

NEW CHROMIUM- AND VANADIUM-BEARING GARNETS FROM TRANOROA, MADAGASCAR

By Karl Schmetzer, Thomas Hainschwang, Heinz-Jürgen Bernhardt, and Lore Kiefert

Pyrope-spessartine garnets from Tranoroa, in southern Madagascar, contain appreciable Cr and somewhat lower V contents. Although these elements are responsible for the color-change behavior of similar garnets from the nearby Bekily area, the Tranoroa samples show only a slight change in color appearance from day or fluorescent light (brownish purple-red) to incandescent light (purplish red). Characteristic internal features in the Tranoroa garnets include networks of rutile needles and strain patterns caused by anomalous double refraction. Additional inclusions are graphite, quartz, negative crystals, apatite, zircon, and monazite. One Cr-bearing spessartine from the same area is also described.

Gem-quality pyrope-spessartine garnets have been known from Tanzania and Sri Lanka since the late 1970s. Recently, two important varieties of these intermediate garnets have come from the Bekily area in southern Madagascar. Pink to pinkish orange Bekily material with variable iron contents but almost no vanadium or chromium has been called "malaya" garnet in the trade (Schmetzer et al., 2001). Bekily garnets with variable amounts of vanadium and lesser chromium generally show a distinct color change between day (or fluorescent) light and incandescent light. These color-change pyrope-spessartine garnets have been subdivided into several groups or types according to the different colors observed under variable illumination (see Schmetzer and Bernhardt, 1999; Krzemnicki et al., 2001).

In June 2001, we obtained a parcel of about 30 faceted garnets from southern Madagascar with unusual coloration (see, e.g., figure 1). According to our supplier, these garnets had been mined recently from a new area near Tranoroa, about 60 km southwest of Bekily (figure 2). We do not know the amount of this material that has been mined to date. Both the Tranoroa and Bekily localities belong to a region formed by several metamorphic belts consisting of high-grade metamorphic rocks of Precambrian age (Windley et al., 1994). More information on the geology, mining, and production of garnets from the Bekily area can be found in Schmetzer et al. (2001).

The present study was undertaken to characterize these new garnets, which differ from those previously described from Madagascar with regard to their color and color behavior.

MATERIALS AND METHODS

For this study we selected seven samples, which ranged from 1.52 to 4.77 ct (see, e.g., figure 1), from the parcel of about 30 faceted garnets. Six were brownish purple-red in daylight and represented the majority of the samples. We also studied one brownish orange garnet from the same parcel (see box A). From several other parcels totaling more

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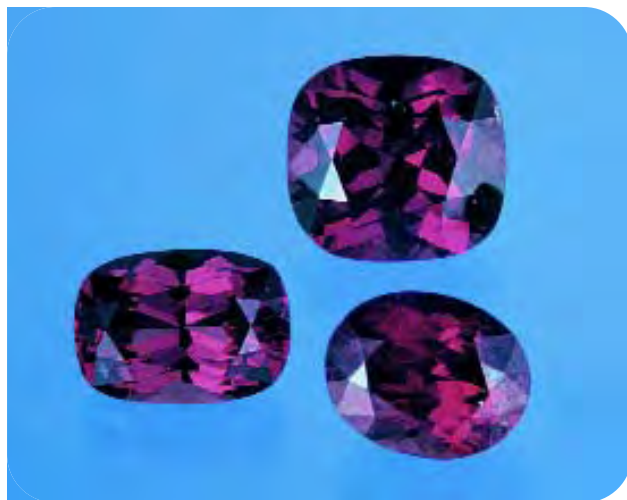
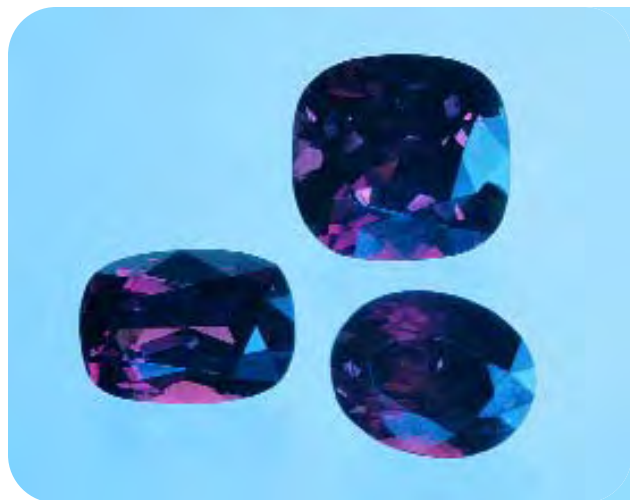


Figure 1. Chemical analysis of these pyrope-spessartine garnets from Tranoroa, Madagascar—shown here in fluorescent light (left) and incandescent light (right)—revealed appreciable amounts of Cr and V. However, they do not show the distinct color change in daylight and incandescent light that is observed in pyrope-spessartines from the nearby deposit at Bekily. The samples weigh 4.77, 3.26, and 2.81 ct. Photos by Maha Tannous.

than 400 garnets from Bekily, we chose about 50 Cr- and V-bearing samples for chemical analysis. From these samples, we selected three representative stones for comparison of their color appearance and composition with the Tranoroa garnets.

The seven Tranoroa samples were tested by standard gemological methods for refractive index, fluorescence to long- and short-wave ultraviolet radiation, and specific gravity. We examined the samples for inclusions and internal structural properties using various microscopes and lighting conditions, both with and without immersion in methylene iodide. In addition, we identified solid inclusions by laser Raman microspectrometry using a Renishaw 1000 system.

For all these Tranoroa samples, we recorded spectra in the UV-visible range with a Leitz-Unicam SP 800 spectrophotometer as well as with an Adamas Advantage SAS 2000 spectrophotometer. To determine quantitative chemical composition, we used a Cameca Camebax SX 50 electron microprobe, with traverses of 10 point analyses each, measured across the tables of the faceted stones. The same instrument was used to analyze the three garnets from Bekily.

RESULTS

The results for the six brownish purple-red Tranoroa samples are listed in table 1 and discussed below. The results for the three Bekily samples are included in table 1 for comparison.

Visual Appearance and Gemological Properties. All samples revealed a homogeneous brownish purple-red color in day or fluorescent light and were pur-

Figure 2. The garnets described here were mined recently near Tranoroa, which is located about 60 km southwest of the Bekily garnet deposits in southern Madagascar.



BOX A: A CHROMIUM-BEARING SPESSARTINE

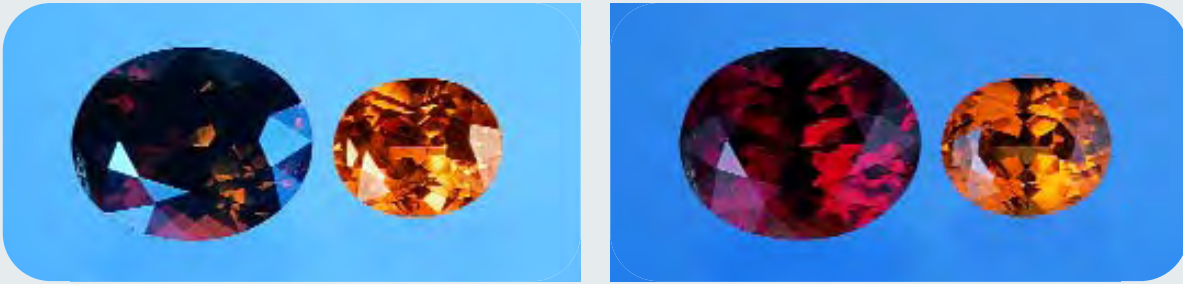


Figure A-1. As seen in day or fluorescent light (left) and incandescent light (right), the color appearance of this 2.84 ct Cr-bearing Tranoroa spessartine (sample G, see table 1) is distinctly different from the 1.03 ct V- and Cr-free Madagascar spessartine (0.02 wt. % V_2O_3 , 0.02 wt. % Cr_2O_3 , 39.34 wt. % MnO, and 2.29 wt. % FeO). Photos by Maha Tannous.

Within the parcel of brownish purple-red garnets from Tranoroa, we observed one sample that appeared brownish orange in day or fluorescent light and reddish orange in incandescent light (figure A-1). Physical and chemical properties of this garnet (sample G) are given in table 1.

This garnet showed distinctly higher R.I. and S.G. values than the other six samples. Microprobe analysis revealed that it was different in composition from the other six garnets, with only about 5 mol. % pyrope and a relatively high spessartine value of just over 88 mol. % (again, see table 1). The almandine content was rather small, and chromium (1.01 wt. % Cr_2O_3) was again more abundant than vanadium (0.32 wt. % V_2O_3). The sample was inert to long- and short-wave UV radiation.

The color behavior of this sample, as compared to that of typical spessartine (again, see figure A-1), was

undoubtedly associated with its high Cr content. The absorption spectrum (figure A-2) was similar to that of the Cr-bearing intermediate pyrope-spessartines from the same area. The spectrum revealed a dominant chromium absorption in the yellow region and weak iron absorption bands. Consistent with the distinctly higher Mn content of the sample, the absorption bands of manganese were stronger, and thus the absorption minimum in the blue-green to violet range was less pronounced than in the intermediate pyrope-spessartine samples from Tranoroa. This difference in transparency in the blue-green to violet region is responsible for the differences in color in daylight and incandescent light observed in the two types of Tranoroa garnets.

Microscopically, the spessartine sample was free of rutile needles or other mineral inclusions. With crossed polarizers, we observed a mosaic-like pattern that showed high-order interference colors (figure A-3).

The garnet from Tranoroa is, to the best of our knowledge, the first chromium-bearing spessartine described as a faceted gemstone.

Figure A-2. The absorption bands observed in the spectrum of the Tranoroa spessartine (sample G) are consistent with those of Cr-bearing pyrope-spessartines. The bands are due to chromium, manganese, and iron (see figure 3 in the main text).

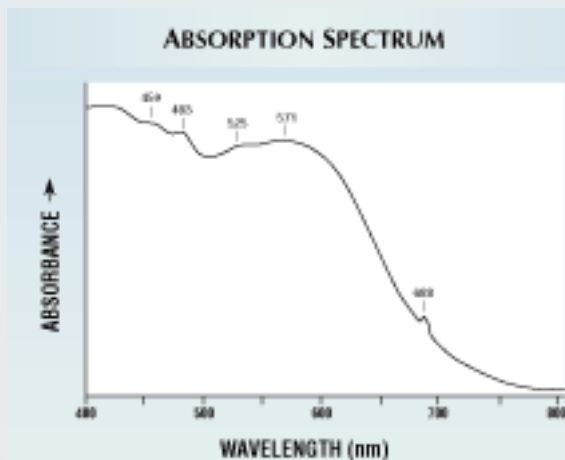
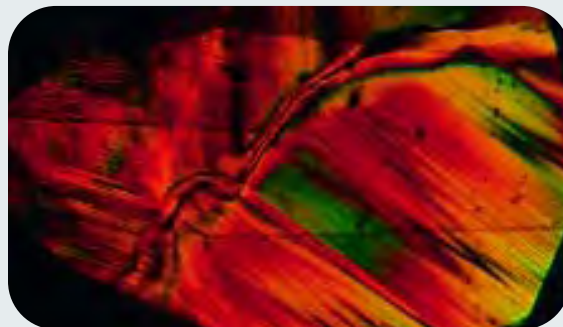


Figure A-3. Microscopic examination of the Tranoroa spessartine revealed high-order interference colors in an irregular mosaic-like structure and strain pattern. Photomicrograph by K. Schmetzer; immersion, crossed polarizers, magnified 40 \times .



plish red in incandescent light (again, see figure 1). Refractive indices for the six samples were found to vary within a small range, from 1.768 to 1.773 (table 1). Likewise, the specific gravity values fell between 3.95 and 3.97, which indicates a narrow range of chemical composition within the pyrope-almandine-

spessartine solid-solution series. These R.I. and S.G. values are within the ranges found for malaya garnets from the same region, although they are higher than the average values recorded for the samples described in Schmetzer et al. (2001). All garnets were inert to both long- and short-wave UV radiation.

TABLE 1. Physical and chemical properties of pyrope-spessartine garnets from Tranoroa and Bekily, Madagascar.

Property	Tranoroa							Bekily			
	A	B	C	D	E	F	G	X	Y	Z	
Weight (ct)	4.77	1.86	3.26	2.81	2.02	1.52	2.84	0.67	0.90	0.78	
Color											
Day or fluorescent light			Brownish purple-red					Brownish orange	Grayish green	Slightly reddish purple	Bluish green-gray
Incandescent light			Purplish red					Reddish orange	Grayish purple	Strongly reddish purple	Pinkish purple
Refractive index	1.768	1.768	1.769	1.770	1.770	1.773	1.808	1.750	1.752	1.755	
Specific gravity	3.95	3.96	3.95	3.96	3.97	3.97	4.15	3.82	3.83	3.86	
Microprobe analyses (wt.%) ^a											
SiO ₂	38.70	37.67	38.82	38.41	37.91	37.88	35.81	40.62	40.83	39.66	
TiO ₂	0.05	0.08	0.04	0.07	0.12	0.16	0.33	0.05	0.07	0.05	
Al ₂ O ₃	21.98	21.75	22.00	21.69	21.46	21.33	20.24	22.92	22.91	22.50	
Cr ₂ O ₃	0.67	0.69	0.68	0.71	0.75	0.75	1.01	0.11	0.53	0.15	
V ₂ O ₃	0.38	0.41	0.35	0.43	0.51	0.58	0.32	0.58	0.56	0.67	
FeO ^b	2.57	2.60	2.55	2.54	2.67	2.32	1.13	1.50	3.69	1.71	
MnO	23.60	23.41	23.44	23.68	24.02	25.00	37.80	15.52	14.27	16.98	
MgO	10.25	10.26	10.24	9.90	9.68	8.40	1.59	14.18	16.10	14.07	
CaO	1.42	1.42	1.42	1.60	1.62	2.50	0.80	5.09	2.02	3.40	
Total	99.62	98.29	99.55	99.03	98.72	98.94	99.04	100.56	100.98	99.19	
Cations ^c											
Si	2.967	2.934	2.975	2.968	2.951	2.959	2.950	2.979	2.972	2.965	
Ti	0.003	0.004	0.002	0.004	0.007	0.009	0.020	0.003	0.004	0.003	
Al	1.986	1.997	1.987	1.976	1.969	1.964	1.965	1.981	1.965	1.982	
Cr	0.041	0.043	0.041	0.043	0.046	0.046	0.066	0.006	0.031	0.009	
V	0.023	0.026	0.022	0.027	0.032	0.037	0.021	0.034	0.033	0.040	
Fe	0.165	0.170	0.163	0.190	0.174	0.152	0.078	0.092	0.224	0.107	
Mn	1.532	1.544	1.522	1.550	1.583	1.654	2.637	0.964	0.879	1.075	
Mg	1.172	1.195	1.170	1.140	1.123	0.978	0.195	1.551	1.746	1.568	
Ca	0.117	0.119	0.177	0.133	0.135	0.209	0.017	0.400	0.157	0.272	
Mol.% end-members											
Pyrope	39.35	39.46	39.37	37.84	37.35	32.68	4.68	51.58	58.08	51.89	
Spessartine	51.31	50.99	51.04	51.44	52.50	55.26	88.46	32.06	29.24	35.57	
Almandine	5.53	5.61	5.48	6.31	5.77	5.08	2.62	3.06	7.45	3.54	
Grossular	0.80	0.59	0.87	0.99	0.67	2.92	—	11.32	2.06	6.59	
Goldmanite	1.12	1.26	1.07	1.32	1.56	1.81	1.02	1.68	1.63	1.99	
Uvarovite	2.00	2.08	2.00	2.10	2.25	2.25	1.36	0.30	1.53	0.42	
Knorringite	—	—	—	—	—	—	1.86 ^d	—	—	—	

^a Average composition of 10 analyses each; all samples were relatively homogeneous in composition.

^b Total iron as FeO.

^c Calculated on the basis of 12 oxygens.

^d Because CaO was smaller than necessary to account for all the chromium and vanadium as uvarovite and goldmanite, the residual chromium in this sample was assigned to the Mg-Cr end member, knorringite [Mg₃Cr₂(SiO₄)₃].

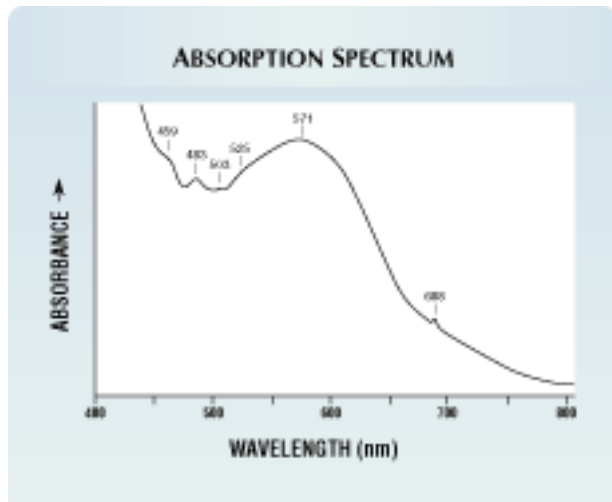


Figure 3. This absorption spectrum of a representative brownish purple-red garnet from Tranoroa (sample E) shows features that are consistent with a chromium-bearing intermediate pyrope-spessartine. The bands labeled are due to Cr^{3+} (571, 688 nm), V^{3+} (571 nm), Mn^{2+} (459, 483, 525 nm), and Fe^{2+} (459, 503, 525 nm).

Chemical Properties. The garnets were members of the pyrope-almandine-spessartine solid-solution series, with 33–39 mol.% pyrope and 51–55 mol.% spessartine (table 1). Almandine percentages varied only between 5 and 7 mol.% for these six samples, with smaller percentages of grossular (0.6–3 mol.%). All samples contained more chromium than vanadium: 0.67–0.75 wt.% Cr_2O_3 (~2 mol.% uvarovite) and 0.35–0.58 wt.% V_2O_3 (1–2 mol.% goldmanite).

Calculations of Fe^{2+} and Fe^{3+} for a garnet com-

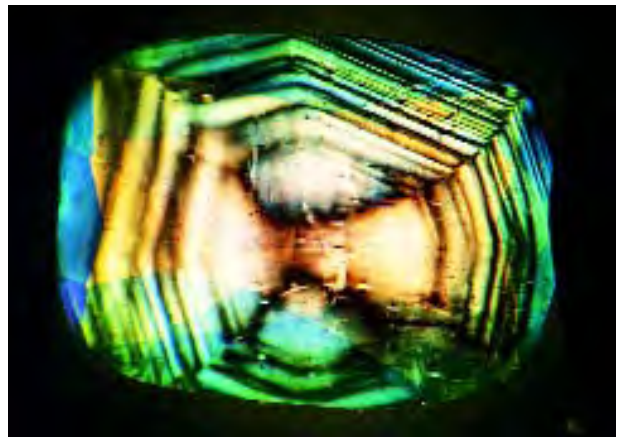


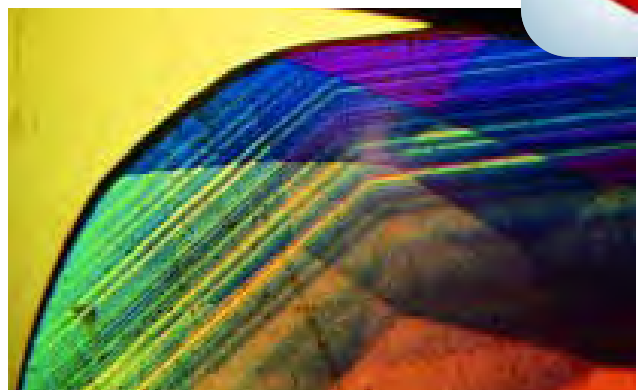
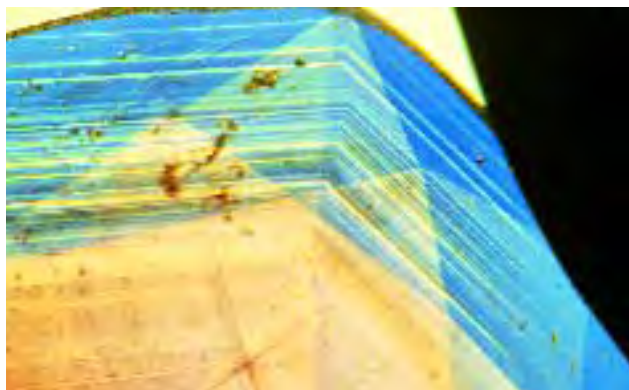
Figure 4. This pyrope-spessartine shows anomalous double refraction and strain parallel to growth planes that were determined as the trapezohedron $\{211\}$. Photomicrograph by K. Schmetzer; immersion, crossed polarizers, magnified 20 \times .

position with 12 oxygens suggested that Fe^{3+} is either not present or present in only a very small amount (<0.01 Fe^{3+} atoms per formula unit). This indicates little or no andradite component in the samples.

In summary, all samples contained more chromium than vanadium. They were intermediate pyrope-spessartine garnets with greater amounts of spessartine than pyrope.

Spectroscopic Properties. The absorption spectra of all six samples consisted of a strong broad absorption band centered at 571 nm; weak bands at 459, 483, 503, 525, and 688 nm; and an absorption edge

Figure 5. In two of the Tranoroa pyrope-spessartine garnets, growth planes were seen to form angles of 132° (left) or 147° (right), which are typical for the trapezohedron $\{211\}$ in the cubic system. Both photomicrographs taken with immersion, magnified 50 \times . The inset shows an idealized drawing (clinographic projection) of a crystal composed of $\{211\}$ faces.



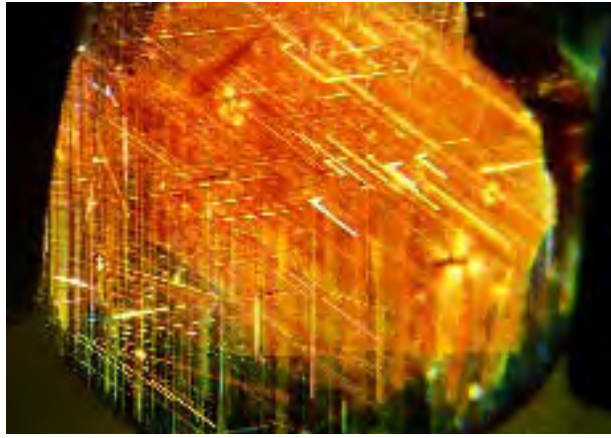


Figure 6. All of the pyrope-spessartine study samples revealed dense, three-dimensional networks of oriented rutile needles. Photomicrograph by K. Schmetzer; immersion, crossed polarizers, magnified 40 \times .

near 440 nm with an almost continuous strong absorption below 440 nm (figure 3).

Features Observed with the Microscope. As illustrated and described for the non-color-change pyrope-spessartines from Bekily (Schmetzer et al., 2001), all of the Tranoroa samples revealed strong anomalous double refraction (ADR) when examined with crossed polarizers (figure 4). In two samples, this ADR was also seen parallel to growth planes of the trapezohedron {211}, which forms pairs of faces with two characteristic angles of 132° and 147° (figure 5). The trapezohedron (figure 5, inset) is one of the two most common forms observed in garnet crystals (the other is the dodeca-

Figure 8. This negative crystal in a pyrope-spessartine represents the garnet morphology. The faces are probably also the trapezohedron {211}. Photomicrograph by L. Kiefert; magnified 200 \times .

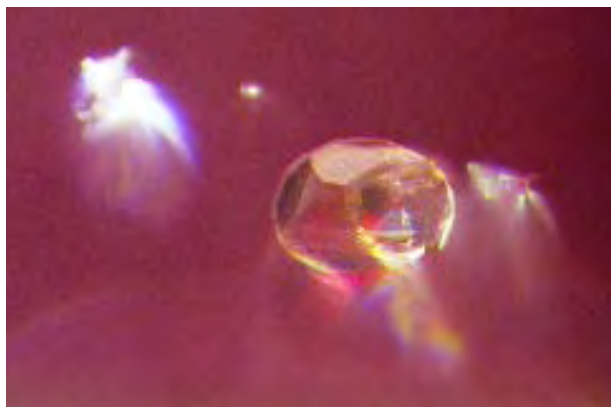


Figure 7. As with the Bekily garnets examined earlier, some of the Tranoroa pyrope-spessartines also contained tabular graphite crystals. Photomicrograph by L. Kiefert; magnified 100 \times .

hedron {110}). Two of these garnets also showed a swirl-like pattern of growth inhomogeneities.

Also as described and illustrated in Schmetzer et al. (2001) for Bekily garnets, all six Tranoroa samples revealed a three-dimensional network of oriented rutile needles (figure 6), and some contained numerous other inclusions, which were identified by laser Raman microspectrometry: irregularly shaped graphite platelets (figure 7) and fragments of quartz crystals; negative crystals reflecting the external garnet morphology (figure 8); prismatic apatite crystals, sometimes with slightly rounded edges; and small zircon crystals with tension cracks. In one of the garnets, we found an irregularly shaped monazite crystal (figure 9).

Figure 9. One of the garnet samples contained this irregularly shaped monazite crystal. Photomicrograph by L. Kiefert; magnified 100 \times .

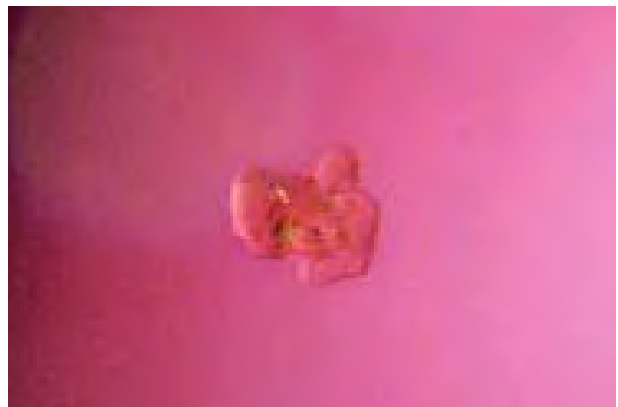




Figure 10. Chemical differences (table 1) are responsible for the different colors shown by the pyrope-spessartines from Tranoroa as compared to pyrope-spessartines from Bekily in day or fluorescent light (left) and incandescent light (right). From left to right: sample E, 2.02 ct from Tranoroa, with Cr>V; sample X, 0.67 ct from Bekily, with V>Cr; sample Y, 0.90 ct from Bekily, with V~Cr; and sample Z, 0.78 ct from Bekily, with V>Cr. Photos by Maha Tannous.

DISCUSSION

Absorption Spectra. The strong band at 571 nm in the absorption spectra of the Tranoroa samples is assigned to Cr³⁺, because a Cr³⁺ absorption band in an almost identical position has been reported in pyropes with high chromium contents (Amthauer, 1976). A chromium absorption maximum at this wavelength also has been found in alexandrite-like intermediate pyrope-spessartine garnets with higher Cr than V contents (Schmetzer and Ottemann, 1979; Schmetzer et al., 1980). In the latter type of garnet, however, the V³⁺ absorption band is located in the same spectral range (Schmetzer and Ottemann, 1979; Manson and Stockton, 1984; Schmetzer and Bernhardt, 1999; Krzemnicki et al., 2001). As a result of this overlap, the absorption bands of chromium and vanadium cannot be separated in intermediate pyrope-spessartine garnets. Rather, they have a combined effect that strengthens the absorption in this region of the spectrum. The weak absorption band at 688 nm is also caused by Cr³⁺ and is commonly observed in various Cr-bearing garnets (Amthauer, 1976).

The four remaining absorption bands are assigned to Fe²⁺ and/or Mn²⁺ as follows: 459 nm = Fe + Mn, 483 nm = Mn, 503 nm = Fe, and 525 nm = Fe + Mn. A detailed discussion of this assignment appears in Schmetzer et al. (2001). The almost continuous absorption below 440 nm is caused by several manganese absorption bands.

Chemical Composition and Color Appearance. The brownish purple-red garnets from Tranoroa are intermediate members of the pyrope-spessartine series. All samples contained greater amounts of chromium than vanadium. Although the Tranoroa garnets did show a perceptible difference in appearance between daylight and incandescent light, these samples did not show the distinct change in hue seen in the Bekily color-change garnets. (Note that “color

change” terminology is not well defined and will be interpreted differently by different viewers and organizations. Because the Tranoroa samples showed a distinct change in color appearance but not from one hue to another, we are not referring to them as “color change” in this article. Some laboratories and other members of the trade might describe these samples as showing a “color shift.”) Color-change garnets with more Cr than V have been known from Tanzania and Sri Lanka for decades (Schmetzer and Ottemann, 1979; Schmetzer et al., 1980; Stockton, 1982; Manson and Stockton, 1984). However, the color-change pyrope-spessartines examined to date from Bekily, Madagascar, typically contain more vanadium than chromium (Schmetzer and Bernhardt, 1999; Krzemnicki et al., 2001; see also figure 10 and table 1). Only six of the 50 color-change Bekily samples analyzed had almost the same amount of vanadium as chromium (again see, figure 10 and table 1).

Color change in pyrope-spessartine garnets is a complex function of the relative amounts of color-causing transition metals (i.e., V, Cr, Mn, and Fe). Colorimetric data have been applied to explain the various changes in color appearance in different lighting environments for garnets and other gem materials (Schmetzer et al., 1980; Liu et al., 1999; Krzemnicki et al., 2001). The Tranoroa samples have absorption characteristics that are similar to the V>Cr-bearing color-change garnets from Bekily, which have an absorption maximum in the yellow region at 571 nm and two areas of transparency in the red and in the blue-green to violet regions (see Schmetzer and Bernhardt, 1999). However, in the Cr>V-bearing samples from Tranoroa, the transparency in the blue-green to violet region is distinctly smaller. This gives rise to the difference in color behavior of the Cr- and V-bearing garnets from Bekily and Tranoroa. It is evident that an

increase in manganese in intermediate pyrope-spessartine garnets causes an increase in the intensity of the manganese absorption bands and a reduction in transparency in the blue-green to violet spectral range (again, see figure 3), thus decreasing the blue color component and increasing the orange.

CONCLUSION

The new pyrope-spessartine garnets from Tranoroa have a brownish purple-red color not seen thus far in the nearby Bekily material. Despite their appreciable Cr and V contents, they do not show the distinct color change from daylight to incandescent light observed in the Bekily material. This is mainly due to their relatively high Mn contents, which reduce their transparency in the blue-green to violet range.

Garnets from both Tranoroa and Bekily formed in high-grade metamorphic Precambrian rocks. Differences in the composition of the host rocks are the most likely source of variations in the chemical properties and color appearance of these garnets.

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