OPTICAL-ABSORPTION AND ELECTRON-MICROPROBE STUDIES OF SOME HIGH-Ti ANDRADITES

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ABSTRACT

Electron-microprobe and optical-absorption spectra are reported of yellow/brown thin sections of some melanites and schorlomites and also of some pink high-Ti andradites from San Benito County, California. Ti^{3+}:Ti^{4+} ratios for the above garnets have been calculated, from which it is concluded that Ti substitutes as Ti^{3+} for octahedral Fe^{3+} in the pink andradites, whereas in the yellow/brown melanites and schorlomites the titanium appears to exist predominantly as Ti^{4+}, substituting in part for tetrahedral silicon. The pink titanian andradites can therefore be considered as a different variety from melanite or schorlomite.

INTRODUCTION

The valence states of Ti ions and their distribution between octahedral and tetrahedral sites in the andradite structure have long been the subject of much discussion. Andradites can contain appreciable amounts of Ti, presumably on account of the relatively large cell dimension of the andradite molecule compared with, for example, pyralspite garnets. Recently, Howie & Woolley (1968) suggested that andradites with $<8\%$ TiO_2 be called melanites and those with $>8\%$ TiO_2, schorlomites.

Zedlitz (1935) suggested that part of the Ti in andradite is present as Ti^{3+}, and this was confirmed by the optical absorption measurements of Manning (1967*a*) on a melanite from San Benito County, California. Ti^{3+}, a $3d^1$ ion, exhibits a single *d–d* absorption band in the visible region at 19,000 cm^{-1}, thus accounting for the brown colours of thin sections of the garnet. Ti^{4+}, having the $3d^0$ configuration, does not exhibit a *d–d* spectrum in the visible region, hence the presence of Ti^{4+} can only be inferred if the extinction coefficient of the Ti^{3+} *d–d* band is known and there is more titanium than can be accounted for by Ti^{3+}. In the current work, a lower limit for the extinction coefficient of the Ti^{3+} *d–d* band has been calculated, from which information can be obtained on the Ti^{3+}:Ti^{4+} ratios in melanites and schorlomites.

Tarte (1960), from studies of the infra-red spectra of garnets, has assigned an absorption band at 650 cm^{-1} to TiO_4 tetrahedra, and he puts most of the Ti in andradites into tetrahedral (Si) sites. Kunitz (1936) had

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earlier looked at chemical data on garnets and also concluded that titanium replaces Si. It is very likely that, because the Ti^{4+} (ionic radius = 0.68 Å) ion is smaller than Ti^{3+} (0.76 Å), the Ti^{4+} ion will predominate in the Si^{4+} sites. Moreover, where, say, 20% or so of the Si sites are occupied by Ti, cation charge-balance will demand that most of the Ti be Ti^{4+}, especially in view of the fact that other 4-valent cations are not usually observed in the Fe^{3+} sites (Howie & Woolley 1968).

Very recently, electron-microprobe studies of zoned titanium garnets have been reported by Lehijarvi (1966), Isaacs (1968) and Howie & Woolley (1968), but the metal–metal relationships deduced are conflicting. Lehijarvi (1966) and Isaacs (1968) showed that the content of titanium is inversely proportional to that of iron, suggesting that most of the Ti is present in octahedral sites. Howie & Woolley (1968), on the other hand, found this titanium–iron relationship in only one of 33 garnets investigated, and in general their electron-probe results indicate that Si is more likely to be replaced than Fe. A reasonable conclusion would seem to be that the roles of Ti in the andradite garnets studied by the above workers are different.

While preparing thin sections of melanites from San Benito County, California, for the current work, it was found that most of the sections were the usual shades of yellow and brown, but a few surprisingly were pink or bluish pink. Because the colours of garnets are due principally to their transition-metal content (Manning 1967*a*, 1967*b*), and because Ti^{3+} absorptions are considerably stronger than Fe^{2+} or Fe^{3+} absorptions in the visible region, the application of optical absorption techniques became self-evident. Of three different schorlomites studied, all were the expected shades of yellow or brown in thin section.

Electron-microprobe analyses are also reported across several yellow-to-pink zoned melanites, and these analyses are used in conjunction with the optical absorption data to calculate the chemical formulae of the yellow and pink melanites.

MATERIALS

Black melanite and schorlomite crystals were obtained from the following localities: melanites—Santa Rita Peak, San Benito County, (M26429), and near the Dallas Gem Mine, San Benito County, California (M28226); schorlomites—Magnet Cove, Arkansas; Knee Lake, Manitoba (M19222) and also one from an unknown locality. The minerals were kindly donated by Mr. H. R. Steacy, Curator of the National Mineral Collection, Geological Survey of Canada, and by Dr. R. I. Gait, Assistant Curator of Mineralogy at the Royal Ontario

Museum. The numbers following the specimens are ROM reference numbers.

EXPERIMENTAL DETAILS

Thin sections of the andradites were prepared by mounting a polished face on glass and thinning the sample to permit resolution of the spectra to 400 nm. Optically, the sections were only weakly anisotropic, and unpolarized-light spectra only are reported here. The specimens were then placed in one window of a two-windowed variable-aperture aluminum crystal holder made to fit the cell-compartment of a Beckman DK-2A double-beam spectrophotometer. Spectra were recorded, at room temperature, in the energy range 3,500 cm^{-1} (2800 nm) to 25,000 cm^{-1} (400 nm). Crystal thicknesses were measured with a micrometer.

Extinction coefficients were calculated from the expression

$$\epsilon = \frac{A}{C\,.\,l},$$

where A is the net absorbance, C is the cation concentration in moles per litre and l the specimen thickness in cm. The units of ϵ are therefore litres per mole-cm.

RESULTS AND DISCUSSION

Features of Ti-andradite spectra

Optical absorption spectra of the garnets are presented in Figs. 1–4. Light-brown sections of the melanites from the two different localities gave very similar spectra, and the spectrum of a specimen from Santa Rita Peak is shown in Fig. 1. The two schorlomites have very similar spectra also, and the spectrum of the Magnet Cove specimen is shown in Fig. 2. The yellow to brown colours of the melanites and schorlomites are due to the similar manner in which the absorption envelopes rise in going from the red-end to the blue-end of the visible region. According to Howie & Woolley (1968), the colours of thin sections of their 33 titanian garnets vary from yellow to brown, hence it would seem that the spectra of Figs. 1 and 2 are typical of yellow/brown melanites and schorlomites.

Figure 3 shows the absorption spectrum of a pink andradite from Santa Rita Peak. The pink colour is due to the steep rise in the absorption envelope at the longer wavelength (red) end of the visible region, while a bluish tinge arises from the valley in the blue region at 23,000 cm^{-1}.

The absorption spectra of low-Ti andradites and of a yellow melanite section have been reported in an earlier work (Manning 1967*a*), and

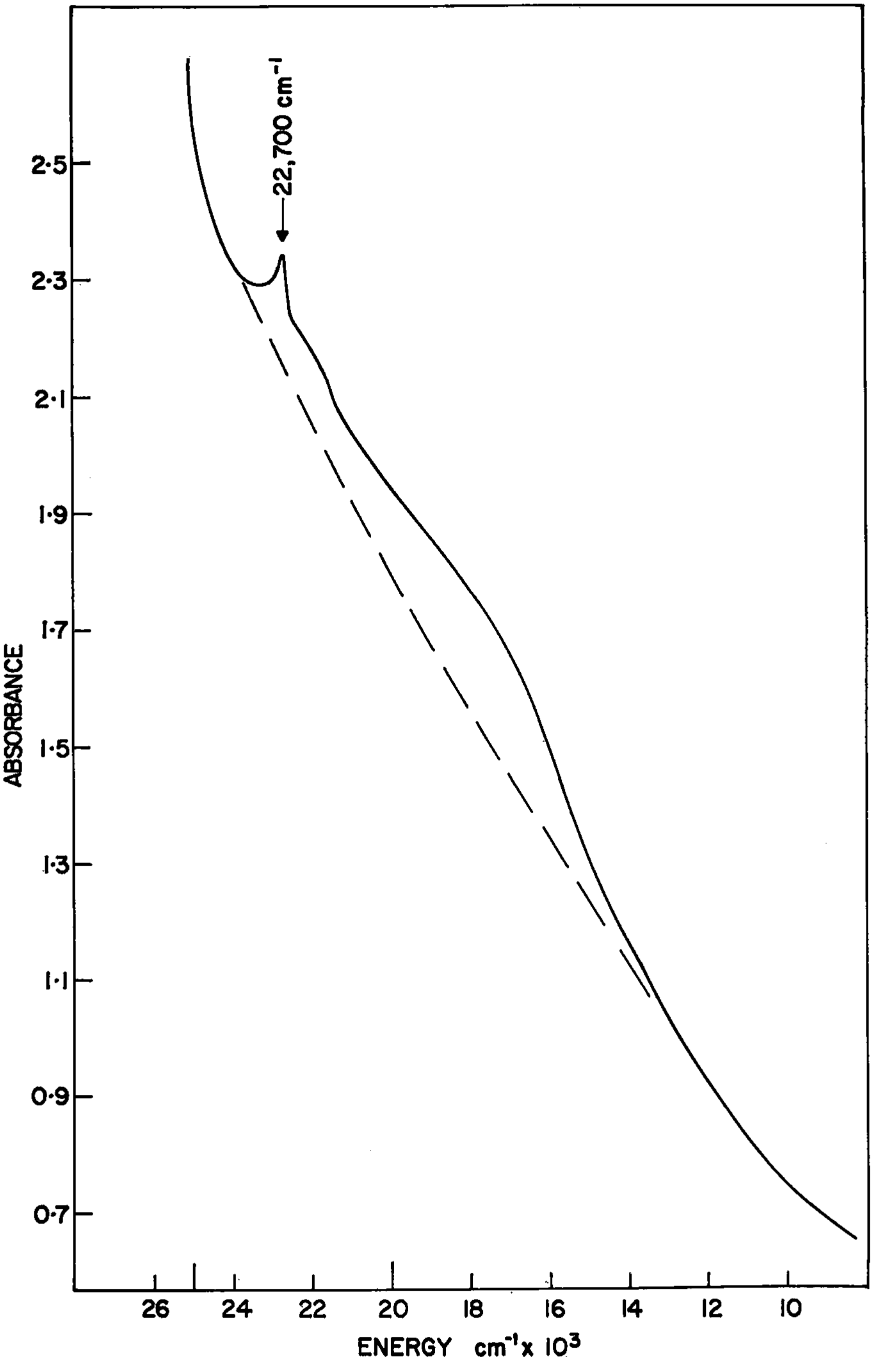

FIG. 1. Spectrum of light-yellow melanite from Santa Rita Peak. l = 0.02 cm.

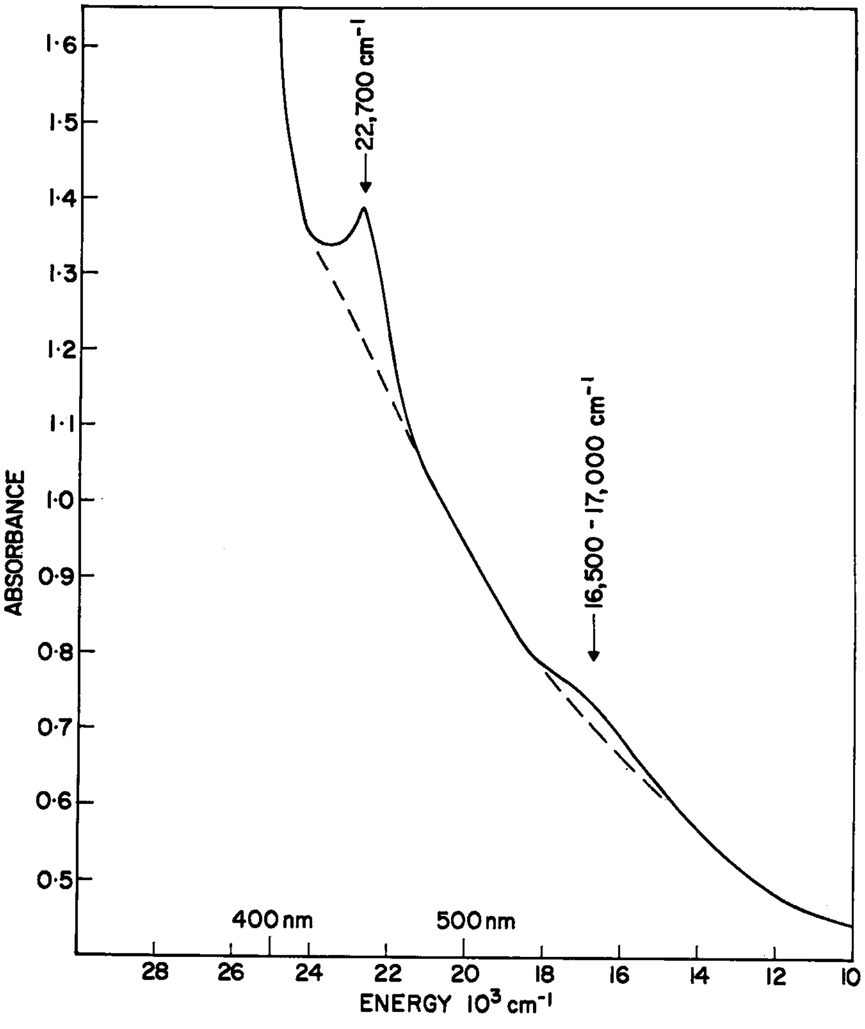

FIG. 2. Absorption spectrum of schorlomite from Magnet Cove. l = 0.0015 cm.

reasonable assignments were made of the principal absorption features. In particular, a very sharp absorption band at 22,700 cm^{-1} was assigned to transitions to the first field-independent state ($^6A_1 \rightarrow {}^4A_1{}^4E(G)$) in octahedrally bonded Fe^{3+}. As in Mn^{2+} complexes, the $^4A_1(G)$ and $^4E(G)$ levels in Fe^{3+} are split by approximately 300 cm^{-1}. The 22,700 cm^{-1} band appears in the spectra in Figs. 1–3, but whereas the Fe $^{3+}$ band is very weak in Fig. 3 and dominated by a strong absorption centred at 19,000 cm^{-1}, it is the dominant absorption in the schorlomite spectrum

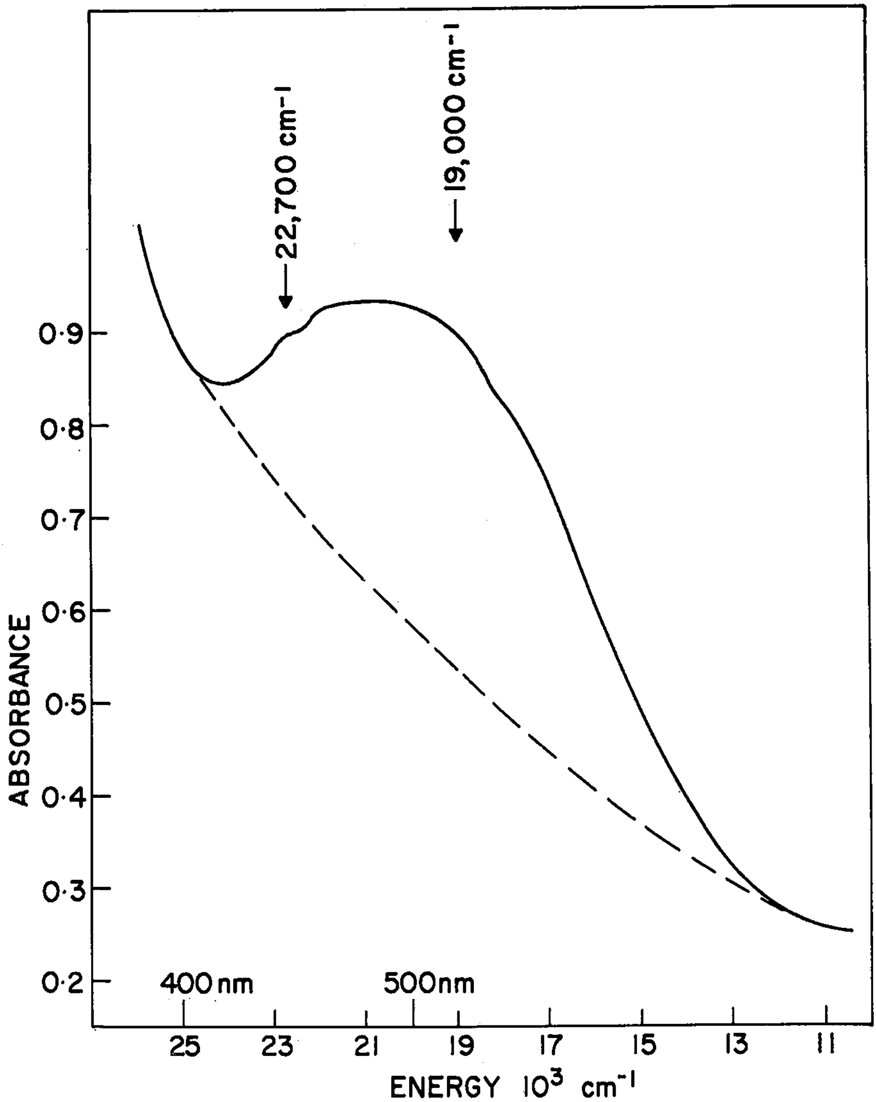

FIG. 3. Absorption spectrum of pink andradite from Santa Rita Peak. $l = 0.0018$ cm.

(Fig. 2). The yellow-melanite spectrum (Fig. 1) has features that put it in an intermediate position, *i.e.* the 22,700 cm^{-1} band is only partially "swamped" by the 19,000 cm^{-1} band.

The broad 19,000 cm^{-1} band is present only in the spectra of some high-Ti andradites, and was earlier assigned to the transition $^2T_2 \rightarrow E(D)$ in octahedrally-bonded Ti^{3+} (Manning 1967*a*). Reliable information on

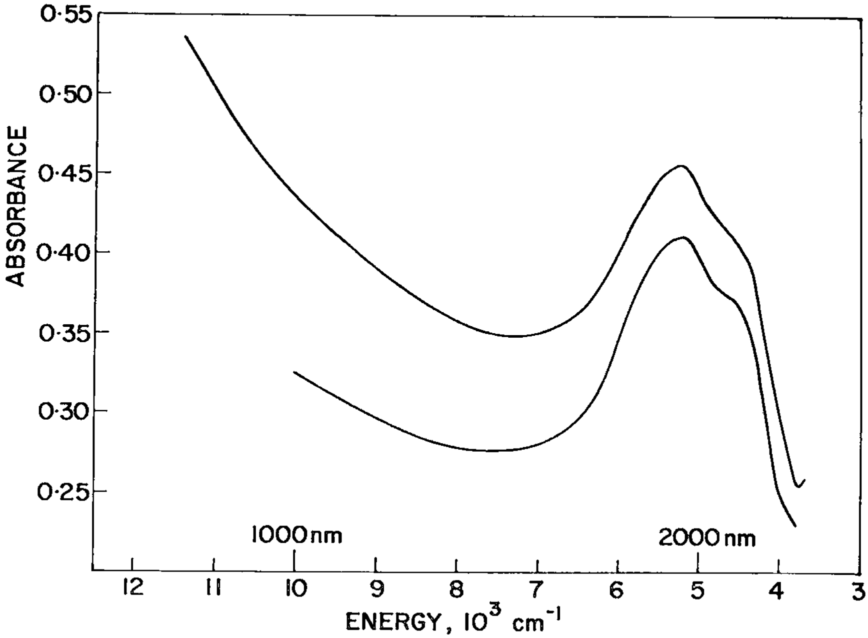

FIG. 4. Absorption spectra of Magnet Cove schorlomite (upper) and Santa Rita Peak pink andradite (lower) in the infrared region. Respectively, l = 0.006 cm and 0.0025 cm.

the Ti^{3+}:Ti^{4+} ratios in melanites could not be obtained because the limits on the value of the extinction coefficient for the Ti^{3+} band could not be defined.

Derivation of molecular formulae of yellow/brown and pink Ti-andradites

Andradite crystals with light yellow rims and pink or bluish pink cores were obtained from both San Benito localities. Electron-microprobe traverses across the yellow-pink areas showed an inverse relationship between Fe and Ti, while Si and Ca analyses remained constant. Although the pink areas were slightly zoned, the chemical analyses over much of the pink area were constant to within ±3%. Average analyses over large areas of both pink and light yellow areas are presented in Table 1, from which the inverse relationship between Fe and Ti is easily evident. This suggests that Ti substitutes in the main for Fe^{3+} in the pink andradites.

The optical absorption spectrum of a bluish-pink crystal from Santa Rita Peak is shown in Fig. 3. A lower limit for the extinction coefficient of the 19,000 cm^{-1} Ti^{3+} band can be calculated from the total Ti concentration (6.5% or 5.1 M), $l = 0.0018$ cm and $A = 0.37$, whence $\epsilon \nless 40$.

TABLE 1. ELECTRON-MICROPROBE ANALYSES (WT %) OF LIGHT YELLOW RIM AND PINK CORE OF SAN BENITO TI-ANDRADITES

	Santa Rita Peak		near Gem Mine*	
Oxide	Rim	Core	Rim	Core
CaO	33.6	33.7	31.3	32.0
SiO_2	34.2	32.5	36.6	34.0
Fe_2O_3	29.2	21.4	29.1	21.5
TiO_2	2.5	11.2	2.5	9.7
Al_2O_3	0.7	0.7	<0.1%	<0.1
MgO	0.2	1.0		

*Al, Mn, Mg, K and Na—not detected.

The spectra in Figs. 1 and 2 are typical of yellow-to-brown sections of melanites and schorlomites. In Fig. 1, for example, based on $\epsilon = 40$, $l = 0.02$ cm and measured $A = 0.20$, the concentration of Ti^{3+} in the specimen is $\ngtr 0.25$ *M* or 0.32%. However, the total Ti concentration is 1.5%, hence <20% of Ti is present as Ti^{3+}. The light yellow rim of the pink andradite from near the Dallas Gem Mine also showed a weak, broad band at approximately 19,000 cm^{-1}, the spectrum being very similar to that shown in Fig. 1. From the following data, $A = 0.05$, $l = 0.01$ cm and $\epsilon = 40$, the concentration of Ti^{3+} in the light yellow rim is ~0.1 *M* (0.13%), which is approximately 10% of the total Ti content of the melanite. It would seem, therefore, that <20% of the Ti in yellow or brown melanites is present as Ti^{3+} in octahedral sites.

The origin of the band at 16,500–17,000 cm^{-1} in the schorlomite spectrum (Fig. 2) is in doubt. The band seems at too low an energy for the $^2T_2 \rightarrow {}^2E(D)$ transition in Ti^{3+}, but it could conceivably be an Fe^{3+} *d–d* band. Fe^{3+} *d–d* bands have been observed at ~16,500 cm^{-1} in spectra of green low-Ti andradites (Manning 1967*a*), epidote (Burns & Strens 1967) and also very prominently in high-Fe^{3+} muscovite (Manning 1969). Hence, it is very likely that the 16,500–17,000 cm^{-1} band in schorlomite is an Fe^{3+} band. No absorption is detectable at ~19,000 cm^{-1} in the schorlomite spectrum; in fact the absorption envelope is almost coincident with background in this region. Nevertheless, assuming that the 16,500 cm^{-1} band is due to Ti^{3+}, the calculated concentration of Ti^{3+} is $(0.05/0.0015 \times 40) = 0.8$ *M*. However, the total Ti concentration is 7 *M* (14.5% TiO_2), hence <12% of the Ti is Ti^{3+}. Significantly, Howie & Woolley (1968) put 80% of the Ti in the Magnet Cove schorlomite into silicon sites, presumably as Ti^{4+}. The current study of the Magnet Cove schorlomite further suggests that most of the Ti in the octahedral sites is also Ti^{4+}.

That the role of Ti is different in the yellow and pink areas of the

San Benito melanites is evident from the electron-microprobe analyses (Table 1) and also the optical absorption spectra (Figs. 1 and 3). The calculated ϵ-value (40) for the 19,000 cm^{-1} Ti^{3+} band in Fig. 3 is very reasonable for a spin-allowed *d–d* band, and suggests that most of the Ti is present as Ti^{3+} in octahedral sites. The electron-probe traverses confirm that Ti displaces Fe^{3+}, and in the absence of considerable amounts of Na^+ in the Ca^{2+} sites or Fe^{2+} in the octahedral sites, it is likely that most of the octahedral Ti is Ti^{3+}.

TABLE 2. ATOMIC RATIOS OF CATIONS PER 24 OXYGENS IN LIGHT YELLOW RIMS AND PINK CORES OF TI-ANDRADITES

	Santa Rita Peak		near Gem Mine	
Cation	Rim[1]	Core[2]	Rim[3]	Core[4]
Ca	6.1	6.0	5.6	6.00
Si	5.8	5.4	6.1	5.94
Al	0.1	0.1	—	—
Fe^{3+}	3.7	2.5	3.65	2.69
Fe^{2+}	—	0.2	—	0.11
Ti^{3+}	—	1.4	—	1.27
Ti^{4+}	0.3*	—	0.31*	—
Mg^{2+}	0.05	0.2		

*Approximately 10%–20% of Ti is Ti^{3+} (see text).

Formulae: 1. $Ca_{6.1}(Fe^{3+}{}_{3.68}Al^{3+}{}_{0.1}Ti^{3+}{}_{0.05})(Si_{5.8}Ti^{4+}{}_{0.2})O_{24}$.
2. $Ca_{6.0}(Fe^{3+}{}_{2.5}Al^{3+}{}_{0.1}Ti^{3+}{}_{>1.0}Mg^{2+}{}_{0.2})$
$(Si_{5.4}Ti^{4+}{}_{<0.4}Fe^{2+}{}_{0.2})O_{24}$.
3. $Ca_{5.6}(Fe^{3+}{}_{3.65}Ti^{3+}{}_{0.03}Ti^{4+}{}_{0.28})(Si_{6.1})O_{24}$.
4. $Ca_{6.00}(Fe^{3+}{}_{2.69}Ti^{3+}{}_{1.1}Ti^{4+}{}_{\sim 0.2})(Si_{5.94}Fe^{2+}{}_{0.1})O_{24}$.

In Table 2 are presented the atomic ratios of the metals per 24 oxygens for the yellow rims and pink cores of two San Benito garnets, together with the molecular formulae. In the Santa Rita Peak specimen, the 8-coordinate sites are completely filled by Ca^{2+}, showing that only minor amounts of Fe^{2+} and Na^+ are present. The garnet from near the Dallas Gem Mine shows no K or Na, while the spectra (Fig. 4) do not show 8-coordinate Fe^{2+} bands (Manning 1967*b*). Also absent from the spectra are *d–d* bands of octahedrally bonded Fe^{2+} at ~10,000 cm^{-1}. Of particular interest is the absence of detectable amounts of Al in the yellow rim and pink core of the sample from near the Dallas Gem Mine, indicating negligible grossular content.

The near-infrared absorption band at ~5,000 cm^{-1} in melanite and schorlomite spectra (Fig. 4) was earlier assigned to the $^2E \rightarrow {}^2T(D)$ transition in tetrahedral-Fe^{2+} (Manning 1967*a*). Curve analysis of the curves in Fig. 4 showed that the 5,000 cm^{-1} envelope is composed of two Gaussian bands at 5,250 cm^{-1} and 4,300 cm^{-1}, but with no detectable absorptions at ~9,000 cm^{-1} due to 8-coordinate Fe^{2+}. Low-Ti andradites from Stanley Peak, Arizona, and Hastings County, Ontario, exhibited no absorptions in the near-infrared (Manning 1967*a*), nor did low-Ti andradites from Tudor, Ontario, Temagami, Ontario, and Karelia, Russia. The 5,000 cm^{-1} system may therefore be associated with the presence of Ti in the andradite, and likely reflects the easier substitution of Fe^{2+} (0.74 Å) for Si^{4+} (0.42 Å) in andradites of relatively large cell-size (Deer, Howie & Zussman 1962). Howie & Woolley (1968) find it necessary to put large amounts of Ti^{4+} (0.68 Å) into Si sites. The tetrahedral Fe^{2+} contents of the garnets have been computed from the intensities of the 5,000 cm^{-1} band system and using an ϵ-value of 100 for a tetrahedral Fe^{2+} *d–d* band. In general, cations in tetrahedral sites absorb 10–100 times more strongly than cations in octahedral sites.

Absorption spectra of the yellow rims of the San Benito garnets showed only weak bands at ~5,000 cm^{-1}, corresponding to less than 0.01 Fe^{2+} ions per 24 oxygens. The molecular formulae of the two yellow melanites, $Ca_{6.1}(Fe^{3+}{}_{3.68}Al^{3+}{}_{0.1}Ti^{3+}{}_{0.05})(Si_{5.8}Ti^{4+}{}_{0.2})O_{24}$ and $Ca_{5.6}(Fe^{3+}{}_{3.65}Ti^{4+}{}_{0.28}Ti^{3+}{}_{0.03})Si_{6.1}O_{24}$ for the Santa Rita Peak and near the Dallas Gem Mine specimens, respectively, are reasonably close to each other, bearing in mind experimental errors in the electron-probe analyses.

The molecular formulae of the two pink andradites from Santa Rita Peak and near the Dallas Gem Mine are, respectively, $Ca_{6.0}(Fe^{3+}{}_{2.5}Al^{3+}{}_{0.1}Mg_{0.2}Ti^{3+}{}_{>1.0})$ $(Si^{4+}{}_{5.4}Ti^{4+}{}_{<0.4}Fe^{2+}{}_{0.2})O_{24}$ and $Ca_{6.0}(Fe^{3+}{}_{2.7}Ti^{3+}{}_{1.1}Ti^{4+}{}_{\sim 0.2})$ $(Si^{4+}{}_{5.94}Fe^{2+}{}_{0.1})O_{24}$. In the latter formula, the excellent cation balance strongly suggests that the Ti ions are present mainly as Ti^{3+}, otherwise electron imbalance would be too great: the 0.2 Ti^{4+} in the octahedral positions have been included to electrostatically balance 0.1 Fe^{2+} in Si^{4+} sites. Moreover, the Ti^{3+} ion attains ligand field stabilization energy (19,000 × 2/5 cm^{-1} or 20 kcal) in octahedral sites.

The molecular formula of the garnet from near the Dallas Gem Mine conforms very closely to the classical andradite formula, with Ca^{2+} and Si^{4+} predominating in the 8-coordinate and tetrahedral sites, respectively. Particularly interesting, however, is the large Ti^{3+} content of the octahedral site, in contrast to the high Ti^{4+} content of melanites and schorlomite; also the Ti^{4+} ions of the latter andradites are partly located in the tetrahedral sites (Howie & Woolley 1968). The pink andradite should, if the current assignments are correct, be considered a different variety of andradite from melanites and schorlomite. Isaacs (1968) observed an inverse relationship between Fe and Ti in an andradite from the Gem Mine in San Benito County, and concluded that Ti was present in the octahedral sites. However, she relied upon wet chemical analysis to show that Ti was present as Ti^{3+}, which cannot be considered conclusive in view of the large amounts of Fe^{3+} oxidant present.

The cell-size of the pink andradite from Santa Rita Peak is 12.076 Å, a value that is smaller than expected for an andradite containing 10.8% TiO_2 (Howie & Woolley 1968). The plot of cell size against weight per cent TiO_2 (Fig. 1d in Howie & Woolley's paper) indicates that for a melanite/schorlomite containing 10.8% TiO_2, the expected cell size is >12.095 Å. The smaller cell size is in keeping with the replacement of Fe^{3+} (0.64 Å) by Ti^{3+} (0.76 Å) rather than Si^{4+} (0.42 Å) by Ti^{4+} (0.68 Å) where the radius difference is considerably larger.

The magnetic susceptibility of the pink andradite from near the Dallas Gem Mine, measured by Mr. J. L. Horwood of the Mines Branch, is 27.6 emu units/gram. This measured value is somewhat lower than the calculated value based on a magnetic moment of 5.9 Bohr magnetons for Fe^{3+}, and suggests some form of interaction between second close-neighbour metals. In line with this, it is interesting to note that the intensity of the 22,700 cm^{-1} Fe^{3+} band in schorlomite spectra (Fig. 2) is about 20 times greater than the intensity of the same band in the spectra of pink andradites. In the case of schorlomite, the high intensity ($\epsilon \sim 15$) of the 22,700 cm^{-1} band could be due to Fe^{3+}—(Fe^{2+} or Ti^{4+})$_{tet}$ interaction.

CONCLUSION

Ti-rich andradites seem to fall into three classes: melanites, schorlomites and a pink variety. The melanites and schorlomites are yellow to brown in thin sections and their absorption spectra are consistent with $<20\%$ of the Ti being octahedral Ti^{3+}. The chemical data of Howie & Woolley (1968) suggest that Ti^{4+} prefers the tetrahedral Si^{4+} sites.

Electron-microprobe and optical absorption studies of pink high-Ti andradites suggest that most of the Ti is present as octahedral Ti^{3+}. If these structural assignments are confirmed, the pink andradites should be considered a different variety from melanites and schorlomites.

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