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OPTICAL-ABSORPTION AND MÖSSBAUER SPECTRAL STUDIES OF IRON AND TITANIUM SITE-POPULATIONS IN VESUVIANITES

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ABSTRACT

The optical absorption and Mössbauer spectra of a suite of differently-coloured vesuvianites are collated and used to determine some site-populations of Fe and Ti ions. The two types of spectra are complex, but a considerable measure of consistency is evident in their interpretation. Mössbauer spectra give definitive information on site distributions of the major Fe species, and aid further in the resolution of the near-infrared envelope in the optical spectrum. Intervalence charge-transfer bands in the optical spectra yield additional information on some minor Fe species and on Ti ions.

In green low-Ti vesuvianites, > 90% of total Fe is Fe^{3+} on octahedral Al/Fe positions, but in crystals in which the TiO_2 concentration exceeds one per cent w/w, most of the Fe is in the ferrous form. At low total-Fe concentrations (< 3.5%) in these Ti-rich vesuvianites, ferrous ions occupy preferentially the 5-coordinate positions, but at higher concentrations these sites are saturated and ferrous ions then favour the Al/Fe positions. A vesuvianite from Wakefield, P.Q., containing 3.65% FeO and 0.95% TiO_2, has the following Fe distributions: Fe^{2+} in 5-coordination 44%, Fe^{2+} on Al/Fe 31%, Fe^{3+} on Al/Fe 13% and Fe^{2+} in 8-coordination 1%. Approximately 10% of the Fe has not been assigned. Titanium ions, as Ti^{4+}, are predominantly on Al/Fe sites, with smaller amounts in 8-coordination and possibly in 5-coordination.

INTRODUCTION

A strongly polarized band at 23000 cm^{-1} (435 nm) in spectra of Ti-bearing vesuvianites has been assigned (Manning 1975) to intervalence charge-transfer between Fe^{2+} and Ti^{4+} ions located at the centres of adjacent face-sharing antiprisms and lying on the 4-fold axis. A second broad absorption at 26750 cm^{-1} (374 nm) in spectra of material from Leurel, P.Q., was assigned to a similar process between ferrous ions on Ca(2) and Ti^{4+} on Al/Fe. In general, however, optical absorption methods are of limited value in determining ferrous and ferric distributions in complex silicates such as vesuvianites, the structures of which contain, besides tetrahedral (Si) positions, one site of 5-coordination, two of 6(octahedral)-coordination and four of 8-coordination. Mössbauer spectroscopy, although restricted to minerals in which the Fe concentration > 1%, can yield definitive information on valencies and site populations. Here, we wish to demonstrate, using a suite of vesuvianites of different Fe:Ti concentrations, that a collation of optical and Mössbauer spectra can be a facile method of elucidating site-populations.

EXPERIMENTAL DETAILS

Polarized optical absorption spectra were run at room-temperature using Glan prisms and a Cary-14 spectrophotometer. Parallel-sided mineral sections of dimensions 3mm × 3mm were cut parallel to the *c*-axis from material supplied by Messrs. G. Ansell and H. R. Steacy, Geological Survey of Canada, and by Professor R. A. Howie, King's College, London. Optical spectra of the Sudan crystals were run several years ago, but unfortunately no more of this material seems available for Mössbauer analysis. Absorption envelopes were resolved using a Dupont Model curve-resolver. Extinction coefficients, expressed in litres mole^{-1} cm^{-1}, are defined by

$$\epsilon = A/C.l$$

where *A* is the net absorbance, *C* is the cation

TABLE 1. COMPOSITIONS OF VESUVIANITES MEASURED BY ELECTRON-MICROPROBE (IN WT.%).

Oxide	Lowell (green)	Leurel (honey-yellow)	Wakefield (brown)	Sudan (reddish-brown)
FeO	4.9*	0.98	3.65	6.85
TiO_2	0.12	2.41	0.95	3.00
MnO		n.d.	n.d.	0.05
MgO		3.39	1.79	3.28
CaO		37.46	37.51	35.20
Al_2O_3		16.60	16.95	12.76
SiO_2		36.88	37.02	34.67

*% Fe_2O_3 (see text) n.d. = not detected.

TABLE 2. VALUES OF $\varepsilon.C(= A/l)$ FOR Fe^{2+} NEAR-INFRARED BANDS IN SPECTRA OF Ti-RICH VESUVIANITES

Band Energy →	9000 cm^{-1}	12000 cm^{-1}	Ratio 12000:9000
Leurel	0.1	0.6	6
Wakefield	1.1*	2.5	2.2
Sudan	3	4	1 - 1.5

* The concentration of Fe^{2+} in Al/Fe positions is 0.54 molar (Table 3), hence $\varepsilon = 2$.

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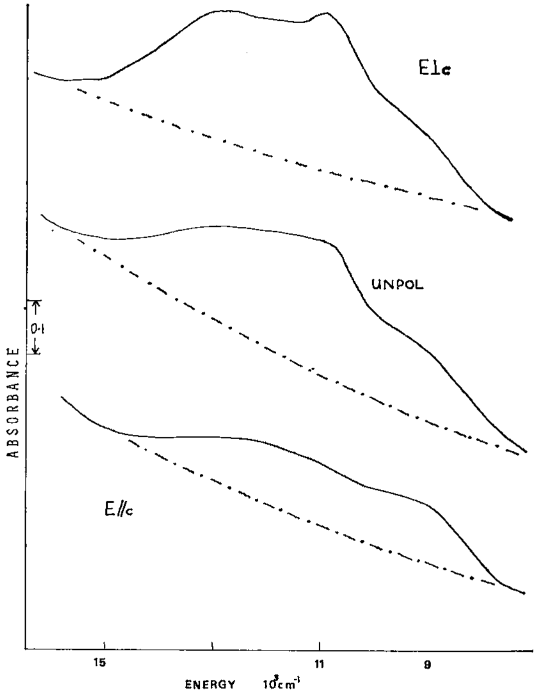

FIG. 1. Optical absorption spectra of Wakefield vesuvianite. Sample thickness 0.083 cm. E represents the polarization direction of incident light; -.-.-. represents estimated background.

concentration in moles litres⁻¹ and *l* is the specimen thickness in cm. Electron-microprobe analyses, performed by Dr. D. C. Harris and Mr. D. Owens, Mines Branch, Ottawa, are presented in Table 1.

Mössbauer spectra were obtained by use of a Harwell Mössbauer spectrometer of the constant-acceleration type. Spectra were accumulated at room-temperature in 256 channels of a multi-channel analyzer using a 10 mc ^{57}Co/Rh source and thin powdered absorbers. The spectrometer was calibrated periodically using a standard iron foil. The experimental Mössbauer envelopes were fitted to sums of Lorentzian line shapes using an iterative non-linear least-squares Algol program on an ICL 4130 computer. It was often found necessary to constrain the area ratios of each peak of a quadrupole doublet to be equal to obtain convergence. X^2 tests and visual examination of the fits were used as criteria of goodness of fit. The X^2 values were, respectively, 219, 281 and 273 for the Lowell, Leurel and Wakefield samples for *ca* 220 degrees of freedom.

RESULTS AND DISCUSSION

The crystal structure of vesuvianite has been determined by Coda *et al.* (1970) and Rucklidge *et al.* (1974), using *x*-ray diffraction methods. Transition-metal ions are concentrated on octahedral Al/Fe and 5-coordinate *B*-sites. Crystal-chemical arguments (Burns & Strens 1967) suggest that the octahedral Al position (Al-O 1.89Å) is too tight for significant transition-metal substitution. Attention is also drawn to the structure along the 4-fold axis which comprises half-occupied 5-coordinate and 8-coordinate (square-antiprisms) *C*-sites separated by 1.06Å. Cations on the two *C*-sites share a face of four oxygens. Average bond distances are: *B*-O 2.11Å, Al/Fe-O 1.945Å and *C*-O 2.48Å.

DESCRIPTION OF OPTICAL ABSORPTION SPECTRA

Selected, near-infrared spectra of three vesuvianites from Wakefield Twp., from the Sudan, and from Leurel, Quebec, are shown in Figures 1-3. Polarized spectra of the Wakefield material are shown in detail in Figures 1 and 2, from which we see that the prominent peak at 11000 cm⁻¹ (900 nm) is apparently extinguished completely in *E*//*c* spectra. Two other absorption envelopes are present at 9000 cm⁻¹ (1100 nm) and ~12000 cm⁻¹ (833 nm), although it is probable, bearing in mind errors inherent in the transcription of spectra to a linear-energy scale and the subjectiveness of the curve-resolving procedure, that the 12000 cm⁻¹ envelope is a composite of two bands at the approximate energies 12200 cm⁻¹ and 13300 cm⁻¹ (for example see Fig. 3D).

The absence of a 11000 cm⁻¹ band in the Leurel spectra (Fig. 2) shows that its origin is different from the origins of the 9000 cm⁻¹ and 12000 cm⁻¹ envelopes. The polarization properties of the band are consistent with metal-metal intervalence charge-transfer in a plane perpendicular to the *c*-axis. Bands caused by $Fe^{2+} \rightarrow Ti^{4+}$ charge-transfer processes have been observed at 23000 cm⁻¹ and 26750 cm⁻¹ in vesuvianite spectra (Manning 1975) and at similar energies in the spectra of other silicates. It seems reasonable, therefore, to assign the 11000 cm⁻¹ band to $Fe^{2+} \rightarrow Fe^{3+}$ charge-transfer between ions on Al/Fe and Ca(3) positions that lie at similar heights along the *c*-direction (Rucklidge *et al.* 1974). Considerations of ionic radii suggest that the Fe^{2+} ions are on Ca(3) positions, but Mössbauer spectra of the Wakefield material (see below) show both Fe^{2+} and Fe^{3+} ions on Al/Fe. If Fe^{2+} ions are on Ca(3), then a broad absorption is anticipated in the range 22000 to 27000 cm⁻¹ marking $Fe^{2+} \rightarrow Ti^{4+}$ interaction, because major amounts of Ti^{4+} ions are probably on Al/Fe. No such absorption is

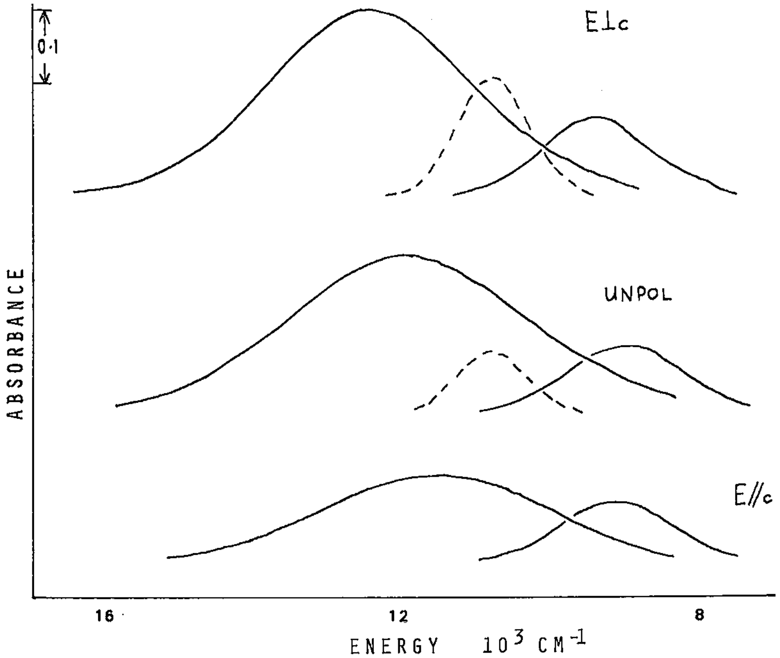

FIG. 2. Component absorption bands in Wakefield spectra. l = 0.083 cm. Dashed line depicts the polarization of the 11000 cm^{-1} band. The broad 12000 cm^{-1} envelope is probably a composite of two bands (see text, Fig. 3D).

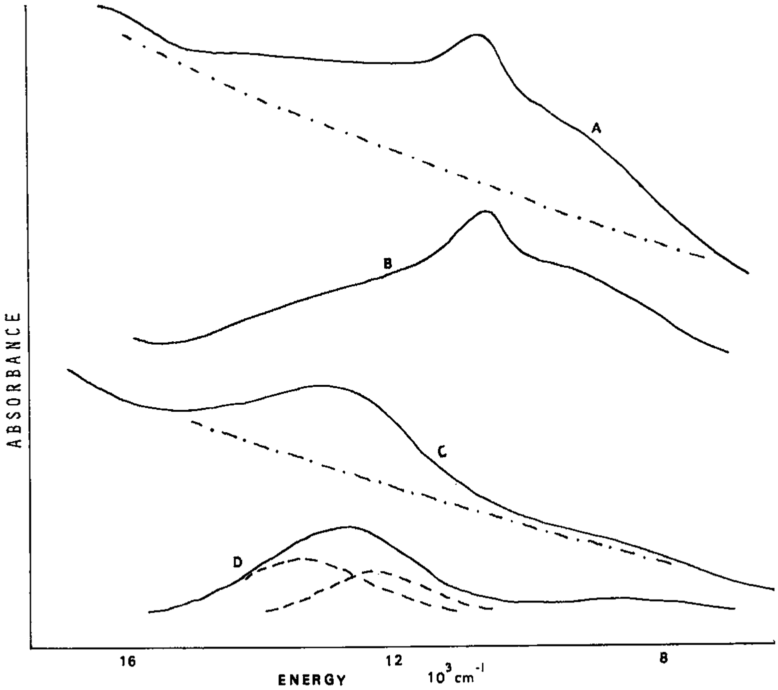

FIG. 3. Unpolarized light spectra of Sudan (A = recorded, B = net) and Leurel (C = recorded, D = net) vesuvianites; specimen thickness 0.03 cm and 0.22 cm respectively. Curve -.-.-. represents estimated background. The broad ~12000 cm^{-1} envelope may itself be a composite of two individual bands (dashed curve in D).

observed in Wakefield spectra, even though the ε-value of the $Fe^{2+} \rightarrow Ti^{4+}$ process is at least an order of magnitude larger than for $Fe^{2+} \rightarrow Fe^{3+}$ (Robbins & Strens 1968; Manning 1975). However, the $Fe^{2+} \rightarrow Ti^{4+}$ process may occur at energies >27000 cm^{-1} in the Wakefield material, so that currently we cannot say whether the 11000 cm^{-1} band marks Fe^{2+} (Al/Fe) → Fe^{3+} (Ca3) or Fe^{2+}(Ca3) → Fe^{3+}(Al/Fe).

The 9000 cm^{-1} band and the 12000 cm^{-1} envelope undoubtedly represent crystal-field transitions in octahedral and/or 5-coordinate ferrous ions. The relative intensities of the 9000 cm^{-1} and 12000 cm^{-1} absorptions differ markedly from one specimen to another (Figs. 1-3; Table 2), indicating either that both are not assignable to transitions within the same cation or that the 12000 cm^{-1} envelope contains a second-component absorption. The 9000 cm^{-1}. band is at too high an energy for 8-coordinate Fe^{2+} (Manning 1967) and at too low an energy for 5-coordinate Fe^{2+}, in the second instance because the absence of an axially-located anion (along the cation d_{z^2} axis) should leave the energy of the $d_{x^2-y^2}$ orbital unchanged from the octahedral case whereas the d_{xz} and d_{yz} orbitals are lowered in energy. The 9000 cm^{-1} band is therefore caused by octahedrally-bonded Fe^{2+}. *X*-ray diffraction evidence (Rucklidge *et al.* 1974) and considerations of ionic sizes suggest further that the octahedral site is the Al/Fe and not the smaller Al (of average Al-O) distance 1.89Å). Reference to Faye's (1972) plot of Δ_{VI} (the crystal-field splitting parameter) against modified *M-O* distance shows that a Δ_{VI} value of 9000 cm^{-1} is far too small to correspond to a Al/Fe-O distance of 1.95Å. The Al/Fe site can be considered to have a modest tetragonal distortion and two bands are expected from the splitting of the two e_g orbitals. If the 13300 cm^{-1} feature is the second component of transitions to the Fe^{2+} e_g levels, the calculated value of Δ_{VI}, equal to (13300 + 9000)/2 or 11100 cm^{-1}, is in better agreement with Faye's plots. The component band at ~ 12200 cm^{-1} may arise from 5-coordinate Fe^{2+}.

DESCRIPTION AND ASSIGNMENT OF MÖSSBAUER SPECTRA

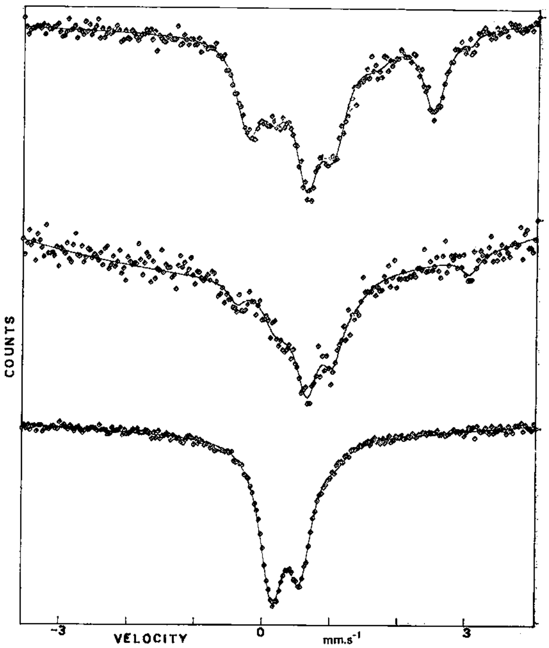

FIG. 4. Mössbauer spectra of Wakefield (upper), Leurel (middle) and Lowell (lower) vesuvianites.

Mössbauer spectra of Lowell, Leurel and Wakefield vesuvianites are shown in Figure 4 and the derived isomer shifts (relative to α-Fe), quadrupole splittings, full line widths at half peak height and site populations are collated in Table 3. It should be noted that some sets of parameters marking a particular site appear in all or two of the spectra making one more confident that the final fits are in fact correct. The parameters LO-1, LE-1 and W-1 are closely similar and the isomer shift and quadrupole splittings are indicative of ferric iron in a close-to-octahedral oxygen environment (Bancroft 1973). The parameters LO-1, LE-1 and W-1 are therefore compatible with the presence of ferric iron in the Al/Fe sites within the three vesuvianites studied. The parameters W-5 of the Wakefield sample are those expected for ferrous iron in moderately distorted octahedral sites (Bancroft 1973) and we therefore assign these to the presence of ferrous iron in the Al/Fe octahedra. Parameters LE-3

TABLE 3. MÖSSBAUER PARAMETERS* AND SITE OCCUPANCIES OF Fe SPECIES IN VESUVIANITES.

	Designation	Isomer Shift (mm/sec)	Quad. Split (mm/sec)	Half-width (mm/sec)	Ion	% Total Fe	Molarity	Position
Lowell	LO-1	0.35	0.42	0.43	Fe^{3+}	90	1.87	Al/Fe
	LO-2	0.62	0.89	0.43	Fe^{3+}	10	0.21	8-coord.
Leurel	LE-1	0.39	0.46	0.43	Fe^{3+}	29	0.14	Al/Fe
	LE-2	0.84	0.37	0.39	Fe^{2+}	51	0.24	5-coord.
	LE-3	1.32	3.44	0.22	Fe^{2+}	9	0.04	8-coord.
	LE-4	0.85	1.04	0.43	Fe^{2+}	12	0.05	
Wakefield	W-1	0.39	0.48	0.39	Fe^{3+}	13	0.22	Al/Fe
	W-2	0.82	0.39	0.48	Fe^{2+}	44	0.76	5-coord.
	W-3	1.32	3.44	0.2	Fe^{2+}	1	0.02	8-coord.
	W-4	0.87	1.55	0.54	Fe^{2+}	11	0.19	
	W-5	1.13	2.74	0.40	Fe^{2+}	31	0.54	Al/Fe

* Measured with respect to Fe foil.
Estimated errors in quadrupole splittings and isomer shifts ± 0.04 mm/sec.

and WE-3 are characterized by large shifts and quadrupole splittings, expected for ferrous iron in eight-coordination, and are similar to those found for cube sites in garnets (Bancroft *et al.* 1967). These parameters therefore demonstrate the presence of ferrous iron on the 8-coordinate Ca sites within the vesuvianites. Which of the four possible sites is occupied cannot be decided on Mössbauer evidence alone, but the sharpness of the lines suggest that one of these sites is preferentially occupied.

The parameters designated LE-2 and W-2 which make up a large fraction of the total iron present in the Leurel and Wakefield sample, are unusual in that the isomer shift and quadrupole splitting fall outside the expected range for ferrous or ferric iron in the more common coordination spheres. We assign these parameters to ferrous iron in the 5-coordinate sites. To our knowledge no parameters for ferrous iron in 5-coordination in silicate minerals have been reported for comparison. We have made the assignment for the following reasons. The isomer shift (0.83 mm s^{-1}) falls within the range predicted for 5-coordinate ferrous in that the isomer shift of ferrous iron decreases in going from 8- to 6-coordination and a similar reduction is expected in going from 6- to 5-coordination. Moreover the isomer shift of 0.83 mm s^{-1} is larger than the value of 0.75 mm s^{-1} observed for the distorted four-fold site of gillespite (Bancroft *et al.* 1968). It is well-known that the quadrupole splitting of ferrous iron in 6-coordination decreases with increasing distortion of the oxygen environment (Bancroft 1973). In this sense the small quadrupole splitting observed for the 5-coordinate site can be rationalized by visualizing the 5-coordinate site as a grossly distorted 6-coordinate site.

The site marked by the parameters LO-2 of the high ferric Lowell sample constitutes less than 10% of the total iron present and is unusual in that the isomer shift is larger than that expected for ferric iron in 6-coordination. An increase in isomer shift of ferric iron is expected to result from an increase of the coordination number from 4 through 6 to 8. It seems reasonable to conclude that a small fraction of the 8-coordinate Ca sites are occupied by ferric iron in the Leurel sample. However, the distribution of the ferric iron over these sites cannot be determined from the Mössbauer parameters obtained in this work. Parameters LE-4 and W-4 account for only a small fraction of the iron present in the Leurel and Wakefield samples. The absorptions arising from these sites are overlapped by the stronger absorptions and accurate determination of the parameters is difficult.* However, it was found necessary to include these absorptions to obtain reasonable fits. We tentatively suggest that the parameters are associated with ferrous iron in the tight aluminium sites. Some support for this conclusion comes from the fact that high-pressure experiments indicate that the isomer shift of ferrous iron decreases with increasing pressure (Greenwood & Gibb 1971). Thus the short Fe^{2+}-O bonds of the tight site may lead to the small isomer shifts observed.

CORRELATIONS OF OPTICAL AND MÖSSBAUER SPECTRA

The Mössbauer measurements confirm earlier optical work (Manning 1968) that the Lowell material is high in Fe^{3+} and low in Fe^{2+}. An absorption band marking the well-known transition ${}^6A_1 \rightarrow {}^4A_1{}^4E(G)$ in Fe^{3+} is observed in Lowell spectra at 21600 cm^{-1} (463 nm) with an ϵ-value of 1.5. No such sharp feature is seen in the optical spectrum of a 0.22-cm section of Leurel material, and a 'blip' of 0.025 absorbance units only is seen in the spectrum of a 0.08-cm section of the Wakefield. From the latter values of A and l, the Fe^{3+} concentration is 0.2 molar, in excellent agreement with the Mössbauer determinations (Table 3).

Optical absorption (A/l values for the 9000 cm^{-1} band, Table 2) and Mössbauer (Table 3) spectra are consistent in showing that the concentration of Fe^{2+} in Al/Fe sites is at least 10 times greater in Wakefield crystals than in Leurel. At low FeO concentrations, $< 3.4\%$ w/w, Fe^{2+} ions occupy preferentialy the 5-coordinate B-sites in Ti-rich vesuvianites, but at higher concentrations a greater proportion enters the Al/Fe sites. Significantly, the 9000 cm^{-1} and 12000 cm^{-1} envelopes in the Sudan optical spectra (Fig. 3) are of approximately equal intensity, indicating that most of the ferrous ion is on Al/Fe positions. Calculation shows that complete occupation of B-sites by Fe^{2+} corresponds to $\sim$ 1 molar ferrous ion ($\sim$ 2.0% FeO w/w).

The relative values of the Fe^{2+} concentrations on Al/Fe sites (Tables 2 and 3) explain why the 11000 cm^{-1} intervalence charge-transfer band is seen in Wakefield and Sudan spectra but not in Leurel. Also, because major amounts of Ti^{4+} ions are expected to substitute into Al/Fe positions, and because there are no indications in

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*Small quantities of 8-coördinate ferrous iron can be detected as the high-velocity component of the quadruple doublet is resolved from the main envelope.

Wakefield spectra of bands at 20000-27000 cm^{-1} polarized parallel to the *c*-axis and marking $Fe^{2+} \rightarrow Ti^{4+}$ intervalence charge-transfer, then charge-transfer processes between ions in neighbouring Al/Fe sites are highly inefficient, probably on account of the large internuclear separation of 5.9Å.

Which of the four available 8-coordinate positions contains the Fe^{2+} ion marked by parameters LE-3 and W-3 in Table 3? Broad absorptions caused by intervalence charge-transfer between Fe^{2+} and Ti^{4+} ions located in the site-pairs *C*-*C* and Ca(2)-Al/Fe were observed at, respectively, 23000 cm^{-1} and 26750 cm^{-1} in Leurel spectra (Manning 1975), and on this basis it was suggested that Fe^{2+} ions occupy preferentially either the *C* or Ca(2) sites, with a greater likelihood of the latter. Neither of these two optical absorption bands is observed in Wakefield spectra, probably because of the lower total-Ti concentration combined with the lower concentration of 8-coordinate ferrous ions (marked by parameters LE-3 and W-3) in the Wakefield material. It does not seem possible, from the Mössbauer parameters alone, to decide between the two sites, but let us assume that the distribution coefficients for Fe^{2+} between the half-occupied *B*- and *C*-sites is constant for different but closely-related vesuvianites. The *B*- and *C*-sites on the 4-fold axis are separated by 1.06Å, and there is *x*-ray diffraction evidence to suggest that, for the two vesuvianites studied at least (Rucklidge *et al.* 1974), the distribution coefficient is approximately constant. Assuming that Mössbauer parameters LE-3 and W-3 mark Fe^{2+} on *C*-sites, the distribution coefficients are 6 for the Leurel crystals and ~40 for the Wakefield (Table 3). This suggests that parameters LE-3 and W-3 mark Fe^{2+} on Ca(2). If LE-3 marked Fe^{2+} on Ca(3) positions, a broad band caused by $Fe^{2+}(Ca3) \rightarrow Ti^{4+}(Al/Fe)$ interaction would be seen in Leurel optical spectra, in addition to the band marking $Fe^{2+}(Ca2) \rightarrow Ti^{4+}$ (Al/Fe).

If the 11000 cm^{-1} band in Wakefield spectra arises from $Fe^{2+}(Al/Fe) \rightarrow Fe^{3+}(Ca3)$ charge-transfer, how much Fe^{3+} is required on Ca(3) sites to account for its intensity? The $\epsilon.C$-value of the band is approximately one (Fig. 2), where C is the concentration of Fe^{2+} - Fe^{3+} pairs in adjacent positions. Each Fe^{2+} ion on Al/Fe positions has two adjacent Ca(3) positions, and let us assume that the concentration of Fe^{3+} on Ca(3) sites is 0.02 molar, corresponding to the occupation of one Ca(3) site out of ~450. Then $C = 0.54 \times 2/450$ or 0.0025 molar (or 1% of total-Fe) and $\epsilon \sim 400$ litres per mole-cm. This is a not unreasonable ϵ-value, but 0.02 molar Fe^{3+} is unlikely to be detectable by Mössbauer methods.

The ratio of concentrations of *B*-site Fe^{2+} ions in Wakefield and Leurel vesuvianites is 3:1 as measured by Mössbauer absorption and ~5:1 as measured from the 12200 cm^{-1} optical absorption. This agreement is not unreasonable bearing in mind the weak absorptions by the low Fe^{2+} concentrations in Leurel specimens.

The 11000 cm^{-1} band is at too high an energy for 8-coordinate Fe^{2+} (Manning 1967), whereas two bands are expected of ferrous ions in the distorted octahedral positions. The Mössbauer determinations show three times as much 5-coordinate Fe^{2+} in Wakefield crystals than in Leurel. The optical spectra (Figs. 1-3) pertain to Leurel crystals of 0.22-cm thickness and to Wakefield crystals of 0.083 cm. There is no indication of a 11000 cm^{-1} band in the Leurel spectra, showing that the 11000 cm^{-1} band does not mark 5-coordinate ferrous ion.

SITE LOCATIONS OF Ti^{4+} IONS

Considerations of ionic sizes and the need for charge-compensation suggest that a major portion of the Ti^{4+} ions substitute into Al/Fe positions. The bulk of the Fe^{3+} ions do likewise (Table 3). The Leurel and Sudan spectra (Manning 1975) show a polarized band at ~23000 cm^{-1} indicative of Ti^{4+} (and Fe^{2+}) ions on the antiprismatic *C*-sites. In contrast, no such band is seen in Wakefield spectra, suggesting that Ti^{4+} ions are absent from *C*-sites. If metal ions do distribute between *B*- and *C*-sites, then there are relatively few Ti^{4+} ions on *B*-sites also in Wakefield vesuvianites.

SUMMARY

In green, low-Ti vesuvianites, > 90% of iron is present as Fe^{3+} on octahedral Al/Fe sites. Ferrous ions predominate in Ti-rich crystals, and at total-Fe concentrations of < 3-4% FeO, the 5-coordinate *B*-site is favoured. At higher FeO concentrations, Fe^{2+} enters preferentially the Al/Fe position. Minor amounts of Fe^{2+}, Fe^{3+} and Ti^{4+} occupy 8-coordinate positions. Ti^{4+} ions favour the Al/Fe position.

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