray gems and even in the corundum itself. As one prominent example of the latter, it has been speculated that the accidental inclusion of chrysoberyl in a sapphire heating run led to the discovery of beryllium treatment of sapphires and the effect that even small traces of Be have on corundum coloration. Consequently, although we don't expect to find visual evidence of high-temperature heating in zircons, observation of any such features is almost always worth documenting.

This was the case with an orangy yellow 0.96 ct transparent mixed-cut zircon from Anakie, Queensland, Australia, that Terry Coldham of Sapphex, in Sydney, loaned the GIA lab for examination. As seen in figure 20, this zircon contained a reflective decrepitation halo surrounding a melted inclusion, which clearly indicated that the zircon had been subjected to high-temperature heat treatment. A ring of solidified melt droplets surrounded an elongated central inclusion that now appeared to contain a transparent solid with a gas bubble frozen in place at its tip. Beyond the melt droplet ring, the presence of a second reflective discoid rim suggests that this inclusion experienced two rupture events during the heat treatment.

John I. Koivula

Figure 18. Intense blue solid inclusions and obvious gas bubbles were discovered in the green flame-fusion synthetic sapphire. Field of view ~0.7 mm.

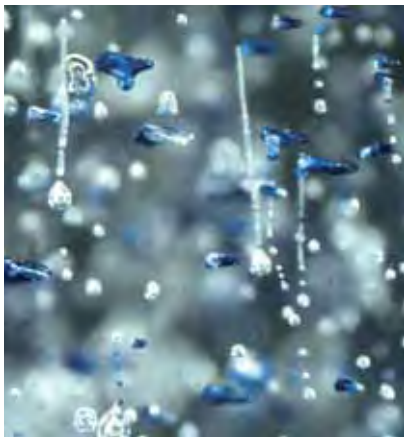


Figure 19. LA-ICP-MS and Raman analysis could not conclusively identify these deep blue spinel-like crystalline dendrites exposed on the surface of the flame-fusion synthetic sapphire boule. Field of view ~3.5 mm.

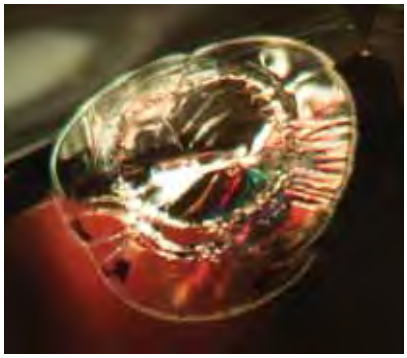


Figure 20. Measuring 0.70 mm in longest dimension, the reflective halo structure surrounding a melted inclusion in this zircon clearly indicates that an atypically high temperature (for zircon) heat treatment has taken place.

ERRATUM

In the Winter 2007 Lab Notes entry on the double-star sapphire (p. 365), the name of the client, Depal Weerashinghe of International-Gem Merchants, Sri Lanka/Rhode Island, was inadvertently left out. *Gems & Gemology* regrets the omission.

PHOTO CREDITS
John I. Koivula—1, 8, 9, 10, 18, 19, and 20; Jian Xin (Jae) Liao—2, 14, 15, and 16 Wuyi Wang—3; Karen M. Chadwick—4 and 5; David M. Kondo—11 and 12; Robert Weldon—17.