GEMOLOGICAL INVESTIGATION OF A NEW TYPE OF RUSSIAN HYDROTHERMAL SYNTHETIC EMERALD

By John I. Koivula, Robert C. Kammerling, Dino DeGhionno, Ilene Reinitz, Emmanuel Fritsch, and Mary L. Johnson

Tairus, in Novosibirsk, has produced yet another new type of Russian hydrothermal synthetic emerald, now being marketed in Bangkok. Examination of eight faceted samples revealed that, with the exception of certain characteristic inclusions, the basic gemological properties shown by this new synthetic are essentially the same as those encountered in other hydrothermally grown synthetic emeralds and some natural emeralds. If the characteristic inclusions are not present, distinctive spectral characteristics in both the mid- and near-infrared regions of the spectrum will serve to separate these synthetic emeralds from their natural counterparts.

The first commercially successful hydrothermal synthesis of beryl is generally attributed to Johann Lechleitner who, in 1960, produced hydrothermal synthetic emerald overgrowth on pre-faceted natural beryl (Nassau, 1980). Today, gem-quality hydrothermal synthetic emeralds are available from Innsbruck, Austria (Lechleitner), from the United States (Regency, formerly Linde), from China, from Japan (formerly Biron, which originated in Australia), and from Russia. The focus of this article is a new product from Russia, specifically from the joint-venture company Tairus.

ABOUT THE AUTHORS

Mr. Koivula is chief research gemologist, the late Mr. Kammerling was vice-president of research and development, Mr. DeGhionno is senior staff gemologist, and Dr. Johnson is research scientist at the GIA Gem Trade Laboratory, Santa Monica. Dr. Reinitz is research scientist at the GIA Gem Trade Laboratory, New York. Dr. Fritsch is professor of physics at the Gemology Laboratory, Physics Department, University of Nantes, France.

Acknowledgments: The authors thank Walter Barshai, director of Pinky Trading Co., Bangkok, for supplying the hydrothermal synthetic emeralds examined for this report. Sam Muhlmeister performed the EDXRF analysis, Yan Liu and Mike Moon assisted with gathering spectra, and Patricia Maddison and Philip Owens helped with the gemological testing. Dr. John Armstrong and Paul Carpenter, of the California Institute of Technology, assisted with the SEM-EDS analyses performed there.

Gems & Gemology, *Vol. 32, No. 1, pp. 32–39.*

The gemological literature contains useful information on previous examinations of hydrothermal synthetic emeralds from the former Soviet Union (Takubo, 1979; Koivula, 1985; Schmetzer, 1988; Henn et al., 1988; "What to look for . . . ," 1989). Since late 1993, Pinky Trading Co. of Bangkok, Thailand, has been marketing a hydrothermally grown synthetic emerald with internal features that are different from those of earlier Russian-grown hydrothermal synthetic emeralds and other colored synthetic beryls. This new type of hydrothermal synthetic is being commercially manufactured through a joint-venture company known as Tairus. The crystals are grown by the Laboratory for Hydrothermal Growth at the Institute of Geology and Geophysics in the Siberian Branch of the Russian Academy of Sciences in Novosibirsk, Siberia. They are fashioned and released to the market in Bangkok. Comparison of these hydrothermal synthetic emeralds to those previously described shows distinct differences, particularly with respect to inclusions, although they can still be conclusively identified as synthetic.

MATERIALS AND METHODS

All the samples used for this study were obtained in Bangkok from the same lot. According to the supplier, they were manufactured in 1993. The eight transparent oval mixed cuts (figure 1) weighed between 0.17 and 0.41 ct, with measurements ranging from $4.87 \times 2.96 \times 1.99$ mm to $5.72 \times 4.15 \times 2.98$ mm. The body color of all eight synthetic emeralds, when examined table up, was a very slightly bluish green of medium dark tone and moderate intensity. To the unaided eye, all the samples appeared flawless.

Refractive index was determined using a Duplex II refractometer with a polarizing filter (to determine birefringence) and a sodium vapor light source. We established specific gravity by the hydrostatic method, using a Mettler AM100 electronic balance. The reaction to ultraviolet radiation was observed under darkroom conditions with a standard UV lamp. The samples were also examined with a Chelsea filter and a Hanneman-Hodgkinson emerald filter (Hodgkinson, 1995), as well as with a standard polariscope, a calcite dichroscope, and a Beck prism spectroscope.

In addition, we submitted these samples to infrared spectroscopy, X-ray fluorescence spectroscopy, and electron microscopy. Mid-infrared spectra were taken using a Nicolet 510 Fourier transform infrared spectrometer (FTIR) in the region from 6600 to 400 cm^{-1} (1515–25,000 nm), at a resolution of 4 cm^{-1}. Ultraviolet-visible-near infrared (UV-Vis-NIR) spectra were taken with a Hitachi U-4001 spectrophotometer in the region 250–2500 nm, with calcite polarizers used to obtain oriented spectra in two crystallographic directions for three faceted ovals—0.19, 0.21, and 0.37 ct.

Energy-dispersive X-ray fluorescence (EDXRF) spectroscopy was performed on four faceted ovals (0.19, 0.23, 0.37, and 0.41 ct) using a Tracor Northern (Spectrace) 5000 unit with a rhodium X-ray tube. Three faceted ovals (0.20, 0.23, and 0.41 ct) were examined using a Camscan Series II analytical scanning electron microscope (SEM) at the Division Analytical Facility, Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena, operating under run conditions of 15 kV excitation voltage and 100 μA specimen current, with a Tracor Northern 5500 energy-dispersive X-ray spectrometer for elemental analyses at selected points.

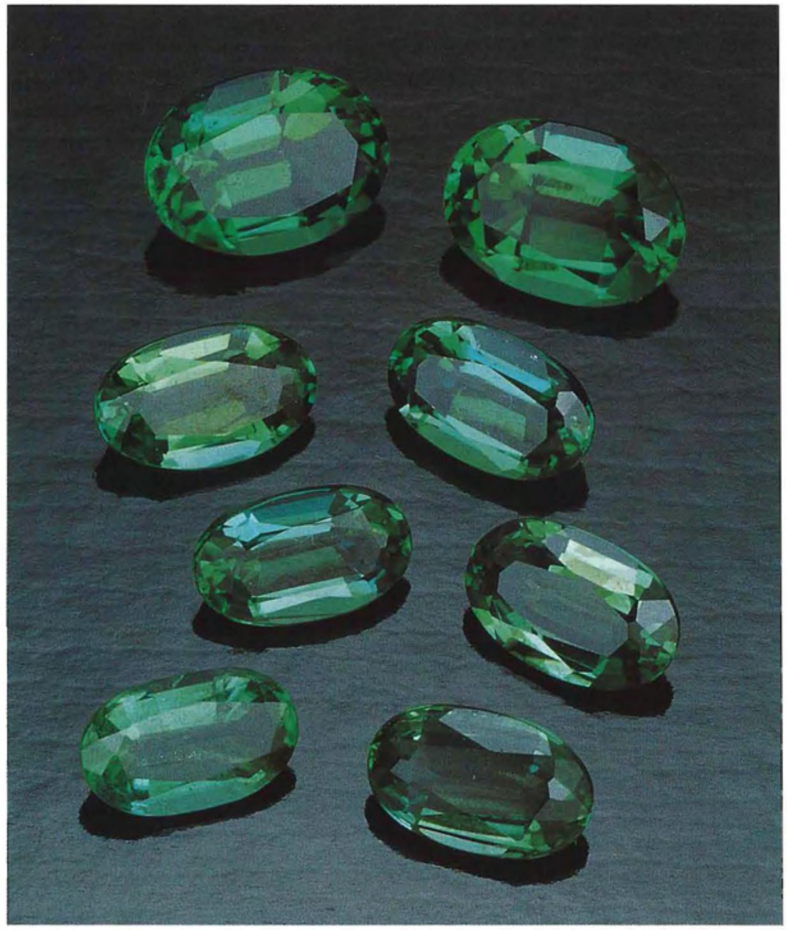


Figure 1. The eight Russian hydrothermal synthetic emeralds examined for this report, all oval mixed cuts, ranged from 0.17 to 0.41 ct. Photo by Maha DeMaggio.

GEMOLOGICAL PROPERTIES

The results of the gemological testing on this collection of Russian hydrothermal synthetic emeralds are summarized in table 1 and discussed below.

Refractive Index. We recorded R.I. ranges of 1.572–1.578 (n_ϵ) and 1.579–1.584 (n_o), with a birefringence of 0.006–0.007 and a uniaxial negative optic character. These refractive indices are comparable to those of previously examined Russian hydrothermal synthetic emeralds (see, e.g., Koivula, 1985; Schmetzer, 1988; Henn et al., 1988; Scarratt, 1994), but they are higher than the values reported for the Biron material (Kane and Liddicoat, 1985). These values also overlap those reported for natural emeralds (Schrader, 1983).

Specific Gravity. The eight samples had average S.G. values for three tests that ranged from 2.67 to 2.73. Although the air weights were consistent for each weighing, the values obtained in water immersion were not, due to the relatively small size of these samples; this led to the variation in the final calculated S.G.'s.

These values are comparable to those previously reported for hydrothermal synthetic emeralds (Takubo, 1979; Koivula, 1985; Kane and Liddicoat, 1985; Schmetzer, 1988; Henn et al., 1988; Scarratt, 1994; "What to look for . . ," 1989). They also overlap those reported for natural emeralds (Schrader, 1983; Webster, 1994).

TABLE 1. Gemological properties of the new Russian hydrothermal synthetic emeralds.

Properties that overlap those of other synthetic and natural emeralds	
Color (through table)	Very slightly bluish green
Refractive index	n_ε = 1.572–1.578; n_o = 1.579–1.584
Birefringence	0.006–0.007
Optic character	Uniaxial negative
Specific gravity (hydrostatic)	2.67–2.73
Ultraviolet fluorescence[a]	Inert to both long- and short-wave UV
Phosphorescence	None
Chelsea color-filter reaction	Weak red
Pleochroism	Moderate yellowish green and bluish green
Optical absorption spectrum	Virtually identical to the spectrum shown by natural and earlier Russian hydrothermal synthetic emeralds
Inclusions	Opaque black hexagonal plates and crystals that look like phenakite
Possible key identifying properties	
Inclusions	Numerous tiny red-brown and white nondescript particles
Infrared spectrum	Weak to moderate absorptions at about 2235, 2320, and 2440 cm^{-1}; weak, sharp peak at about 2358 cm^{-1}; broad shoulder at 4052 cm^{-1}.

[a]*Testing done in total darkness (darkroom conditions).*

Reaction to Ultraviolet Radiation. As with natural emeralds and other hydrothermal synthetic emeralds reported in the literature, all of the samples were inert to long-wave (365 nm) and short-wave (254 nm) UV radiation.

Color-Filter Reactions. When placed on the tip of a fiber-optic illuminator and observed through the Chelsea color filter at a low angle to the direction of illumination, all eight samples revealed a weak red glow. These stones also showed a very weak red transmission luminescence in white light when no filter was used. (The angle of observation is important, and the only visible light source in the room should be the fiber-optic illuminator.) Similar reactions have been observed in both natural and synthetic emeralds. Like natural emerald, these synthetics showed no reaction to the Hanneman-Hodgkinson emerald filter.

Polariscope Reaction. Each stone exhibited typical double refraction and standard uniaxial optic figures. Because of facet interference, we had to immerse the three smallest stones in methylene iodide to observe their optic figures.

Dichroism. All eight specimens showed distinct dichroism of yellowish green (perpendicular to the optic axis) and bluish green (parallel to the optic axis), as is typical of many natural and synthetic emeralds. No specific optic orientation was noted in the eight samples.

Spectroscopy. Using both transmitted and internally reflected light, we observed a relatively weak absorption spectrum in all eight stones, but it was typical of emerald (Liddicoat, 1987). The features noted were located in the red at approximately 652 (weak), 632 (moderate), and 606 (moderate) nm. In addition, there was a weak, "smudged" band of general absorption in the orange-red between 584 and 603 nm, and a cutoff in the red starting at about 660 nm.

Internal Characteristics. The most obvious characteristic seen with the microscope (with any illumi-

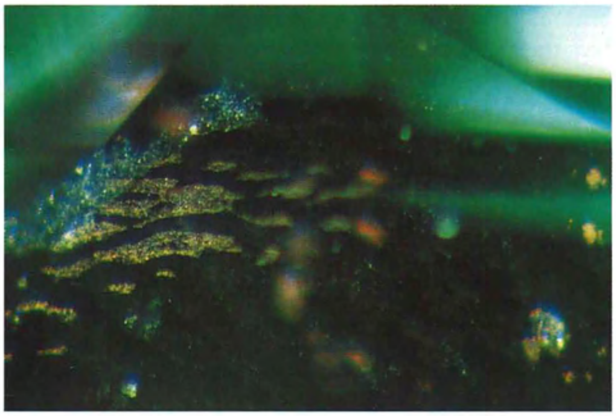


Figure 2. Clouds of tiny red-brown particles, like those shown here, were seen in all eight of the new Russian hydrothermal synthetic emeralds examined. They have not been reported before in natural or other hydrothermal synthetic emeralds. Photomicrograph by John I. Koivula, magnified 50×.

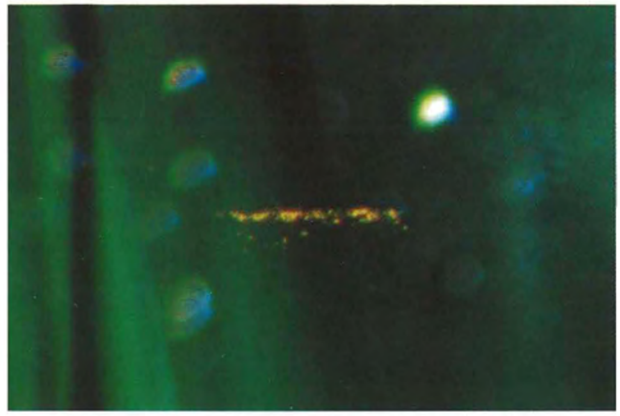


Figure 3. In one of the Russian synthetics, the tiny red-brown particles appeared in a linear arrangement. Photomicrograph by John I. Koivula, magnified 50×.

nation technique, in all eight samples) was the lack of the distinctive and highly developed chevron- or V-shaped growth zoning that is typical of all other Russian hydrothermal synthetic beryls (Takubo, 1979; Koivula, 1985; Gübelin and Koivula, 1986; Schmetzer, 1988; Henn et al., 1988). Also, the internal motif observed in these new hydrothermal synthetics does not resemble the suite of characteristic inclusions recognized so far in natural emeralds (Gübelin and Koivula, 1986; Schwarz, 1987). These unusual internal characteristics serve to identify them as a new type of Russian hydrothermal synthetic.

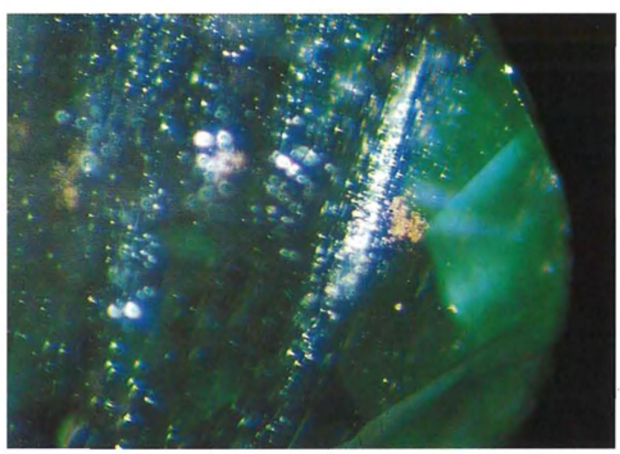
Specifically, all eight stones contained numerous tiny red-brown particles (visible even at 10× in some cases), which were so small that they could not be resolved microscopically into any recognizable crystal habit (even at 120×). These particles usually were arranged in dense clouds with no particular orientation or form (figure 2); in one instance, they appeared in a linear arrangement (figure 3).

With fiber-optic illumination and 30× magnification, we also saw clouds and layers of tiny, randomly oriented, white-appearing particles in all eight of the synthetic emeralds. These inclusions were extremely dense (figure 4) and easily observed in four of the eight samples, but they were very difficult to detect in the other four, even with strong pinpoint fiber-optic illumination. As with the red-brown inclusions, these white-appearing particles were too small to be resolved completely with a standard gemological microscope. Because of their small size, their white appearance may be due in part to light reflection and scattering rather than to their true color.

One 0.20 ct stone had a small fingerprint-like accumulation of white particles under the table facet that resembled a partially healed fracture (figure 5). This was the only evidence of fracturing or fracture healing noted.

Only two samples contained inclusions large enough to be identified as crystals. One 0.37 ct sample contained a 0.2-mm-long, birefringent, euhedral crystal that had the habit of phenakite (figure 6). The 0.23 ct sample contained two opaque black hexagonal plates that showed a silvery gray metallic luster in reflected light. One of these

Figure 4. Dense concentrations of extremely fine, white-appearing particles are another distinctive internal feature noted in the new Russian hydrothermal synthetic emeralds. Photomicrograph by John I. Koivula, magnified 30×.



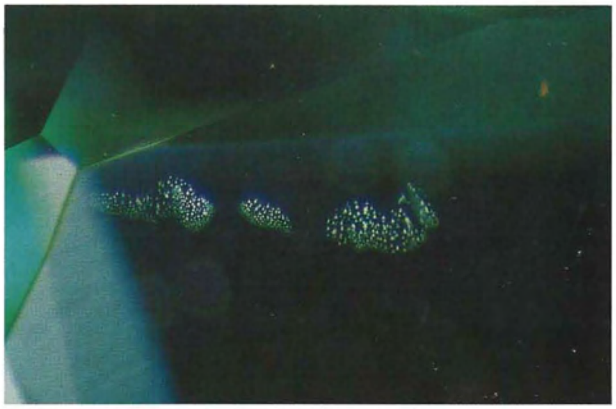


Figure 5. Only one fingerprint-like pattern was observed in any of the eight samples of Russian synthetic emeralds. Photomicrograph by John I. Koivula, magnified 35×.

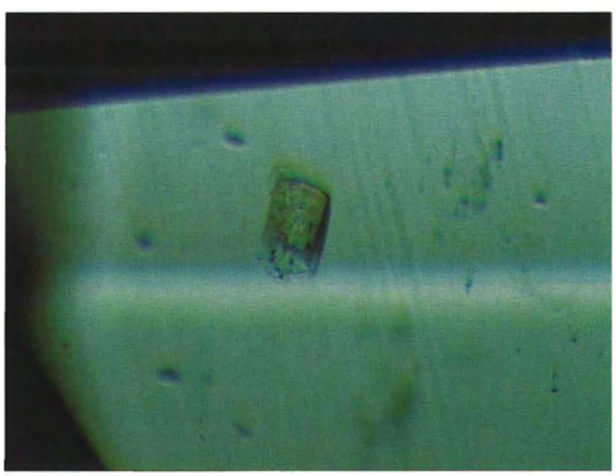
hexagonal plates (figure 7) caused growth blockage in the form of two conical growth zones extending away from one flat surface, which was visible in shadowed transmitted light.

ADVANCED TESTING

Infrared Spectroscopy. Features due to water and hydroxides are easily seen in the infrared spectra of emeralds and other beryls, and are useful in differentiating natural stones from their synthetic counterparts (Wood and Nassau, 1968; Schmetzer and Kiefert, 1990). Absorption features from other chemical groups (such as CO_2) are also present.

The mid-infrared spectra of our eight samples are similar in overall appearance to those of natural emeralds and other Russian hydrothermal emeralds, but they differ significantly from those of both flux and other (non-Russian) hydrothermal synthetic emeralds (figure 8). Other hydrothermal synthetic emeralds have high water contents and, thus, very strong absorptions in the region around 3600 cm^{-1} as well as strong absorptions between 3000 and 2000 cm^{-1}. However, these Russian hydrothermal synthetic emeralds have only moderate to strong water-related peaks at 3600 cm^{-1} and are quite transparent at 3000 cm^{-1}. Nevertheless, such a spectrum still contrasts sharply with that of a flux-grown synthetic emerald, which is essentially free of water.

Figure 6. This 0.2-mm-long crystal, seen in the 0.37 ct Russian hydrothermal synthetic emerald, looks like phenakite. Photomicrograph by John I. Koivula.



Wood and Nassau (1968) described two positions that water molecules can occupy within the channels in a beryl's structure. The different orientations of these "type I and type II water" molecules are clearly reflected in the positions of their absorption peaks in the ordinary- versus extraordinary-ray spectra. Both types of water cause several sharp absorption peaks between 3510 and 3825 cm^{-1}; however, only type II water causes absorptions at about 3910 cm^{-1} and 3230 cm^{-1}. Wood and Nassau found that all natural emeralds and Linde hydrothermal synthetic emeralds contained type I water, but that only natural emeralds showed type II water, although in greatly varying amounts. In 1990, however, Schmetzer and Kiefert reported type II water bands in Lechleitner and some Russian hydrothermal synthetic emeralds as well.

Because of the difficulties inherent in taking the spectra of faceted gems, we could only obtain unoriented mid-infrared spectra for our samples, which made the interpretation of mid-infrared water bands more difficult. Weak type II peaks can be seen in the spectra of both the natural emerald and the representative Russian hydrothermal synthetic emerald from our study sample, as shown in figure 8.

The gross spectral similarities in the mid-infrared between these Russian hydrothermal emeralds and natural emeralds do not extend to the finer structure seen in the region around 2300 cm^{-1} (figure 9A). Natural emeralds have a moderate to strong, sharp absorption at 2358 cm^{-1}, much stronger in the ordinary-ray spectrum, which Wood and Nassau assign to CO_2 oriented within the beryl structure. Stockton (1987) describes a distinct peak at 2290 cm^{-1} and a peak or shoulder at about 2340 cm^{-1}, in addition to the peak at 2358 cm^{-1} (which she asserts is always stronger than the 2340 cm^{-1} in natural emeralds), but she does not identify the causes of these absorptions. All three features also have been observed in the

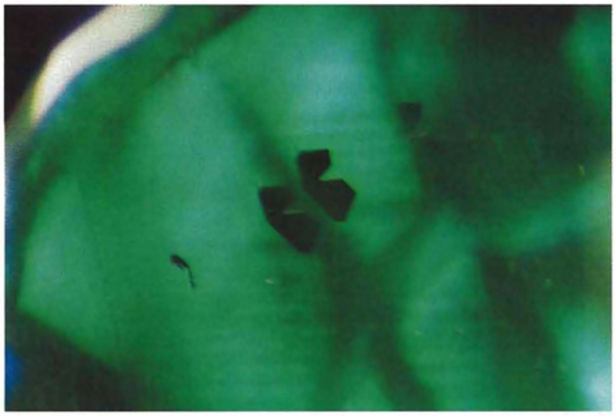


Figure 7. One of the samples contained two black opaque hexagonal plates like this one, here multiply reflected by facets. Photomicrograph by John I. Koivula, magnified 50×.

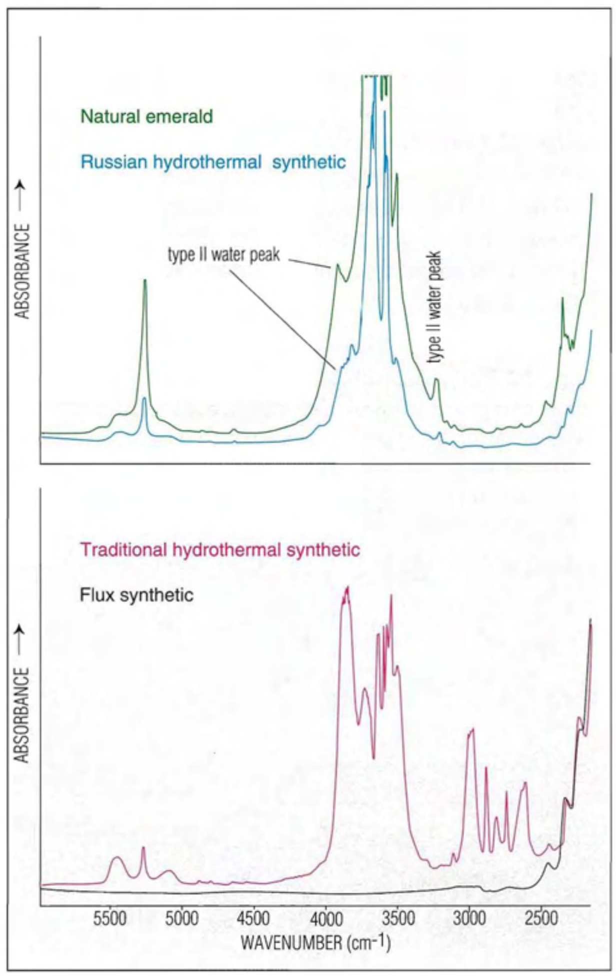
spectra of 67 natural emeralds identified by standard gemological techniques in the GIA Gem Trade Laboratory over the last four years. Although these peaks vary considerably in magnitude from one spectrum to another, probably due in part to the fact that these are unoriented spectra, our data support Stockton's statement regarding their relative strengths in natural emeralds.

In this region around 2300 cm^{-1}, however, our eight Russian hydrothermal synthetic emeralds showed a structure very different from that seen for natural emeralds. These synthetics have weak to moderate, somewhat broad absorptions at about 2235, 2320, and 2440 cm^{-1}, and a weak, sharp peak at about 2358 cm^{-1}. They show no peak at 2290 cm^{-1}. Accepting Stockton's assertion that the "2340 cm^{-1}" band may be found as far away as 2310 cm^{-1} in synthetic emeralds, we see that in these Russian hydrothermal synthetics, too, the "2340" peak (actually at 2320 cm^{-1} for our samples) is stronger than the absorption at 2358 cm^{-1}.

Stockton's examination of three Russian hydrothermal emeralds available at that time also revealed weak features at 4375 cm^{-1} and 4052 cm^{-1}, which had not been seen in natural emeralds. The spectra of the Russian synthetic emeralds examined for this study have no features at 4375 cm^{-1}, but all show a broad shoulder at 4052 cm^{-1} (figure 9B).

Water in beryl also absorbs in the near-infrared at about 1400 and 1900 nm, and in these regions we were able to obtain oriented spectra for three samples. The extraordinary-ray near-infrared spectra (figure 10A) of a natural emerald and all three synthetics showed strong water-related peaks at about 1896 nm and 1400 nm, a moderate peak around 1464 nm, and weak peaks at 1149 nm and 2145 nm. In the ordinary-ray spectra (figure 10B), there are three strong peaks at 1950, 1895, and 1830 nm, and two moderate peaks around 1400 nm. Comparison of these results with Wood and Nassau's figure 4 confirms that both the natural emerald used for reference and these Russian hydrothermal synthetic emeralds contain small amounts of type II water, similar to Schmetzer and Kiefert's "group II" emeralds.

Figure 8. Representative mid-infrared spectra of a natural emerald, a "traditional" hydrothermal synthetic emerald, a flux synthetic emerald, and one of the new Russian hydrothermal synthetic emeralds are shown here for comparison. Note that the spectrum of the Russian hydrothermal synthetic is more like that of the natural emerald than like that of either the typical hydrothermal synthetic or the flux synthetic.



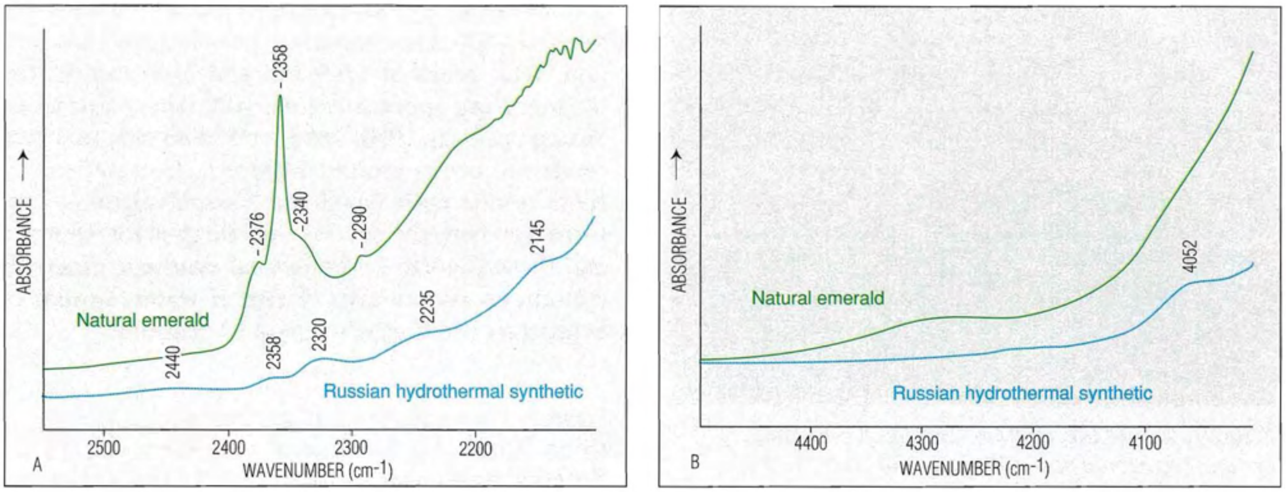


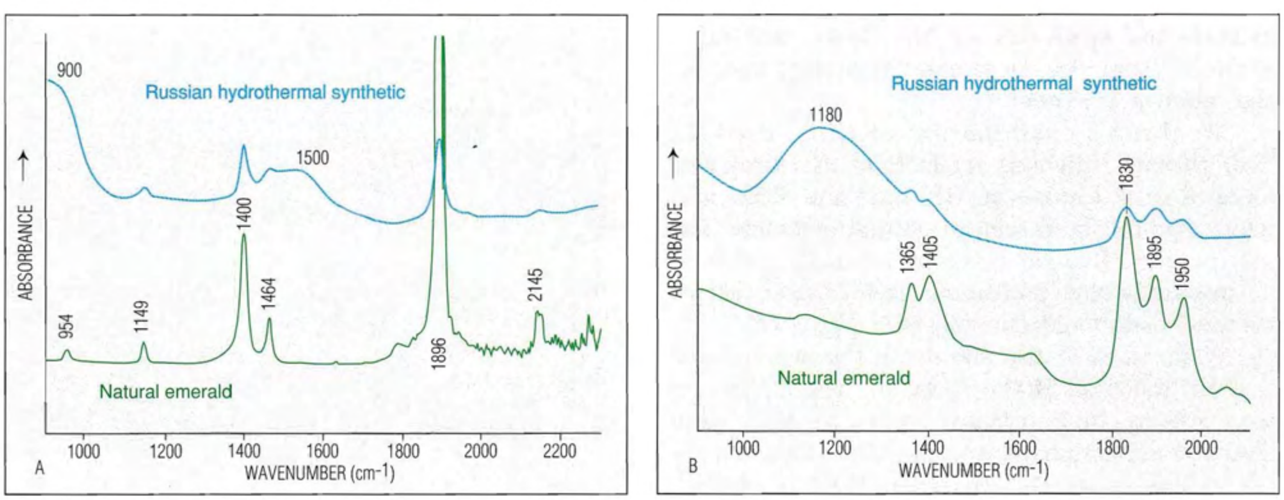
Figure 9. (A) The fine structure of their spectra around 2300 cm^{-1} (mid-infrared) reveals marked differences between natural emerald (green curve) and the Russian hydrothermal synthetic emeralds tested for this study (blue curve). (B) In the region around 4200 cm^{-1}, these synthetics display one of the features reported by Stockton (1987) for other Russian hydrothermal synthetics, at 4052 cm^{-1}. Such a shoulder has not been seen in natural emeralds.

There are, however, some dramatic differences in the near-infrared spectra of these Russian (manufactured by Tairus) synthetic emeralds as compared to those of natural stones. The synthetic emeralds produced two broad absorptions in the extraordinary-ray spectrum (figure 10A), one centered around 1500 nm and the other at about 900 nm, and one in the ordinary-ray spectrum (figure 10B) at about 1180 nm; none of these features has been reported in natural emeralds.

Thus, in both the mid- and near-infrared, even for unoriented spectra, these Russian hydrothermal synthetic emeralds display diagnostic features that distinguish them from all natural emeralds.

Ultraviolet-Visible Spectroscopy. The UV-Vis absorption spectra of all eight Russian hydrothermal synthetic emeralds studied showed comparable features, which are similar to those published by Schmetzer (1988) for Russian hydrothermal syn-

Figure 10. These near-infrared extraordinary-ray (A) and ordinary-ray (B) spectra of a natural emerald (green curve) and a sample new Russian hydrothermal synthetic emerald (blue curve) show that both contain small amounts of type II water, which was once believed to occur only in natural emeralds. Note, however, the broad absorption peaks in the synthetic that are not seen in the natural stone.



thetic emeralds. The green color is due to a transmission window around 500 nm, surrounded by two broad absorptions centered at about 435 and 600 nm. These measurements are in partial disagreement with handheld spectroscope observations. For example, the lines observed at 632 and 652 nm with the spectroscope are probably those noted at 637 and 661 nm with the spectrometer.

Chemical Analysis. *EDXRF.* Four of the synthetic emeralds were selected for EDXRF analysis. Only some of the elements present in emerald are detectable by X-ray fluorescence; oxygen, hydrogen, and beryllium are not. In addition to aluminum and silicon, a minor amount of iron and traces of chromium, potassium, calcium, titanium, nickel, and copper were detected in the four faceted stones. Unlike some other (non-Russian) hydrothermal synthetic emeralds (see, e.g., Hänni and Kiefert, 1994), our samples did not show any chlorine.

SEM-EDS. In an effort to identify the minute white and red-brown particles in these synthetic emeralds, we submitted three samples to SEM-EDS analysis. Only one white-appearing inclusion, in a 0.20 ct sample, reached the surface. Within this inclusion, we found a micron-sized calcium- and sulfur-bearing grain—possibly synthetic gypsum. Traces of sodium, potassium, titanium, iron, and chlorine—found in the dark pit on the emerald's surface—may be the evaporated residue of the hydrothermal solution in which the emerald grew, or may represent residue from the polishing compound.

CONCLUSION

These eight Russian synthetic emeralds represent a new type of hydrothermal product. Their standard gemological properties, such as R.I. and S.G., overlap those of both natural and other hydrothermal synthetic emeralds. However, microscopy and spectroscopy provide information useful for gemological identification.

Although the roiled, chevron-shaped growth zoning that is generally considered to be characteristic of Russian synthetic beryls was absent in this new product, other internal characteristics, if present, would readily identify this material as synthetic. In particular, the tiny red-brown particles (of undetermined nature) observed in all eight faceted ovals have not been previously noted in natural emeralds or in the "traditional" Russian hydrothermal product. In the absence of such particles, advanced testing by such techniques as infrared spectroscopy or EDXRF analysis may be needed to identify this material conclusively as a synthetic.

REFERENCES

Gübelin E.J., Koivula J.I. (1986) *Photoatlas of Inclusions in Gemstones*, ABC Edition, Zurich, Switzerland.

Hänni H.A., Kiefert L. (1994) AGEE hydrothermal synthetic emeralds. *JewelSiam*, October/November, pp. 80–85.

Henn U., Lind T., Bank H. (1988) Hydrothermally grown synthetic emeralds from USSR. *Canadian Gemmologist*, Vol. 9, No. 3, pp. 66–72.

Hodgkinson A. (1995) The Hanneman-Hodgkinson synthetic emerald filter. *Canadian Gemmologist*, Vol. 16, No. 1, pp. 18–22.

Kane R.E., Liddicoat R.T. Jr. (1985) The Biron hydrothermal synthetic emerald. *Gems & Gemology*, Vol. 21, No. 3, pp. 156–170.

Koivula J.I. (1985) Gem news: More on Russian hydrothermal synthetic emeralds. *Gems & Gemology*, Vol. 21, No. 1, p. 59.

Liddicoat R.T. Jr. (1987) *Handbook of Gem Identification*, 11th ed. Gemological Institute of America, Santa Monica, CA.

Nassau K. (1980) *Gems Made by Man*. Chilton Book Co., Radnor, PA.

Scarratt K. (1994) Lab report: Hydrothermal synthetic emerald. *JewelSiam*, Vol. 5, No. 1, pp. 67–68.

Schmetzer K. (1988) Characterization of Russian hydrothermally-grown synthetic emeralds. *Journal of Gemmology*, Vol. 21, No. 3, pp. 145–162.

Schmetzer K., Kiefert L. (1990) Water in beryl: a contribution to the separability of natural and synthetic emeralds by infrared spectroscopy. *Journal of Gemmology*, Vol. 22, No. 4, pp. 215–223.

Schrader H.W. (1983) Contributions to the study of the distinction of natural and synthetic emeralds. *Journal of Gemmology*, Vol. 18, No. 6, pp. 530–543.

Schwarz D. (1987) *Esmeraldas: Inclusões em Gemas.* Escola de Minas, Universidade Federal de Ouro Preto, Ouro Preto, Brazil.

Stockton C.M. (1987) The separation of natural from synthetic emeralds by infrared spectroscopy. *Gems & Gemology*, Vol. 23, No. 2, pp. 96–99.

Takubo H. (1979) Characteristics of synthetic hydrothermal emeralds from USA and USSR. *Journal of the Gemmological Society of Japan*, Vol. 6, No. 4, pp. 3–4.

Webster R. (1994) *Gems: Their Sources, Descriptions and Identification*, 5th ed. Revised by Peter Read, Butterworths, London.

What to look for in Vasar synthetic emeralds (1989). *Jewellery News Asia*, September, pp. 178–179.

Wood D.L., Nassau K. (1968) The characterization of beryl and emerald by visible and infrared absorption spectroscopy. *American Mineralogist*, Vol. 53, No. 5-6, pp. 777–799.