Demantoid and Topazolite from Antetezambato, Northern Madagascar: Review and New Data

Federico Pezzotta, Ilaria Adamo, and Valeria Diella

An important deposit of andradite, containing demantoid and topazolite varieties, has been mined near the village of Antetezambato in northern Madagascar since early 2009. Most of the activity took place from April through November 2009, and yielded a large quantity of rough material in a wide range of colors. The deposit has a skarn origin, related to contact metamorphism between Cenozoic magmatic intrusions and Mesozoic calcareous sediments. The garnets' internal features consist mainly of fluid inclusions, fractures, wollastonite needles (or their remnant channels), and diopside aggregates. The chemical composition is close to pure andradite, with negligible Cr and V contents; thus, iron is likely the main chromophore. LA-ICP-MS analysis showed a relatively high content of light rare-earth elements.

Since early 2009, the village of Antetezambato in northern Madagascar has become known for producing fine andradite gem rough and crystal specimens. The deposit has yielded a range of andradite colors, including yellow-green to bluish green demantoid (figure 1), greenish/brownish yellow to brown topazolite, and rare dark brownish red to red material. Several articles describing the locality and its andradite production have been published. Following the preliminary gemological data reported by Mocquet et al. (2009a), further details were provided by Danet (2009), Mocquet et al. (2009b), Rondeau et al. (2009a), and the authors listed below. Pezzotta (2010a) provided historical, geological, and mineralogical information, including the andradite's paragenesis and crystal morphology; some mineralogical information also appeared in Praszkier and Gajowniczek (2010) and Pezzotta (2010b). Local newspaper articles (e.g., Razafindramiadana, 2009) and various websites documented the rush of miners, brokers, and dealers to the site, as well as the many social and security problems that have plagued the area.

The notable features of gem andradite from this locality can be summarized as:

- A skarn origin (Pezzotta, 2010a).
- A wide range of color varieties, mostly demantoid but also topazolite, as documented by several authors, particularly Rondeau et al. (2009b) and Pezzotta (2010a,b); a review of andradite color variety names appears in Pezzotta (2010a).
- Growth zoning, anomalous extinction (strain), and the absence of horsetail inclusions (Rondeau et al., 2009b).
- An almost pure andradite composition, as documented on one sample by Bocchio et al. (2010) and on two samples by Adamo et al. (2011).
- The relative absence of chromium, as documented by Rondeau et al. (2009b); nevertheless, Schmetzer and Karampelas (2009) reported that

See end of article for About the Authors and Acknowledgments.

Gems & Gemology, Vol. 47, No. 1, pp. 2–14.

Figure 1. Since early 2009, substantial quantities of attractive demantoid have emerged from the Antetezambato area of northern Madagascar. The stones shown here range from 1.86 to 3.99 ct. Courtesy of Fine Gemstones Madagascar; photo by Matteo Chinellato.

minor amounts of chromium were responsible, at least in part, for the green color.

- The significant presence of rare-earth elements (REEs), as pointed out on one sample by Bocchio et al. (2010).

This article provides an update on the mining activity and production and distribution of demantoid from the Antetezambato deposit. A complete gemological characterization, including quantitative chemical data, is also presented. This study confirms previously published data, establishes the characteristic features of gem andradite from this locality, and offers new information concerning inclusions, trace-element profiles, and UV-Vis-NIR spectra. In addition, a genetic model for the andradite's formation is presented.

LOCATION

The andradite deposit is located in the Antsiranana region of northern Madagascar, ~2.5 km west of the village of Antetezambato (figure 2). The mining area covers ~20 hectares and is centered at 13°30.460'S, 48°32.652'E; most of the mining takes place within a mangrove swamp that is subject to daily tidal flooding (figure 3). Detailed information about the locality and its geomorphology, including tidal effects, was presented by Pezzotta (2010a).

HISTORY

Lacroix (1922) reported finding pale green andradite crystals in the cavities of a nepheline syenite of Mount Bezavona, an intrusive massif of Cretaceous age located south of the Nosy Be archipelago on the Ampasindava peninsula. Beyond this one entry, there is no other mention in the literature of green andradite from Madagascar. Gem-quality green grossular (tsavorite) has been found at Gogogogo in the Toliara region (Mercier et al., 1997), and at Itrafo in the Antananarivo region.

A detailed description of the Antetezambato deposit's discovery and mining activity up to early 2010 appears in Pezzotta (2010a), and a brief review is given here. Between 2006 and 2008, a few local people from Antetezambato (at the time a small village of ~20 huts) recovered a small quantity of stones from a tidal estuary that were initially thought to be zircon or sapphire. As word spread that they had found demantoid, thousands of people rushed to the site in 2009 (e.g., figures 4 and 5).

Unfortunately, the situation deteriorated quickly. Armed robberies became more frequent as organized crime from the Ilakaka and Ambondromifehy sapphire trade spread to the Ambanja and Antetezambato areas. Since October 2009, authorities have brought the situation somewhat under control, though the area is still considered very dangerous.

Production has also diminished significantly since October 2009—largely because of the difficulty and danger of continued mining as deeper pits are required to reach productive zones—and most of the workers have left the area. In April 2010, a few groups of miners began working with better-organized systems, but the infiltration of seawater into the pits and tunnels during high tide greatly limited output. At the beginning of the rainy season in November 2010, only a few dozen miners were still working, and Antetezambato had shrunk to a population of about 200.

In December 2010, all the claims covering the demantoid deposit were legally acquired by a joint venture of Italian, German, and Malagasy mining operators, with the aim of investigating the down-dip extension of the demantoid occurrence and eval-

Figure 2. The Antetezambato garnet deposit is located just southeast of the Nosy Be archipelago in the Antsiranana region of northern Madagascar.

uating the economic potential of organized mining in the future.

PRODUCTION AND DISTRIBUTION

No official production figures exist for the Antetezambato deposit, and any estimates are approximate due to the lack of any organization and regulation. Based on the experience of the lead author and information gathered from several gem and mineral dealers in Madagascar, however, it is certain that most of the production (probably more than 90% of the total to date) was mined between April and November 2009. Only a very small percentage was mined subsequently, and virtually none since November 2010.

Numerous mineral specimens also have been produced (e.g., figure 6), and by far the finest one observed by the lead author consisted of several lustrous eye-clean crystals up to 2.8 cm across on matrix, each characterized by a green core with a thin brown-yellow overgrowth.

During the peak of the mining activity in 2009, ~20 kg of gem material were produced weekly, as well as a much larger quantity of low-quality rough. Thus, the total production of gem rough (e.g., figure 7) can be estimated to be on the order of hundreds of kilograms. However, high-quality pieces weighing 1+ g with good clarity and green color have always been scarce, and the total production is probably no more than a few kilograms. Eye-clean rough material of good color weighing 2.5+ g is exceptionally rare. High-quality cut gemstones weighing 4+ ct are very scarce, and those larger than 6 ct (e.g., figure 8) are exceptional. Most of the cut andradite consists of demantoid, while some topazolite and a small amount of red-brown material also has been faceted (e.g., figure 9).

The outlook for future production is uncertain. Small-scale and hand mining have become very difficult and unproductive, mostly because of the daily tidal flooding. Nevertheless, large reserves of demantoid are inferred at deeper levels of the deposit, as most of the garnet-rich veins dip steeply and occur over an area of several hectares. Since the present tunnels reach a depth of no more than 5–20 m, it is reasonable to speculate that only a small percentage of the total deposit has been mined. Still, a large and well-organized mining operation will be necessary to overcome the flooding problems and achieve significant production.

The vast majority of the gem demantoid production from Antetezambato has been traded out of Madagascar by Thai dealers. The first significant quantity of rough and cut stones reached the Bangkok market in September-October 2009, followed by a notable amount (including sets of calibrated stones) at the February 2010 Tucson gem shows. In the early stages of production, prices for top-quality material were very high, but they have since stabilized. Larger good-quality cut stones continue to command high prices.

NEED TO KNOW

- Commercial quantities of gem-quality andradite have been produced at Antetezambato in northern Madagascar, mainly in 2009.
- The production consists primarily of yellow-green to bluish green demantoid and greenish/brownish yellow to brown topazolite.
- The skarn origin is reflected by inclusions of wollastonite and diopside (but no "horsetails"), as well as relatively high concentrations of light rare-earth elements.
- The demantoid contains very low Cr and V; the green color appears related to intrinsic Fe^{3+}.

Figure 3. The garnet mining area is located in a mangrove swamp, seen here during low tide in November 2009 (left, photo by F. Pezzotta) and at high tide in September 2009 (right, photo by Marco Lorenzoni).

GEOLOGY AND GARNET FORMATION

Northwestern Madagascar is characterized by significant magmatism of Upper Mesozoic to Cenozoic age, affecting both the Pan-African crystalline basement and the Permo-Mesozoic sedimentary sequence of the Mahajunga Basin. The plutonic and volcanic complexes are distributed from the Nosy Be archipelago and the Ampasindava peninsula to the southeast toward Antongil Bay, forming an elongate area presumed to be related to a rift zone (de Wit, 2003). The Antetezambato garnet deposit occurs on the northwestern side of this magmatic area and represents the first important gem deposit in Madagascar formed by contact metamorphism within the Permian-Mesozoic sedimentary cover.

The Antetezambato area (again, see figure 2) is composed of sediments of the Isalo Formation (mostly sandstone) and intrusive rocks of the Ambato alkaline-granite massif (Melluso et al., 2007). The garnet deposit consists of a tilted block of layered sediments (dipping 45–60° south) that is intruded by a network of lamprophyric dikes (figure 10). The lamprophyric rocks (not reported in the geologic map of Besairie, 1962) bound the garnet deposit on the north and west

Figure 4. In this September 2009 photo, two Malagasy women hand-pick andradite crystals from material they have washed using metal sieves. Photo by Marco Lorenzoni.

Figure 5. Thousands of miners have dug numerous pits in search of demantoid at the Antetezambato deposit. Because of the tidal influx, they must carefully reinforce their diggings and pump seawater out of the pits before mining can resume each day. Photo by F. Pezzotta, November 2009.

Figure 6. The Antetezambato deposit is the source of fine garnet specimens, such as these demantoid (left and center) and topazolite crystals (right). The largest crystals measure 1.2 cm (left) and 2.2 cm (center); the specimen on the right is 4.2 cm tall. Courtesy of Daniel Trinchillo; photos by James Elliott.

sides. The sediments, originally composed of fine- to medium-grained fossiliferous sandstones interlayered with silica-rich limestones, are metasomatically altered along structural discontinuities such as layer boundaries, fractures, and contacts with the lamprophyric intrusions. The alteration is related to pneumatolytic and hydrothermal fluid circulations generated by the intrusions, resulting in a network of veins consisting of very fine-grained, garnet-rich skarn rock that is white to pale green. Locally, even fossil shells and corals in the sediments have been replaced by the fine-grained skarn minerals. Cavities in the skarn veins contain the garnet crystals.

The relative absence of titanium in the sedimentary rocks resulted in the crystallization of the andradite as green to brown demantoid and topazolite varieties (sometimes as color-zoned crystals; see figure 11), rather than the more common titanium-rich andradite (melanite), which is black.

Figure 7. This parcel of gem-quality demantoid was shown by a Malagasy dealer in Antetezambato in May 2010. Photo by F. Pezzotta.

MATERIALS AND METHODS

We examined 24 representative samples (20 demantoid and 4 topazolite; tables 1 and 2), consisting of 11 faceted gems (0.67–4.22 ct; figure 12) and 13 pieces of partially polished rough (~0.1–8.5 g). Two samples of matrix rock were prepared as polished thin sections.

The faceted samples were examined by standard gemological methods at the Italian Gemological Institute in Milan to determine their optical properties, hydrostatic SG, UV fluorescence, and microscopic features. Raman analysis of inclusions in the 7.17 ct sample pictured in figure 8 were performed at the GIA Laboratory in Carlsbad.

Quantitative chemical analysis was performed on all of the rough samples at the Earth Sciences

Figure 8. This faceted demantoid (7.17 ct) is representative of the finest material from Antetezambato. Photo by Matteo Chinellato.

Figure 9. This topazolite (left, 1.38 ct) and rare brownish red andradite (right, 1.86 ct) were faceted from material recovered at Antetezambato. Courtesy of Vadim Fedder; photos by Matteo Chinellato.

Department of the University of Milan. We used a JEOL JXA-8200 electron microprobe in wavelength-dispersive mode, with an accelerating voltage of 15 kV, a beam current of 15 nA, count times of 60 seconds on peaks and 30 seconds on background, and a beam diameter of ~1 μm. The following elements were analyzed: Na, Mg, Al, Si, K, Ca, Ti, V, Cr, Mn, and Fe. We corrected the raw data for matrix effects using a conventional ϕρZ routine in the JEOL software package. The two polished thin sections were examined with a petrographic microscope and analyzed by microprobe as well as by a scanning electron microscope (JEOL JSM 5610 LV) equipped with an energy-dispersive spectrometer.

The trace-element composition of the same 13 rough samples was determined by laser ablation–inductively coupled plasma–mass spectrometry (LA-ICP-MS) at the CNR Geosciences and Georesources Institute of Pavia, Italy. The instrument consisted of a Quantel Brilliant 266 nm Nd:YAG laser coupled to a PerkinElmer DRCe quadrupole ICP-MS. Spot size was 50 μm. NIST-SRM612 glass was used as the external calibration standard, while ^{43}Ca was the internal standard. In each analytical run, USGS reference sample BCR2 was analyzed together with unknowns for quality control; precision and accuracy were better than 5% and 10%, respectively. Data reduction was carried out using the Glitter software package (van Achterbergh et al., 2001) to analyze the following elements: Li, Be, B, Na, Mg, Al, Sc, Ti, V, Cr, Mn, Co, Ni, Cu, Zn, Rb, Sr, Y, Zr, Nb, Cs, Ba, Hf, Ta, Th, U, Pb, and the rare-earth elements from La to Lu.

Ultraviolet/visible/near-infrared (UV-Vis-NIR) spectroscopic measurements over the 250–900 nm range were performed at the Materials Science Department of the University of Milan-Bicocca with a PerkinElmer Lambda 950 spectrophotometer, equipped with an integrating sphere and operating with a spectral resolution of 0.05 and 0.30 nm/minute for the UV-Vis and NIR intervals, respectively, at a 1 nm/minute scan rate. Spectra were collected on two of the rough samples (nos. 1 and 13).

Spectroscopic measurements of all the rough

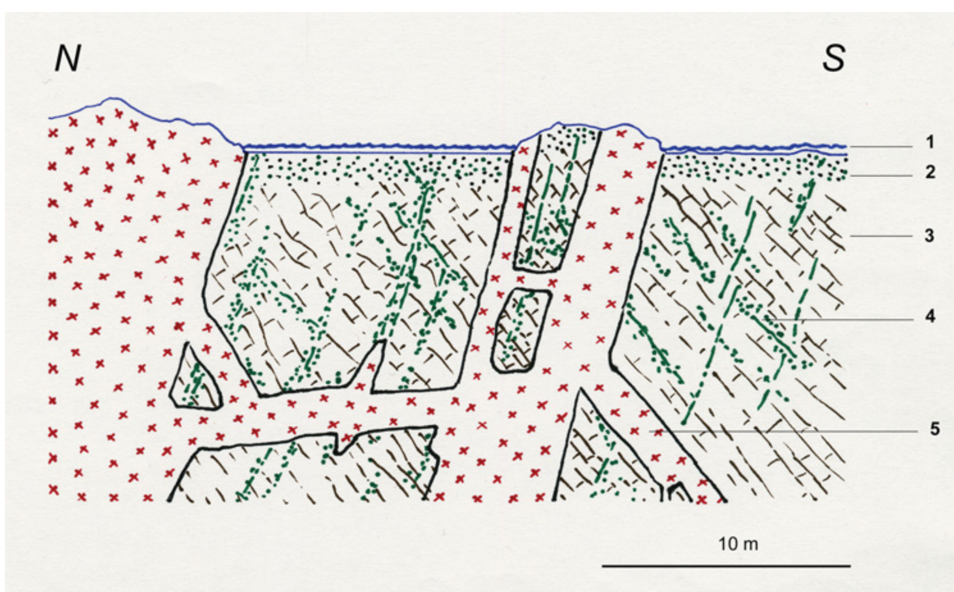


Figure 10. The Antetezambato deposit is located within a mangrove swamp (1), and the geology is characterized by a weathered horizon with dispersed broken crystals of andradite (2), which is underlain by sandstone and limestone (3) that are locally metasomatized and contain andradite-bearing skarn veins (4). The veins developed along fractures in the sedimentary rocks and along contacts with lamprophyre intrusions (5).

TABLE 1. Properties of the 11 faceted andradite samples investigated in this study.

Properties	A	B	D	E	I	M	L	H	C	G	F
Color (in daylight)	Bluish green	Green	Green	Green	Green	Green	Yellowish green	Yellow-green	Greenish brown	Yellowish brown	Brown
Weight (ct)	1.37	1.15	3.04	1.99	4.22	2.82	1.88	2.30	0.67	3.17	1.23
Specific gravity	3.81	3.86	3.83	3.88	3.81	3.79	3.82	3.83	3.90	3.84	3.86
Internal features[a]	Fractures (some partially healed), wollastonite and diopside inclusions, straight and angular growth structures, growth channels	Two-phase inclusions, wollastonite inclusions	Two-phase inclusions, fractures (some partially healed)	Diopside inclusions, straight and angular growth structures, growth channels	Fractures (some partially healed), wollastonite and diopside inclusions	Fractures, diopside inclusions	Two-phase inclusions, fractures (some partially healed), diopside and pyrite inclusions	Fractures	Two-phase inclusions, diopside inclusions	Fractures	Wollastonite inclusions, growth channels, color zoning

[a] *Liquid inclusions were observed in all samples.*

samples over the mid-infrared range (4000–400 cm^{-1}) were performed with a Nicolet Nexus Fourier-transform infrared (FTIR) spectrometer, equipped with a Spectra-Tech diffuse reflectance (DRIFT) accessory, at a resolution of 4 cm^{-1} and 200 scans per sample.

RESULTS

Color and Morphology. The demantoid ranged from yellow-green to bluish green, with low to moderate saturation (see tables 1–2 and figure 12). The topazolite samples were greenish brown, yellowish brown, and brown. Five of the samples (rough nos. 9 and 10, and faceted samples G, H, and L) showed a significant color shift from yellowish green in daylight to pinkish yellow in incandescent light. Moreover, an unusual bluish green hue was noted in two samples (12 and A) only in daylight and not under incandescent light (in which they appeared green).

Figure 11. This andradite crystal (1.8 cm in diameter) from Antetezambato shows a green core and a yellowish brown rim. Courtesy of Riccardo Caprilli; photo by Roberto Appiani.

The most common forms exhibited by the crystals investigated here consisted of various combinations of the dodecahedron {110} and trapezohedron {110}, the former more typical in demantoid and the latter in topazolite. Several more-complex forms were reported by Pezzotta (2010a).

Gemological Properties. The standard gemological properties of the faceted samples are provided in table 1. All the stones were transparent, singly refractive with moderate anomalous double refraction, and had an RI value of >1.81 and SGs of 3.79–3.90. They were inert to long- and short-wave UV radiation.

With magnification, we observed liquid inclusions in all the stones, mostly consisting of liquid veils, with some two-phase inclusions (figure 13A). Fractures were common, and some of them were partially healed into "fingerprints." In addition, some samples contained white acicular crystalline inclusions, often in aggregates, that SEM-EDS identified as wollastonite (figure 14); most of these were strongly corroded or completely leached, leaving empty channels. Also present were birefringent aggregates of white crystals identified by Raman spectroscopy in one sample as diopside (figure 13B). In another sample, an opaque crystalline inclusion with a brassy yellow color, metallic luster, and cubic morphology with striated faces was visually identified as pyrite. We also observed some growth channels (figure 13C) distinct from those left behind by leached wollastonite, as well as distinct straight and angular growth structures (figure 13D) and color zoning. Most samples showed moderate to strong anomalous double refraction between crossed polarizers (again, see figure 13D).

Chemical Composition. The chemical compositions of the 13 rough samples are reported in tables 2 and 3. Electron microprobe analyses showed that the garnets consisted of nearly pure andradite (≥98 mol.%). Ti, Al, Mn, Na, and K were present in very low amounts (<0.2 wt.%), while Cr and V were below the detection limit (0.01 wt.%) in all samples. The main trace elements measured by LA-ICP-MS were Mg (307–1423 ppm), Al (15–5467 ppm), and Mn (9–92 ppm). Sc, Ti, V, and Cr contents were consistently very low, with a maximum of only 7.5 ppm for Ti (table 3). Rare-earth element concentrations ranged from 0.037 to 100.8 ppm.

Figure 12. These 11 andradites from Antetezambato (0.67–4.22 ct) are among those studied for this report. Photo by Roberto Appiani.

Microprobe analyses of granular garnet in the skarn host rock showed compositions intermediate between andradite (Adr) and grossular (Grs), ranging from $Adr_{63}Grs_{37}$ to $Adr_{29}Grs_{71}$.

Spectroscopy. *UV-Vis-NIR.* The absorption spectra of representative green and brown samples are shown in

TABLE 2. Average chemical composition obtained by electron microprobe analyses of 13 rough andradite samples from Antetezambato, Madagascar.[a]

Chemical composition	12	1	2	3	4	5	6	7	8	9	10	11	13
Color (in daylight)	Bluish green	Green	Green	Green	Green	Green	Green	Green	Yellowish green	Yellowish green	Yellowish green	Yellowish green	Brown
Weight (g)	0.11	1.51	0.12	0.32	0.58	2.00	0.19	8.49	1.70	0.43	0.38	0.10	0.14
No. points analyzed	10	10	15	15	15	15	10	15	5	8	5	12	15
Oxides (wt.%)													
SiO_2	35.47	34.90	34.90	34.23	34.63	36.09	34.00	34.39	35.94	35.60	35.70	35.05	35.52
TiO_2	0.01	nd	nd	0.01	nd	nd	nd	0.01	0.01	nd	nd	0.01	nd
Al_2O_3	0.01	0.01	0.01	0.02	0.03	nd	nd	0.03	0.08	nd	nd	0.18	0.02
Fe_2O_3[b]	31.93	31.54	31.43	31.34	31.50	31.51	31.42	31.18	31.54	31.59	31.46	31.61	31.23
MnO	0.01	0.01	0.01	0.01	0.01	0.01	nd	0.01	0.01	0.01	0.01	0.01	0.01
MgO	0.07	0.08	0.08	0.08	0.06	0.08	0.13	0.10	0.30	0.11	0.12	0.09	0.06
CaO	33.24	32.95	33.20	32.84	32.95	32.67	32.90	33.02	33.38	33.00	32.99	33.28	32.84
Na_2O	nd	0.05	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
K_2O	nd	0.02	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Total	100.74	99.56	99.63	98.53	99.18	100.36	98.45	98.74	101.26	100.31	100.28	100.23	99.68
Ions per 12 oxygens													
Si	2.979	2.964	2.962	2.940	2.954	3.013	2.922	2.945	2.995	3.001	3.009	2.956	3.005
Ti	0.001	nd	nd	0.001	nd	nd	nd	0.001	0.001	nd	nd	0.001	nd
Al	0.001	0.001	0.001	0.002	0.003	nd	nd	0.003	0.008	nd	nd	0.018	0.002
Fe^{3+}	2.018	2.016	2.007	2.025	2.022	1.990	2.032	2.009	1.978	1.998	1.981	2.006	1.988
Mn	0.001	0.001	0.001	0.001	0.001	0.001	nd	0.001	0.001	0.001	0.001	0.001	0.001
Mg	0.009	0.010	0.010	0.010	0.008	0.011	0.017	0.013	0.037	0.014	0.015	0.011	0.008
Ca	2.991	2.998	3.019	3.022	3.012	2.970	3.029	3.029	2.981	2.981	2.979	3.007	2.977
Na	nd	0.008	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
K	nd	0.002	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Mol.% end members													
Andradite	99.70	99.60	99.40	99.60	99.70	99.50	99.50	99.50	98.30	99.50	99.20	99.60	99.60
Others	0.03	0.04	0.06	0.04	0.03	0.05	0.05	0.05	1.40	0.05	0.08	0.04	0.04

[a] *Standards: natural wollastonite (Si, Ca), anorthite (Al), fayalite (Fe), olivine (Mg), rhodonite (Mn), omphacite (Na), ilmenite (Ti), K-feldspar (K), and pure Cr and V for those elements. Abbreviation: nd = not detected (<0.01 wt.%). Chromium and vanadium were below detection limit in all analyses.*
[b] *Total iron is calculated as Fe_2O_3.*

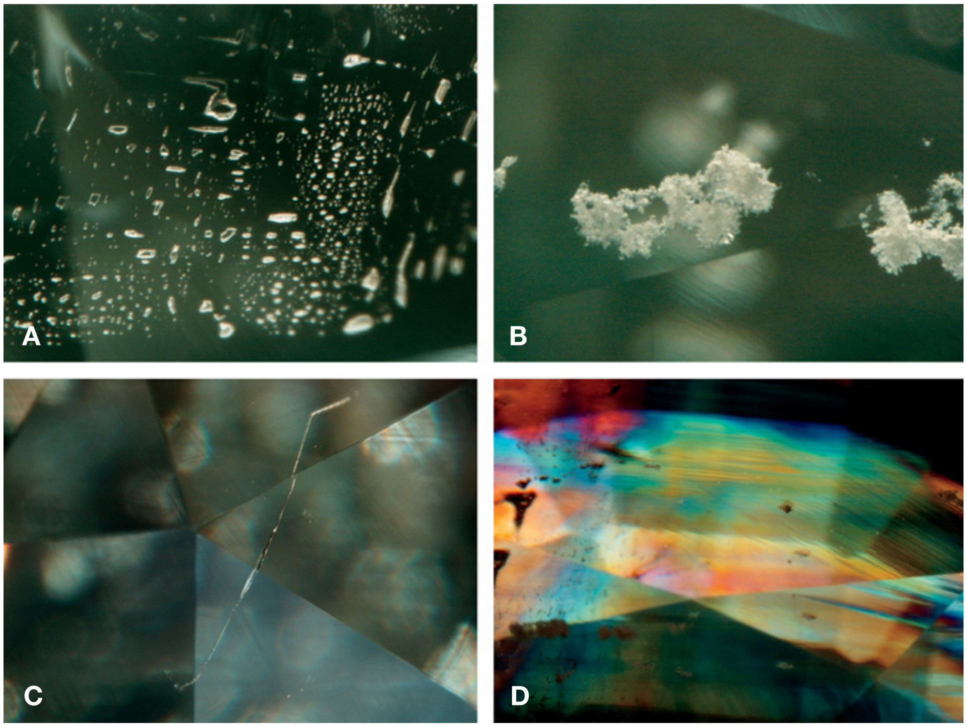


Figure 13. Typical internal features in andradite from Antetezambato are fluid inclusions (A, magnified 55×), crystalline aggregates of diopside (B, 50×), etch channels (C, 35×), and growth structures and strain (D, 15×; crossed polarizers). Photomicrographs by Nathan Renfro.

figure 15. The spectra displayed similar features: total absorption below 390 nm; an intense peak at about 440 nm; a broad band at ~600 nm consisting of two distinct components located at 575 and 610 nm, clearly visible in the spectrum of the green sample (figure 15, inset); and a band at ~850–860 nm. In addition, the brown sample showed continuously increasing absorption in the visible to ultraviolet range.

Mid-Infrared. The mid-IR spectra of all samples showed areas of total absorption in the 2250–400 cm^{-1} range, intrinsic to garnet, along with absorption bands between 3650 and 3500 cm^{-1} (e.g., figure 16). In particular, we observed three distinct peaks at 3610, 3581, and 3560 cm^{-1}.

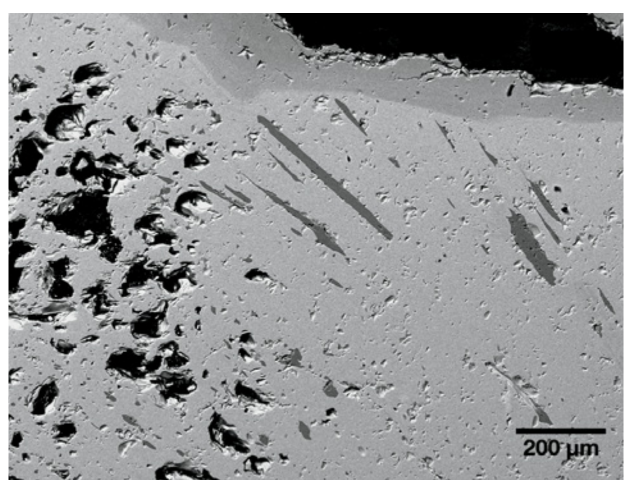
DISCUSSION

The gemological properties reported here for demantoid and topazolite from Antetezambato are typical of andradite (e.g., O'Donoghue, 2006). They also agree with the results obtained by Rondeau et al. (2009b) and Schmetzer and Karampelas (2009) on samples from this locality. As pointed out by Rondeau et al. (2009a), these garnets show strain exhibited as anomalous double refraction with undulating extinction and "tatami" patterns. Strain is typical in andradite (e.g., Meagher, 1980).

The inclusion features in andradite from Antetezambato differ significantly from those observed in serpentinite-hosted andradites, such as demantoid from Russia and Italy (Phillips and Talantsev, 1996; Adamo et al., 2009). We did not find any "horsetail" inclusions, which are common in demantoid from serpentinites. The inclusions in the Madagascar demantoid are similar to those found in specimens from Namibia (Gübelin and Koivula, 2005), which also are hosted by skarns.

Gem varieties of andradite typically have a near-end-member composition (Adamo et al., 2009;

Figure 14. This backscattered electron image shows wollastonite crystal inclusions up to 0.4 mm long (medium gray) in andradite. Micrograph by Michele Zilioli.



Bocchio et al., 2010), and this was the case for our samples from Antetezambato. Only the garnet microcrystals constituting the skarn host rocks showed chemical zoning, in the grossular-andradite solid solution range. The color zoning exhibited by some andradite crystals reflects inhomogeneities in the distribution of the trace elements, similar to what was described by Meagher (1980).

LA-ICP-MS analyses revealed very low levels of most trace elements, especially chromophore elements. Except for iron (Fe^{3+}), which is intrinsic to andradite, no chromophores were present in significant amounts, and there were no consistent variations in color according to composition. Although traces of chromium were reported in samples from Antetezambato by Schmetzer and Karampelas (2009), we found only extremely low quantities (up to ~3 ppm), consistent with Rondeau et al. (2009b). S. Karampelas and T. Hainschwang (pers. comm., 2011) reported that even photoluminescence spectra (after long acquisitions) showed no evidence of Cr emission lines. It seems likely that the EDXRF spectroscopy (a bulk analysis technique) performed by Schmetzer and Karampelas (2009) indicated the presence of Cr-bearing inclusions, probably sub-microscopic. In fact, one of the first demantoid samples collected at the locality contained tiny inclusions rich in Cr, as revealed by microprobe analysis (G. Parodi, pers. comm., 2009).

Although Lind et al. (1998) measured small amounts of Cr (0.02–0.13 wt.% Cr_2O_3) in demantoid from Namibia, the results of Bocchio et al. (2010) and our own analyses of Namibian samples found no significant Cr. This is in agreement with the genetic similarity between these deposits (cf., Cairncross and Bahmann, 2006).

The REE distribution of andradite from Antetezambato shows a general enrichment in light rare-earth elements and a depletion of heavy REE (see plot in *G&G* Data Depository at gia.edu/gandg), which is typical of andradite (see Bocchio et al., 2010, and references therein). Moreover, this andra-

TABLE 3. Trace-element composition obtained by LA-ICP-MS analyses of 13 rough andradite samples from Antetezambato, Madagascar.[a]

Element (ppm)	12	1	2	3	4	5	6	7	8	9	10	11	13
Color	Bluish green	Green	Green	Green	Green	Green	Green	Green	Yellowish green	Yellowish green	Yellowish green	Yellowish green	Brown
Mg	418.4	395.9	358.9	449.5	336.0	503.3	408.7	720.3	1423	677.5	720.0	601.5	306.8
Al	26.37	15.14	16.84	58.58	99.02	24.47	42.81	32.10	5467	302.8	180.7	24.97	37.82
Sc	0.58	1.50	1.20	0.89	0.73	0.55	0.97	0.70	1.14	1.13	1.04	0.52	0.55
Ti	2.05	0.17	0.61	3.09	0.95	1.70	1.30	0.24	7.50	5.30	1.23	0.82	0.40
V	0.06	nd	0.03	0.04	0.04	0.02	0.02	nd	3.09	0.36	0.03	0.04	nd
Cr	1.15	0.59	0.59	0.99	0.98	0.00	0.63	0.50	2.20	2.35	2.74	0.50	1.35
Mn	53.98	85.91	37.63	18.09	34.98	9.01	37.12	13.73	29.88	33.45	26.07	91.53	56.45
La	1.24	0.019	0.118	0.515	1.11	0.171	0.386	0.592	0.194	2.60	8.34	0.669	2.74
Ce	12.04	0.009	0.324	3.41	2.66	1.73	1.63	4.26	0.389	7.54	54.21	1.02	22.18
Pr	1.03	0.002	0.026	0.388	0.208	0.203	0.165	0.715	0.036	0.670	8.685	0.056	3.54
Nd	1.25	0.008	0.039	1.04	0.431	0.361	0.375	2.18	0.123	2.16	26.81	0.162	9.93
Sm	0.037	0.002	0.009	0.057	0.019	0.017	0.021	0.036	0.010	0.151	0.729	0.000	0.321
Eu	0.199	0.006	0.006	0.075	0.102	0.053	0.048	0.124	0.085	0.377	1.85	0.013	1.40
Gd	0.034	nd	0.007	0.012	0.004	0.007	0.006	0.017	0.007	0.095	0.136	0.020	0.061
Tb	0.002	nd	nd	0.003	0.002	0.001	0.001	0.002	0.001	0.004	0.007	0.001	0.008
Dy	0.013	0.001	0.002	nd	0.003	0.002	0.002	nd	0.002	0.034	0.004	0.009	0.023
Ho	0.003	0.001	0.001	nd	0.001	0.001	0.001	0.001	0.001	0.010	0.002	nd	0.002
Er	nd	0.003	0.003	0.003	0.002	0.002	0.003	0.002	nd	0.036	0.002	0.003	0.002
Tm	nd	nd	0.001	0.001	nd	0.002	0.001	0.001	nd	0.005	nd	0.001	nd
Yb	0.003	0.002	0.007	0.002	0.008	0.003	0.004	0.003	0.006	0.022	0.002	0.002	0.008
Lu	0.001	0.001	nd	nd	0.001	0.001	0.001	0.001	0.001	0.004	0.001	0.001	0.001
Σ REE	15.85	0.037	0.542	5.51	4.54	2.55	2.64	7.93	0.853	13.70	100.8	1.96	40.21
Σ LREE (La+Ce+Pr+Nd)	15.56	0.030	0.507	5.35	4.40	2.46	2.55	7.75	0.742	12.97	98.04	1.91	38.39
Σ HREE (Er+Tm+Yb+Lu)	0.004	0.005	0.010	0.007	0.010	0.008	0.009	0.007	0.007	0.066	0.005	0.007	0.011

[a] *Other elements (Li, Be, B, Na, Co, Ni, Cu, Zn, Rb, Sr, Y, Zr, Nb, Cs, Ba, Hf, Ta, Th, U, and Pb) were <1 ppm (by weight) in all samples.*
Abbreviations: nd = not detected, REE = rare-earth elements, LREE = light rare-earth elements, HREE = heavy rare-earth elements.

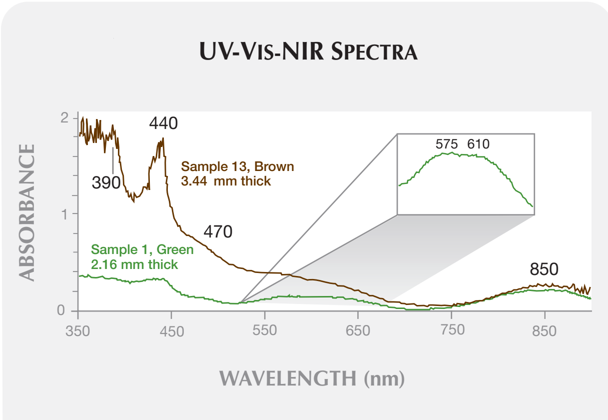


Figure 15. UV-Vis-NIR spectra of two representative andradite samples from Antetezambato show features related to Fe^{3+}, which is likely the main chromophore.

dite has a relatively high total REE content, similar to that of Namibian demantoid and generally higher than that of andradite from serpentinites (Bocchio et al., 2010). This relatively high REE content could be caused by the mobility and enrichment of these elements in skarn rocks. The alkaline intrusive rocks associated with the Antetezambato andradite could also be a source of hydrothermally transported REEs (Pezzotta, 2010a).

The UV-Vis-NIR spectra of the green and brown samples showed spectral features related to octahedral Fe^{3+} (Manning, 1972; Moore and White, 1972; Amthauer, 1976; Lind et al., 1998). The gradual increase in absorption from the visible to UV wavelengths, evident in the brown sample's spectrum, is the main cause of its coloration. This absorption feature is usually attributed to an Fe^{2+}-Ti^{4+} intervalence charge transfer (Fritsch and Rossman, 1993; Rondeau et al., 2009b), but this interpretation is not consistent with the very low Ti content (up to ~7 ppm) in our samples. Because our LA-ICP-MS data did not show significant chromophores except iron, it appears likely that Fe^{2+}-Fe^{3+} interactions or tetrahedral Fe^{3+} (Moore and White, 1972) contribute to this continuous absorption. However, further research is needed to assess the cause of the brown coloration.

The color-shift behavior shown by some samples is similar to that seen in demantoid from Quebec, Canada (Amabili et al., 2009). The rare-earth elements cerium and neodymium, though detected only in trace amounts in our specimens, could be involved in the color shift, as documented in color-change glass (Quinn and Muhlmeister, 2005) and in minerals such as apatite. Further investigation, including systematic trace-element analyses and a detailed study of UV-Vis-NIR spectra, would be necessary to fully characterize this phenomenon.

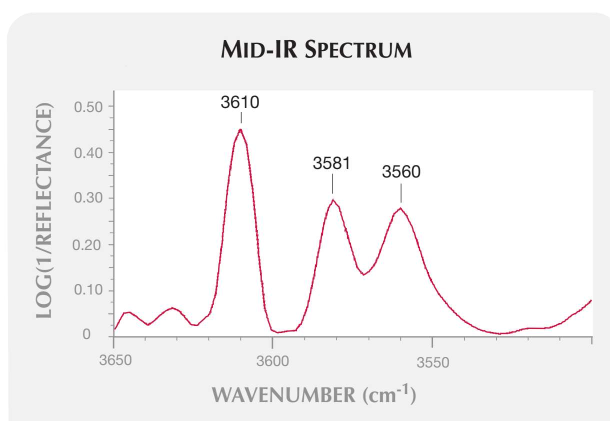
The mid-IR absorption features at 3610, 3581, and 3560 cm^{-1} are related to structurally bonded OH^- (Amthauer and Rossman, 1998). Our spectra are very similar to those of andradite from skarn reported by Amthauer and Rossman (1998).

Stephenson and Kouznetsov (2009) reported that Russian demantoid can be heat-treated at temperatures of 640–720°C in a graphite-powder reducing atmosphere to enhance their color. Indeed, this treatment is able to minimize, if not totally eliminate, the yellow color component, giving rise to pure green gems. Despite the rumors in the Madagascar market that Thai treaters can improve the demantoids' color, heating experiments performed recently by G. Pocobelli in collaboration with the lead author did not show any significant changes in color. The experiments were done in oxidizing and reducing atmospheres, at temperatures up to 800°C; further investigations are in progress.

CONCLUSION

A relatively new deposit of demantoid and topazolite at Antetezambato in northern Madagascar has produced attractive gem material (e.g., figure 17), mainly in 2009. This study, performed on representative rough and cut samples selected from a large quantity of material produced since the discovery of the

Figure 16. Peaks at 3610, 3581, and 3560 cm^{-1} in the mid-IR spectrum (reflectance mode) of Antetezambato andradite are related to hydroxides.



deposit, has confirmed previously published data and significantly added to knowledge of the most typical mineral inclusions (wollastonite and diopside) and the trace-element composition. The relatively high REE content, with a light-REE enrichment, is of particular interest as it characterizes andradite from skarn-type deposits. The skarn origin and some of the gemological features of the Antetezambato demantoid are similar to material from Namibia, but significantly different from those shown by demantoid from serpentinite-related deposits.

The trace-element data show no evidence of systematic compositional variations associated with the wide variety of colors. Moreover, the very low contents of Cr and V, combined with the UV-Vis-NIR spectroscopic results, suggest that the demantoid's green color is related to the constituent Fe^{3+}.

Studies of the Antetezambato mining area by author FP have provided a good understanding of the geologic processes involved in garnet formation. Modeling of the deposit suggests that there is significant potential for further production at depth, although the daily tidal flooding will seriously limit additional mining activities.

Figure 17. Madagascar's Antetezambato deposit became an important source of demantoid and topazolite in 2009. Additional production of fine stones such as these (0.90–1.71 ct) will depend on overcoming the logistical problems associated with daily tidal flooding. Photo by Robert Weldon.

ABOUT THE AUTHORS

Dr. Pezzotta (fpezzotta@yahoo.com) is the mineralogy curator of the Natural History Museum of Milan, Italy. Dr. Adamo is a postdoctoral fellow in the Earth Sciences Department at the University of Milan. Dr. Diella is a senior researcher at the Institute for the Study of the Dynamics of Environmental Processes, National Research Council (CNR), Milan.

ACKNOWLEDGMENTS

The authors thank Andrea Risplendente (University of Milan) for assistance with microprobe analyses, Dr. Massimo Tiepolo (CNR Geosciences and Georesources Institute, Milan) for assistance with LA-ICP-MS measurements, and Cristina Pogliani and Dr. Giorgio Spinolo (Materials Science Department, University of Milan-Bicocca) for assistance with UV-Vis-NIR spectroscopy. Nathan Renfro (GIA Laboratory, Carlsbad) is thanked for photomicrographs and Raman analysis of inclusions. Giuseppe Pocobelli (Fine Gemstones Madagascar, Antananarivo) and his colleagues arranged author FP's visit to the mine and provided samples. Georges Rakotonirina (Madagascar Ministry of Energy and Mines, Antananarivo) facilitated contacts with the local authorities. Vadim Fedder (Mineral Treasure, Antananarivo) generously loaned samples for study. Laurent Thomas (Polychrom France, Chambray-lès-Tours, France) provided the initial garnet fragments for analysis. Luciano Merlo Pich (San Francesco al Campo, Italy) faceted the gemstone samples, and Dr. Margherita Superchi (Segrate, Italy) and Thomas Hainschwang (GGTL Gemlab–Gemtechlab Laboratory, Balzers, Liechtenstein) offered useful comments and suggestions. We also thank Drs. Benjamin Rondeau, Stefanos Karampelas, and Mary Johnson for their reviews of the manuscript.

REFERENCES

van Achterbergh E., Ryan C.G., Jackson S.E., Griffin W. (2001) Data reduction software for LA-ICP-MS. In P. Sylvester, Ed., *Laser Ablation-ICP-MS in the Earth Sciences: Principles and Applications*, Mineralogical Association of Canada Short Course Handbook, Vol. 29, Mineralogical Association of Canada, Quebec, pp. 239–243.

Adamo I., Bocchio R., Diella V., Pavese A., Vignola P., Prosperi L., Palanza V. (2009) Demantoid from Val Malenco, Italy: Review and update. *G&G*, Vol. 45, No. 4, pp. 280–287.

Adamo I., Gatta G.D., Rotiroti N., Diella V., Pavese A. (2011) Green andradite stones: Gemmological and mineralogical characterisation. *European Journal of Mineralogy*, Vol. 23, pp. 91–100.

Amabili M., Spertini F., Auguste M.B., Bonin G. (2009) Famous mineral localities: The Lac d'Amiante mine, Black Lake, Thetford mines, Quebec. *Mineralogical Record*, Vol. 40, No. 4, pp. 297–304.

Amthauer G. (1976) Crystal chemistry and colour of chromium-bearing garnets. *Neues Jahrbuch für Mineralogie, Abhand-*

lungen, Vol. 126, No. 2, pp. 158–186.
Amthauer G., Rossman G.R. (1998) The hydrous component in andradite garnet. *American Mineralogist*, Vol. 83, No. 7/8, pp. 835–840.
Besairie H. (1962) *Nosy-Be–Ambato*. Geologic map R33–S33, scale 1:100,000, Service Géologique, Antananarivo, Madagascar.
Bocchio R., Adamo I., Diella V. (2010) The profile of trace elements, including the REE, in gem-quality green andradite from classic localities. *Canadian Mineralogist*, Vol. 48, pp. 1205–1216.
Cairncross B., Bahmann U. (2006) The Erongo Mountains, Namibia. *Mineralogical Record*, Vol. 37, No. 5, pp. 361–470.
Danet F. (2009) Gem News International: New discovery of demantoid from Ambanja, Madagascar. *G&G*, Vol. 45, No. 3, pp. 218–219.
Fritsch E., Rossman G.R. (1993) The causes of color in garnets. *Mineralogical Record*, Vol. 24, No. 1, p. 63.
Gübelin E.J., Koivula J.I. (2005) *Photoatlas of Inclusions in Gemstones*, Vol. 2. Opinio Publishers, Basel, Switzerland.
Lacroix A. (1922) *Minéralogie de Madagascar*, Vol. 1. Augustin Challamel Éditeur, Paris, 624 pp.
Lind Th., Henn U., Bank H. (1998) New occurrence of demantoid from Namibia. *Australian Gemmologist*, Vol. 20, No. 2, pp. 75–79.
Manning P.G. (1972) Optical absorption spectra of Fe^{3+} in octahedral and tetrahedral sites in natural garnets. *Canadian Mineralogist*, Vol. 11, No. 4, pp. 826–839.
Meagher E.P. (1980) *Silicate Garnets*. *Reviews in Mineralogy*, Vol. 5, Mineralogical Society of America, Washington, DC, pp. 25–66.
Melluso L., Morra V., Brotzu P., Franciosi L., Grifa C., Lustrino M., Morbidelli P., Riziky H., Vincent M. (2007) The Cenozoic alkaline magmatism in central-northern Madagascar: A brief overview. *Periodico di Mineralogia*, Vol. 76, No. 3, pp. 169–180.
Mercier A., Moine B., Delorme J., Rakotondrazafy M.A.F. (1997) A note on a new occurrence of vanadian grossular garnet from Madagascar. *Journal of Gemmology*, Vol. 25, No. 6, pp. 391–393.
Mocquet B., Lulzac Y., Rondeau B. (2009a) Nouveau gisement de andradite démantoïde à Madagascar. www.gemnantes.fr/recherche/autre/demantoide_mada.php, May 30.
Mocquet B., Lulzac Y., Rondeau B., Fritsch E., Le Quéré J., Mohamady B., Crenn G., Lamiraud C., Scalie S. (2009b) Ambanja, premier gisement d'andradite démantoïde gemme à Madagascar. *Revue de Gemmologie a.f.g.*, No. 169, pp. 4–8.
Moore R.K., White W.B. (1972) Electronic spectra of transition metal ions in silicate garnets. *Canadian Mineralogist*, Vol. 11, No. 4, pp. 791–811.
O'Donoghue M., Ed. (2006) *Gems*, 6th ed. Butterworth-Heinemann, Oxford, UK.
Pezzotta F. (2010a) Andradite from Antetezambato, north Madagascar. *Mineralogical Record*, Vol. 41, No. 3, pp. 209–229.
Pezzotta F. (2010b) Demantoid und Topazolith aus Antetezambato, Nordmadagaskar. *Lapis*, Vol. 35, No. 10, pp. 31–39.
Phillips W.R., Talantsev A.S. (1996) Russian demantoid, czar of the garnet family. *G&G*, Vol. 32, No. 2, pp. 100–111.
Praszkier T., Gajowniczek J. (2010) Demantoide aus Antetezambato auf Madagascar. *Mineralien Welt*, Vol. 21, pp. 32–41.
Quinn E.P., Muhlmeister S. (2005) Gem News International: "Color-change" glass update. *G&G*, Vol. 41, No. 4, pp. 364–365.
Razafindramiadana L. (2009) Un gisement de démantoïde à Ambanja. *Express de Madagascar*, Antananarivo, No. 4327, June 6.
Rondeau B., Fritsch E., Mocquet B., Lulzac Y. (2009a) Ambanja (Madagascar)—A new source of gem demantoid garnet. *InColor*, No. 11, pp. 22–24.
Rondeau B., Mocquet B., Lulzac Y., Fritsch E. (2009b) Les nouveaux grenats démantoïdes d'Ambanja, Province d'Antsiranana, Madagascar. *Le Règne Minéral*, Vol. 90, pp. 41–46.
Schmetzer K., Karampelas S. (2009) Demantoid from a new source. *Gems & Jewellery*, Vol. 18, No. 4, pp. 10–12.
Stephenson J., Kouznetsov N. (2009) Major deposits of demantoid around the world. *InColor*, No. 11, pp. 16–20.
de Wit M.J. (2003) Madagascar: Heads it's a continent, tails it's an island. *Annual Review of Earth and Planetary Sciences*, Vol. 31, pp. 213–248.