CRYSTAL CHEMISTRY OF TITANIAN AND ZIRCONIAN GARNET: I. REVIEW AND SPECTRAL STUDIES

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Abstract

Chemical analyses provide very little information about the site distribution and valence of titanium in garnet. Mössbauer spectra of titanian garnet specimens show that as titanium enters the structure of andradite, ferric iron is forced into the tetrahedral site, displacing silicon. The spectra also suggest that a small amount of ferrous iron is in tetrahedral coordination. The amount of tetrahedral iron is not sufficient, however, to account for all of the deficiency in silicon, and although one would suppose that tetrahedral aluminum accounts for most of the remainder, the possibility of some tetrahedral titanium remains open.

The widely-quoted arguments of Tarte (1961), supposedly demonstrating the existence of tetrahedral titanium from IR spectra, are refuted by reference to spectra of synthetic garnet containing tetrahedral Fe^{3+} and Al: the features in the titanian garnet spectra allegedly due to tetrahedral titanium are better explained as due to Fe^{3+} and Al.

Optical spectra of Ti-garnet from all but one locality, in which the presence of an interfering contaminant is suspected, show no evidence for the presence of Ti^{3+}. The dark brown color of titanian garnet is due to charge-transfer absorptions. A band in the near infrared can be assigned to tetrahedral ferrous iron, tending to corroborate the Mössbauer evidence.

The preference for Fe^{3+} over Ti^{4+} in tetrahedral coordination may be ascribed to covalency factors. Values of isomer shift for the tetrahedral site, measured in Mössbauer spectra, suggest that the bonding of this site is more covalent than normal for tetrahedral sites in oxides and silicates.

Introduction

The garnet structure normally assumes the space group $Ia3d$, and has eight of the formula units, $X_3Y_2Z_3O_{12}$, per elementary cell. Oxygen atoms are in the general position, $96h$, and the cations all occupy special positions: X cations in $24c$, Y cations in $16a$, and Z cations in $24d$. The X cations are coordinated by eight oxygens in the form of a distorted cube (described by some as a triangular dodecahedron), with point symmetry 222; the Y cations are octahedrally coordinated, with point symmetry $\bar{3}$, and the Z cations are tetrahedrally coordinated, with point symmetry $\bar{4}$. The tetrahedra are independent in that they do not share corners with each other. There is edge and corner sharing among the various polyhedra, but the structure does not lend itself easily to a description as sheets, chains, or other units.

Appreciable titanium content in natural garnet is usually restricted to specimens which are otherwise predominantly andradite, $Ca_3Fe_2Si_3O_{12}$, with a small to moderate amount of the grossular component, $Ca_3Al_2Si_3O_{12}$.

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The site distribution and valence of most cations in natural and synthetic garnet are fairly well understood, but the location and valence of titanium remain topics of much discussion. It is the aim of the present paper to try to define the problems relating to the site distribution and valence of cations in titanian garnet, to discuss certain previously published conclusions, and to present some new chemical and spectral data on ten specimens of garnet, which may help to clarify these problems. These new data are in some respects only qualitative or semi-quantitative, and while they may set limits on the cation distribution, they do not suffice to determine it completely. In Part II (Dowty and Appleman, in preparation) a more quantitative approach will be taken, and results from X-ray refinement of selected specimens will be combined with spectral data.

POSSIBLE SUBSTITUTIONS IN RELATION TO CHEMISTRY

Two structural roles have been advocated for titanium in garnet: substituting for silicon in the tetrahedral Z site; and substituting for ferric iron in the octahedral Y site. By the same token two valence states have been advocated for titanium. Although it is generally four-valent in minerals it has often been proposed that some, or in certain cases, all, of the titanium is three-valent in garnet. The bulk chemistry of titanian garnet provides some information about these possibilities but chemical data is inadequate for the most critical distinctions (Essene 1971). Substitutions of titanium into garnet may be classified into two categories, depending on their effect on the bulk chemistry; these which cause a *silicon deficiency* and those which cause a *cation imbalance*.

To illustrate these types of substitutions an analysis is recalculated into the number of cations per twelve oxygens as in Table 1. All the two-valent cations are included in the X group all the three-valent cations plus titanium and zirconium provisionally in the Y group, and silicon in the Z group. The *silicon deficiency* is the amount by which silicon falls short of the theoretical three atoms. It is caused either by titanium substituting directly for silicon which, when carried to its extreme, would be

$$Ca_3Fe_2^{3+}Ti_3^{4+}O_{12};$$
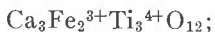
or by substitution of titanium or zirconium for ferric iron and concomitant substitution of aluminum or ferric iron for silicon:

$$Ca_3Ti_2^{4+}(Al, Fe^{3+})_2SiO_{12}.$$

As is to be expected, the silicon deficiency is roughly proportional to the titanium content. This is shown in Figure 1 (a similar plot is given in

Table 1. Chemical Analysis of Zirconian Schorlomite from Iron Hill, Colorado.

	weight %	atoms/12 oxygens					
SiO_2	26.0	2.28 — 2.28		3.00 − 2.28	theoretical Z silicon		
ZrO_2	4.0	.17		0.72	silicon deficiency		
TiO_2	12.1	.79		2.45 − 0.72	sum Y silicon deficiency		
Al_2O_3	3.4	.35	} 2.45				
Fe_2O_3	17.6	1.14		1.73	adjusted sum Y		
FeO	2.8	.20		2.00 − 1.73	theoretical Y adjusted sum Y	3.32 − 3.00	sum X theoretical X
MnO	0.4	.03		0.27		0.32	
MgO	1.0	.13	} 3.32	cation imbalance = (0.27+0.32)/2 = 0.29			
CaO	31.6	2.92					
Na_2O	0.3	.04		silicon deficiency + cation imbalance = 1.01			
	99.6 [a]			Ti + Zr			= 0.96

Analyst: Prof. Dr. Max Weibel, Eidgenossische Technische Hochschule, Zurich.

[a] Loss on ignition of 0.2 brings total to 99.8%.

Howie and Woolley, 1968, Fig. 3). It may be seen, however, that the silicon deficiency is in general not large enough to account for all the titanium, but on the average, only about two thirds of it.

If enough of the Y cations are transferred to the Z site to make up the silicon deficiency (without specifying at this point which particular ones), there are now too few Y cations. There are also too many X cations, and the amount by which the X cations exceed the theoretical three atoms is about the same as the amount by which the Y cations fall short of the theoretical two atoms. The *cation imbalance* is defined as the average of these two discrepancies, or, in a simplified formula:

cation imbalance = (sum X − sum Y − Si + 2.0)/2.0.

The cation imbalance may be a result of any of four causes. First, a two-valent cation may compensate for the excess charge of titanium or zirconium entering the octahedral site by also entering the octahedral site:

$$Ca_3Ti^{4+}Me^{2+}Si_3O_{12},$$

where "Me^{2+}" is ferrous iron or magnesium, for example. Second, there may be very minor substitutions of alkalis:

$$NaCaTi^{4+}Me^{3+}Si_3O_{12}.$$

Third, if a two-valent cation substitutes for silicon, two atoms of four-
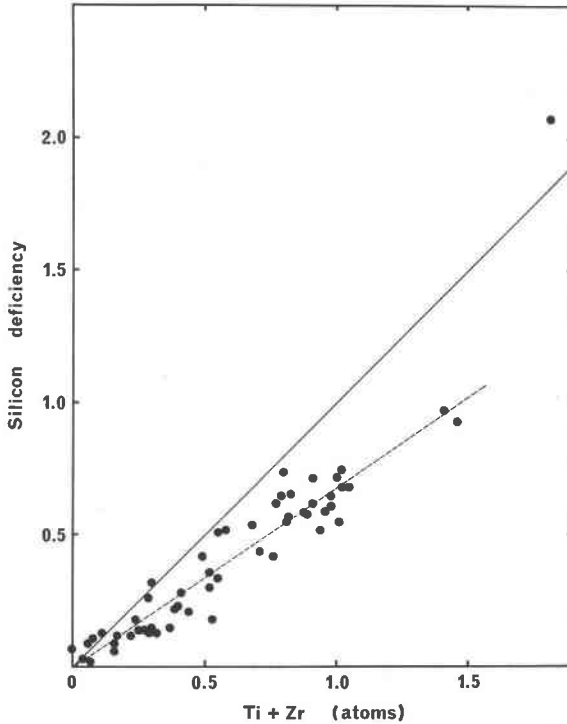
FIG. 1. Correlation of silicon deficiency with titanium and zirconium. Analyses are from the literature. The solid line represents one-to-one correlation, and the dashed line is a least-squares fit to the points (excluding the point near the upper right-hand corner, representing kimzeyite). Slope of the dashed line is 0.68.

valent titanium or zirconium could enter the octahedral site:

$$Ca_3Ti_2{}^{4+}Me^{2+}Si_2O_{12}.$$

Note that this substitution would also increase the silicon deficiency. This substitution may appear extremely unlikely, in view of the fact that most two-valent cations are much larger than silicon, but some evidence in favor of its existence will be presented in this paper. Fourth, part or all of the cation imbalance may be caused by some of the titanium being three-valent, instead of four-valent. This possibility stems from the fact that it is not normally possible to determine directly the amounts of all four of the species Fe^{2+}, Fe^{3+}, Ti^{3+}, and Ti^{4+} in a wet chemical analysis. In a conventional analysis only total iron, total titanium, and total reducing capacity are determined. Total reducing capacity includes all oxidizable species, which is this case are Fe^{2+} and Ti^{3+}. It is normally

assumed that Ti^{3+} is not present, and the total reducing capacity is ascribed to Fe^{2+}, because Ti^{3+} is known to be a strong reducing agent, and substantial quantities do not exist in aqueous solutions in the presence of Fe^{3+}. This is not necessarily the case in a crystalline solid, however, where structural factors might stabilize Ti^{3+} (Strens, 1967). Therefore, there is no way to tell from an analysis whether the ferrous iron is real, or actually represents three-valent titanium, *in toto* or in part.

The silicon deficiency and the cation imbalance together account for nearly all of the titanium and zirconium in garnet, as shown in Figure 2. There is still considerable scatter in the plot, but the fit of the line of one-to-one correlation to the data is good. The scatter must be accepted as due to analytical error unless some of the garnet specimens are non-stoichiometric, which is unlikely. The fact that there are about as many points on one side of the line as the other is in itself an argument in favor
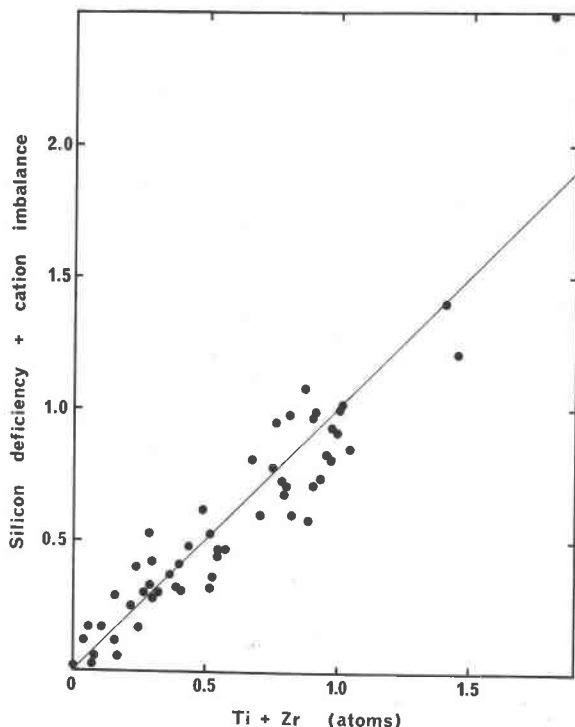

Fig. 2. Correlation of silicon deficiency and cation imbalance with titanium and zirconium. The solid line represents one-to-one correlation. Silicon deficiency plus cation imbalance has been adjusted to take account of such minor substitutions as Na^+ for Ca^{2+}, which would allow concomitant substitution of Ti^{4+} for Fe^{3+}.

of the general stoichiometry of titanian garnet. If stoichiometry is assumed, then the maximum amount of Ti^{3+} which could be present is limited to the cation imbalance or the total reducing capacity, whichever is smaller. Essene (1971) has calculated the maximum amount of Ti^{3+} which could be present in a number of published analyses.

Although the average ratio of the silicon deficiency to the cation imbalance is about two to one, there is no apparent reason why this ratio should hold exactly for every specimen: there may be a predominance of the silicon deficiency type of substitution in certain circumstances, and a predominance of the cation imbalance in others. A variation of this sort seems to have been observed in the electron microprobe studies of Lehijärvi (1961), Isaacs (1968), Leake (1968), Howie and Woolley (1968), and Gomes (1969). Sometimes iron or aluminum varies inversely with titanium in microprobe traverses, but perhaps more often silicon shows a distinct negative correlation. However, determining which type of substitution is predominant in certain cases, or in general, does not completely determine the site distribution of titanium, or its valence.

The silicon deficiency obviously involves the replacement of silicon, but it is not obvious, or even determinate from the type of data we have examined so far, that it is titanium which directly replaces silicon. The cation imbalance presumably corresponds to the amount of titanium in excess of the silicon deficiency, and this amount must therefore be present in the octahedral site. However, the problem with respect to the cation imbalance is not the location of this amount of titanium, but its valence. Further discussion of uncertainty in the site distribution of titanium will refer only to an amount corresponding to the silicon deficiency.

For the purpose of the present study, there are basically two hypotheses to account for the silicon deficiency: either titanium substitutes directly for silicon; or else it and/or zirconium goes into octahedral coordination while silicon is replaced by aluminum or ferric iron, or perhaps two-valent cations. Naturally, the silicon deficiency could be accounted for by a combination of the two basic hypotheses. At the risk of belaboring the point, it will be emphasized again that the choice between the two hypotheses cannot be made on the basis of chemical analyses, and that the correlation between the silicon deficiency and the titanium-zirconium content shown by Figure 1 does not by any means prove that titanium (or zirconium) is directly replacing silicon.

Aluminum is known to take tetrahedral coordination in all types of silicates, and it is common practice when recalculating analyses to make up any deficiency in silicon with aluminum. However, in the most titanium-rich garnet, there is simply not enough aluminum to make up

the silicon deficiency; this is the case for the analysis in Table 1 (see also Howie and Woolley, 1968, Fig. 2). Consequently, many mineralogists have favored the hypothesis that titanium substitutes directly for silicon. Actually, when aluminum is not sufficient alone to account for the silicon deficiency, it would seem that we are faced with a choice between ferric iron and titanium. Trying to decide on the basis of accepted crystal chemical principles which of these two is more likely to substitute for silicon is difficult.

The radii of the two ions, Fe^{3+} and Ti^{4+}, are apparently similar enough that some tabulations have Fe^{3+} as the larger, others Ti^{4+}. On electrostatic grounds, Ti^{4+} should be favored for the tetrahedral site, since it has the same charge as silicon. In natural garnet with the formula $X^{2+}_3Y^{3+}_2Z^{4+}_3O_{12}$, as well as synthetic garnets of the YIG type (yttrium-iron garnet, $Y_3Fe^{3+}_2Fe^{3+}_3O_{12}$), Pauling's electrostatic valence rule (Pauling, 1960) is satisfied exactly, but substitution of Fe^{3+} or Al for Si would be a violation of the rule, causing local charge imbalance. However, this factor cannot be of overriding importance, since aluminum commonly substitutes for silicon in many silicates. Crystal field considerations are no help; neither Fe^{3+} nor Ti^{4+} is stabilized by any particular type of coordination. Perhaps the last remaining theoretical criterion, and one that is not often employed in the prediction of site occupancies, is the bond type criterion, *i.e.*, whether a cation forms bonds of the particular degree of covalency that is required in a structure or site. We shall see some evidence below that this may indeed be the deciding factor in the case of titanian garnet.

On the other hand, empirical results from the study of other crystal systems containing Fe^{3+} and Ti^{4+} seem to favor Fe^{3+} as a substitute for silicon. Hartman (1969) has summarized arguments why the decreasing order of preference for substitution of silicon is Al, Fe^{3+}, and Ti^{4+}. These arguments are well based in experiment, but do not make use of any fundamental crystal chemical principles; it is simply found that Fe^{3+} substitutes more easily into tetrahedral sites.

The location of zirconium seems to be somewhat better established than that of titanium. The Zr^{4+} ion is generally considered to be so large as to preclude its occupying the tetrahedral site in silicate garnet, and the principal question seems to be whether it may occupy the 8-fold, as well as the octahedral site. Since calcium is usually present in sufficient quantity to fill or nearly fill the 8-fold site in natural zirconian garnet, zirconium is probably almost entirely restricted to octahedral coordination. There is also little doubt that the valence of zirconium in garnet is always four. Zirconian garnet is considered in this paper along with titanian garnet because titanium apparently always accompanies zir-

conium in garnet. Also, as detailed above, some of the effects of substitution of zirconium are identical to those expected for certain of the substitutions involving titanium.

<div align="center">EXPERIMENTAL</div>

Specimens. Physical properties and partial chemical composition of the ten specimens used in this study are shown in Table 2. The physical properties and composition of specimen 10 (kimzeyite) are those previously published by Milton, Ingram, and Blade (1961). A complete wet chemical analysis was carried out on specimen 8 (Table 1).

Titanium and zirconium were determined in the other specimens by X-ray fluorescence, using a semi-quantitative loose-powder technique. The total precision of the Ti determinations, in terms of standard error, is estimated at 10 to 15 percent of the amount of oxide present, and of the Zr determinations, 20 to 50 percent. About 0.3 percent yttrium was found in specimen 3, and lesser amounts in specimens 7 and 8. Traces of niobium (less than 0.1 percent) were found in specimens 7 and 8.

Precision in determining the physical properties was limited because of ubiquitous zoning. Refractive indices of all the specimens showed considerable variation, and are only reported to the nearest hundredth. Standard error of the cell edge determinations is 0.001 to 0.002 Å, and of the densities, which were determined in most cases by pycnometer, 0.01 to 0.02 g/cc.

Table 2.   Physical Properties and Partial Chemical Composition of Specimens

	Specimen, locality	cell edge ångstroms	density g/cc	refractive index	TiO_2, wt. %	ZrO_2, wt. %
1)	Andradite Adelaide, Nevada	12.049	3.85	1.88	nil	nil
2)	Andradite Garnet Hill, Calif.	11.995	3.80	1.85	nil	nil
3)	Melanite Granite Mtn., Alaska	12.035	3.81	1.86	3.8	0.7
4)	Melanite Magnet Cove, Arkansas	12.050	3.80	1.88	3.2	0.1
5)	Melanite Magnet Cove, Arkansas	12.099	3.78	1.90	6.9	0.7
6)	Schorlomite Atlas Mts., Morocco	12.086	3.79	1.90	7.6	0.3
7)	Schorlomite Iron Hill, Colorado	12.095	3.78	1.91	11.0	0.2
8)	Zirconian schorlomite Iron Hill, Colorado	12.148	3.81	1.92	12.1	4.0
9)	Schorlomite Iiwaara, Finland	12.130	3.81	1.95	15.5	0.4
10)	Kimzeyite Magnet Cove, Arkansas	12.458	3.94	1.94	5.6	29.9

See text for precision of measurements.

Mössbauer. Two parameters describe the shape of a Lorentzian absorption peak in Mossbauer spectroscopy: height, and width at half-height. The area under the peak is equal to the product of height and width. In general, the heights of the two peaks of a doublet are not exactly equal (Goldanskii, Makarov, and Khrapov, 1963), but in a cubic substance such as garnet, for which preferred orientation is impossible and the point symmetries of the iron sites are high, the height and width of the two peaks are probably identical within the precision of the measurement. It has also been found that ferric iron doublets are in general much more symmetric than ferrous. In thin absorbers, the area under each doublet is proportional to the amount of the particular type of iron giving rise to it, but the constant of proportionality may be somewhat different for each site. This constant is determined by the recoil-free fraction, or Mössbauer coefficient, which is a function of both the rigidity of binding of the atom in the material and the temperature at which the experiment is conducted. Since the Mössbauer coefficients for different sites tend toward a uniformly high value at low temperatures, spectra taken at liquid nitrogen (77°K) or liquid helium (4°K) temperatures may yield more accurate estimates of site distribution than those taken at room temperature. In the present study, the precision of most of the chemical data was not thought sufficient to warrant taking low-temperature spectra of all the specimens.

Chi-square, the sum of the squared differences between the predicted and measured counts, divided by the predicted counts at each channel, seems to be the best criterion of the goodness of the fit to a spectrum. Theoretically, for perfect fits the average value of chi-square is equal to the number of degrees of freedom, which in this case is the number of data points minus the number of adjustable parameters. In practice, instrumental effects cause chi-square for the ideal fit to be somewhat larger. It should be kept in mind, however, that "goodness" of the fit is not necessarily equated with correctness. For a given degree of correctness, in terms of the absolute deviation of a set of fitted parameters from the real parameters, the value of chi-square is dependent on the variance at each data point, that is, on the number of counts. In other words, a given incorrect set of parameters will yield a higher value of chi-square for a spectrum with a large number of counts than for a spectrum of the same sample with a small number of counts. Experience has shown that for the number of counts taken in the present study, values of chi-square less than about 20 percent greater than the number of degrees of freedom are rather good, and indicate essentially correct fits.

The spectra reported in this study were taken with a time-mode spectrometer, using a 256-channel analyzer. The source of gamma-rays was Co^{57} in copper, which gave a line width of less than 0.25 mm/sec. Spectra were calibrated with metallic iron, and the isomer shifts are reported with respect to metallic iron. The mirror-image halves of the spectra were combined, giving 128 data points, except in some spectra taken on a wide velocity scale, from which the outer 18 channels were deleted. The variable metric minimization method of Davidon (1959) was used to fit Lorentzian curves to the spectra; Davidon's computer program was modified for use on the IBM 360/67 by Mr. Robert Mark, Stanford University. Linear constraints were applied to the peak parameters in fitting all spectra except the non-titanian andradite (specimen 1); both heights and widths of the peaks of each doublet were constrained to be equal.

Infrared spectra. A Beckman IR-10 spectrophotometer was used to record the spectra. The samples were prepared by the KBr disc method.

Optical spectra. Absorption spectra were taken on thin doubly-polished plates, using a Carey 14-IR spectrophotometer. Identical aluminum masks were inserted into the sample

and reference beams when necessary to isolate small grains. The spectra shown in Figure 10 were transferred point-by-point from the wavelength-linear scale of the instrument to the energy-linear scale of the figure.

Mössbauer Spectra

Mössbauer data for eight of the ten specimens are given in Table 3, and a representative spectrum is shown in Figure 3. At least four different types of iron are distinguishable in Mössbauer spectra of titanian garnet, corresponding to the four columns labeled O_1, O_2, T_1, and T_2 in Table 3.

The O_1 Doublet. This is the only doublet present in the non-titanian andradite, and its parameters are very similar to those previously reported for andradite (Bancroft, Maddock, and Burns, 1967), except that for specimen 1, no significant difference in the widths of the two peaks was observed. This doublet is unquestionably due to ferric iron in octahedral coordination.

The O_2 Doublet. It was found that satisfactory values of chi-square could not be obtained for the titanian garnet spectra when only one doublet for octahedral ferric iron was fitted. When two closely spaced doublets, O_1 and O_2, were fitted, chi-square dropped by over 50 percent in some cases. It was hypothesized at one time, partly on the basis of these results, that two distinct octahedral sites may exist in the structure of titanian garnet; but this has now been disproven by extensive X-ray work, including the refinements mentioned earlier (Part II). The "split" of the octahedral ferric iron absorption may stem from the existence of distinct differences in the short-range ordering around the octahedral cations, *i.e.*, the fact that some of the iron atoms may have a different number of four-valent versus three-valent or two-valent cations as second-nearest neighbors. It could also be an artifact of the fitting process, or some type of domain structure, as yet undetected otherwise, may exist. In any case, the isomer shifts for the O_1 and O_2 doublets are very similar, and the quadrupole splittings show very similar variation (to be discussed below). This makes it probable that the absorption of the O_2 doublet is due to octahedral ferric iron and not to some other type of iron.

The T_1 Doublet. The parameters of this doublet are similar to those reported for tetrahedral ferric iron in YIG and rare-earth iron garnet (Nicholson and Burns, 1964). The intensity of this doublet, as a percentage of the total area, is roughly proportional to the amount of titanium plus zirconium present. The assignment of the T_1 doublet to

Table 3. Mössbauer data.

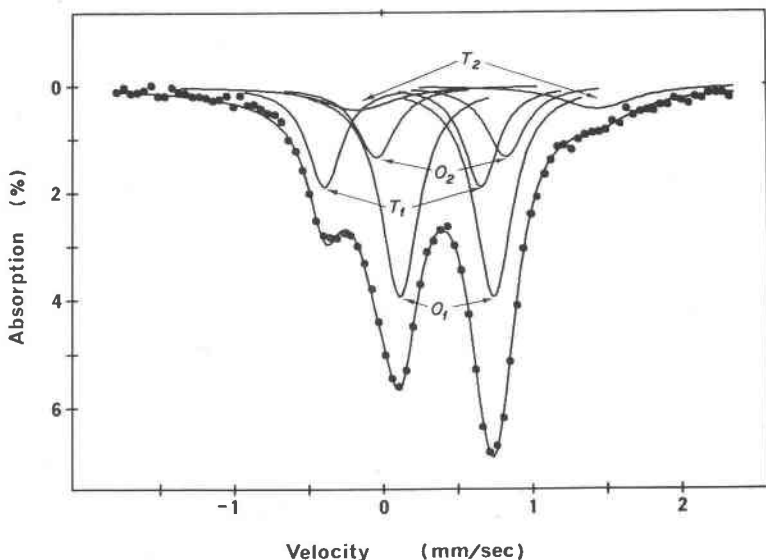| no.	a	O_1				O_2				T_1				T_2				X^2	d.f.[b]	cts.[c]
		Q.S.	I.S.	width	% area	Q.S.	I.S.	width	% area	Q.S.	I.S.	width	% area	Q.S.	I.S.	width	% area			
1	nil	0.53	0.43	0.26	100.0													121	121	0.8
4	3.3	.57	.41	.25	83.8 ±1.5	0.90	0.42	0.30	11.9 ±1.5	1.08 ±.02	0.04 ±.02	0.24 ±.03	4.3 ±.8					145	115	1.6
5	7.4	.57	.42	.22	44.5 ±2.2	.78	.42	.31	41.6 ±2.4	1.08	.10	.28	13.9 ±1.0					131	115	1.6
6	7.8	.57	.42	.24	51.4 ±1.9	.80	.42	.33	31.4 ±2.4	1.06	.08	.33	12.5 ±1.2	1.53 ±.06	0.75 ±.06	0.55 ±.07	4.8 ±1.1	168	111	1.5
7	11.1	.58	.43	.23	41.4 ±1.2	.85	.41	.31	34.0 ±1.5	1.09	.11	.30	17.7 ±1.0	1.80 ±.08	.68 ±.08	.81 ±.08	6.9 ±1.1	115	111	4.5
8	14.9	.60	.45	.23	23.5 ±3.1	.83	.43	.34	43.6 ±4.4	1.07	.13	.29	20.3 ±1.8	1.99 ±.08	.79 ±.08	.87 ±.08	12.6 ±2.1	143	93	1.8
9	15.8	.64	.43	.31	51.9 ±5.0	.88 ±.05	.40 ±.05	.32 ±.05	8.6 ±3.6	1.05	.14	.26	20.7 ±1.9	1.62 ±.10	.63 ±.10	.60 ±.10	10.9 ±3.8	147	93	2.2
10						1.01 ±.06	.45 ±.06	.43 ±.08	7.0 ±1.8	1.08	.19	.30	93.0 ±.6					132	119	2.0

FIG. 3. Mössbauer spectrum of specimen 9, Ti-garnet.

tetrahedral ferric iron is quite certain, and it is therefore confirmed beyond doubt that significant quantities of ferric iron take tetrahedral coordination in natural titanian garnet.

The T_2 Doublet. The right-hand peak of this doublet is visible to the eye in spectra of the specimens with the highest Ti-Zr content, although its parameters are only revealed by computer fitting. Owing to its low intensity and larger width, and the fact that the low-velocity peak is buried beneath the larger peaks, its parameters are not as reliable as those of the other doublets, but there is enough consistency among the different specimens to make it fairly certain that the peaks have been correctly located. The relatively high values of the isomer shift and quadrupole splitting suggested that this doublet is due to ferrous, rather than ferric iron. This

←·《《《

[a] $TiO_2 + 0.7\ ZrO_2$. Multiple of 0.7 for ZrO_2 converts it to roughly the same mole-percent scale as TiO_2.

[b] Degrees of freedom.

[c] Background counts in millions.

Quadrupole splitting (Q.S.), isomer shift (I.S.) and width (full width at half-height) given in mm/sec. Standard deviation is smaller than 0.01 mm/sec except where given explicitly. However, this applies only to the computer fitting stage of the experiment. Actual standard error is unknown, and necessarily somewhat larger than the figures given, which may be taken as minima.

was confirmed by the fact that the splitting increased to about 2.2 mm/ sec in a spectrum of specimen 9 taken at liquid nitrogen temperature. Temperature dependence of this magnitude, attributed to Boltzmann population of the crystal-field split d orbitals in ferrous iron (Werthein, 1964, p. 66), is not expected to occur in ferric iron.

Ferrous iron normally takes the 8-fold site in natural garnet. Quadrupole splittings of 3.53 to 3.60 mm/sec, and isomer shifts of 1.30 to 1.35 mm/sec have been reported for ferrous iron in almandine (Bancroft, Maddock and Burns, 1967) and andradite-almandine (Marfunin, et al., 1967). Obviously these parameters are very different from those measured for the T_2 doublet. We might ask next if the measured parameters are consistent with octahedral ferrous iron, since one of the hypotheses for explaining the cation imbalance involved the presence of two-valent cations in octahedral coordination. The answer is again negative; the quadrupole splitting and particularly isomer shift of ferrous iron in even very distorted octahedra are generally distinctly higher than the values for the T_2 doublet. If only by a process of elimination, we come to the possibility of ferrous iron in tetrahedral coordination. In fact, the measured parameters are fairly reasonable for tetrahedral ferrous iron. The isomer shift is generally thought to be the critical parameter with respect to coordination number, a lower value indicating a lower coordination number; for example, the tetrahedral ferrous iron in staurolite gives an isomer shift of 0.96 mm/sec (Bancroft, Maddock, and Burns, 1967), versus values generally over 1.05 for octahedral sites in silicates.

Another case of ferrous iron substituting for silicon has now apparently been found in lunar plagioclase (Appleman, et al., 1971). There the quadrupole splitting is 1.55 mm/sec and isomer shift is 0.92 mm/sec. Thus, despite the rarity of ferrous iron substituting for silicon, this is the most reasonable assignment of the T_2 doublet. Manning (1967) has also found evidence in the optical spectra of titanian garnet that tetrahedral Fe^{2+} is present (see below).

In some of the spectra, notably numbers 6, 8, and 9, chi-square is still somewhat high. It is likely that in these spectra, and perhaps in the others, minor absorptions due to eight-fold or octahedral ferrous iron are present. In one spectrum of specimen 9 it was possible to fit a fifth doublet constituting 2 percent of the total area, with quadrupole splitting of 3.0 mm/sec and isomer shift of 1.3 mm/sec. This doublet has also been found in the spectra of the specimens which have been refined by X-ray, and will be reported in more detail in Part II.

The Mössbauer spectrum of kimzeyite shows that almost all the ferric iron is in the tetrahedral site, which is in good agreement with the formula originally proposed (Milton, Ingram, and Blade, 1961). No ferrous iron

was detected, the significance of which will be discussed below in the section on optical spectroscopy.

In discussion of the site distribution of iron as determined from Mössbauer spectra, it is assumed for convenience that the area under a doublet, as a percentage of the total area, is equivalent to the percentage of the total iron giving rise to that particular absorption. This is done with the reservation that the true percentages may be somewhat different, because of differences in the relative recoil-free fractions. In particular, the recoil-free fraction of tetrahedral iron may be somewhat larger than that of octahedral iron, owing to stronger bonding. Therefore, the amounts of iron in tetrahedral coordination indicated by the relative areas of the Mössbauer spectra probably represent upper limits, although the true values are not likely to be too much lower.

Figure 4, a plot of total iron on the tetrahedral site versus Ti+Zr, shows that iron appears in tetrahedral coordination at a low value of Ti+Zr, and that the fraction of total iron in the tetrahedral site is approximately proportional to the Ti+Zr content. Some more precise figures may be obtained for the analyzed specimen, number 8 (Table 1). The total area for tetrahedral iron corresponds to 0.44 atoms. If this is subtracted from the silicon deficiency of 0.72 atoms, the remainder, 0.28 atoms, could be accounted for by aluminum, which totals 0.35 atoms, if one were inclined to prefer aluminum over titanium as a replacement for silicon. Note that if tetrahedral ferric iron alone, 0.27 atoms, is subtracted from the silicon deficiency, the remainder, 0.45 atoms, is larger than total aluminum; this implies that if there is no tetrahedral ferrous iron, some titanium is in the tetrahedral site.

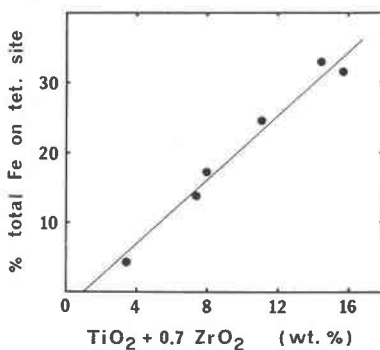The area for ferrous iron measured in the Mössbauer spectrum of

Fig. 4. Correlation of total iron in tetrahedral coordination with titanium and zirconium for specimens 4 through 9. ZrO_2 has been multiplied by 0.7 in order to convert roughly to the same mole percent scale as TiO_2.

specimen 8, corresponding to 0.17 atoms, accounts for most of that reported in the chemical analysis, 0.20 atoms. Its total, however, is somewhat less than the cation imbalance, 0.27 atoms. The difference between the cation imbalance and the area for ferrous iron suggests that some other two-valent cations are in the octahedral or tetrahedral sites, and the difference between the ferrous iron determined chemically and through Mössbauer areas leaves open the possibility that a small amount of Ti^{3+} (0.03 atoms) may be present. However, with respect to the latter, the difference is probably within the experimental error. Because of differences in relative recoil-free fractions, the value for tetrahedral Fe^{2+} may be somewhat high, but it is probable also that small amounts of 8-fold or octahedral ferrous iron have been overlooked. The existence of more than a very small amount of Ti^{3+} in this specimen is therefore rather unlikely, and a large amount is impossible.

Trends in the Parameters. Several of the parameters in Table 3 appear to show systematic variation through the titanian garnet series. The quadrupole splitting for both the O_1 and O_2 doublets increases with the amount of iron in the tetrahedral site in all the specimens including kimzeyite (but excepting specimen 4 in the case of the O_2 doublet). This is to be expected, as the local symmetry about the octahedral site decreases through the series, owing to increasingly heterogeneous population of the tetrahedral site and other disruptive influences.

The isomer shift for T_1 increases through the titanian garnet series (Fig. 5) and kimzeyite, but for the titanian garnet specimens, the highest values are still significantly lower than the values of 0.18 to 0.23 mm/sec reported for yttrium- and rare-earth-iron garnet (Nicholson and Burns, 1964), and very markedly lower than other values which have been reported for tetrahedral ferric iron in oxides and silicates. In orthoclase, for
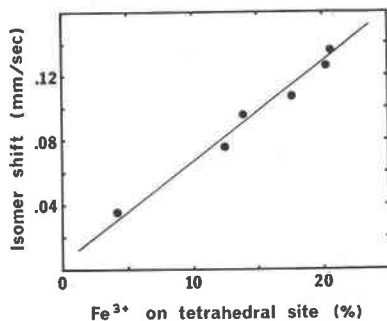

FIG. 5. Correlation of isomer shift of tetrahedral ferric iron with the amount of ferric iron in tetrahedral coordination (as a percentage of total iron).

example, tetrahedral Fe^{3+} has an isomer shift of .46 mm/sec (Brown and Pritchard, 1969). Nicholson and Burns considered the values they measured for tetrahedral ferric iron in synthetic garnet specimens to be exceptionally low, and this was taken by them and others (Van Loef, 1966) to be a possible indication of greater-than-normal covalency for this site. The isomer shift of the T_2 doublet also seems to be markedly lower than values which have been reported for tetrahedral ferrous iron (in staurolite and feldspar, for example, above). If the interpretation of the low values of isomer shift as due to increased covalency is correct, then the bonding of tetrahedral iron in titanian garnet must indeed be abnormally covalent with respect to oxides. Apparently, the covalency decreases somewhat as aluminum and iron are substituted for silicon. The implications of the idea of increased covalency will be discussed further below.

Infrared Spectra

The infrared spectra of specimens in the andradite-schorlomite series have been examined by Tarte (1961 and 1965) as part of a more extensive study of the spectra of natural garnet. He found that the spectra of nontitanian silicate garnet specimens with various cations in the X and Y positions were quite similar in general aspect, differing mainly in the exact location of the bands. The spectra of titanian garnet specimens, however, showed marked deviations from this pattern.

Representative spectra of specimens from the andradite-schorlomite series are shown in Figure 6. The titanian garnet spectra differ from the andradite spectrum in two important ways. First, a new, broad absorption appears at about 650 cm^{-1}, and its intensity increases with the titanium content. The new absorption in this area is indicated in Figure 6 by the hatching. Second, the spectrum loses definition, the sharp bands tending to become obscured. Tarte called particular attention to the region from 800 to 1000 cm^{-1}, the characteristic region for Si-O stretching vibrations, where four bands are distinguishable in the andradite spectrum, but only two diffuse ones in titanian garnet.

It is clear that both of these changes are related to the entrance of titanium into the structure; the new band at 650 cm^{-1} is probably caused by a cation or cations other than silicon occupying the tetrahedral site. In his 1961 paper, Tarte apparently failed to consider the possibility of aluminum and iron occupying the tetrahedral site, and assigned this band to tetrahedral titanium-oxygen stretching. In the later paper (1965), he reconsidered, and concluded that most of this absorption could be due to tetrahedral Al-O or Fe^{3+}-O. However, he pointed out two minor, sharp bands at 740 and 700 cm^{-1}, and suggested that these might be tetrahedral Ti^{4+}-O bands.
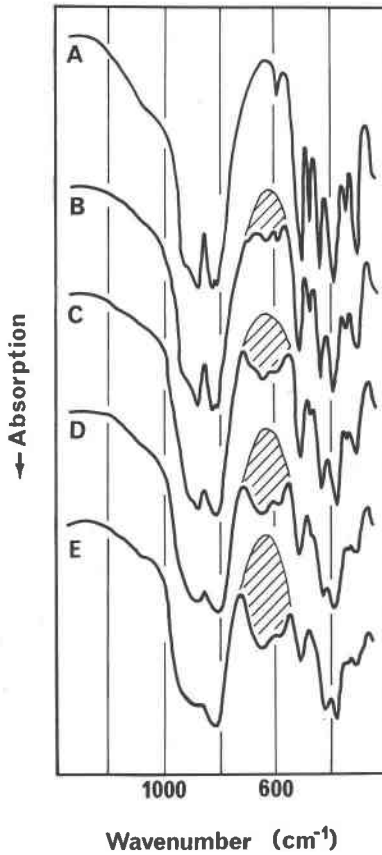
FIG. 6. Infrared spectra: (A) specimen 1, andradite; and (B)–(E) specimens 3, 6, 7, and 9, respectively, titanian garnet.

The spectra of synthetic yttrium-iron and yttrium-aluminum garnet are shown in Figure 7. The tetrahedral Fe^{3+}-O and Al-O stretching bands may be easily located in these spectra by analogy with the silicate garnet spectra; in YIG, the absorption centers at 600 cm^{-1}, and in YAG, between 700 and 800 cm^{-1}. The main part of both these absorptions are within the range of the new, broad band in titanian garnet. With respect to the sharp bands at 740 and 700 cm^{-1} mentioned by Tarte (only one of which is faintly visible in curves B and C in Figure 6, the one at 700 cm^{-1}) it may be noted that that spectrum of YAG shows two sharp bands at very nearly these locations. Therefore, the new absorptions centering at 650 cm^{-1} in the spectra of titanian garnet appear to be completely explicable as due to tetrahedral Fe^{3+}-O and Al-O stretching vibrations.
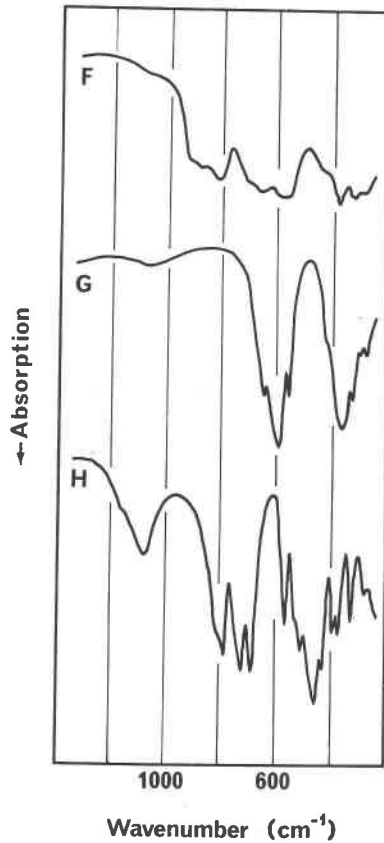
FIG. 7. Infrared spectra: (F) specimen 10, kimzeyite; (G) yttrium iron garnet; and (H) yttrium aluminum garnet.

The second feature of the titanian garnet spectra, the general deterioration, which Tarte attributed in his 1965 paper to the disruptive influence of titanium replacing silicon, is also much more likely to be caused by iron and aluminum replacing silicon. The substitution of three-valent iron or aluminum, rather than four-valent titanium, for some of the silicon, would produce heterogeneities in the local charge distribution at both the octahedral and tetrahedral sites which would be expected to lead to just this sort of blurring of the bands. Thus the infrared spectra at this level of analysis provide absolutely no justification for assigning titanium to the tetrahedral site.

The spectrum of kimzeyite (Figure 7) shows a much reduced Si-O band, and a band due to other tetrahedral cations which has a somewhat
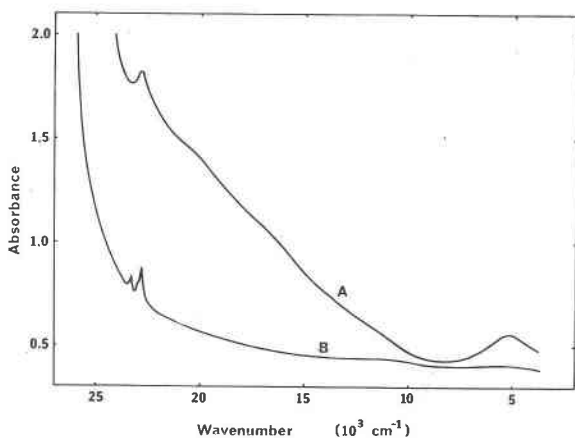
Fig. 8. Optical spectra: (A) specimen 8, zirconian schorlomite, thickness 0.04 mm; (B) specimen 2, andradite, thickness 0.07 mm. Curve (B) has been displaced downward about 0.4 absorbance units to facilitate comparison.

greater intensity. This is in good agreement with the original formula proposed for kimzeyite (Milton, Ingram, and Blade, 1961) wherein aluminum and iron totaling about two atoms out of three were assigned to tetrahedral coordination along with silicon, totaling about one atom.

The band at about 1100 cm^{-1} in the spectrum of YAG is somewhat of a mystery. Less intense bands at the same location are present in several of the other spectra shown in Figures 6 and 7, and in other published garnet spectra. This band may be due to a contaminant or to some other consequence of the experimental technique, although attempts failed to isolate a contaminant or remove it from the YAG sample. In any case, its presence does not seem to be particularly pertinent to the present discussion.

Optical Spectra

Visible and near-infrared spectra of titanian garnet specimens have been reported by Manning (1967), Manning and Harris (1970), and Moore and White (1971). Transmittance spectra of specimens 3, 6, 7, 8, and 10 have been taken in this study; a typical spectrum is shown in Figure 8.

All the titanian garnet spectra have two features which distinguish them from the spectra of ordinary andradites; an increased background absorption which slants upward with increasing wavenumber beginning at about 8,000 cm^{-1}, and a moderately intense band at about 5,000 cm^{-1}. The yellow to dark brown color of titanian garnet may be attributed to

the first feature. Manning (1967) and Manning and Harris (1970) also found a broad band at 18–19,000 cm⁻¹, but only in certain specimens from one locality, San Benito County, California. Manning assigned this band to the crystal field absorption of Ti^{3+} in the octahedral site, and originally ascribed the brown color to it, but Manning and Harris found that the specimens in which the band was most intense were actually pink, rather than brown. Moore and White also reported finding this band in diffuse reflectance spectra of several specimens, but since a transmittance spectrum of one of the same specimens did not show the band, and they apparently did not take a reflectance spectrum of andradite for comparison, their reflectance findings must be regarded as questionable.

The slanting increased background absorption in titanian garnet is very probably due to some type of charge transfer interaction. There are basically two types of charge transfers which must be considered as possible causes of this absorption: first, those involving direct transfer of an electron between two cations, and second, those involving anions either as receptors of charge or as intermediaries between two cations. The first type is often between two valence states of the same element, such as Fe^{3+} and Fe^{2+}, and requires that the cations be relatively close to each other; generally, their coordination polyhedra share edges. In garnet the octahedral and tetrahedral sites do not share edges among themselves or with each other; all edge sharing involves the eight-fold site. The only transition-metal cation likely to occupy the eight-fold site is Fe^{2+} (see also the cation-cation distances for garnet in Novak and Gibbs, 1971) As far as transfer between eight-fold Fe^{2+} and octahedral Fe^{3+} is concerned, the same possibility is present in ordinary andradite. We are left, then, with transfer between eight-fold Fe^{2+}, and either octahedral Ti^{4+} or tetrahedral Fe^{3+}, as the most likely possibilities for charge transfer of the first type. There is no definite ground for eliminating either of these, but on the other hand, there is no positive evidence that any eight-fold Fe^{2+} is present. In view of the latter, and the strength and shape of the increased background absorption in titananian garnet, it seems more likely that its cause is a transfer of the second type. An "absorption edge" due presumably to this type of transfer, involving Fe^{3+}, is present in andradite, but it does not impinge on the visible region, so that andradite is generally not strongly colored in transmitted light. The absorption edge is much stronger in synthetic YIG and other oxides with high Fe^{3+} contents (Wickersheim and Lefever, 1962).

Although the content of Fe^{3+} is not generally higher in titanian garnet than ordinary andradite, there are at least two alternate reasons why part of the absorption edge may be shifted to lower energy, leading to

more absorption in the visible region. First, if the transfer is basically cation-anion, tetrahedral Fe^{3+}-O bonds would be shorter than octahedral Fe^{3+}-O bonds, which might allow transfer at lower energy. Second, if the transfer is basically between two cations with oxygen only as intermediary, the different site distribution of iron in titanian garnet opens up possibilities of different interactions than in andradite. In particular, an electron could jump between octahedral Fe^{3+} and tetrahedral Fe^{3+} *via* an oxygen bonded to both cations, since the different polyhedra share corners. The octahedra do not share corners with each other, nor do the tetrahedra. An electron from octahedral Fe^{3+} would have to jump across two oxygens to reach another octahedral Fe^{3+} ion.

Octahedral Ti^{4+} might perform a role similar to Fe^{3+} in charge transfer, and increase the total area under the band, but by itself would not be expected to cause appreciable absorption in the visible, for the same reasons that octahedral Fe^{3+} alone does not. For example, if the charge of the octahedral Ti^{4+} were compensated solely by substitution of tetrahedral Al for Si, an increase in color would not be expected.

The transmittance spectra of all titanian garnet specimens from localities other than San Benito County show no definite evidence for the presence of a band at 18–19,000 cm^{-1} which could be assigned to Ti^{3+}; its presence in some San Benito specimens is therefore somewhat surprising. Crystal structural factors should be required to stabilize Ti^{3+} in the presence of Fe^{3+}, and it would be supposed that if these factors are operative in some specimens, they should be operative in all. The major element chemistry of San Benito specimens does not appear to be substantially different from that of other localities. Therefore, Manning's (1967) assignment of the 18–19,000 cm^{-1} band to Ti^{3+} must be regarded as questionable. It is suggested that this band is not due to Ti^{4+}, but to a crystal-field or charge-transfer absorption connected with some other element present in minor or trace quantities. San Benito specimens are unique in that they are found in secondary deposits associated with serpentinite, rather than in rocks of carbonatite or nepheline-syenite association which is the usual provenance of titanian garnet. The ultramafic-serpentinite environment carries larger quantities of first transition—period elements which are likely to give rise to such an absorption. It should be kept in mind that these elements may not give the same spectra that they normally do in end-member garnet types since their site distribution and/or valence may be different.

Alternatively, some of the San Benito specimens may be more reduced than those from other localities. If most of the iron were ferrous, not ferric, substantial quantities of Ti^{3+} might not be unexpected. Issacs (1968) reported a reducing capacity for one specimen from San Benito

County which is very much higher than any other in the literature for titanian garnet.

The band at 5,000 cm^{-1} was assigned by Manning (1967) to the crystal field absorption of tetrahedral ferrous iron. If the Mössbauer assignment of most of the ferrous iron to tetrahedral coordination is correct, and there is little or no Ti^{3+} present, this is, in fact, the only crystal field band that would be expected, since Fe^{3+} and Ti^{4+} do not have allowed crystal field absorptions. The tetrahedral ferrous iron band would be relatively strong, due to lack of a center of symmetry, and so would appear at low concentrations of Fe^{2+}.

There is also a possibility that the band could be due to a direct cation-cation charge transfer. Moore and White (1971) found that its temperature behavior was apparently not completely consistent with a crystal field absorption. They also found an increased electrical conductivity in titanian garnet over andradite and an activation energy in titanian garnet of about 3,800 cm^{-1} suggesting that some charge transfer was taking place in the region of the 5,000 cm^{-1} band. However, increased conductivity would also be expected from the shift of the absorption edge due to cation-anion interactions. From considerations given above, it seems that the only real possibilities for a direct cation-cation transfer would involve eight-fold Fe^{2+}, and lack of evidence for the presence of eight-fold Fe^{2+} does not lend support to these possibilities. The shape of the band also seems more characteristic of crystal field than charge transfer absorptions; it is actually composed of a closely spaced doublet (this is not apparent in Figure 10, but is shown clearly in Manning and Harris, 1971, Figure 4). Probably the choice between the two assignments should not be made on the basis of evidence discussed in this section alone, but the optical and Mössbauer results together do seem to indicate tetrahedral ferrous iron.

Bands in the neighborhood of 5,000 cm^{-1} in the spectra of diopside and enstatite were originally assigned by White and Keester (1966) to tetrahedral ferrous iron, but Bancroft and Burns (1967) showed that these bands were more reasonably explained on the basis of a non-degeneracy of the lower, t_{2g} state of octahedral ferrous iron, due to severe distortion. This would give a low-energy band not present for perfect octahedral coordination. The latter explanation is not acceptable in the present case, because no absorption is observed corresponding to the main, $t_{2g}-e_g$ splitting. This should give a band or bands centering at about 10,000 cm^{-1}. Furthermore, the high point symmetry of the octahedral site in garnet, $\bar{3}$, would not be conducive to a distortion large enough to produce appreciate splitting of the lower levels.

The spectrum of kimzeyite (not shown) is similar to those of the

titanian garnet specimens, except that both the background absorption and the band at 5,000 cm⁻¹ seem to be weaker. The difference in the background absorption causes kimzeyite to have a brownish yellow color in thin section, instead of the deeper brown of specimens with the same titanium content but less zirconium. It may be due to a somewhat lower total content of iron in kimzeyite, but it could be caused by elimination of most octahedral Fe^{3+}-O-tetrahedral Fe^{3+} charge transfer, since almost all of the ferric iron in kimzeyite is in the tetrahedral site.

The weakness of the 5,000 cm⁻¹ band suggests that there is very little ferrous iron in kimzeyite: none, in fact, was detected in the Mössbauer spectrum. Nor is there any evidence in the optical spectrum of a band at 18–22,000 cm⁻¹ which might indicate Ti^{3+}. These facts together are anomalous, since the original analysis of kimzeyite (Milton, Ingram, and Blade, 1961) reported a fairly large reducing capacity, equal to one-third of the iron or all of the titanium. It is possible that a large positive error in the determination of the reducing capacity was made in the original analysis of kimzeyite, or else some contaminant was present which caused a similar effect[1]. In Figure 2, it may be seen that the point representing kimzeyite, in the extreme upper right corner, is the point which is furthest from the predicted one-to-one line. The original analysis apparently gives a composition which is distinctly unstoichiometric; this deviation from stoichiometry is almost eliminated if it is assumed that there are essentially no reduced species present.

Tetrahedral Bonding in the Titanian Garnet Structure

As pointed out above, some traditional crystal chemical principles are not much help in predicting site occupancies of iron and titanium in garnet. In fact, the substitution of ferric iron, and particularly ferrous iron for silicon, are in violation of both Goldschmidt's radius ratio rule and Pauling's electrostatic valence rule. Of course, tetrahedral coordination of iron and even substitution of ferric iron for silicon are known in other substances; the present case may be regarded as another illustration of the limitations of such rules. The fact that unusually large cations are found to substitute for silicon may not be too surprising in view of the silicon "undersaturation" of the normal environment of formation of titanian garnet. Also, the garnet structure seems to be more than usually receptive to large cations in the tetrahedral site; for example, in cryolithionite, a type of garnet with fluorine as anion, the tetrahedral bonds are actually longer than the octahedral bonds (Geller, 1971). However,

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[1] Note added in proof: A re-analysis of kimzeyite by B. L. Ingram yielded a much smaller reducing capacity than that originally found.

the concern here is with the distribution of cations among sites in a mineral with a given composition. It is still surprising that ferric iron is preferred over titanium for the tetrahedral site, considering that the Ti^{4+} ion may actually be slightly smaller than Fe^{3+} and that Ti^{4+} should be more at home electrostatically in the tetrahedral site. The apparent substitution of ferrous iron for silicon is even more anomalous, with respect to both ionic radius and charge balance.

Therefore, it would seem that some special explanation is required for the inapplicability of the crystal chemical rules mentioned above. In the case of titanian garnet, the best guess seems to be that the covalency of the bonding plays a critical role. Although the radius ratio rule and electrostatic valence rule have been used with success in the solution of many problems in silicate crystallography, they are applicable in the strictest sense only for completely ionic bonding, and the silicon-oxygen bond is normally as much covalent as it is ionic. We have seen that the isomer shift of both ferric and ferrous iron in tetrahedral coordination is notably low in titanian garnet, which implies that the Fe-O bonding is somewhat more covalent than normal for tetrahedral sites in oxides and silicates.

Iron has a greater tendency to form covalent bonds than titanium, and this might be sufficient to cause it to be favored as a replacement for silicon in a site where the bonding is particularly covalent. A measure of the tendency to form covalent bonds is the electronegativity difference between the atoms involved; the smaller the difference, the more covalent character is expected. Since the anion is the same in all cases, oxygen, with electronegativity 3.5, the electronegativities of ferric and ferrous iron, 1.9 and 1.8 respectively, may be compared directly with those of silicon, 1.8, aluminum, 1.5, and titanium, 1.5 (values from Pauling, 1960, p. 93). The values for iron and silicon are similar, and somewhat higher than those for aluminum and titanium.

SUMMARY: SITE DISTRIBUTION AND VALENCE OF TITANIUM

Mössbauer spectra taken in the present study show that substantial quantities of ferric and probably ferrous iron assume tetrahedral coordination. The maximum possible amount of tetrahedral titanium is limited to the silicon deficiency minus the amount of tetrahedral iron; in most cases, this seems to be about half the silicon deficiency. Although it is most reasonable to assume that the portion of the silicon deficiency not accounted for by iron is due principally to aluminum, the possibility that some or even all of it could be due to tetrahedral titanium cannot be excluded on the basis of the evidence given in this paper. More data

are needed in order to determine quantitatively how much titanium, if any, is in the tetrahedral site.

In Part II, X-ray diffraction data will be given which hopefully will provide this extra information. X-ray refinement alone would not uniquely define the cation distribution, since there are at least three species involved, distributed over two sites. The X-ray scattering factor of titanium is intermediate to those of iron and aluminum, and thus a certain combination of iron and aluminum would give the same electron density on a particular site as titanium. Mössbauer data alone are not sufficient either, since they say nothing about the distribution of titanium *versus* aluminum. However, combined X-ray and Mössbauer data should furnish enough information to determine the site distribution of titanium, provided that the site distribution of other cations excepting aluminum and titanium can be assumed, that the Mössbauer assignments are complete and correct, and that the relative Mössbauer coefficients for the sites are known.

The evidence points toward the absence of three-valent titanium from most, if not all, titanian garnet. The optical spectra of specimens from all but one locality show no definite evidence for the presence of Ti^{3+}. Some specimens from San Benito County, however, do show a band in the optical spectrum which could be the crystal field absorption of Ti^{3+}, but it is also possible that this band could be caused by some other element. Further chemical work is necessary on these specimens. The brown color of titanian garnet is due to a charge-transfer process, probably a cation-anion transfer involving chiefly Fe^{3+}. The amount of ferrous iron detected in the Mössbauer spectrum of one specimen from Iron Hill accounts for almost all of the reducing capacity, and the remainder is within the error of the Mössbauer area ratio.

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