DEMANTOID FROM VAL MALENCO, ITALY: REVIEW AND UPDATE

Ilaria Adamo, Rosangela Bocchio, Valeria Diella, Alessandro Pavese, Pietro Vignola,
Loredana Prosperi, and Valentina Palanza

New data are presented for demantoid from Val Malenco, Italy, as obtained by classical gemological methods, electron microprobe and LA-ICP-MS chemical analyses, and UV-Vis-NIR and mid-IR spectroscopy. The results confirmed that these garnets are almost pure andradite (≥98 mol%, RI >1.81, SG = 3.81–3.88). All 18 samples studied contained "horsetail" inclusions, which are characteristic of a serpentinite geologic origin. Fe and Cr control the coloration of demantoid, though color variations in these samples were mainly correlated to Cr content.

Demantoid is the Cr-bearing yellowish green to green variety of andradite [$Ca_3Fe_2(SiO_4)_3$] (O'Donoghue, 2006). Very popular in Russia (where it was first discovered) from about 1875 to the start of the Russian Revolution in 1917, this gem has enjoyed a resurgence in demand since the beginning of the 21st century (Furuya, 2007).

One of the most notable localities for demantoid is Val Malenco, located in Sondrio Province in the Lombardy region of northern Italy. Several deposits in this area have produced well-formed rhombic dodecahedral crystals (e.g., figure 1, left) that are coveted by collectors (Bedogné and Pagano, 1972; Amthauer et al., 1974; Bedogné et al., 1993, 1999). A limited quantity (some thousands of carats) of Val Malenco demantoids have been cut, producing gemstones that are attractive but rarely exceed 2 or 3 ct (e.g., figure 1, right).

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Val Malenco demantoid was first documented by Cossa (1880), who studied a sample recovered by T. Taramelli in 1876. In the next century, Sigismund (1948) and Quareni and De Pieri (1966) described the morphology and some physical and chemical properties of this garnet. Subsequently, the demantoid was investigated by Bedogné and Pagano (1972), Amthauer et al. (1974), Stockton and Manson (1983), and Bedogné et al. (1993, 1999). Because some of these data are more than 20 years old, and some publications are in Italian, we prepared this review and update on the physical, chemical, and gemological properties of demantoid from Val Malenco.

Note that *demantoid*—although commonly used as a trade or variety name—is not approved by the International Mineralogical Association as a mineral name (Nickel and Mandarino, 1987; O'Donoghue, 2006). However, for reasons of brevity and consistent with gemological convention, throughout this article we will use *demantoid* instead of *andradite, variety demantoid*.

HISTORY AND PRODUCTION

Most of the demantoid recovered from Val Malenco thus far has been found in asbestos mines located in a small area between Dossi di Franscia and Coston d'Acquanegra (figure 2). The most famous localities are: Cengiàsc (including the Sferlùn quarry), Dossi di Franscia, Coston d'Acquanegra, Valbrutta, and Al Ross (Bedogné et al., 1999). These asbestos deposits are located at ~1800–2200 m above sea level, and are not easily accessible.

Probably the most beautiful Italian demantoid

Figure 1. The demantoid crystal (9.01 × 9.42 mm) and 1.98 ct faceted cushion cut are from the Sferlùn mine in Val Malenco, Italy. Left image courtesy of the Museo di Storia Naturale di Milano, Italy, and Dr. Federico Pezzotta; photo by Matteo Chinellato. Right image courtesy of Francesco Bedogné; photo by Roberto Appiani.

crystals were found at the Sferlùn mine by L. Magistretti in 1947 (Sigismund, 1948). Some were given to Università degli Studi di Milano, while others were sold to jewelers and collectors. Other important finds were made during the second half of the 1960s (Bedogné et al., 1999).

At present, all the asbestos mines are closed, so the possibility of collecting fine demantoid specimens is very remote. The existing demantoid crystals and cut stones on the market came from commercial exploitation before the mines closed toward the end of the 1970s (Bedogné et al., 1999).

GEOLOGIC SETTING

The Val Malenco ultramafic rocks (again, see figure 2) mainly consist of magnetite-, diopside-, and antigorite-bearing serpentinites that formed by metamorphism of mantle rocks during the Alpine orogenesis (Montrasio et al., 2005; Trommsdorff et al., 2005). The demantoid is found within foliated serpentinites in the eastern part of the Val Malenco ultramafic unit, where it is hosted by asbestos (chrysotile)–filled brittle fractures, generally oriented perpendicular to the foliation. The demantoid may be found as crystals up to 2 cm in diameter (see figures 1 [left] and 3), or as aggregates of tiny crystals that are locally dubbed "asbestos seed."

The demantoid crystals are generally associated with magnetite, Cr-bearing magnetite, calcite, hydromagnesite, brucite, clinochlore, and rarely, transparent green masses of forsterite. This assemblage has hydrothermal origins and formed in a retrograde metamorphic process during the late Alpine orogenesis at temperatures below 370°C and pressures ranging from 0.5 to 1.5 kbar (Amthauer et al., 1974).

MATERIALS AND METHODS

We examined 18 samples from Val Malenco consisting of eight faceted (0.31–3.84 ct; see, e.g., figure 4) and 10 rough (0.01–0.4 g) specimens taken from 10 different rock samples, the latter all from the Sferlùn mine. All the faceted samples were examined by standard gemological methods to determine their optical properties, hydrostatic specific gravity, UV fluorescence, and microscopic features.

Quantitative chemical analyses were performed on eight of the rough samples, selected on the basis of color (representing a range from yellowish green to green to intense green). We used a JEOL JXA-8200 electron microprobe in wavelength-dispersive mode. The following elements were measured: Na, Mg, Al, Si, K, Ca, Ti, V, Cr, Mn, and Fe. We corrected the raw data for matrix effects using a conventional ZAF routine. The oxidation state of Fe was determined for all the samples, using the flank method, which allows one to directly determine the ferric iron content from microprobe data (Höfer and Brey, 2007).

Laser ablation–inductively coupled plasma–mass spectroscopy (LA-ICP-MS) chemical analyses were performed on the same samples analyzed by electron microprobe. The instrument consisted of an Elan DRC-e mass spectrometer coupled with a Q-switched Nd:YAG laser source, with a fundamental emission (1064 nm) that was converted to 266 nm by two harmonic generators. Helium was used as a carrier gas, mixed with an Ar stream in the ablation cell. The following elements were analyzed: Li, Be, B, Sc, Ti, V, Cr, Co, Ni, Zn, Rb, Sr, and the rare-earth elements from La to Lu.

Ultraviolet-visible–near infrared (UV-Vis-NIR) spectroscopic measurements over the 250–1000 nm range were performed with a Lambda 950 PerkinElmer spectrophotometer, equipped with an integrating sphere, on four rough samples (nos. 1, 2, 6, and 8, having thicknesses of 1.90, 2.04, 1.82, and 1.40 mm, respectively).

Spectroscopic measurements of all the rough samples over the mid-infrared range (4000–400 cm^{-1}) were performed with a Nicolet Nexus Fourier-transform infrared (FTIR) spectrometer, operating in dif-

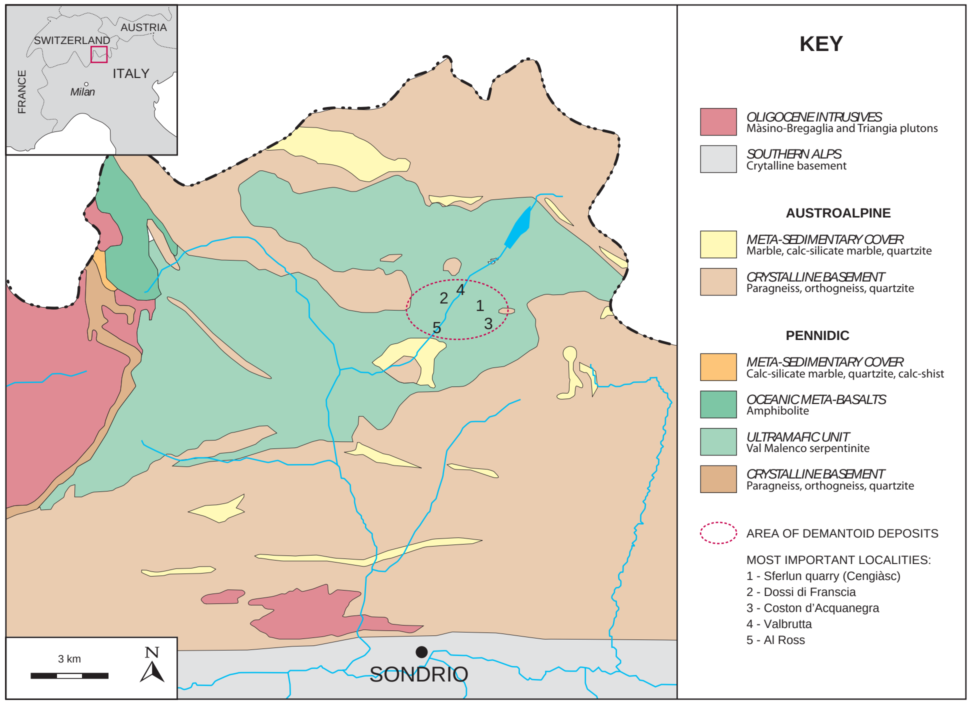


Figure 2. Demantoid is hosted by serpentinites in the eastern part of the Val Malenco ultramafic unit, northern Italy. The presence of "horsetail" inclusions in the garnet is consistent with the serpentinite origin.

fuse reflectance (DRIFT) mode, with a resolution of 4 cm^{-1} and 200 scans per sample. Three crystals were also tested in transmission mode using the same operating conditions.

Figure 3. A group of well-formed demantoid crystals are associated with asbestos on a serpentine matrix in this sample from the Sferlùn mine. The largest crystal is ~20 mm across. Courtesy of the Earth Sciences Department Museum of the Università degli Studi di Milano, Italy (Magistretti Collection); photo by R. Bocchio.

RESULTS AND DISCUSSION

Standard Gemological Properties. The color of both the rough and faceted samples ranged from yellowish green to green, including a rare bright intense "emerald" green (seen in six samples, especially the smallest ones), with a medium-to-dark tone. The color was generally homogeneous, but one rough sample (no. 10) contained inclusions near the core that darkened the overall appearance. All the crystals studied had dodecahedral habits, often modified by trapezohedron faces that were finely striated lengthwise.

The standard gemological properties, summarized in table 1, are typical of andradite (O'Donoghue, 2006). The properties are also comparable to those obtained by Stockton and Manson (1983) on seven samples of demantoid reportedly from Italy.

All of our samples contained fibrous inclusions, identified as chrysotile on the basis of morphology, in the typical "horsetail" arrangement (figure 5). One stone had been cut with these fibers placed under the table facet to emphasize their distinctive beauty. "Horsetail" inclusions have been previously documented in samples from Val Malenco (e.g., Hoskin et al., 2003; Gübelin and Koivula, 2005), and such internal features are typical of demantoid hosted by serpentinite. The faceted samples also contained many fractures, some healed with liquid or solid materials. Straight growth lines were observed in one stone, and two samples contained white inclusions of what was probably a serpentine-group mineral (e.g., antigorite; see figure 5, left), as documented by Gübelin and Koivula (2005) in demantoid from this locality.

Chemical Composition. The chemical compositions of the eight analyzed samples from Val Malenco are summarized in table 2.

NEED TO KNOW

- Demantoid is a variety name for Cr-bearing yellowish green to green andradite.
- Demantoid from Val Malenco has been known since the late 19th century, but only limited amounts have been cut.
- Val Malenco demantoid is almost pure andradite, and contains "horsetail" inclusions.
- The intensity of the green coloration correlates to Cr content, which was measured in relatively low concentrations (up to ~5500 ppm).

Electron microprobe analyses showed that all the garnets consisted of nearly pure andradite (≥98 mol%), and that Ti, V, Al, Cr, Mn, Mg, Na, and K were present only in amounts of <1 wt.% oxide, which is consistent with data previously reported by Amthauer et al. (1974), Stockton and Manson (1983), and Bedogné et al. (1999). Chromium was the most important chromophore other than iron, with average values ranging up to 0.58 wt.% Cr_2O_3. Moreover, this element was heterogeneously distributed within each sample (see, e.g., figure 6). Amthauer et al. (1974) also measured variable Cr_2O_3 contents in different colors of demantoid from Val Malenco (i.e., 0.02–1.30 wt.%; the highest contents were measured in intense green samples). Bedogné et al. (1999) reported a strong Cr_2O_3 variation (from traces up to 2.48 wt.%) between different samples. Stockton and Manson (1983) reported small amounts of Cr_2O_3 (approaching the detection limit of the microprobe) in almost all the yellowish green samples investigated from this locality, noting also a heterogeneous composition, especially with regard to chromium.

LA-ICP-MS analyses measured significant values (more than a few parts per million) of only three elements: Cr, Ti, and V (table 2). Ti and V were rather constant, and did not show any correlation with color; Cr, however, was quite variable and did correlate to the intensity of green coloration (figure 7). In

Figure 4. These faceted demantoids from Val Malenco (0.31–0.91 ct) are some of the cut samples tested for this study. Photo by Matteo Chinellato.

the yellowish green specimens (nos. 1–3), Cr contents were below or very close to the detection limit of the microprobe, with levels ranging up to 250 ppm measured by LA-ICP-MS. The greener stones (nos. 4–8) contained higher Cr contents, up to ~5500 ppm. The variation of Cr within a single sample (again, see figure 6) was also evident in the LA-ICP-MS data (see ranges in table 2). The content and distribution of the rare-earth elements, as measured by LA-ICP-MS, will be discussed in a separate article.

Chemical analysis of the dark inclusions in sample no. 10 (figure 8) identified them as Cr-bearing magnetite, with 16.63–23.08 wt.% Cr_2O_3. Magnetite and Cr-bearing magnetite are common in demantoid associated with serpentinite, and were observed by Bedogné and Pagano (1972) as small grains in

TABLE 1. Gemological and spectroscopic properties of andradite/demantoid from Val Malenco, Italy, investigated in this study.

Color	Yellowish green to green, medium to dark
Diaphaneity	Transparent
Optic character	Singly refractive with moderate-to-strong anomalous double refraction
Refractive index	>1.81
Specific gravity	3.81–3.88
UV fluorescence	Inert
Internal features	"Horsetail" inclusions, crystalline inclusions (probably belonging to the serpentine mineral group), fractures (some partially healed), straight growth lines
UV-Vis-NIR spectroscopy	Total absorption below 390 nm, strong bands at 435–440 nm, broad feature at 480 nm, absorptions at 575, 620, 640 nm, a doublet at 695–700 nm, and a broad band at 860 nm
Mid-IR spectroscopy	Areas of total absorption between 2250 and 400 cm^{-1} intrinsic to garnet; bands at 3560 and 3604 cm^{-1} related to structurally bonded OH^-

TABLE 2. Chemical composition of eight andradites from Val Malenco, Italy.

Chemical composition	No. 1 Yellowish green	No. 2 Yellowish green	No. 3 Yellowish green	No. 4 Green	No. 5 Green	No. 6 Green	No. 7 Green	No. 8 Green
Electron microprobe analyses (average)[a]								
No. points analyzed	11	10	7	11	11	10	10	10
Oxides (wt.%)								
SiO_2	35.95	35.39	35.37	35.93	35.76	35.73	35.88	35.81
TiO_2	0.02	0.03	0.01	0.01	0.04	0.05	0.03	0.02
Al_2O_3	0.06	0.08	0.07	0.15	0.06	0.08	0.06	0.05
Cr_2O_3	bdl	0.01	0.03	0.18	0.19	0.29	0.47	0.58
Fe_2O_3[b]	31.60	31.51	31.60	31.05	31.27	30.98	31.07	31.01
MnO	0.01	0.03	0.03	0.02	0.02	0.03	0.02	0.04
MgO	0.10	0.12	0.13	0.15	0.13	0.17	0.09	0.11
CaO	33.04	33.04	33.04	33.06	33.02	32.98	32.99	33.04
Na_2O	0.01	0.01	0.01	0.01	bdl	bdl	bdl	bdl
Total	100.79	100.22	100.29	100.56	100.49	100.31	100.61	100.66
Ions per 12 oxygens								
Si	3.011	2.987	2.985	3.014	3.005	3.007	3.010	3.004
Ti	0.001	0.002	0.001	0.001	0.003	0.003	0.002	0.001
Al	0.006	0.008	0.007	0.015	0.006	0.008	0.006	0.006
Cr	bdl	0.001	0.002	0.012	0.013	0.019	0.031	0.039
Fe^{3+}	1.992	2.001	2.006	1.960	1.977	1.962	1.961	1.958
Mn	0.001	0.002	0.002	0.001	0.001	0.002	0.001	0.003
Mg	0.012	0.015	0.016	0.019	0.016	0.021	0.011	0.014
Ca	2.965	2.988	2.987	2.971	2.975	2.974	2.965	2.970
Na	0.001	0.002	0.002	0.002	bdl	bdl	bdl	bdl
Mol% end members								
Andradite	99.6	99.9	99.9	98.7	99.2	98.6	98.8	98.3
Uvarovite	0.0	0.0	0.0	0.6	0.2	1.0	0.8	1.1
Others	0.4	0.1	0.1	0.7	0.6	0.4	0.4	0.6
LA-ICP-MS analyses[c]								
No. points analyzed	3	6	6	3	4	3	3	3
Element (ppm)								
Cr	6–23 (12)	2–188 (67)	11–250 (113)	16–5089 (682)	1621–3302 (2553)	1028–1467 (1271)	690–5468 (2568)	3899–4480 (4189)
Ti	113–233 (180)	78–649 (266)	110–152 (126)	7–157 (89)	157–292 (228)	156–458 (300)	67–195 (120)	68–87 (60)
V	35–41 (37)	33–86 (52)	26–28 (28)	12–43 (35)	52–70 (62)	51–69 (57)	65–91 (74)	39–46 (43)

[a] *Electron microprobe operating conditions: accelerating voltage = 15 kV, beam current = 15 nA, count time = 60 seconds on peaks and 30 seconds on background. Standards: natural wollastonite (Si, Ca), anorthite (Al), fayalite (Fe), olivine (Mg), rhodonite (Mn), omphacite (Na), ilmenite (Ti), K-feldspar (K), and pure V and Cr for those elements. Abbreviation: bdl = below detection limit (0.01 wt.%). Potassium and vanadium were below the detection limit in all analyses.*

[b] *Total iron calculated as Fe_2O_3. The flank method established that all iron is Fe^{3+}.*

[c] *LA-ICP-MS operating conditions: spot size = 40 μm; external standard = NIST SRM 610 glass; internal standard = Ca. Precision and accuracy estimated on the basaltic glass BCR2 standard were better than 10%. Data include ranges, with average values in parentheses. Several other elements (see text) were present at no more than a few ppm, and are not included here.*

samples from Val Malenco. In sample no. 10, enriched amounts of Cr (and relatively low Fe) were also present in the garnet adjacent to these inclusions (figure 8). The Cr_2O_3 content varied from 10.09 to 3.78 wt.% with increasing distance from the Cr-bearing magnetite grain.

Spectroscopy. The most significant spectroscopic features in the investigated samples are summarized in table 1 and described below.

UV-Vis-NIR. As illustrated by the two representative samples in figure 9, the UV-Vis-NIR absorption spectra are characterized by total absorption below 390 nm, an intense peak at ~440 nm with a second component at ~435 nm, two bands at 575 and 620

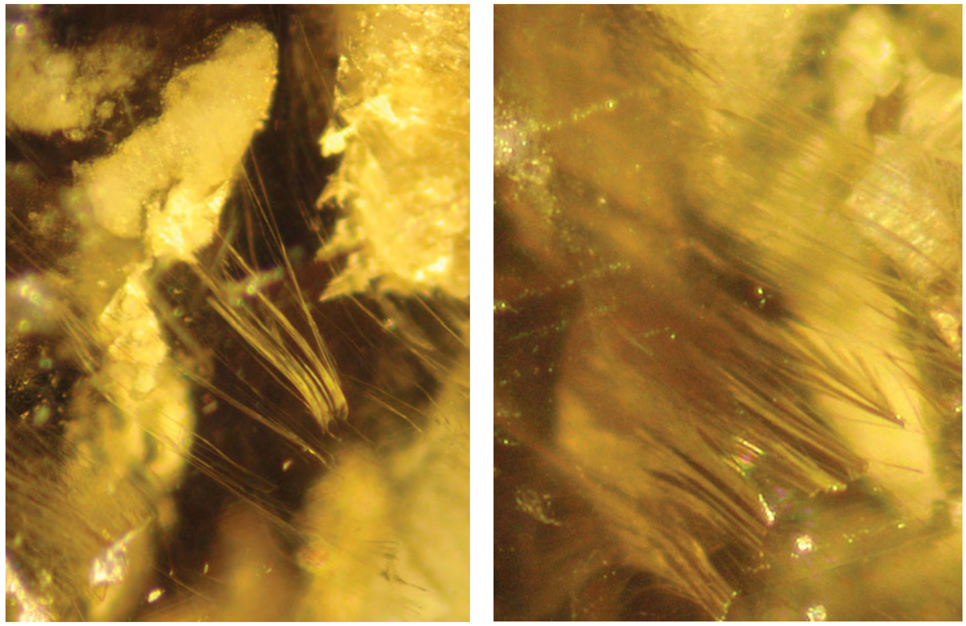


Figure 5. All the Val Malenco samples investigated for this study contained fine fibers of chrysotile in a "horsetail" arrangement, as is typical of demantoids occurring in serpentinite. The white masses in the left photo were identified as a serpentine mineral such as antigorite. Photomicrographs by Vanda Rolandi; magnified 45×.

nm that sometimes overlap, and a broad band at ~860 nm. These spectral features are all related to Fe^{3+} and Cr^{3+}. In particular, the features at 390, 440, 575, and 860 nm are related to Fe^{3+}. The 440 nm band is also attributed to Cr^{3+}, as is a feature at ~480 nm; both of these were seen to increase proportionally to chromium content in spectra taken from slabs of the same thickness. The 620 nm band is also assigned to Cr^{3+}, though we cannot exclude a weak contribution from Fe^{3+} (for all these assignments see, e.g., Manning, 1972; Moore and White, 1972; Amthauer et al., 1974; Amthauer, 1976). Absorption in the 500–700 nm range could be a rough indicator of Cr content in demantoid, although this correlation is in need of proper calibration. In samples with very low Cr (e.g., no. 2, with 67 ppm Cr average), the 575 nm band was clearly evident, whereas the 620 nm feature was only suggested. However, the 575

Figure 6. This X-ray map obtained with the electron microprobe shows the Cr distribution in sample no. 7.

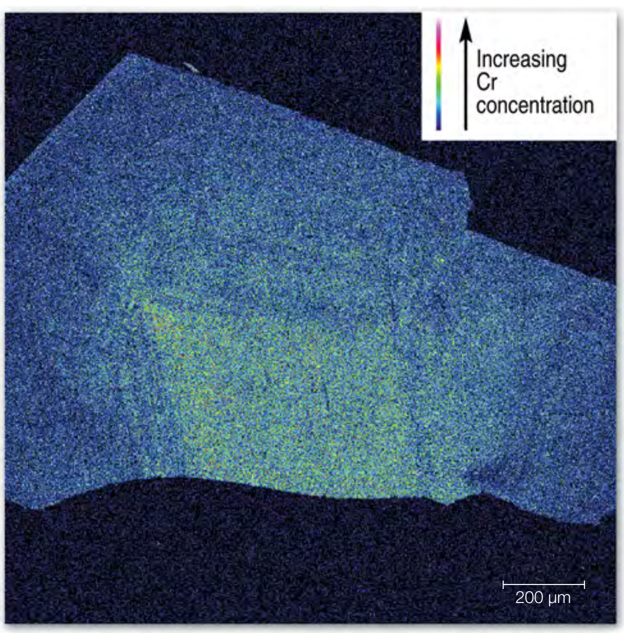
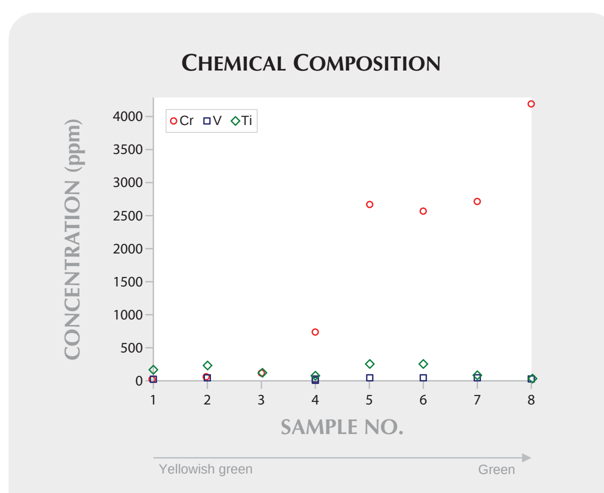


Figure 7. The average contents of Cr, V, and Ti obtained by LA-ICP-MS are shown for eight rough andradite/demantoid samples investigated for this study, according to the intensity of their color (see table 2 for data).



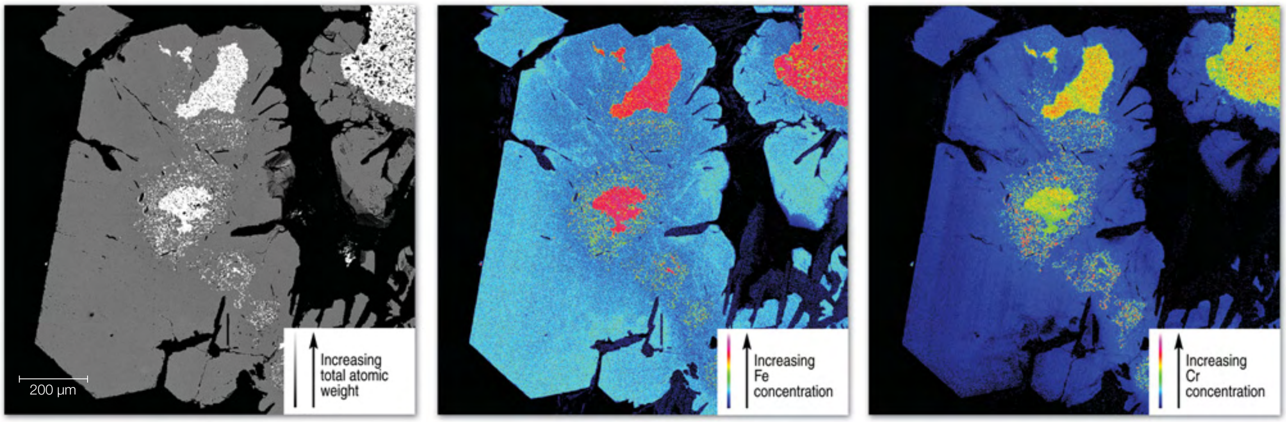
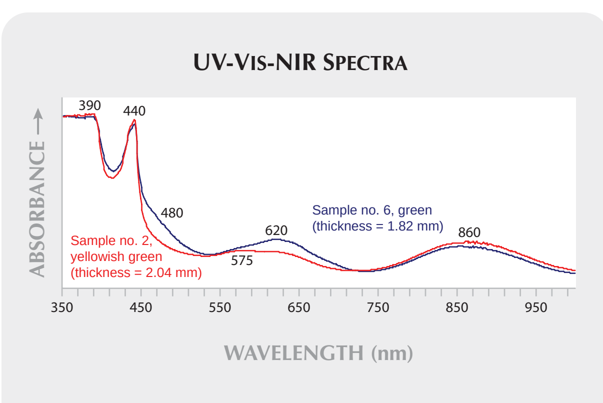


Figure 8. The white areas in the backscattered electron image on the left are inclusions of Cr-bearing magnetite in sample no. 10. The X-ray maps (center and right) show the distribution of Fe and Cr in the inclusions and the host garnet.

nm band was obscured in the Cr-abundant samples by the more intense 620 nm feature. A 695–700 nm doublet and a weak peak at 640 nm, both related to Cr^{3+} (Burns, 1993; O'Donoghue, 2006), were also seen—though with difficulty—in specimens with a higher Cr content (e.g., no. 6).

Mid-Infrared. The mid-IR spectra of all the rough samples—both in diffuse reflectance and transmission modes—showed areas of total absorption in the 2250–400 cm^{-1} range, intrinsic to garnet, along with one or more bands between 3650 and 3450 cm^{-1} (figure 10). The dominant absorption peak at ~3560 cm^{-1} and the weaker absorption at 3604 cm^{-1} are related to hydroxide, which can be present in andradite as a minor component, in the form of structurally bonded OH^- (Amthauer and Rossman, 1998).

Figure 9. UV-Vis-NIR spectra are shown here for two representative samples from Val Malenco: no. 2 (average Cr = 67 ppm) and no. 6 (average Cr = 1271 ppm).

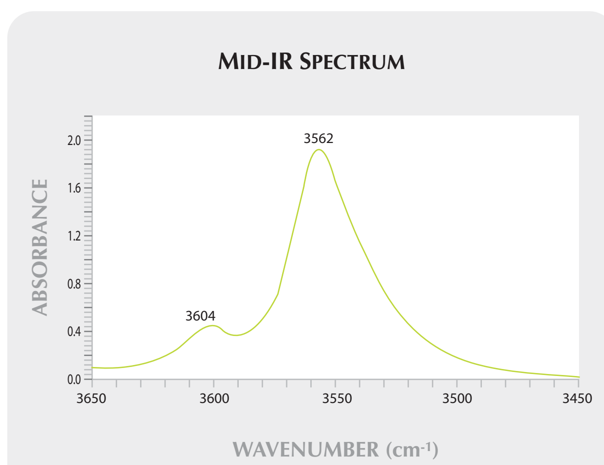


CONCLUSION

Demantoid from Val Malenco is an attractive gem material that consists of almost pure andradite (≥ 98 mol%) and has typical gemological properties for this garnet variety. "Horsetail" inclusions are common and are consistent with the demantoid's geologic origin related to serpentinite. Infrared spectroscopy showed that hydroxide is a minor component of this garnet.

The color, ranging from yellowish green to green, is due to intrinsic iron and traces of chromium, as shown by chemical analyses and UV-Vis-NIR spectroscopy. In particular, Cr^{3+} causes the purer green coloration, despite the often low amounts present. Mining at Val Malenco is no longer active, but thousands of carats of faceted demantoid from this area have entered the market over the years.

Figure 10 The mid-IR spectrum in transmission mode of Val Malenco demantoid (here, sample no. 4, 1.50 mm thick) shows absorption features related to OH^- at 3604 and 3562 cm^{-1}.



ABOUT THE AUTHORS

Dr. Adamo (ilaria.adamo@unimi.it) is a postdoctoral fellow, and Drs. Bocchio and Pavese are professors of mineralogy, in the Earth Sciences Department at Università degli Studi di Milano, Italy. Drs. Diella and Vignola are researchers at the Institute for Dynamics of Environmental Processes (IDPA), National Research Council (CNR), Section of Milan, to which Drs. Bocchio and Pavese also belong. Dr. Prosperi is director of the Italian Gemological Institute (IGI) laboratory in Milan. Dr. Palanza is a study grant holder in the Materials Science Department at Università degli Studi di Milano–Bicocca, Italy.

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