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CHARGE-TRANSFER PROCESSES AND THE ORIGIN OF COLOUR AND PLEOCHROISM OF SOME TITANIUM-RICH VESUVIANITES

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ABSTRACT

The optical absorption spectra of high-titanium vesuvianites from three different localities are described and are shown to be dominated by bands marking $Fe^{2+} \rightarrow Ti^{4+}$ intervalence and oxygen→Fe charge-transfer processes. The spectra of all three crystals show a polarized band centred at 23000-24000 cm^{-1} (435-415 nm) that is assigned to charge-transfer between Fe^{2+} and Ti^{4+} ions in adjacent *C* positions in columns along the 4-fold axis and parallel to the crystallographic *c*-axis. A vesuvianite from Leurel, Quebec, containing 0.98% FeO and 2.41% TiO_2, in addition absorbs at 26750 cm^{-1} (374 nm) and this is attributed tentatively to charge-transfer between Fe^{2+} and Ti^{4+} ions in adjacent Al/Fe and Ca(2) posititons. The spectra indicate a non-uniform distribution of Fe^{2+} over the four different Ca sites; one of these sites, the highly-distorted Ca(3), contains an immeasurably small amount, <7%, of total iron. These occupancies could not be confirmed because of the absence or weakness of Fe^{2+} crystal-field bands. No evidence of Fe^{3+} or Ti^{3+} crystal-field absorption is observed and calculation suggests that the minerals are richer in Fe^{2+} ions than in Fe^{3+} and also that <1% of total Ti is Ti^{3+}.

The UV-centred background absorption is polarized in $E /\!/ c$ spectra, where E is the polarization direction of the electric vector of incident light. This absorption and that at ~23000 cm^{-1} are mainly responsible for the yellow and pinkish-brown colours and the pleochroism of Ti-rich vesuvianites.

INTRODUCTION

Optical absorption can be a facile method of studying the chemistry of Ti in minerals. Assuming reasonable extinction of coefficients, the strength of Ti^{3+} crystal-field absorption can lead to estimates of $Ti^{3+}:Ti^{4+}$ ratios (Manning & Harris 1970). The substitution of Ti^{4+} into Ca^{2+} and Al^{3+} sites requires parallel charge compensation through changes in local crystal composition, and this can cause the intensification, broadening and shifting of Fe^{2+} and Fe^{3+} bands (Manning & Townsend 1970; Robbins & Strens 1972; Manning 1973; Faye *et al.* 1974). In addition, Ti^{4+} is an acceptor ion in directional intervalence charge-transfer processes (Manning 1969a; Townsend 1968; Faye & Harris 1969).

Broad absorption bands in the energy-range 20000 - 24000 cm^{-1} are not uncommon features of the optical spectra of Ti-bearing minerals (Manning 1969a; 1969b; Faye & Harris 1969). The bands are polarized along metal-metal directions, hence the reason for the current belief that they mark $M^{n+} \rightarrow Ti^{4+}$ intervalence charge-transfer, where M^{n+} is more likely to be Fe^{2+} than Ti^{3+} (Faye *et al.* 1974; Townsend 1968). Vesuvianites are silicates of complex structure containing, insofar as transition-metal ion substitutions are concerned, 'tight' Al-centred and Al/Fe-centred octahedral sites, a 5-coordinate site and four 8-coordinate Ca^{2+} sites of significantly different local site symmetry. Vesuvianites can contain several per cent Fe and Ti; those low in Ti are often green and those rich in Ti brown or yellow (Deer, Howie & Zussman 1962). Here, the polarization properties of absorption bands in the blue and near-ultra-violet regions of the spectra of three Ti-bearing vesuvianites are used to determine the electronic transitions responsible for the colour and pleochroism. Because the bands mark directional intervalence charge-transfer processes, information can be obtained on some Fe^{2+} and Ti^{4+} site occupancies. Optical absorption evidence (Grum-Grzhimailo *et al.* 1963; Manning 1968) indicates that almost all the Fe in low-Ti vesuvianites is Fe^{3+}.

EXPERIMENTAL

Polarized absorption spectra were recorded on a Cary-14 spectrophotometer using Glan polarizing prisms. Spectra were measured at room-temperature. Gem-quality, honey-yellow crystals of vesuvianites from Leurel, Quebec, were donated by Messrs. H. R. Steacy and H. G. Ansell, curators of the National Mineral Collection, Geological Survey of Canada. They also gave crystals from Salinas, Mexico. A thin section of pinkish-brown vesuvianite from Sudan was sent to me some years ago by Dr. R. A. Howie,

King's College, London, U.K. Electron microprobe analyses (Table 1) were performed by Dr. D. C. Harris and Mr. D. Owens, Mines Branch, Ottawa, and Dr. W. Petruk of the same address aided in orientation of specimens.

TABLE 1. MICROPROBE ANALYSES OF VESUVIANITES IN WEIGHT PER CENT

	Leurel	Salinas	Sudan
FeO	0.98	1.29	7.62*
TiO_2	2.41	0.90	3.00
MnO	n.d.	0.05	0.06
SiO_2	36.88	36.76	34.67
CaO	37.46	37.70	35.24
Al_2O_3	16.60	16.12	12.76
MgO	3.39	4.51	3.28
Total	97.72	97.33	96.63

n.d.=not detected *expressed as Fe_2O_3, otherwise total is even lower (96%). Balance to 100% is probably made up of OH, to a lesser extent by Fe^{3+}, and by Na^+ (not measured).

Extinction coefficients, expressed in litres/mole-cm, are calculated from

$$\epsilon = A/Cl$$

where A is net absorbance, C is the cation concentration in moles/litre and l is the specimen thickness. In the text, metal concentrations are given according to mineralogical custom as weight per cent oxide. Pleochroic schemes are given in Table 2.

TABLE 2. PLEOCHROIC SCHEMES OF Ti-RICH VESUVIANITES

Specimen	Thickness	$E/\!/c$	$E\perp c$
Leurel	0.0085 cm	yellow	colourless
Salinas	0.10 cm	yellow	colourless
Sudan	0.01 cm	pinkish-brown	yellow-brown

E represents the polarization direction of incident light.

Structure of Vesuvianite

The structure of vesuvianite has been determined by Warren & Modell (1931) and more recently and accurately by Coda *et al.* (1970) and Rucklidge *et al.* (1975). The structures proposed by the Coda and Rucklidge groups are virtually identical but differ significantly from the Warren & Modell structure in the distribution of atoms on the 4-fold axis. The latter suggested that two Ca ions separated by 2.84Å are on the 4-fold axis, each cation sharing a face of an antiprism of oxygens. The newly determined structure on the 4-fold axis is shown in Figure 1; Ca ions in C sites are in antiprismatic co-ordination and Fe ions in B sites are in square-pyramidal coordination. The C-C separation is 2.60 Å and the C-B 1.06 Å. Least-squares refinement of site occupancies placed Al on the smaller 8-fold octahedral positions and Al, Fe, Ti, Mn and Mg on both the 16-fold general octahedral AlFe site and the B site. Average metal-oxygen distances are: Al-O 1.89Å, Al/Fe-O 1.95Å, C-O 2.47 Å, B-O 2.11 Å, Ca(1)-O 2.42 Å, Ca(2)-O 2.47 Å and Ca(3)-O 2.50Å. the B and C positions are half occupied, and presumably if a B position is filled the adjacent C position is unfilled.

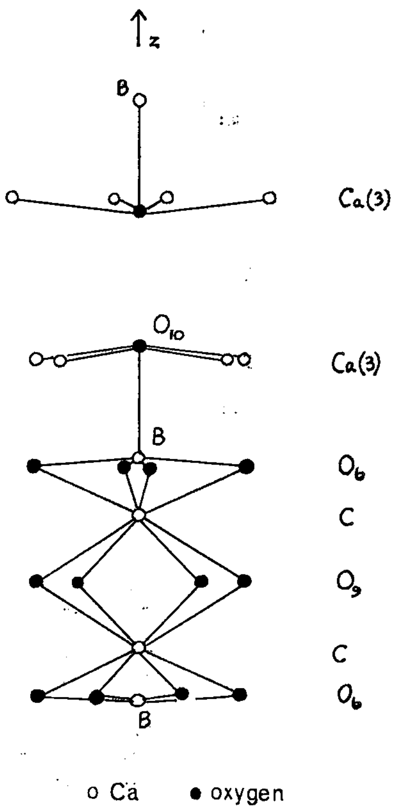

FIG. 1. Diagrammatic representation of 4-fold axis at $x=\frac{1}{4}$ and $y=\frac{1}{4}$. Projection is on a plane containing the c-direction.

Results and Discussion

Description of spectra.

Figures 2-4 present the polarized- and unpolarized-light spectra of irrational and oriented sections of Leurel and Salinas vesuvianites. Spectra of the Leurel material show two broad absorption bands at 23000 cm^{-1} (435 nm) and 26750 cm^{-1} (374 nm) superimposed on strong UV-centred charge-transfer absorption. The 23000 cm^{-1} band is strongly polarized, having maximum intensity in $E/\!/c$ spectra and zero intensity in $E\perp c$ (Figs. 2 and 3). Spectra of the Salinas (Fig. 4) and Sudan crystals show the one band at 23000 cm^{-1} and ~24000 cm^{-1}, respectively, also polarized, although not shown here,

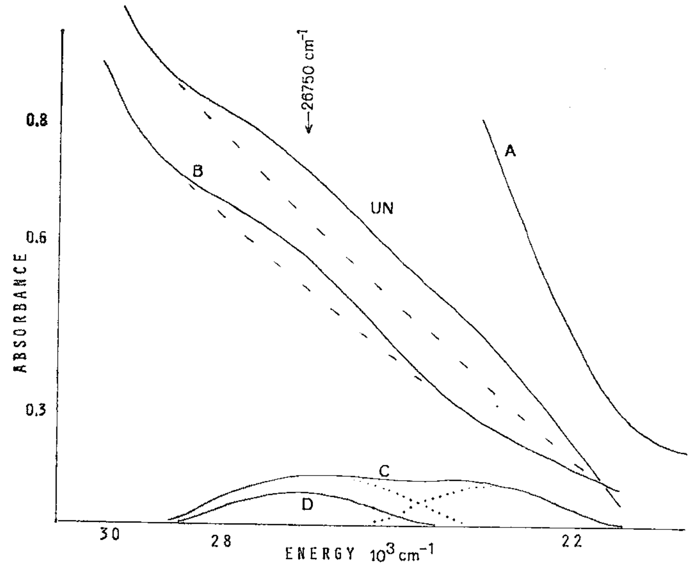

FIG. 2. Optical absorption spectra of a section of Leurel vesuvianite cut parallel to the *c*-axis. Spectrum A represents $E \parallel c$, B $E \perp c$, and UN unpolarized light. (*E* is the polarization direction of incident light). Profiles and D are obtained by subtracting the ultraviolet-centered background absorption from UN and B, respectively. Dashed lines indicate approximate backgrounds for curves B and UN. Specimen thickness 0.0085 cm.

in $E \parallel c$ spectra. The two broad Leurel bands therefore mark two electronic processes involving differently-situated pairs of cations. These same bands are associated unquestionably with the presence of Ti because two of the three Ti-

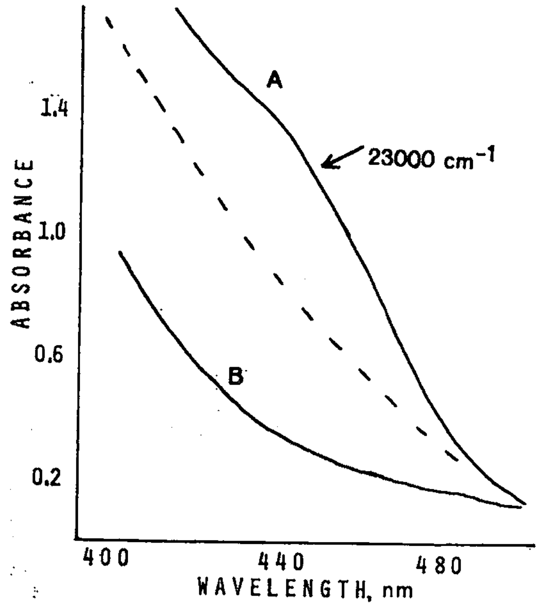

FIG. 3. Polarized absorption spectra of Leurel vesuvianite. A is for $E \parallel c$ and B for $E \perp c$. Dashed line indicates background absorption. Sample thickness 0.038 cm.

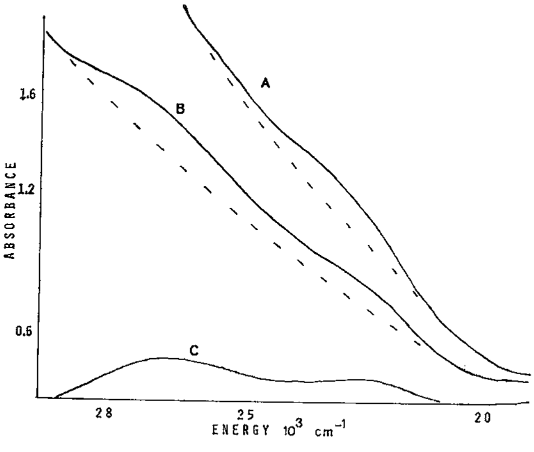

FIG. 4. Unpolarized-light spectra of Salinas (A) and Leurel (B) vesuvianites. Curve C is that of B minus background. Specimen thicknesses: 0.043 cm for A and 0.019 cm for B.

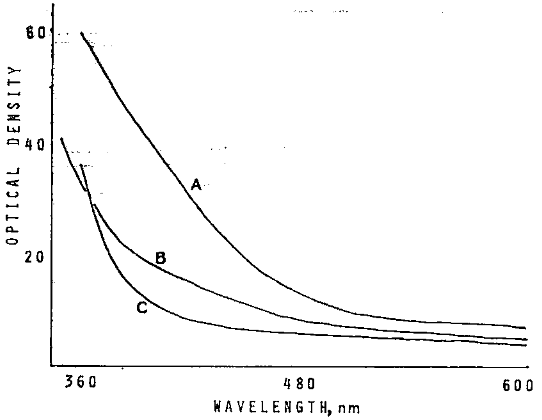

FIG. 5. Absorption coefficient (absorbance/thickness, in cm^{-1}) versus wavelength for Leurel (A), Salinas (B) and Lowell (C) vesuvianites. For A, B, C respectively, $l = 0.0215$, 0.043, 0.033cm; FeO = 0.98, 1.29, 4.4%; TiO_2 = 2.41, 0.90, 0.12%.

bearing vesuvianites are relatively low in Fe and relatively high in Ti compared with the Fe^{3+}-bearing Lowell crystals studied earlier (4.9% Fe_2O_3; 0.20% TiO_2; Manning 1968), the spectrum of which showed neither of these two bands. Three interpretations are possible: firstly, the bands represent crystal-field transitions in Ti^{3+}; secondly, they mark directional metal → Ti^{4+} intervalence charge-transfer, and thirdly, they mark crystal-field transitions in ferrous and ferric ions intensified and broadened by the substitution of Ti^{4+} ions into next-neighbour Ca^{2+}, Mg^{2+} or Al sites. Substitutional effects have been noted in schorlomite garnet (Manning & Townsend 1970; Manning 1973), Ti-bearing biotites (Robbins & Strens 1972) and tourmalines (Faye *et al.* 1974). Intervalance charge-transfer absorption is polarized accurately along metal-metal directions (Manning 1969a; Faye & Harris 1969). Reference to garnets shows that the solubility of Ti in grossular (~1% w/w TiO_2; Al-O 1.945Å; Deer, Howie & Zussman 1962; Abrahams & Geller 1958) is too low for measurable crystal-field absorption, whereas in andradite Ti^{3+} solubility is greater (equivalent to 10% TiO_2; Fe^{3+}–O 2.02Å) and crystal-field absorption is strong (Manning & Harris 1970). It therefore seems unlikely that the solubility of Ti^{3+} in octahedral sites in vesuvianites (Mg-O 1.89Å; Al-O 1.95Å) will be great enough for measurable *d-d* absorption. Ti^{3+} ions in 8-coordinate Ca positions will absorb, from comparisons with spectra of Ti^{3+}-andradite, at $19000 \times 8/9 \times (2.0/2.4)^5$ cm^{-1}, or ~7000 cm^{-1}, where (2.0/2.4) is the ratio of metal-oxygen distances in andradite and vesuvianite.

Origin of the 23000 cm^{-1} band.

The polarization properties of the 23000 cm^{-1} band indicate $Fe^{2+} \rightarrow Ti^{4+}$ or $Ti^{3+} \rightarrow Ti^{4+}$ charge-transfer between cations in adjacent sites lying along the *c*-direction. The vesuvianite structure shows Al-Al, Al/Fe and also *B*-*C* and *C*-*C* vectors parallel to the *c*-axis. The structure of the column at $x = ¼$ and $y = ¼$ is shown in Figure 1. Cations in adjacent *C* positions share a face of an antiprism and according to Randic (1960) the odd 3*d* electron of the donor ion occupies the axially-symmetrical $3d_{z^2}$ orbital, which here is directed along the 4-fold axis and which in turn coincides with the crystallographic *c*-direction. Intervalence charge transfer is particularly favourable because of the short *C*-*C* separation (2.60 Å) and extensive overlap from bridging O_9 $2p\pi$ orbitals. Charge-transfer between metal ions in non-adjacent *B* and *C* sites is much less favourable, firstly on account of the large 3.8 Å separation and secondly because of the unavailability of bridging oxygen π orbitals. The Al-Al and Al/Fe-Al/Fe separations must be considered far too long for intervalence charge-transfer, particularly because the cations do not share octahedral edges of oxygens and the t_{2g} orbitals are not directed along the metal-metal axis. The 23000 cm^{-1} band would therefore seem to arise from Fe^{2+}/Ti^{3+} $3d_{z^2} - O_{2_{p\pi}} - Ti^{4+}$ $3d_{z^2}$ charge-transfer in adjacent *C* sites.

Origin of the 26750 cm^{-1} Leurel band.

Because of very intense ultraviolet-centred background absorption, the 26750 cm^{-1} band in the Leurel spectrum was not resolved in $E /\!/ c$, but $E \perp c$ and unpolarized-light spectra (Fig. 2) show that the band has maximum intensity in $E /\!/ c$. The band after approximate background subtraction is 25-60 per cent more intense in the unpolarized-light spectrum, hence the $E /\!/ c$: $E \perp c$ intensity ratio will be around two. The 26750 cm^{-1} band will probably be too weak to measure if crystals could be thinned sufficiently to permit resolution of the near-ultraviolet spectrum. The half-width and energy of the band suggest metal → Ti^{4+} interaction and the polarization properties indicate metal-Ti^{4+} vectors having a greater projection onto the *c*-axis than onto a plane perpendicular to *c*. This criterion eliminates $Fe^{2+}/Ti^{3+} \rightarrow Ti^{4+}$ charge-transfer in the site-pairs Al-Al/Fe, Al-Ca, Ca(1)-Ca(2) and Ca(3)-Al/Fe. The *C*-Ca(3) site-pair can be eliminated because the odd 3*d* electron of Fe^{2+} ions in *C* sites is localized in the $3d_{z^2}$ orbital that is oriented parallel to the *c*-axis and away from

Ca(3) ions. Possible site-pairs are Ca(2)-Al/Fe, Ca(2)-Ca(2), Ca(2)-Ca(3) and Ca(3)-Ca(3).

Crystal-chemical arguments (Burns & Strens 1967) and *x*-ray diffraction evidence (Coda *et al.* 1970; Rucklidge *et al.* 1974) suggest that major amounts of transition-metal Ti^{4+} ions occupy the octahedral Al/Fe sites in vesuvianites. In schorlomite garnets, for example, there is no evidence to suggest that Ti^{4+} ions occupy other than the octahedral Al sites (Hartman 1969; Manning & Harris 1970; Burns 1972; Dowty 1971). Optical-absorption and Mössbauer studies of tourmalines (Herman *et al.* 1973; Faye *et al.* 1974; Burns 1972) demonstrate that ferrous ions are present in Al positions (Al-O 1.93 Å) although the larger Mg site (Mg-O 2.05Å) is usually favoured. The availability of several Ca sites in the vesuvianite structure suggests that ferrous substitution into 'tight' Al/Fe sites will be on a smaller scale than for Ti^{4+} substitution. Moreover, ions in the Al/Fe and Ca(2) sites share a pair of oxygens and a 3*d*-orbital lobe of the Al/Fe ion is directed toward a Ca(2) ion. For these reasons, Fe^{2+}/Ti^{3+} and Ti^{4+} substitution into Ca(2) and Al/Fe sites is attractive as the cause of the 26750 cm^{-1} band. The internuclear separation is 3.3Å. The donor ions, Fe^{2+} or Ti^{3+}, are probably on the Ca(2) site.

Some site occupancies of Fe^{2+} and Fe^{3+} ions.

None of the spectra showed a sharp absorption band at 21600 cm^{-1} (463 nm) marking the field-independent transition $^6A_1 \rightarrow {}^4A_1{}^4E(G)$ in Fe^{3+} ions in Al/Fe positions (Manning 1968). Assuming for the Leurel material that a sharp band of 0.05 absorbance units would be observed, if it existed, at 21600 cm^{-1} in the spectrum of a Leurel section 0.22 cm thick and that $\epsilon = 1.5$, the maximum calculated concentration of Fe^{3+} ions in Al/Fe sites is 0.15 molar or 30% of total Fe. Lesser amounts of Fe^{3+} ions are expected in Al and *B* sites, in the former instance because of the tightness of the site and in the latter because the ϵ-value is expected to be ~10 as there are no covalently-bonded next-nearest neighbour cations around O_{10} (Manning 1973; Fig. 1). It would appear, therefore, that the Ti-rich minerals, in contrast to the Lowell, are richer in Fe^{2+} than in Fe^{3+} ions. Assuming for the Leurel material that a broad band of 0.1 absorbance units would be easily seen, if it existed, in the 5000-20000 cm^{-1} spectrum of a section 0.22 cm thick and that $\epsilon = 40$ litres/mole-cm, as it is for the Ti^{3+} $^2E \rightarrow {}^2T_2(D)$ transition in regular octahedral sites in garnets (Manning & Harris 1970), then the Ti^{3+} concentration is ~0.01 molar, which is 1% of total Ti. Absorption bands of the different 8-coordinate Ti^{3+} ions are expected to overlap and any broad envelope seen would have contributions from several Ti^{3+} ions. The odds are that the 23000 cm^{-1} band in spectra of titanian vesuvianites is caused by $Fe^{2+} \rightarrow Ti^{4+}$ charge-transfer. It has been suggested that such processes occur at 14000 to 24000 cm^{-1} in spectra of several natural and synthetic materials (Faye 1968; Townsend 1968; Ferguson & Fielding 1971; van der Graf *et al.* 1973; Dowty & Clark 1973). Polarized bands assigned earlier in spectra of tourmalines (Manning 1969a) and andalusite (Faye & Harris 1969) to $Ti^{3+} \rightarrow Ti^{4+}$ can probably be re-assigned to $Fe^{2+} \rightarrow Ti^{4+}$ (Faye *et al.* 1974). The 23000 cm^{-1} band is of comparable intensity in spectra of all three vesuvianites, indicating similar concentrations of Fe^{2+}-Ti^{4+} ion-pairs and presumably individual Fe^{2+} and Ti^{4+} ions in *C* positions.

If this assignment is correct, the absence of a broad band polarized in $E \perp c$ spectra of the three vesuvianites suggest Fe^{2+} Ca(2)-site : Ca(3)-site occupancy ratios of, say ~4:1. Ions in the Al/Fe and Ca(3) sites lie in a plane approximately perpendicular to the *c*-axis, share a pair of oxygens, and a 3*d* orbital lobe of the Al/Fe-site ion is directed towards Ca(3). (A band at ~11000 cm^{-1} with maximum intensity in $E \perp c$ spectra and zero intensity in $E /\!/ c$ has been observed by me in spectra of some low-Ti vesuvianites; the origin of the band is uncertain but it may mark $Fe^{2+} \rightarrow Fe^{3+}$ charge-transfer). Intervalence charge-transfer involving ions in Ca(3) and other metal sites, can therefore be eliminated. (Note that the principal reason for favouring the Al/Fe-Ca(2) site-pair over Ca(2)-Ca(2) is based on the crystal-chemistry of Ti^{4+}).

The Fe^{2+} - Ti^{4+} process causing the Leurel 26750 cm^{-1} band is probably less efficient than that causing the 23000 cm^{-1} on account of the greater internuclear separation. There are 32 Ca(2) plus Al/Fe sites in the unit cell against four *C*, hence in order to counteract the greater dilution it would appear that more Fe^{2+} and Ti^{4+} ions are present in Ca(2) and Al/Fe sites than in *C*. The solubility of Fe^{2+} in the 'tight' Al sites is probably very low (Burns & Strens 1967), whereas reference to tourmalines (Faye *et al.* 1974; Hermon *et al.* 1973) suggests that Fe^{2+} may be appreciably soluble in Al/Fe sites. No band stronger than 0.03 absorbance units is observed in the featureless 5000-8000 cm^{-1} region of the spectrum of a 0.22 cm section of the Leurel crystal, where bands of 8-coordinate ferrous ions are expected to occur (Manning 1967; Moore & White 1973). Assuming ϵ-values of one, the maximum concentration of Fe^{2+} ions in a Ca position is ~28% of total Fe. Because bands arising from Fe^{2+} in the different Ca positions are expected to overlap, the total concentration of Fe^{2+} in 8-coordinate positions is probably not greater than 28%. The weak, ill-defined envelope in the 8000-14000 cm^{-1} region reflects ferrous occupancy of either or both of the Al/Fe and 5-coordinate positions. The maximum $\epsilon \cdot C$*-value* $(=A/l)$ of the envelope is 0.6 cm^{-1}, and if $\epsilon = 4$ litres/mole-cm then the concentration of absorbing ion is 0.15 molar or ~30% of total Fe. This admittedly approximate ϵ-value is not unreasonable for either 6- or 5-coordinate ferrous, but the purpose of the calculation is to show that major amounts of ferrous ions are on either or both of the Al/Fe and *B* positions.

We have, therefore, for the Leurel material that (i) total Fe^{2+} in Ca positions <28% of total Fe, (ii) Fe^{3+} in Al/Fe positions <30% of total Fe, (iii) Fe^{3+} in *B* sites <5% of total Fe, and (iv) Fe^{2+} in Al/Fe plus *B* sites ~30% of total Fe. Of the Ca positions, Fe^{2+} may be most abundant in Ca(2). The absence of a 26750 cm^{-1} band in the Salinas and Sudan crystals indicates lesser concentrations of Fe^{2+} ions in Ca(2) positions. The stronger near-infrared envelope in the Sudan spectra ($\epsilon C \sim 12$) reflects greater ferrous occupancy of *B* and Al/Fe sites; however, the envelope cannot be resolved unambiguously. The determination of more accurate site-occupancies awaits Mössbauer studies and optical-absorption studies of thicker crystals (for better resolution of the near-infrared).

Assuming that 20% of total-Fe is Fe^{2+} on Ca(2) positions, then one Ca(2) site out of 20 is occupied by Fe^{2+}. If we now place 50% (0.5 molar) of total Ti as Ti^{4+} onto Al/Fe positions, the concentration of adjacent ion-pairs is 0.5/90 or 0.0055 molar. The ϵ-value for the 26750 cm^{-1} band in Leurel spectra can be obtained from $\epsilon = 0.15/(0.0085 \times 0.0055)$ or 3500 litres/mole-cm, where 0.15 is the anticipated absorbance of the band in $E /\!/ c$ spectra (Fig. 2), 0.0085 is the specimen thickness in cm and 0.0055 is the molar concentration of ion-pairs. This is a reasonable ϵ-value because values of 1000 have been calculated for similar bands in spectra of andalusite (Faye & Harris 1969) and green tourmalines (Faye *et al.* 1974) based on Ti concentrations only.

My interpretation of the origin of the 23000 cm^{-1} band requires the presence of Ti^{4+} ions on 8-coordinate *C* sites. This unusual coordination of Ti^{4+} may be related in some way to the occupation of *B* sites by transition-metal ions generally. The metal-oxygen distances of ~2.1Å measured for the *B* site are representative of Fe^{2+}-bearing minerals. Possibly each metal ion on *B* distributes to some degree between *B* and *C* sites, both being half occupied. The simple calculations presented here suggest that Fe^{2+} ions prefer *B* and over *C*, and crystal-chemical considerations suggest that Ti^{4+} does likewise.

Iron is present mostly as Fe^{3+} in the low-Ti Lowell vesuvianite and as Fe^{2+} in the high-Ti crystals. Hydroxyl absorption at 1430 nm is more intense in the Leurel spectra than in Lowell, indicating that the Ti substitutional reaction is mainly

$$Fe^{3+} + Al^{3+}_{oct} \rightleftharpoons Fe^{2+} + Ti^{4+}_{oct}$$

and possibly $Ca^{2+} + Al^{3+}_{oct} \rightleftharpoons Na^{+} + Ti^{4+}_{oct}$,

but not Fe^{3+} (or Al^{3+}) $+ OH^{-} \rightleftharpoons Ti^{4+} + O^{2-}$,

as for example in tourmalines (Faye *et al.* 1974). Other substitutional reactions proposed have included

$$R^{2+}_{oct} + 2Si^{4+}_{tet} \rightleftharpoons Ti^{4+}_{oct} + 2Al^{3+}_{tet}$$

in Appollo 11 pyroxenes (Burns *et al.* 1972),

$$2Fe^{3+}_{oct} \rightleftharpoons Fe^{3+}_{oct} + Ti^{3+}_{oct}$$

in some high-Ti andradites (Manning & Harris 1970),

and $\quad Fe^{3+}_{oct} + Si^{4+}_{tet} \rightleftharpoons Ti^{4+}_{oct} + Al/Fe^{3+}_{tet}$

in schorlomites (Manning & Harris 1970).

SUMMARY

The colour and pleochroism of three Ti-bearing vesuvianites arise mainly from $Fe^{2+} \rightarrow Ti^{4+}$ and $O^{2} \rightarrow Fe$ charge-transfer processes. The polarization properties of the bands reflect Fe^{2+} and Ti^{4} occupancy of *B* and *C* positions in channels running parallel to the *c*-axis, and, in the case of the vesuvianite from Leurel, Quebec, Fe^{2+} and Ti^{4+} occupation of adjacent Ca(2) and Al/Fe positions. The distorted Ca(3) site contains no measurable amount of Fe^{2+} (<7% of total Fe^{2+} in the Leurel material). No direct information can be gleaned on ferric iron but approximate calculations suggest that <30% of total Fe is Fe^{3+}. Not more than 1% of total-Ti is Ti^{3+}. Appreciable amounts of Fe^{2+} are present (15-60%) in the octahedral Al/Fe and 5-coordinate *B* positions.

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