The role of titanium and the effect of TiO_2 *on the cell-size, refractive index, and specific gravity in the andradite–melanite–schorlomite series*

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Summary. New chemical analyses, cell-sizes, and specific gravities are given for 12 garnets, and TiO_2 values, cell-sizes, and refractive indices are presented for a further 33 garnets all belonging to the andradite–melanite–schorlomite series. The increase of refractive index, cell-size, and specific gravity with increasing titania is shown graphically. A plot of Ti against Si atoms in the unit cell suggests that Ti replaces Si rather than Fe^{3+} in the structure, while electron-probe results indicate that Si or (Si+Fe) may be replaced by Ti. The chemical and infra-red absorption data are considered in a discussion of the structural role of titanium in these garnets: both Ti^{4+} and Ti^{3+} may be present.

THE exact role of titanium in the andradite–melanite–schorlomite series has for long remained problematical. Zedlitz (1935) suggested that part of the titanium is present in the trivalent state, while Kunitz (1936), from a study of chemical data, concluded that the titanium replaces silicon. Tarte (1959, 1960, 1961, 1965), as a result of infra-red studies these on garnets, has suggested that the titanium replaces silicon and is present in the tetrahedral sites. Recent electron-microprobe studies of zoned titanian garnets (Lehijärvi, 1966; Isaacs, 1968) have shown that for the garnets investigated the content of titanium is inversely proportional to that of iron.

The published diagrams relating chemical composition of garnets to their physical properties do not allow for the titanium garnet series. It has long been known, however, that there is an increase of refractive index with increasing titanium content (Washington, 1920; Kunitz, 1936), while Zedlitz (1933, 1935) has shown that the cell dimensions increase linearly in proportion to the titanium, a conclusion that has recently been confirmed for synthetic garnets along the andradite–schorlomite join (Ito and Frondel, 1967).

The relative rarity of these garnets has restricted past workers to the investigation of only a few specimens, but the recent increase of interest in the alkaline rocks and carbonatites, among which titanian garnet is often an important rock-forming mineral, has made more material available for study. Many of the garnets investigated are from well-documented localities: brief references to the occurrences of some of the garnets from less well known localities whose analyses are here reported are given by Sukheswala, Udas, and Heinrich (1965) for the melanite from the Amba Dongar carbonatite (anal. 6), by Agard (1960) for the schorlomite from the Tamazert carbonatite (anal. 8), and by Ruxton (1956) for the schorlomite associated with grossular, idocrase, and diopside in a skarn zone, some four square miles in area, around a norite intruded into calcareous sediments at Dirbat Well (36° 29′ E., 19° 55′ N.), Sudan (anal. 9). Magnet Cove, Arkansas, is the original locality for schorlomite (Koenig, 1886); the alkaline igneous rocks of this area containing schorlomite (anal. 11) have been described recently by Erickson and Blade (1963).

The new chemical analyses of table I were made using classical methods, in general those of Washington (1930) modified by the spectrophotometric determination of total iron using 2,2′-dipyridyl and by the flame-photometric determination of the small amounts of alkalis present. The analyses were carried out after the specific gravities of the pure mineral powders had been determined in a pycnometer over a period of 8–10 days and the powders air-dried at 105° C. The specimens subjected to full chemical analyses were selected from several times their number to show a range in TiO_2 content, on the basis of preliminary spectrophotometric determinations, and after examination in thin section to reject those showing obvious zoning, an extremely common feature in many of these garnets. The determination of ferrous iron in these garnets is difficult due to their resistance to attack in a gently boiling mixture of HF and H_2SO_4 and to the dark colour of the resulting solution, which makes the titrimetric end-point difficult to detect. Reproducible results were, however, obtained when the determinations were repeated five times, the acid attack being continued for up to 20 min. In several of the analyses of table I (anals. 5, 6, 7, 10, and 11) the Fe^{3+}/Fe^{2+} ratios can be seen to be unsatisfactory; the Fe^{2+} is apparently too high, bringing the X group to above 6·0, whereas the Y group is below the ideal value of 4·0 by an equivalent amount, i.e. the sum of the X and Y group ions approximates closely to the ideal value of 10·0. The direction of this error is the opposite to what would arise from incomplete attack or from oxidation during the process. The optical absorption spectra (see later) suggest that some of the Ti in garnets of this series is present as Ti^{3+} in addition to the normal Ti^{4+} state: such trivalent ions would not be analytically distinguished from quadrivalent ions in the determination of titanium. The titration against potassium dichromate to determine ferrous iron measures only the total oxidation state in the sample (usually assumed to be due to the oxidation of Fe^{2+} to Fe^{3+}, but also affected by the presence of other multivalent ions such as Mn, V, and, as in this case, Ti). The separate TiO_2 determinations were done spectrophotometrically by A. J. Easton using the yellow peroxide complex, phosphoric acid being added to complex any iron present.

Physical properties. In thin-section the colour of the titanian garnets varies from colourless to pale-yellow or brown at the andradite end to black in the schorlomites, with intermediate shades of yellow or brown. That the depth of colour is related to the titanium content, and not to the iron, is rather well shown by material from the Borolan Complex in Scotland. Melanite is a ubiquitous component, by definition, of the rock borolanite, and this garnet contains about 4 % TiO_2 (table I, no. 4) and is commonly altered to sphene (30 to 40 % TiO_2). In the immediate vicinity of the sphene crystals the garnet is drained of its usual brown colour and becomes a honey yellow. It would seem, therefore, that the preferential concentration of the titanium in the sphene is responsible for the loss in the depth of colour of the surrounding garnet. The dependence of the colour on the titanium content is also confirmed by electron-probe traverses across garnets that are zoned from pale yellow or almost colourless to deep brown (fig. 4, A and B). The iron is essentially constant across the colour zones, while the titanium increases in proportion to the depth of colour.

On fig. 1 (*a*) are plotted refractive indices against weight percent TiO_2 for the data presented in table II, with a number of determinations taken from the literature. There is a considerable scatter at the high titania end, which is probably partly to be accounted for by the difficulties of measurement entailed by the deep brown colour of these garnets. The new data at the high-titania end plot consistently lower

TABLE I. New analyses of titanium garnets

	1	2	3	4	5	6	7	8	9	10	11	12
SiO_2	36·59	35·76	35·31	33·58	31·66	30·41	34·01	31·35	28·15	27·01	26·76	28·52
TiO_2	0·45	1·27	2·51	3·96	4·70	7·70	8·44	8·65	13·24	14·30	14·46	15·10
Al_2O_3	4·98	10·75	4·09	2·61	4·23	3·29	2·69	1·44	5·85	5·38	5·36	2·12
Fe_2O_3	25·59	17·49	24·87	24·63	24·56	23·06	19·24	23·73	20·37	16·45	16·90	18·25
FeO	0·19	1·95	4·47	1·67	2·10	2·24	2·26	2·00	0·75	5·44	3·37	4·15
MnO	0·35	1·54	0·66	0·69	0·69	0·28	0·03	0·65	0·25	0·34	0·70	0·65
MgO	0·87	1·14	0·65	0·84	tr.	0·43	0·80	0·69	0·94	0·62	1·43	0·49
CaO	31·06	29·75	27·01	30·04	31·61	31·80	32·14	30·79	30·48	30·76	30·91	31·03
Na_2O	—	—	0·45	—	0·25	0·31	0·12	—	—	—	—	—
K_2O	—	—	0·14	—	—	0·09	0·02	—	—	—	—	—
Total	100·08	99·65	100·16	98·02	99·80	99·52	99·75	99·30	100·03	100·30	99·89	100·31
Numbers of metal ions on the basis of 24 oxygens												
Si	5·991	5·772	5·867	5·717	5·349	5·162	5·635	5·325	4·677	4·554	4·507	4·816
Ti	0·009	0·154	0·133	0·283	0·597	0·838	0·365	0·675	1·323	1·446	1·493	1·184
Al	—	0·074	—	—	0·054	—	—	—	—	—	—	—
Ti	0·046	—	0·180	0·224	—	0·145	0·687	0·430	0·331	0·368	0·339	0·734
Al	0·961	1·971	0·801	0·524	0·789	0·659	0·526	0·288	1·145	1·070	1·064	0·422
Fe^{3+}	3·153	2·124	3·109	3·156	3·122	2·946	2·389	3·034	2·547	2·087	2·142	2·320
ΣY	4·160	4·095	4·090	3·904	3·911	3·750	3·602	3·752	4·023	3·525	3·545	3·476

Fe^{2+}	0·026	0·263	0·621	0·238	0·296	0·318	0·313	0·284	0·104	0·768	0·475	0·587
Mn	0·049	0·211	0·093	0·099	0·099	0·040	0·004	0·093	0·035	0·049	0·100	0·093
Mg	0·212	0·275	0·161	0·213	—	0·108	0·197	0·174	0·232	0·156	0·359	0·123
Ca	5·450	5·146	4·809	5·481	5·723	5·784	5·705	5·604	5·427	5·557	5·579	5·615
Na	—	—	0·146	—	0·081	0·100	0·038	—	—	—	—	—
K	—	—	0·030	—	—	—	0·004	—	—	—	—	—
ΣX	5·737	5·895	5·860	6·031	6·199	6·350	6·261	6·155	5·798	6·530	6·513	6·418
$\Sigma X+Y$	9·897	9·990	9·950	9·935	10·110	10·100	9·863	9·907	9·821	10·055	10·058	9·894
a (Å)	12·030	11·962	12·020	12·068	12·061	12·075	12·085	12·096	12·104	—	12·133	12·151
D	3·73	3·75	3·75	3·77	3·78	3·83	3·82	3·854	3·813	—	3·916	3·88

1. Andradite, alkali syenite, Semarule, Botswana (anal. R. C. Tyler).
2. Melanite crystal, Monte Somma, Vesuvius (anal. R. C. Tyler).
3. Melanite crystal (loc. unknown) (anal. R. C. Tyler).
4. Melanite, nepheline syenite, Loch Borolan, Scotland (anal. R. C. Tyler).
5. Melanite, jacupirangite, Iron Hill, Colorado (anal. J. N. Walsh).
6. Melanite, ijolite, carbonatite complex, Amba Dongar, Gujarat State, India (anal. J. N. Walsh).
7. Melanite, on serpentinite, near Dallas gem mine, San Benito Co., California (anal. J. N. Walsh).
8. Schorlomite, carbonatite, Tamazert, Haut Atlas de Midelt, Morocco (anal. R. C. Tyler).
9. Schorlomite, skarn, Dirbat Well, Northern Red Sea Hills, Sudan (anal. R. A. Howie).
10. Schorlomite, pegmatite with ferroan wollastonite and titanaugite, 1100 yd E. 15° S. of Camphouse, Ardnamurchan, Scotland (anal. J. H. Scoon).
11. Schorlomite, carbonatite complex, Magnet Cove, Arkansas (anal. J. N. Walsh).
12. Schorlomite, melanite–nephelinite agglomerate, Rusinga Island, Kenya (anal. R. C. Tyler).

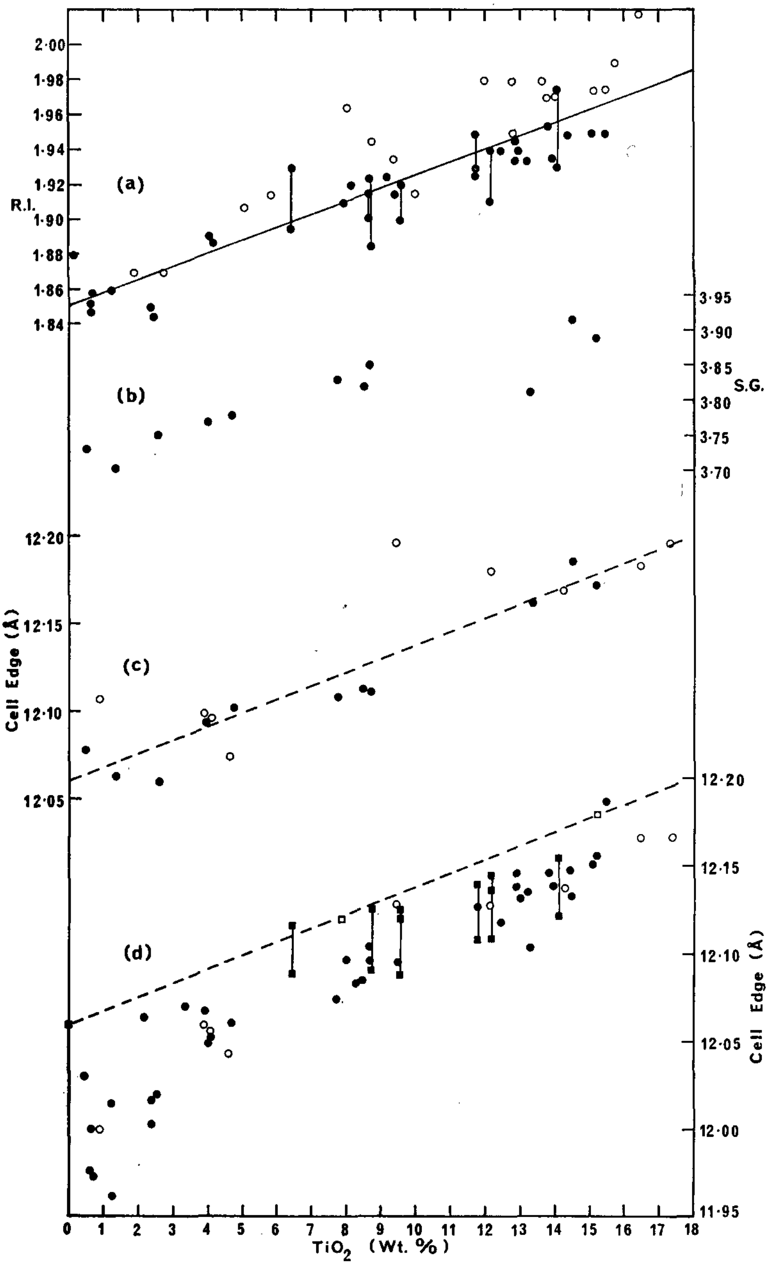

FIG. 1. (*a*) Variation of refractive index against wt. % TiO_2; tie lines indicate range of refractive indices of zoned garnets. (*b*) Variation of specific gravity against wt. % TiO_2 for data given in table I. (*c*) Variation of cell-size against wt. % TiO_2 adjusted to allow for grossular content. (*d*) Variation of cell-size against wt. % TiO_2; tie lines join multiphase garnet values.

● = New data. W ○ Data taken from literature. ——□—— = Synthetic andradite–schorlomite series (Ito and Frondel, 1967).

than the data taken from the literature. A number of the specimens have a range of refractive index, related to zoning, and for these lines have been drawn showing the range of values measured. The titania values for such garnets are, of course, bulk compositional values, but if the extreme titania values were known the tie lines would be rotated in a clockwise direction. The slope of the line on fig. 1 is somewhat flatter and the line itself is rather lower than that inferred by Kunitz on the basis of six analyses (1936, fig. 1).

TABLE II. Cell-size, refractive index, and TiO_2 content of 33 garnets

	Wt. % TiO_2	n	Cell-size (Å)
1.	9·43	1·915	12·096 ±0·002
2.	0·63	1·86	12·000 ±0·001
3.	0·67	1·85	11·9735 ±0·002
4.	0·63	1·85	11·976 ±0·002
5.	$< 0{\cdot}05$	1·88	12·055 ±0·002
6.	15·20	1·95	12·156 ±0·001
7.	1·23	1·86	12·015 ±0·001
8.	4·04	1·89	12·049 ±0·002
9.	4·09	1·89	12·056
10.	2·37	1·85	12·017 ±0·002
11.	2·40	1·845	12·0035 ±0·001
12.	9·20	1·925	—
13.	15·45	1·95	12·187 ±0·001
14.	2·18	1·87	12·064 ±0·001
15.	12·85	1·935	12·139 ±0·002
16.	13·94	1·935	12·139 ±0·002
17.	13·17	1·935	12·135 ±0·001
18.	8·00	1·91	12·097 ±0·001
19.	12·44	1·94	12·118 ±0·002
20.	12·98	1·94	12·131 ±0·001
21.	13·80	1·955	12·147 ±0·002
22.	8·14	1·92	—
23.	11·72	1·93–1·95	12·1395 ±0·002 12·109 ±0·002
24.	12·13	1·91–1·94	12·145 ±0·002 12·137 ±0·002 12·109 ±0·001
25.	12·88	1·945	12·146 ±0·002
26.	14·03	1·93–1·965	12·155 ±0·003 12·121 ±0·001
27.	14·39	1·95	12·148 ±0·002
28.	11·73	1·925	12·127 ±0·002
29.	8·65	1·90–1·915	12·1065 ±0·001 12·106 ±0·001
30.	8·68	1·885–1·925	12·0915 ±0·001 12·126 ±0·004
31.	9·54	1·90–1·92	12·127 ±0·003 12·120 ±0·002 12·085 ±0·002
32.	6·41	1·895–1·93	12·117 ±0·0005 12·089 ±0·001
33.	—	1·92–1·93	12·122 ±0·002 12·1425 ±0·002

TiO_2 determinations by A. J. Easton. TiO_2 of 7 from Sturt and Ramsay (1965, p. 159); 9 from Deer, Howie, and Zussman (1962, p. 91, anal. 8).

1. Fen Complex, Norway (B.M. 1942, 72(6)).
2. Arendal, Norway (B.M. 14394).
3. Arendal, Norway (B.M. 34083).
4. Gjerestad, Nedenaes, Norway (B.M. 1912, 588).
5. Philipstad, Wermland, Sweden (B.M. 28709).
6. Iivaara, Finland (B.M. 50014).
7. Sørøy, Northern Norway.
8. Borolan Complex, Scotland (B98).
9. Kangerdlugssuaq, E. Greenland.
10. Kaiserstuhl, Germany (B.M. 51587).
11. Frascati, Rome, Italy (B.M. 55150).
12. Magnet Cove, Arkansas, U.S.A. (B.M. 32024).
13. Magnet Cove, Arkansas, U.S.A. (B.M. 32025).
14. Semarule, Botswana.
15. Rusinga Island, Kenya.
16. Rusinga Island, Kenya (B.M. 1942, 51).
17. Ankole, Uganda (B.M. 1938, 1267).

Specimens 18 to 33 from Napak Complex of Uganda. Specimens 14, 15, and 18 to 33 from Department of Geology, Bedford College. B.M. numbers in the collection of the Department of Mineralogy, British Museum (Natural History). Specimen 8 from the author's collection.

The specific gravities for the garnets of table I are plotted against weight percent TiO_2 on fig. 1 (*b*), where the influence of titanium is evident. The specific gravity data given in the compilation of Sobolev (1964) were found to give a random scatter.

The data now available relating cell-size to weight percent TiO_2 are assembled in fig. 1 (*d*). The resulting plot coincides almost exactly with that produced by Zedlitz (1933) using only three points. In the X-ray powder patterns certain of the Napak garnets show doubling and even tripling of some of the high angle reflections, which correspond to two and three garnet phases. The calculated cell-sizes are given in tables I and II and the results from multiphase garnets are linked by tie-lines in fig. 1 (*d*). The dashed line joins points determined on synthetic material by Ito and Frondel (1967). The smaller cell of the natural material when compared with the synthetic, particularly at the low titania end, is almost certainly to be ascribed to the ubiquitous aluminium of the natural garnets, which is, in terms of number of atoms, often as abundant as titanium. To test this the measured cell-sizes were corrected for the molecular percentage of the grossular molecule present, using the values for pure synthetic grossular and andradite. These calculated cell-sizes have been plotted as fig. 1 (*c*), and it will be seen that their trend now approximates the curve of Ito and Frondel.

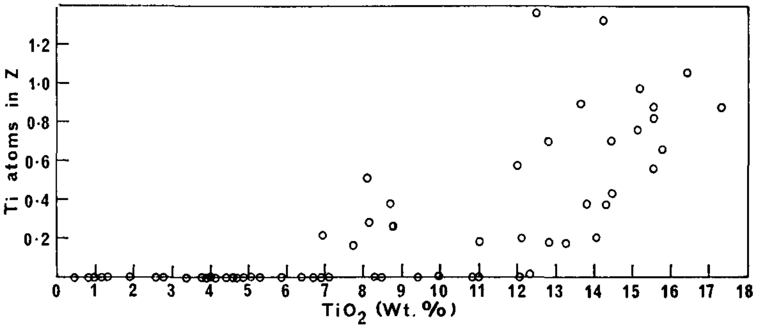

FIG. 2. Plot of wt. % TiO_2 against Ti in the *Z* position after putting Al in *Z* preferentially.

Chemistry. It has for a long time been realized that when calculating a molecular formula for the garnets that are very rich in titanium there is often a deficiency in the *Z* group after including all available Al with the Si, and that to make up the total it is necessary to include a part of the titanium. This point is brought out by fig. 2 which shows that the *Z* group deficiency for garnets with more than 7 to 8 % TiO_2 necessitates the entry of Ti to bring the *Z* group metal ions up to the ideal value of 6·0. To investigate further the chemical relationships that might exist between the titanium and the silicon, ferric iron, and aluminium, fig. 3 has been constructed using analyses taken from the

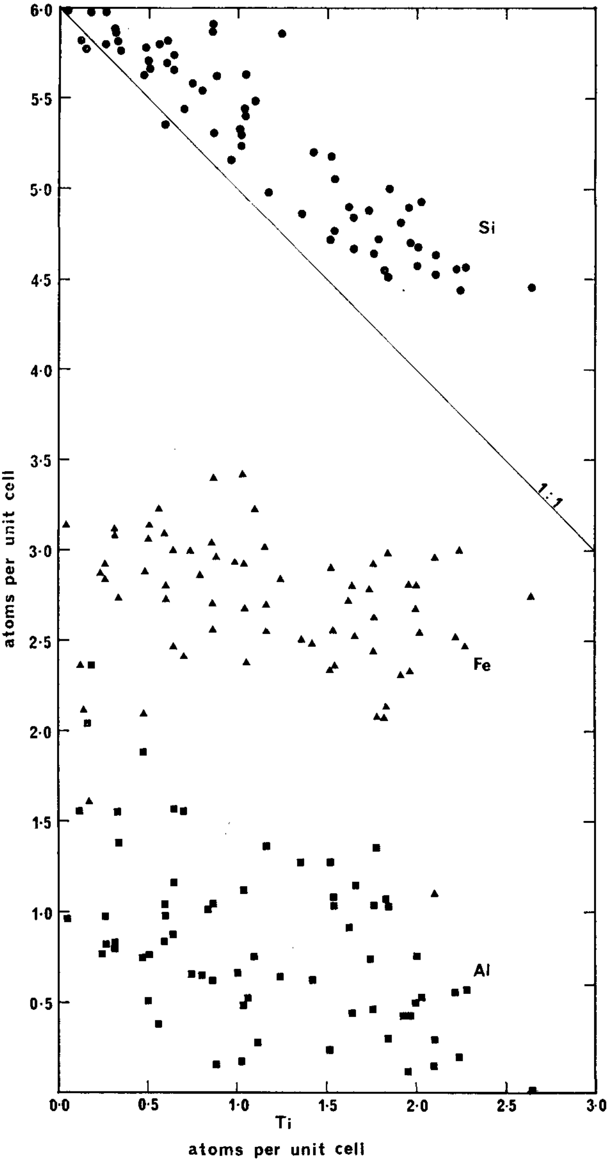

FIG. 3. Plot of atoms of Ti against Si, Fe^{3+}, and Al on the basis of 24 oxygens. ● = Si; ▲ = Fe^{3+}; ■ = Al. The diagonal line indicates the slope for 1 : 1 replacement of Si by Ti. Data from Sobolev (1964) and table I.

literature and from table I. The correlation coefficients are Ti:Fe^{3+} $r = 0{\cdot}1607$, Ti:Al $r = 0{\cdot}5319$, Ti:Si $r = 0{\cdot}9138$, all with 63° of freedom. The first is clearly insignificant, the second is significant at the 0·1 % level, and the third is highly significant ($\leqslant 0{\cdot}1$ % level). These results suggest that titanium in the titanian garnets increases principally at the expense of silicon, confirming the opinion of Kunitz (1936). The plots of Si against Ti lie above the line of 1:1 replacement; indeed there are usually about one and a half times as many titanium atoms as 'missing' silicon atoms; therefore, either the titanium replaces another element besides silicon, in which case the titanium occupies both the *Z* and *Y* sites, or there may be vacancies in the Si sites. The correlation coefficients point to a replacement of aluminium, but not of ferric iron, by titanium. The lack of correlation between titanium and iron is at variance with the electron-probe results of Lehijärvi (1966) and Isaacs (1968). To clarify this apparent discrepancy a number of traverses with an electron-probe were made across zoned garnets to investigate the relations among Si, Fe, and Ti. The garnets chosen were from melanite ijolites of the Usaki Complex, south Nyanza, Kenya. They are particularly suitable because the majority of the garnet individuals have an homogeneous, very dark brown, and therefore highly titanian core surrounded by a narrow, strongly defined rim that quickly passes outwards into almost pure andradite. The traverse results and photomicrographs of the garnets are given as fig. 4, A, B, and C. A and B are seen to be similar and show an increasing titanium content matched by decreasing silicon; the iron is effectively constant. These results appear to substantiate the conclusions based on the chemical evidence. However, fig. 4 C, representing a traverse across a small garnet in another specimen of ijolite, shows titanium values inversely proportional to iron as well as to silicon, although the relative importance of iron and silicon in any replacement has not been determined. The iron–titanium relationship discovered by Lehijärvi (1966) and Isaacs (1968) has thus been confirmed for garnets from one rock, but it would appear that this relationship does not hold invariably; indeed the inverse relationship between silicon and titanium seems to be the more usual and fundamental. This inverse relationship between Si and Ti has also been shown in electron-probe runs by Leake (1968).

The strong negative correlation between silicon and titanium suggests that in assigning a molecular formula to these garnets titanium should be placed in the *Z* group in preference to aluminium, a procedure that has been followed by Sobolev (1964) and is also adopted here (table I).

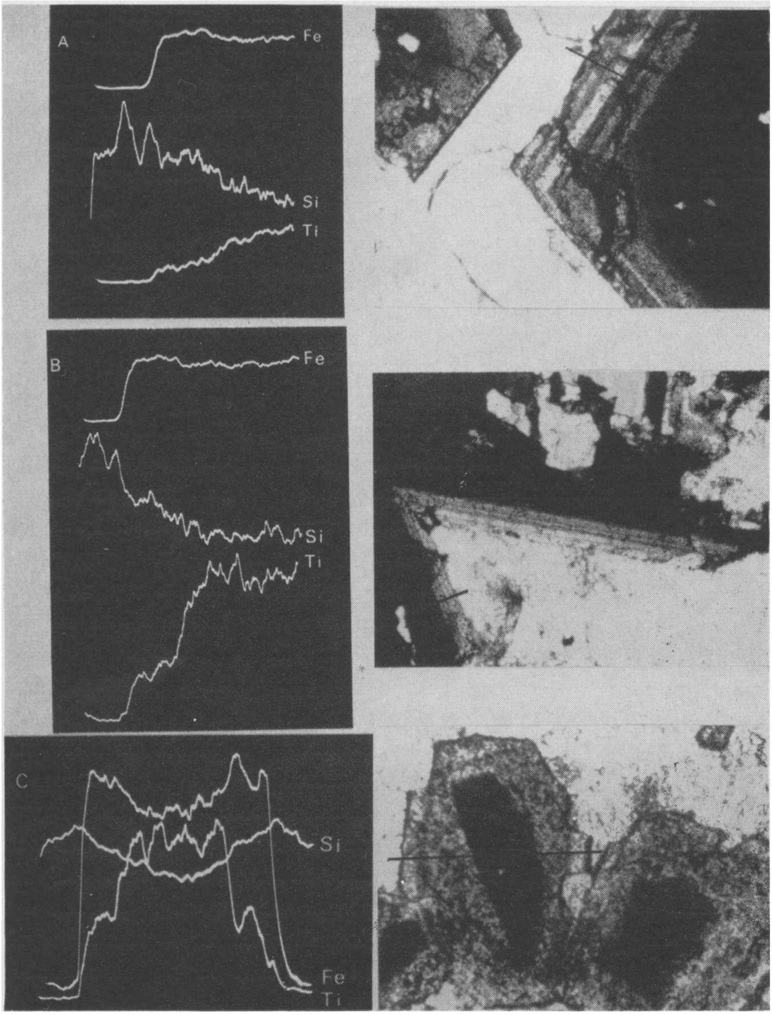

FIG. 4. Electron-probe traverses across zoned garnets from melanite ijolites of the Usaki Complex, Kenya, to determine titanium, silicon, and iron. The path of each traverse is indicated by lines on the photomicrographs.

It may be noteworthy that garnets in the middle titania range, 5 to 8 %, are relatively rare, and this gap tends to separate garnets of different parageneses. As might be expected the titania-poorer garnets are developed dominantly in syenites and nepheline syenites, while the garnets richest in titania (and low in silica) are concentrated in rocks characterized by extreme silica under-saturation—the ijolites. However, in certain melanite ijolites, such as those of the Usaki Complex and the Napak Complex of Uganda (King and Sutherland, 1966, p. 108), high-titanium garnets are rimmed by almost pure andradite, and in the case of the Napak rocks individual andradite crystals are also present. The coexistence of titanium-rich and titanium-poor garnets, and the dearth of garnets in the 5 to 8 % TiO_2 range, suggests that there may be an immiscibility gap in the titanian garnet series, a conclusion also reached by B. C. King (personal communication).

The structural role of titanium. The principal problem presented by the titanian garnets hinges on the structural role of the titanium ion. There are several possibilities for the garnets with high TiO_2 values. The titanium may be tetrahedrally co-ordinated, i.e. substituting for silicon; there may be vacancies in the tetrahedrally co-ordinated positions, the titanium being octahedrally co-ordinated; or titanium may be shared between the tetrahedral and octahedral sites. It seems unlikely that this problem can be resolved without a full structural study, but there are a number of ancillary approaches, such as calculations based on analytical data and the use of infra-red absorption techniques, that seem to shed some light on the problem.

The chemical evidence already cited suggests a strong interdependence of silicon and titanium, and hence either that some of the titanium is tetrahedral or that there are vacant sites in the Si positions. The concept of vacant sites would explain the shortage of silicon but does not dispose of the problem of the excess of titanium, which must then occupy sites in the *Y* group in the more titanium-rich garnets. Chemical analyses do not furnish any information as to the valency state of the titanium. In most geological environments, however, it appears to have a valency of four. The ionic radius of Ti^{4+} is smaller than that of Ti^{3+} and this would make it more probable that the titanium found to be replacing silicon is present as Ti^{4+}.

As a result of work on Zn_2SiO_4, Zn_2TiO_4, $Zn_2(Si,Ti)O_4$, and $Zn_2(Si,Ge)O_4$, and the corresponding barium compounds, Tarte claims to be able to identify the characteristic infra-red absorption bands of tetrahedral and octahedral titanium (1961, p. 1002). One of the new absorption bands that occurs when titanium is substituted for silicon in $Zn_2(Si,Ti)O_4$ is at 750 cm^{-1}, and is proportional to the amount of titanium substituted, and this band is within the absorption range of (GeO_4) tetrahedra as observed in orthogermanates (Tarte, 1961, p. 1002). Similar results were obtained for $Zn_2(Si,Ge)O_4$ and therefore, Tarte concludes, this is an important reason for considering that the titanium is present as (TiO_4) tetrahedra. The work on the barium compounds seems to confirm this. His results for the garnets (1959, 1965) show that in general the characteristic infra-red absorption of the silicate group is not modified by the isomorphous replacement Fe^{2+}–Mg–Mn or Al–Fe^{3+}–Cr^{3+} in the *X* or *Y* groups (1959, p. 172). The spectra of titanian garnets, however, are modified in two ways: a new absorption band occurs in the region 650 cm^{-1}, and the profile of the part of the spectrum caused by the silicate group is changed in the range 800 to 1000 cm^{-1} (Tarte, 1959, p. 172). The magnitude of the change is proportional to the titanium content of the garnets. Tarte argues that the absence of the 650 cm^{-1} band in the non-titanian garnets points to its generation by titanium, and further that a comparison of the titanian garnet spectra with the spectra of (TiO_4)- and (TiO_6)-bearing compounds suggests that the 650 cm^{-1} band is promoted by tetrahedral (TiO_4) groups. The modification of the spectrum in the 800 to 1000 cm^{-1} range could not, he claims, be caused by octahedral titanium, because octahedrally co-ordinated aluminium and iron do not cause such changes. A broad *d–d* absorption band was reported by Manning (1967) in the optical absorption spectra of a melanite (4·9 % Ti) at 19 000 cm^{-1}, and assigned to octahedrally bonded Ti^{3+}. No evidence is available from Manning's work, however, on the presence or absence of Ti^{4+} and it seems likely that titanium is present in both valency states in the titanium garnets, possibly with Ti^{4+} concentrated in the tetrahedral positions and Ti^{3+} in the octahedral positions.

C. J. Elliott of the Mineralogy Department, British Museum (Natural History) has recorded the spectra of all the garnets included in table II on a Grubb–Parsons Spectromaster in the region 2000 to 400 cm^{-1}, using a Nujol mull pressed between polished KBr plates. Tarte's results on the garnets are confirmed by this work, and a range of the spectra obtained are presented in fig. 5. Although the infra-red results cannot, at present, be relied upon absolutely to confirm or disprove the presence of tetrahedral titanium, it would seem that the modifications of the spectra in the 800 to 1000 cm^{-1} range, as they are proportional to the TiO_2 content, suggest that the titanium is having an additive effect on the silicate part of the molecule. The consistent growth of the 650 cm^{-1} band with increasing TiO_2 is well shown by fig. 5, but this band is rather broad and, as fig. 3 indicates, there is probably an increase of octahedral titanium approximately proportional to the over-all

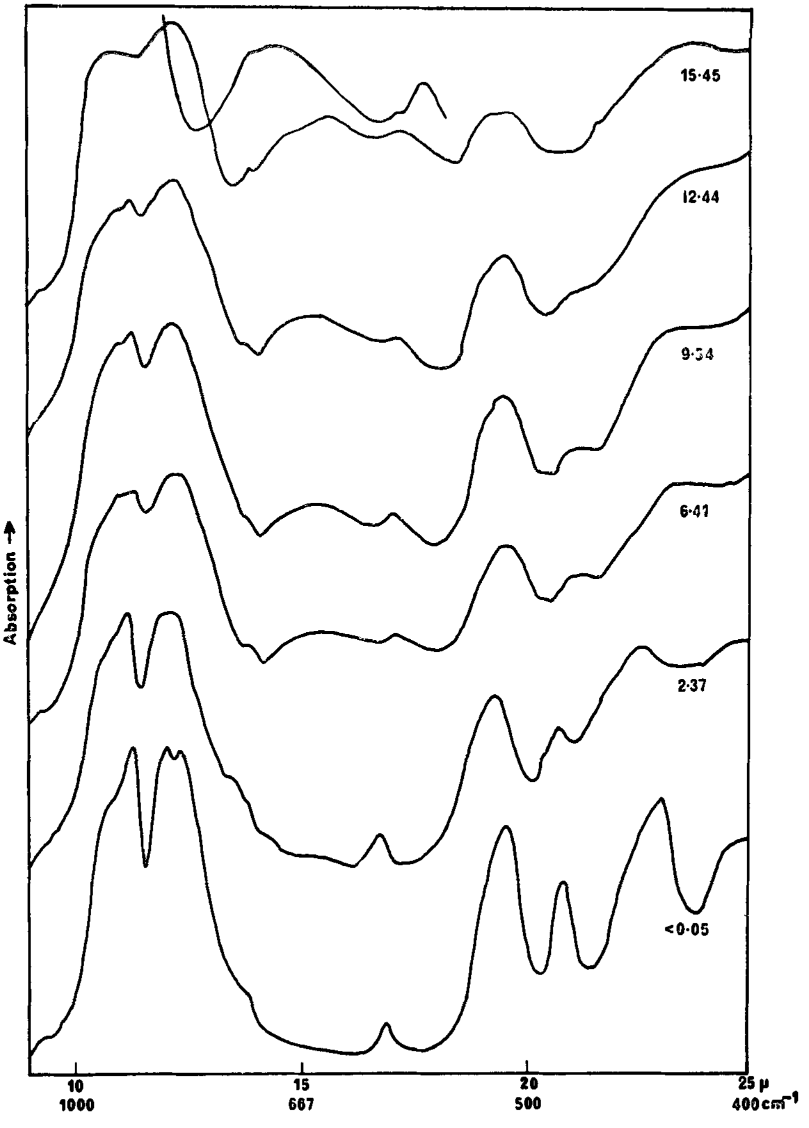

FIG. 5. Infra-red absorption spectra for a range of titanian garnets and for sphene. The weight percentage of TiO_2 for each garnet is indicated on the right-hand side. The change in profile of the absorption in the range 800 to 1000 cm^{-1} and the growth of a band at 650 cm^{-1} with increasing TiO_2 is noteworthy. Part of a sphene spectrum is shown at the top of the diagram, and attention is drawn to its similarity to the spectra of the garnets richer in titanium.

titanium increase, and thus a part of the increasing infra-red absorption in the 650 cm^{-1} region may be due to this.

Some doubt as to the interpretation of the 650 cm^{-1} absorption as being due to (TiO_4) tetrahedra is suggested by the spectra of sphene that have been obtained by Elliott, part of one of which is shown at the top of fig. 5. This shows a broad medium absorption between 667 and 700 cm^{-1}, which can be assigned to (TiO_6) octahedra, as previous structural work has shown the titanium to be in octahedral sites (Zachariasen, 1930). Tarte, however, notes that octahedrally co-ordinated titanium absorbs in the 600 to 500 cm^{-1} range, not above 600 cm^{-1} (1961, p. 1002). These results for sphene suggest, therefore, that the assignment of the 650 cm^{-1} absorption to tetrahedral titanium alone should be treated with some caution.

Nomenclature. Titanium-bearing Ca–Fe garnets have been called melanite and the more titanium-rich types schorlomite. Although Lehijärvi (1960) preferred to use the name iivaarite for the titanium-rich Ca–Fe garnets of Iivaara, Kuusamo, Finland, on the grounds that this name had been used for these garnets as early as 1852 by Nordenskiöld, this name has not been generally adopted and is unfamiliar to most mineralogists. Although Zedlitz (1933) proposed a boundary between melanite and schorlomite at 15 % TiO_2 this seems too high and we here propose that the boundary be placed at 1·0 Ti in the structural formula when calculated on the basis of 24 oxygens: this would amount to a TiO_2 content of approximately 8 %. Such a division is supported by the evidence of fig. 2, which shows that at about this point some Ti has to be accommodated with Si in the tetrahedral sites, and may also be of petrological significance in that it splits the occurrence of melanite in syenites and nepheline syenites from that of schorlomite in rocks extremely under-saturated with respect to silica—the ijolites and carbonatite assemblages.

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