

HIBONITE: A NEW GEM MINERAL

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A 0.23 g orangy brown crystal, a 0.39 ct step-cut gem later faceted from it, and a 0.71 g crystal—all reportedly from Myanmar—were characterized for this report. Infrared spectroscopy, X-ray diffraction, and chemical analysis identified the material as hibonite. These samples represent the first gem-quality hibonite ever recorded.

In late 2009, two transparent orangy brown crystals weighing 0.23 and 0.71 g (figures 1 and 2) were submitted to the AIGS Gemological Laboratory in Bangkok for identification. The crystals were said to originate from

ther analysis and was identified as hibonite; it was subsequently cut into a 0.39 ct gemstone (figure 2, right). We believe these are the first gem-quality specimens of hibonite ever documented.

Hibonite is a hexagonal mineral with the chemical formula $(\text{Ca,Ce})(\text{Al,Ti,Mg})_{12}\text{O}_{19}$. It has a Mohs hardness of 7.5–8 and an SG of 3.84, and it is uniaxial negative with refractive indices of $\omega = 1.807$ and $\varepsilon = 1.790$ (Roberts et al., 1974). Hibonite was discovered in 1955 as opaque to partially translucent black grains in the Esiva alluvial thorianite and phlogopite deposit, located in Toliara (Tuléar) Province, Madagascar (Curien et al., 1956). This rather rare mineral was named after Paul Hibon, the French prospector who discovered it (Fleischer, 1957). Hibonite is known to occur in meteorites, but it is most often associated with moderate- to high-grade metamorphic calcareous rocks,

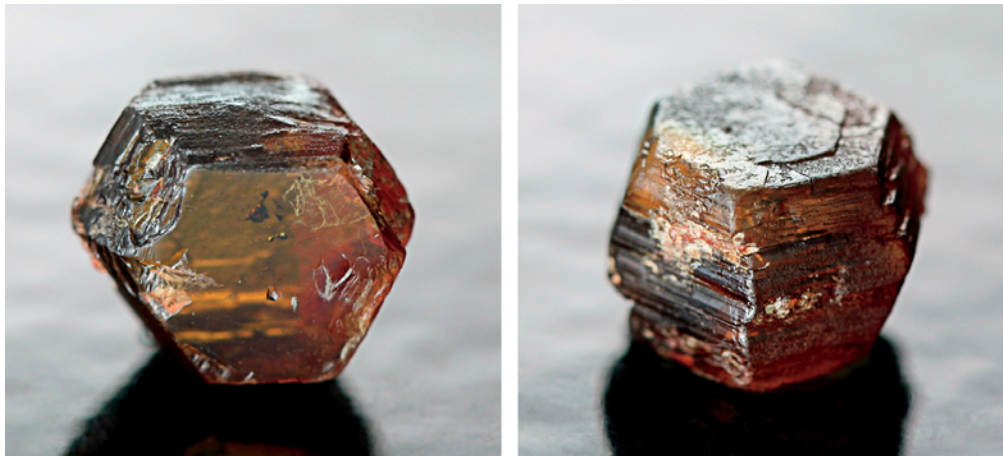


Figure 1. The 0.71 g ($7.02 \times 7.32 \times 5.44$ mm) gem-quality hibonite crystal, reportedly from Myanmar, is shown from two different angles. Photos by L. Massi.

Myanmar, with no additional specifics given. Standard gemological testing and semiquantitative chemical analysis were inconclusive. The smaller crystal underwent fur-

sometimes with corundum, spinel and/or sapphire, as documented at Andranondambo in Madagascar (Schwarz et al., 1996), in southern Tanzania (Maaskant et al., 1980), at Chyulu Hills in Kenya (Ulianov et al., 2005), and in the Achankovil shear zone in southern India (Rajesh, 2010). Macroscopic samples of hibonite are generally opaque and at best translucent, though very small transparent pale yellow to brown crystals were reported from the Tanzanian occurrence.

See end of article for About the Authors and Acknowledgments.

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Figure 2. The 0.23 g hibonite crystal (left) was fashioned into a 0.39 ct step-cut gem (right). The smooth surface on the rough is a polished facet, which corresponds to the table of the faceted gem. The *c*-axis is nearly vertical. Photos by T. Hainschwang (left) and F. Notari (right).

Materials and Methods. Standard gemological properties of the two crystals and the faceted gem that was subsequently cut were determined at the AIGS and GemTechLab laboratories using a refractometer (RI), hydrostatic balance (SG), and 6W long- and short-wave UV lamp (fluorescence). Internal features were observed with standard gemological microscopes at up to 120× magnification.

Advanced testing was performed on the smaller crystal. Reflectance infrared spectra were recorded in the 7500–400 cm^{-1} range at 4 cm^{-1} resolution with Nicolet Nexus and Perkin Elmer BXII Fourier-transform infrared (FTIR) spectrometers at GemTechLab and Gemlab, respectively. Raman spectra were recorded at the IMN–University of Nantes with a Horiba T64000 dispersive Raman spectrometer employing a 514 nm argon laser. Single-crystal X-ray diffraction analysis was performed at the University of Bern using a Bruker Apex diffractometer with $\text{MoK}\alpha$ radiation and an X-ray power of 50 kV/30 mA. Semiquantitative chemical analysis was performed by energy-dispersive X-ray fluorescence (EDXRF) spectroscopy with an Eagle III system at AIGS, a Thermo QuanX system at GemTechLab, and a custom-built EDXRF spectrometer with a thermoelectrically cooled detector at Gemlab. Quantitative chemical analysis was achieved at the IMN–University of Nantes with two scanning electron microscopes (Zeiss Evo 40XVP and JEOL

5800LV), each equipped with a Princeton Gamma Tech energy-dispersive IMIX-PTS detector. Polarized ultraviolet-visible–near infrared (UV-Vis-NIR) absorption spectra were recorded with a xenon-based prototype spectrometer at 0.6 nm resolution in the 240–1050 nm range at Gemlab, and with a Hitachi spectrometer at 1 nm resolution in the 190–900 nm range at GemTechLab.

Results and Discussion. Standard gemological testing of the crystals and the faceted gem gave an SG of 3.84 and RIs of ~1.79–1.81, consistent with the reference values for hibonite cited above. Since the upper RI values were at the limit of the refractometer, the optic character and birefringence could not be measured with certainty. The samples were inert to UV radiation.

With magnification, a variety of inclusions were visible in all the samples, most of them hexagonal and some triangular (figure 3). SEM-EDX analysis of several surface-reaching grains gave a chemical composition indicative of very pure corundum. A tiny (~50 nm) inclusion within one of these inclusions was found to be fluorite by the same method. Some of the other inclusions may be micas, similar to those found in association with blue sapphire and hibonite in the Andranondambo deposit (Schwarz et al., 1996), but they could not be identified by Raman analysis due to the interfering luminescence from the host (see below).

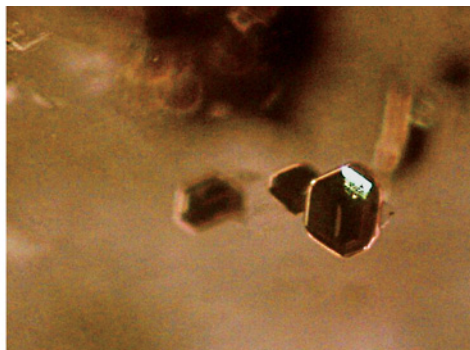
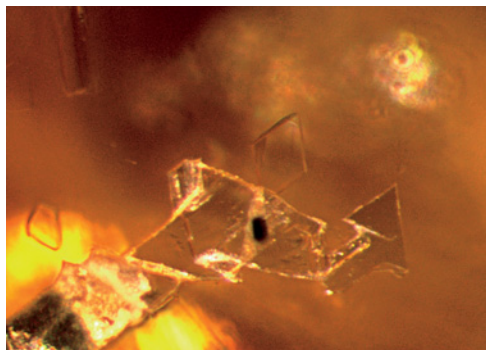


Figure 3. Small triangular and hexagonal inclusions (possibly corundum and mica) were present in the hibonite. Photomicrographs by T. Hainschwang (left, field of view 0.5 mm) and L. Massi (right, magnified 50×).

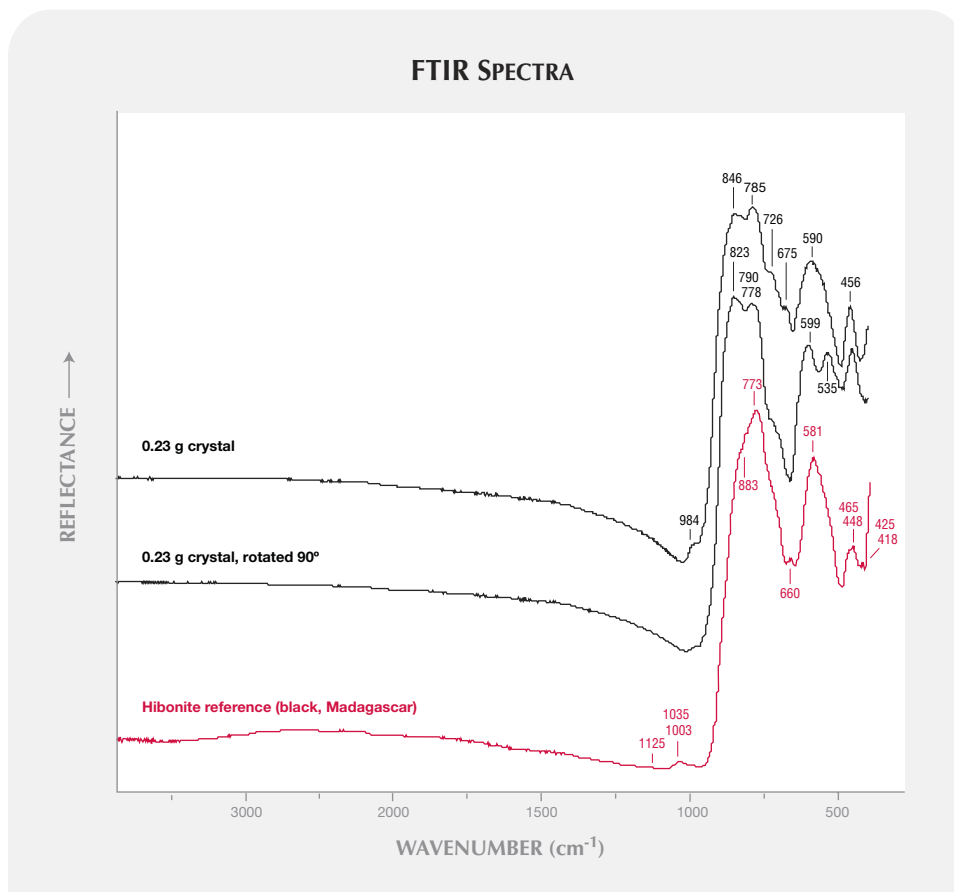


Figure 4. Reflectance FTIR spectra of the smaller crystal, taken in two orientations, show some similarities to the reference spectrum of black hibonite from Madagascar.

TABLE 1. Gemological properties and SEM-EDX quantitative chemical analysis of the 0.23 g hibonite.

Gemological Properties	
Color	Orangy brown
Refractive indices	1.79–1.81
Specific gravity	3.84
Mohs hardness	7 ½–8
Fluorescence	Inert to long- and short-wave UV
Internal features	Triangular and hexagonal crystal inclusions, among others
Quantitative Chemical Analysis ^a	
Element	Atomic %
Al	32.93
Ca	3.37
Mg	1.98
Ti	1.97
Zn	0.46
Fe	0.08
O	59.21

^aResults are normalized to 100%.

Reflectance IR spectroscopy of the smaller crystal yielded patterns relatively close to that of a reference spectrum of hibonite from Madagascar (internal reference, GemTechLab and Gemlab). Nevertheless, the spectra recorded from the sample were sufficiently different that the crystal’s identity remained in doubt (figure 4).

It proved very difficult to obtain useful Raman data, and the spectrum recorded on the smaller crystal was inconclusive. The main features were two weak bands at 903 and 880 cm^{-1} , a more distinct broad band at 740 cm^{-1} , and a weak broad band at 330 cm^{-1} . Hibonite appears to have a weak Raman signal, as many of the published spectra are of poor quality. The hibonite reference spectra in the RRUFF database (<http://rruff.info>), for example, are not pure Raman scattering signals, but appear to consist of luminescence signals.

The identification as hibonite was further supported by X-ray diffraction analysis, which established the material as hexagonal with unit-cell dimensions of $a = 5.592(2) \text{ \AA}$, $c = 21.989(3) \text{ \AA}$, and volume = 595.5(3) \AA^3 . This limited the possible mineral groups to taaffeite, högbomite, or hibonite. A crystal-structure refinement achieved from the X-ray diffraction data indicated near-end member hibonite.

This result was confirmed by chemical analysis. EDXRF spectroscopy of several areas of the smaller crystal indicated mainly Al, plus Ca, Ti, Mg, Zn, and traces of Fe

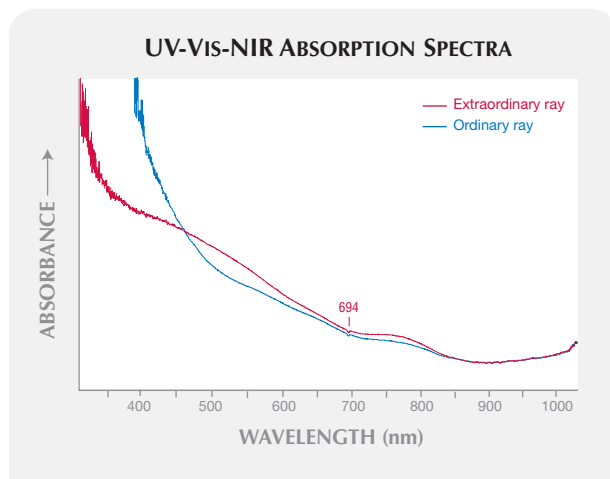


Figure 5. The polarized UV-Vis-NIR spectra of the smaller hibonite crystal are characterized by an absorption continuum with superimposed broad bands, which is responsible for the orangy brown color. The small negative peak at 694 nm is due to Cr^{3+} luminescence.

and Sr; Cr was barely detectable (detection limit ~20 ppm). Quantitative SEM-EDX chemical analysis of this crystal gave a similar result, with slight differences due to the lower sensitivity of this method (detection limit ~100 ppm; see table 1). The significant traces of Zn are surprising for hibonite, as Zn is regarded as an uncommon impu-

rity in this mineral (e.g., Maaskant et al., 1980; Hofmeister et al., 2004). Also, we did not detect Ce (or any other rare-earth element), which is usually present in hibonite.

The polarized UV-Vis-NIR spectra (figure 5) were characterized by broad bands overlaying an absorption continuum with increasing absorbance from lower to higher energies (higher to lower wavelengths). This continuum is responsible for the orangy brown color. Its origin is unclear, but it could be due to an Fe-Ti intervalence charge transfer, as both elements were detected by chemical analysis. Because this color mechanism absorbs light efficiently, it does not require high concentrations of these elements. This mechanism gives similar colors to a number of minerals and gems such as dravite, andalusite, and micas (Fritsch and Rossman, 1988). The origin of the superimposed broad bands is uncertain; they contribute only very slightly to the color. The absence or very low concentrations of Ce and Fe, both potential light absorbers, may explain why this sample is lightly colored when hibonite is usually black and opaque.

Conclusions. Hibonite can be identified by its gemological properties (RI = 1.79–1.81, SG = 3.84, no UV fluorescence) and composition as determined by semiquantitative or quantitative chemical analysis. Gem-quality hibonite can now be added to the list of known gem minerals. Its rarity classifies it as an exotic collector's stone. If more of this material is discovered, its qualities (hardness, attractive color, etc.) make it suitable for general use in jewelry.

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