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SYNTHETIC ZIRCONIUM AND TITANIUM GARNETS

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ABSTRACT

Nearly complete solid solubility is found at 1050°C in the ternary system $Ca_3Fe_2Si_3O_{12}$ (andradite)-$Ca_3Zr_2Fe_2SiO_{12}$ (kimzeyite)-$Ca_3Ti_2Fe_2SiO_{12}$ (schorlomite). A small solubility gap exists near the center of the field, and is associated with abnormal changes of *a* with composition. Some compositions in this region break down on prolonged heating at 1050°C into a mixture of two garnet solid solutions. The syntheses were effected by sintering co-precipitated gels of the desired composition at 1050°C in air for 20 hours.

Thirteen successful and 12 unsuccessful syntheses of garnets containing Zr but with compositions outside of the ternary field stated also are reported. Evidence is given that Zr can go into both 8 and 6 coordination and Ti into both 6 and 4 coordination in garnets.

TABLE 1. GARNET COMPOSITIONS SYNTHESIZED

A: $Ca_3Fe_2Si_3O_{12}$; K: $Ca_3Zr_2Fe_2SiO_{12}$; S: $Ca_3Ti_2Fe_2SiO_{12}$

Composition	*a*, (Å)	Composition	*a*, (Å)
A75-S25	12.12	A	12.06
A50-S50	12.18	K	12.62
A25-S75	12.24	S	12.27
A75-K25	12.22	A25-K40-S35	12.38
A50-K50	12.38	A32.8-K34.5-S32.8	12.34
A25-K75	12.51	A33.1-K33.9-S33.1	12.34
S75-K25	12.38	A33.8-K32.5-S33.8	12.34
S50-K50	12.47	A32.5-K32.5-S35	12.35
S25-K75	12.57	A35-K35-S30	12.36
A33.3-K33.3-S33.3	12.43	A35-K30-S35	12.34
A66.6-K16.6-S16.6	12.23	A37.5-K37.5-S25	12.37
A16.6-K66.6-S16.6	12.47	A40-K30-S30	12.32
A16.6-K16.6-S66.6	12.34	A40-K26.5-S33.5	12.32
A20-K40-S40	12.33	A37-K31.5-S31.5	12.33
A30-K35-S35	12.36	A42.5-K42.5-S15	12.38
A31.9-K36.2-S31.9	12.36	A10-K80-S10	12.57
A30-K30-S40	12.36	A15-K45-S40	12.42
A30-K40-S30	12.38	A22.5-K55-S22.5	12.44
A35-K50-S15	12.39	A42.5-K15-S42.5	12.27

This study was undertaken to contribute to the knowledge of the role of Zr and Ti in garnets. The garnet compositions synthesized include the end-compositions $Ca_3Fe_2Si_3O_{12}$ (andradite), $Ca_3Zr_2Fe_2SiO_{12}$ (kimzeyite),

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$Ca_3Ti_2Fe_2SiO_{12}$ (schorlomite), and 35 intermediate compositions as listed in Table 1 and shown graphically in Figure 1. The end-compositions will be referred to hereafter as A, K and S. A number of additional Zr garnet compositions outside of the A-K-S field also were synthesized. These are listed in Tables 2 and 3.

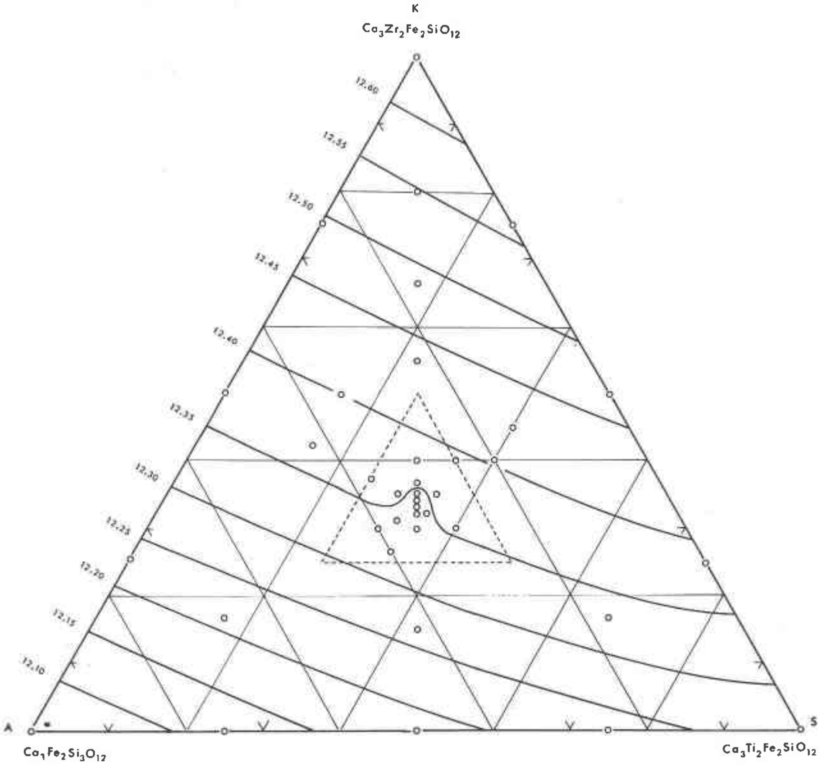

FIG. 1. Variation in *a* as a function of composition. Dotted triangle represents area shown in Fig. 2.

METHOD OF PREPARATION

The garnets were prepared as microcrystalline powders by sintering coprecipitated gels at 1050°C in air. The heating period in general was 20 hours. It was found that crystallization proceeded rapidly at 1050°C, and there was little significant increase in crystallinity in heating periods longer than about 10 minutes (Figure 3). The gels were made from appropriate amounts of the following solutions: 0.2M sodium silicate, 0.2M calcium nitrate, 0.2M ferric chloride, 0.2M zirconyl nitrate, and 0.2M titanium tetrachloride in 6N HCl. Exact amounts of the required stock

TABLE 2. SUPPLEMENTARY GARNET SYNTHESES

Composition	Temp., °C	Pressure, atm.	Time, hours	*a*, Å
$Ca_2LaZr_2Fe_3O_{12}$	1050°	1	20	12.82
$Ca_2ThZrFe_4O_{12}$	1050°	1	24	12.68
$Ca_3Zr_2Al_2SiO_{12}$	680°	2000	48	12.46
$Ca_3Al_2Si_3O_{12}$	550°	2000	48	11.87
$Ca_3Zr_2Fe_2SiO_{12}$	680°	2000	48	12.58
$Ca_3Zr_2Fe_{0.5}Al_{1.5}SiO_{12}$	680°	2000	48	12.56
$Ca_3Zr_2Fe_1Al_1SiO_{12}$	680°	2000	48	12.52
$Ca_3Zr_2Fe_{1.5}Al_{0.5}SiO_{12}$	680°	2000	48	12.50
$Ca_{2.5}Zr_{0.5}Zr_2Fe_3O_{12}$	1200°	1	3	12.65
$Ca_{2.5}Th_{0.5}Zr_2Fe_3O_{12}$	1200°	1	20	12.74
$Ca_{2.5}Ce_{0.5}Zr_2Fe_3O_{12}$	1200°	1	3	12.69
$Ca_3Zr_{1.5}Ti_{1.5}Fe_2O_{12}$	1200°	1	3	12.68
$Ca_3Zr_2TiFe_2O_{12}$	1200°	1	20	12.73

solutions were pipetted into a 250 ml. beaker and were diluted with H_2O to 150 ml. The solution was brought to pH 12 by addition of 7*M* NaOH and a 10 ml. excess of NaOH was added. The gelatinous precipitate was stirred magnetically for one minute and was centrifuged. It was then washed twice with cold distilled H_2O to a total of 300 ml. In this procedure all of the required elements are retained quantitatively in the precipitate. After washing, the gels were spread on filter paper and dried at 110°. They were then ground thoroughly in an agate mortar. The dried gels are not hygroscopic. Approximately 100 mg samples were used in the furnace runs. A few runs on gel compositions outside of the A-K-S field were made hydrothermally; these are indicated in Table 2.

TABLE 3. UNSUCCESSFUL GARNET SYNTHESES

Composition	Temp., °C	Pressure, atm.	Time, hours	Other phases
$Ca_3Zr_{0.5}Al_{1.5}Al_2SiO_{12}$	680°	2000	48	Two garnets, *a* 12.31 and 11.86
$Ca_3Zr_{1.5}Al_{0.5}Al_2SiO_{12}$	680°	2000	48	Two garnets, *a* 12.34 and 11.88
$Ca_3Zr_1Al_1Al_2SiO_{12}$	680°	2000	48	Two garnets, *a* 12.34 and 11.85
$Ca_2ZrZrFeFe_3O_{12}$	1200°	1	3	Garnet *a* 12.65, $CaZrO_3$, Fe_2O_3
$Ca_2ThZrFeFe_3O_{12}$	1200°	1	3	Garnet *a* 12.68, ThO_2
$Ca_2ZrTiFeFe_3O_{12}$	1200°	1	3	Garnet *a* 12.65, Fe_2O_3
$Ca_3Zr_2ZrFe_2O_{12}$	1200°	1	3	$CaZrO_3$, Fe_2O_3, trace garnet
$Ca_3Ti_2TiFe_2O_{12}$	1200°	1	3	$CaTiO_3$, Fe_2O_3
$Ca_3ZrTiTiFe_2O_{12}$	1200°	1	3	Garnet *a* 12.66, Fe_2O_3
$Ca_{2.5}Zr_{.5}Ti_2Fe_3O_{12}$	1200°	1	3	Garnet *a* 12.66, Fe_2O_3, ZrO_2
$Ca_{1.5}Zr_{1.5}Fe_2Fe_3O_{12}$	1200°	1	3	$CaZrO_3$, Fe_2O_3, trace garnet
$Ca_3ZrFeFe_2SiO_{12}$	1050°	1	20	$CaFe_2O_4$, garnet *a* 12.55

EXPERIMENTAL RESULTS

X-ray diffractometer charts were taken of all runs in filtered Cu radiation, with Si as internal standard. The unit cell dimension was obtained by numerical averaging of values obtained from the reflections (400), (420), (422), (611), (640) and (642). The precision is not high because of poor line quality at high angles and is estimated at ±0.01 Å. The variation in a as a function of composition is shown in Figure 1.

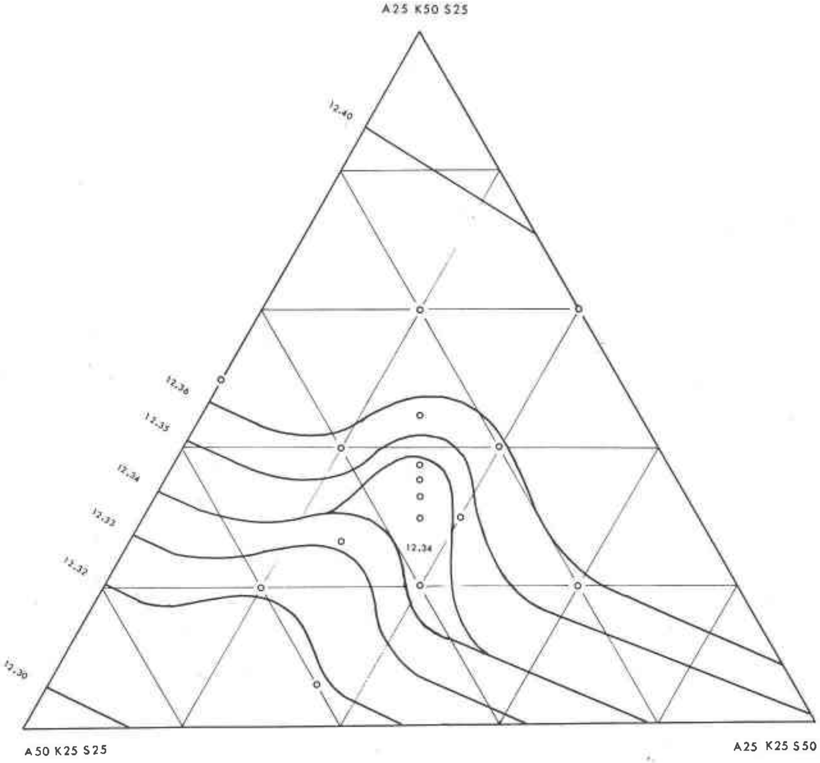

FIG. 2. Enlargement of dotted area in Fig. 1, showing solubility gap and associated variation in a.

In the central part of the ternary field there is a small area, interpreted as a solubility gap, in which the value of a remains essentially constant. This area is shown in enlarged scale in Figure 2. The contouring of a in this region is uncertain, but does indicate that the gap is associated with local abnormalities in the otherwise rather uniform rate of change of a with composition.

The garnets within the gap all have *a* of approximately 12.34 Å on heating periods of 20 hours. There was no clear evidence of admixture in the X-ray patterns. One of the garnets in this region, with the composition A33-K33-S33, was studied as a function of heating time of the gel at 1050°C, as shown in Figures 3 and 4. The gel gives a good pattern after heating for only a few minutes. The initial value of *a*, 12.43 Å, gradually decreases to 12.34 and after about 20 hours line broadening and splitting begins. The material finally separates into two garnet phases. Line broadening at heating periods of 20 hours also was observed in the compositions A37-K31.5-S31.5, A25-K40-S35, K50-A50 and K75-S25.

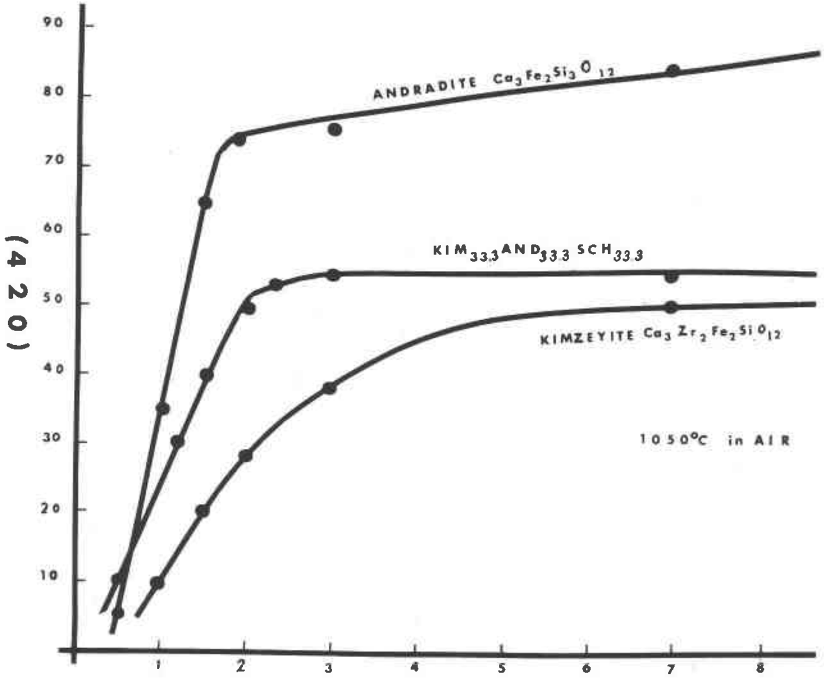

FIG. 3. Crystallization of synthetic garnets as a function of time. Ordinate is heating period of sample in minutes at 1050°C, abscissa is the peak height of (420) in arbitrary chart units.

The following melting phenomena in air at 1 atmosphere were observed: $Ca_3Zr_2Fe_2SiO_{12}$ stable at 1280° ± 10°, melted at 1290° ± 10°; $Ca_3Ti_2Fe_2SiO_{12}$, stable at 1180° ± 10°, melted at 1190° ± 10°; $Ca_3Fe_2Si_3O_{12}$ broke down to hematite and α-$CaSiO_3$ at 1150° ± 10°, melted at 1180° ± 10°C.

DISCUSSION

The interpretation of the crystallochemical mechanisms by which the observed compositional variation is effected is not wholly apparent, particularly with regard to Zr. Garnet belongs to the space group *Ia3d* and contains 8 units of the formula-type $A_3B_2X_3O_{12}$. The cations are in special positions with 24 A in *c*, 16 B in *a*, 24X in *d* and the 96 oxygens are in the general position *h*. In terms of coordination polyhedra, the independent (XO_4) tetrahedra are linked by octahedra of the B ions, and the large A ions are in 8-coordination in this framework. The oxygen polyhedra are more or less distorted depending on the sizes of the cations present.

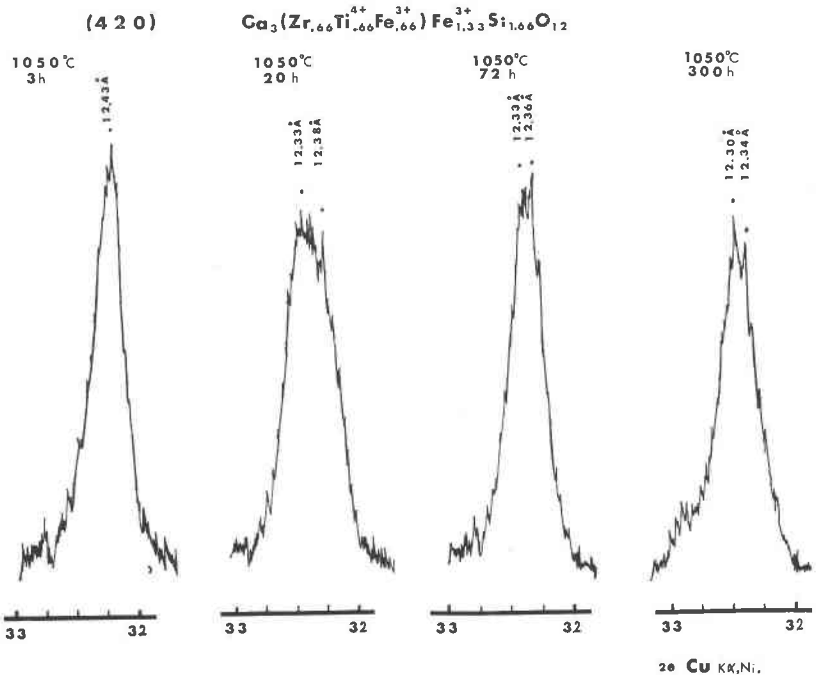

FIG. 4. Line broadening and splitting in garnet of the composition A33-K33-S33 as a function of heating time at 1050°C.

About 40 different cations (including all of the rare-earths) have been found to enter the garnet structure-type as major constituents in synthetic or natural material. The site preferences of these cations have been discussed by Geller (1960) and need not be summarized here. In some garnets individual cations may be distributed between two different sites, usually *a* and *d*. Ordered distributions within a single site have not been demonstrated.

Zr prefers exclusively the 6-coordinated sites in yttrium-iron garnet (Geller *et al.*, 1960, 1964). This coordination number also is indicated in certain compositions synthesized in the present study, including $Ca_2LaZr_2Fe_3O_{12}$, $Ca_2ThZrFe_4O_{12}$ and the aluminous Zr-garnets listed in Table 2. In these garnets, the well established preference of Fe^{3+} and Al for tetrahedral coordination in the absence of Si, and the relatively large size of La and Th, which both normally enter 8-coordination in synthetic garnets, relegate the Zr to 6-coordination. Other synthetic garnets for which 6-coordination is indicated for the Zr include $Ca_3ZrMgGe_3O_{12}$ (Geller and Miller, 1960), $CaGd_2ZrFeFe_3O_{12}$ (Geller *et al.*, 1965) and $Ca_2YZrFeFe_2GeO_{12}$ (Geller, *et al.*, 1964).

The possibility that Zr may enter 8-coordination in place of Ca also should be considered. Zr is the closest in size to Ca of the ions involved in the A-K-S series, and, like Ca, goes into both 6 and higher coordination with oxygen. Zr is 8-coordinated in $ZrSiO_4$ and in the high temperature polymorph of ZrO_2 (where Ca is present as a stabilizing ion). It is 7-coordinated in the low temperature polymorph of ZrO_2, and it is 6-coordinated in ZrO and other compounds. We have synthesized $Ca_{2.5}Zr_{0.5}Zr_2Fe_3O_{12}$, in which the site preferences indicate that the 8-coordinated site is occupied by $(Ca_{2.5}Zr_{0.5})$ and the 6-coordinated site by Zr_2. The garnets $Ca_{2.5}Th_{0.5}Zr_2Fe_3O_{12}$ and $Ca_{2.5}Ce_{0.5}Zr_2Fe_3O_{12}$ also were prepared. Efforts failed to make $Ca_2ZrZrFeFe_3O_{12}$, $Ca_{1.5}Zr_{1.5}Fe_2Fe_3O_{12}$, $Ca_3Zr_3Fe_2O_{12}$, $CaZr_2CuFeFe_3O_{12}$ and $CaZr_2NiFeFe_3O_{12}$. Efforts by Geller and Miller (1960) to synthesize $CaGd_2Co_2Zr_3O_{12}$ also failed. It may be noted that the Mn^2 ion, somewhat larger than Zr^4, goes into both 8 and 6 coordination in synthetic garnets.

The site preferences of Ti in synthetic and natural garnets are not yet well understood. Ti generally takes 6-coordination with oxygen, and it enters the 6-coordinated site in the synthetic garnets $Ca_3TiNiGe_3O_{12}$, $Ca_3TiCoGe_3O_{12}$ and $Ca_3TiMgGe_3O_{12}$ (Geller and Miller, 1960), and in $Ca_2YTi_2Ga_3O_{12}$ (Espinosa, 1964). A special situation, however, exists in iron garnets where the tetrahedral site is not wholly occupied by Si, as in the A-K-S series here described, or in garnets of the yttrium-iron type, where Si is wholly lacking. Here the competition for the tetrahedral sites is with Fe^{3+}, and Ti may be favored because of its slightly smaller size. The site preference is not influenced by the electronic configuration of the Ti^{4+} ion, which should be spherical in both octahedral and tetrahedral fields. However, our efforts to synthesize $Ca_3Ti_2TiFe_2O_{12}$ failed. Both octahedrally and tetrahedrally coordinated Ti is present in the garnet $(Ca_{2.5}Y_{0.5})ZrTi(Ga_{2.5}Ti_{0.5})O_{12}$ (Espinosa, 1964). We also have synthesized $Ca_3Zr_2TiFe_2O_{12}$, in which 4-coordinated Ti is clearly indicated. Tarte (1960) states that infrared spectra indicate both tetrahedral and octahedral Ti in andradite.

We believe that the anomalies in *a* found in the central area of the A-K-S field may be connected with the distribution of Zr and/or Ti between two different sites or with ordering in a shared site.

NATURAL Ti AND Zr GARNETS

Natural calcium garnets high in ferric iron (andradite) and containing more or less Ti are well known. The highest content of Ti yet reported is in the orginal schorlomite from Magnet Cove, Arkansas. The analysis by Koenig (1886) of this material corresponds to

$$(Ca_{2.89}Mg_{0.16}Mn_{.03})(Ti_{1.12}Fe_{0.82})(Si_{2.22}Fe_{0.68}Al_{0.10})O_{12}.$$

Some older analyses are higher in Ti but are unsatisfactory. Analyses of material from other localities, cited by Dana (1892), Kunitz (1936) and by Deer, Howie and Zussman (1962), leave no doubt that a continuous series extends from schorlomite to andradite. This series corresponds to the A-S join in the ternary A-K-S solid solution described above. Some of the natural material is rather aluminous, but with Fe> Al in all instances.

Two calcium garnets high in Zr in addition to Ti and Fe^{3+} have been described by Borodin and Bykova (1961) from the Guli and Vuoriyarvi massifs of ultrabasic-alkalic rocks in Russia. The formulas derived by these authors in which Ti is assigned to the tetrahedral positions are

$$(Ca_{2.91}Mg_{0.09})(\overset{3+}{Fe}_{1.16}Zr_{0.44}\overset{2+}{Fe}_{0.22}Ti_{0.11}Mg_{0.07})(Si_{2.11}Ti_{0.89})O_{12}$$

and

$$(Ca_{2.79}Na_{0.13}Mg_{0.08})(\overset{3+}{Fe}_{0.98}Zr_{0.57}Mg_{0.18}\overset{2+}{Fe}_{0.14}Ti_{0.11})(Si_{2.02}Ti_{0.83}Al_{0.15})O_{12}.$$

These garnets contain small amounts of Fe^{2+} and Na in the 6-coordinated position, which contribute to valence compensation in the structure, but the main mechanism of compositional variation conforms to the ternary A-K-S series described. Zr also has been reported in amounts up to a few weight percent in titanian andradite (melanite) and schorlomite from other localities.

The only known garnet containing Zr as a major constituent, kimzeyite, was described by Milton, Ingram and Blade (1961) from Magnet Cove. The composition is close to

$$Ca_{3.11}(Zr_{1.42}Ti_{0.40}Mg_{0.07}Fe_{0.07}Nb_{0.05})(Al_{1.26}\overset{3}{Fe}_{0.98}Si_{0.94})O_{12}.$$

This garnet has Al> Fe in atomic percent in the tetrahedral position as formulated. The data cited in Table 1 indicate that a complete series extends between $Ca_3Zr_2Fe_2SiO_{12}$ and $Ca_3Zr_2Al_2SiO_{12}$ under hydrothermal conditions at 680° and 2000 atm. (A complete series involving Fe^{3+} and Al also is found between $Ca_3Fe_2Si_3O_{12}$, andradite, and $Ca_3Al_2Si_3O_{12}$, grossularite, but here in the 6-coordinated rather than the 4-coordinated position). A series probably also extends from $Ca_3Ti_2Fe_2SiO_{12}$ to $Ca_3Ti_2Al_2SiO_{12}$ but we have no experimental data.

The nomenclature to be applied to the natural Ti and Zr garnets presents difficulties in view both of the uncertainities as to the actual cation distribution, and in limiting, if this is desired, the total amount of (Fe^{3+}, Al) and the Fe^{3+}/Al ratio in the tetrahedral position. It is suggested that the species names andradite, schorlomite and kimzeyite be applied to calcium garnets with Fe^{3+}, Ti or Zr dominant in atomic percent when referred to the 6-coordinated position, and containing either Fe or Al as the compensating ion in the 4-coordinated position. In andradite containing significant amounts of Ti the existing varietal name melanite or, preferably, the term titanian andradite may be employed. The garnets described by Borodin and Bykova (1961) correspond to zirconian schorlomite in our definition.

The substitution of Ti in some natural silicate garnets is limited, as shown by the presence of exsolved rutile needles (Brauns, 1907; Walcott, 1937).

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