KIMZEYITE, A ZIRCONIUM GARNET FROM MAGNET COVE, ARKANSAS*

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ABSTRACT

Kimzeyite, $Ca_3(Zr, Ti, Mg, Fe'', Nb)_2(Al, Fe''', Si)_3O_{12}$, is a new type of garnet occurring as dodecahedrons modified by trapezohedron at Magnet Cove, Arkansas, in a carbonatite with abundant apatite, monticellite, calcite, perovskite (dysanalyte), magnetite, and minor biotite, pyrite, and vesuvianite. It is dark brown, H about 7, isotropic, insoluble in acids, infusible before the blowpipe, $D=4.0$, $n=1.94$. The three strongest x-ray powder pattern lines with intensities as measured are 1.667 (10), 2.539 (9), 2.79 (8); the unit cell constant is 12.46 Å. Microchemical analysis gave CaO 29.8, ZrO_2 29.9, Ti_2O_3 5.0, MgO 0.5, FeO 0.8, Nb_2O_5 1.0, Al_2O_3 11.0, Fe_2O_3 13.4, SiO_2 9.6, sum 101.0 which computes to $Ca_{3.11}(Zr_{1.42}{}^{+4}Ti_{0.40}{}^{+3}Mg_{0.07}{}^{+2}Fe_{0.07}{}^{+2}Nb_{0.05}{}^{+5})(Al_{1.26}{}^{+3}Fe_{0.98}{}^{+3}Si_{0.94}{}^{+4})O_{12.00}$. Basically, this is $Ca_3Zr_2(Al_2Si)O_{12}$ with Ti replacing Zr and Fe replacing Al. Zirconium has been found in other garnets (schorlomite from Magnet Cove, melanite from Kaiserstuhl, Germany, and titanian andradite from Oka, Quebec) in quantity up to several per cent, but in none of these is it a major constituent. Kimzeyite is named in honor of the Kimzey family, long known in connection with Magnet Cove mineralogy.

INTRODUCTION

During geological study of the Magnet Cove, Arkansas, carbonatite by Erickson and Blade (1956), their attention was directed by Mr. Joe Kimzey of Malvern, Arkansas, to small dark brown garnets about 1 mm. diameter in the Kimzey calcite quarry. Because garnet of various types, including titanian andradite (melanite) and schorlomite with up to 16.9% TiO_2, have long been known from Magnet Cove, the unusual character of the garnets from this limestone quarry was not realized until a spectrographic analysis (by A. T. Myers of the U. S. Geological Survey) indicated zirconium as a major constituent. A second spectrographic analysis of especially cleaned material (by H. Bastron of the U. S. Geological Survey) confirmed the major zirconium content of the garnet. A preliminary note on kimzeyite was published in Science (Milton and Blade, 1958), giving Bastron's spectrographic data which shows more than 20% ZrO_2 to be present.

* Publication authorized by the Director, U. S. Geological Survey.

Kimzeyite, although certainly a garnet, as will be shown, differs greatly in its composition from all garnets previously known. It appears that two-thirds of the normal tetrahedral silicon positions are occupied by aluminum and iron atoms, and of the normal octahedral aluminum-iron positions, almost all are occupied by zirconium and titanium. Correspondingly, the SiO_2 content is only 9.6%; most garnets contain 30 to 40%, and even the least siliceous types (titanian) contain over 25% SiO_2.

Kimzeyite is of further interest in being the first known zirconium silicate containing substantial aluminum, contrary to Frondel's observation (1957) "The (zirconium) silicates without exception lack aluminum. . . . " However, with a bare third of the normal silicon positions of garnet occupied by this element, the question may be raised as to kimzeyite being a silicate even though a garnet, since such compounds as $Gd_3Fe_2Fe_3O_{12}$ or $Y_3Al_2Al_3O_{12}$ are considered garnets, even though not silicates.

Occurrence

Kimzeyite occurs in a light colored phase of carbonatite (Fig. 1) which is associated with ijolite in the Kimzey calcite quarry. With the dominant white coarsely crystallized calcite are scattered irregular zones enriched in white to pale greenish finely prismatic apatite, massive light brown monticellite, and smaller but conspicuous black magnetite and perovskite, and in minor amount some yellow vesuvianite, green mica, and pyrite. The garnet in this rock forms small and far from abundant dark brown crystals, with prominent dodecahedron and almost equally developed trapezohedron (Fig. 2). All so far found are small, usually under 1 mm. diameter. Larger garnets also occur in weathered apatite rock coated with buff clay, in the same quarry; these contain no zirconium.

Kimzeyite is easily differentiated from perovskite with a hand lens in being brown with subrounded crystals (dodecahedron-trapezohedron), whereas perovskite is almost black and sharply angular (octahedron with minor cube). In thin section, the two minerals are easily distinguished by the pale brown of kimzeyite with its subrounded outlines, contrasted with the dark brown sharply angular perovskite. Perovskite also shows the usual segmented anisotropy, whereas kimzeyite is isotropic. Magnetite is easily distinguished by its magnetism, and in section by its opacity.

A typical thin section of the carbonatite showing kimzeyite and some of its associated minerals is shown in Fig. 3.

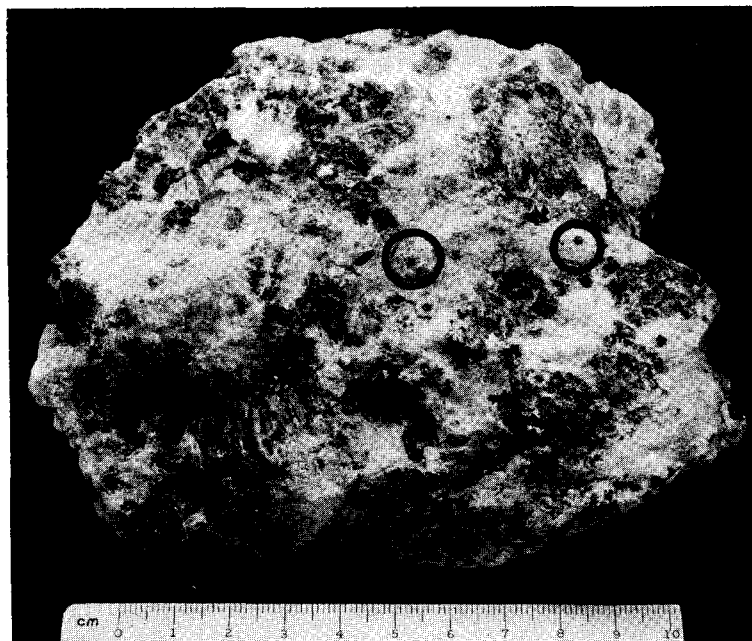The crystals as shown in Fig. 3 contain considerable visible inclusions,

FIG. 1. Kimzeyite-bearing limestone, Magnet Cove, Ark. Two crystals of kimzeyite are present, indicated by circles. These are about average size. The white areas are fibrous apatite and calcite, the slightly darker glossy pale brownish monticellite. Rather coarse black magnetite (lower left) and disseminated black perovskite (dysanalyte) can also be seen.
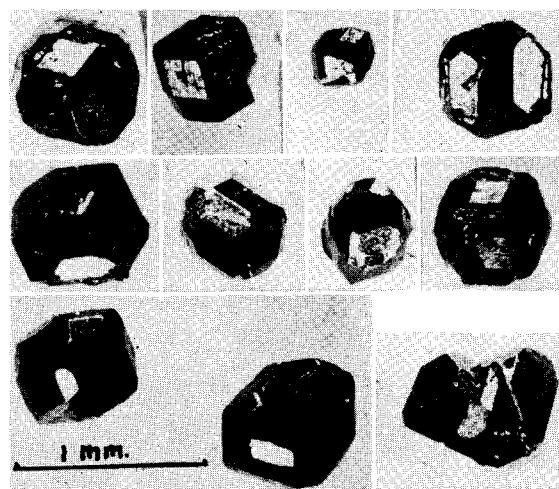

FIG. 2. Kimzeyite crystals isolated from carbonatite matrix. At the lower right is a kimzeyite crystal intergrown with a perovskite crystal.

mainly of apatite, calcite, and monticellite. Only the very smallest appear to be fairly free from such inclusions. In preparing the sample for chemical analysis, single crystals were crushed, and many were found to contain microscopic clear euhedral (?) crystals of anhydrite, confirmed microchemically, optically, and by x-ray powder pattern (by E. C. T. Chao, U. S. Geological Survey). Whether or not equally minute anhydrite exists dispersed in the rock matrix of the kimzeyite would be difficult to determine.

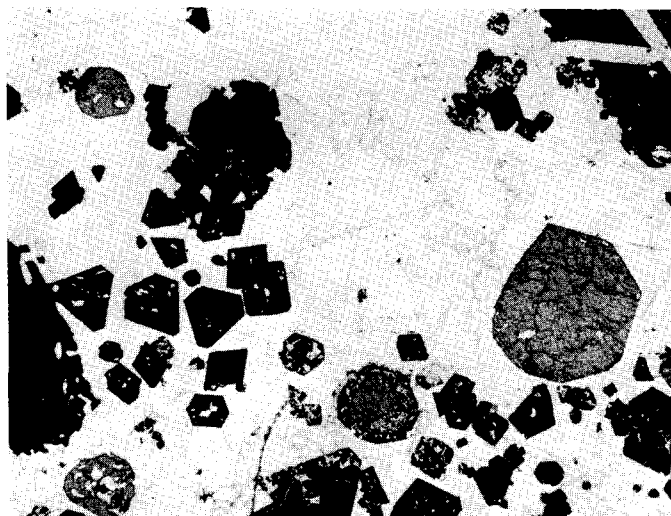Because of these inclusions, which could not be dissolved out com-

Fig. 3. Thin section of carbonatite, showing four rounded kimzeyite crystals (gray), and numerous smaller angular perovskite crystals (black) in calcitic matrix. The large black masses are magnetite; at the upper right two apatite crystals cut the magnetite.

pletely by acids or otherwise removed except by tedious hand picking under the microscope, preparation of sufficiently clean material for analysis was a long drawn-out task, extending over available time for some years.

DENSITY, INDEX OF REFRACTION, AND OTHER PHYSICAL PROPERTIES

The approximate density of whole kimzeyite crystals showing few or no visible inclusions was determined by finding the density of a diluted Clerici solution in which they barely floated or sank, namely 3.94. Because of the impossibility of verifying complete purity of any particle of kimzeyite, only an approximation to a true density is possible. Actually, as explained below, this is low, and a better value would be nearer 4.0.

The index of refraction determined by the immersion method was found to be $1.94 \pm .01$, using liquids prepared and standardized by Robert L. Meyrowitz of the U. S. Geological Survey.

Using Gladstone and Dale's equation relating composition, index of refraction, and density (Larsen and Berman, 1934), with specific refractivities given by these authors (except for substitution of $k_{Fe_2O_3}$ $= 0.290$ instead of 0.308, as suggested by Jaffe (1946)), it is found that $n = 1.92$ (against measured 1.94) if the measured density is assumed correct, or $d = 4.00$ gm. cm.$^{-3}$ (against measured 3.94) if the measured index of refraction is assumed correct.*

The discrepancy between observed and calculated density is not large and it is more likely that the measured refractive index is nearer the true value than is the measured density. Therefore, it may be inferred that the whole garnet crystals used in the density determinations contained substantial inclusions of lower density, *i.e.*, apatite 3.2, monticellite, 3.2, calcite 2.7, or anhydrite 2.9 gm. cm.$^{-3}$. For example, a crystal of density 4 with 10% (by volume) of admixture with density 3 would have a net density of 3.9, and from the illustration (Fig. 3) showing the heterogeneity of kimzeyite this degree of admixture is quite possible. Accordingly the density of kimzeyite is most probably greater than the measured 3.94.

However, we can also calculate the density, using the formula for kimzeyite developed in Table 3, the cell edge constant measured by Axelrod, and the value 8 for Z (moles per unit cell) for the garnet structure: resulting in $d = 4.03$. Using this value for d in Gladstone and Dale's equation gives $n = 1.946$ in fair agreement with the measured 1.94.

The streak of kimzeyite or the color of its powder is light brown; and the hardness is about that of quartz—7. It is almost if not entirely insoluble in hot concentrated HCl or HNO_3 or $HF + H_2SO_4$, and is infusible before the blowpipe. Here again the highly poikilitic character of the kimzeyite necessitated a special procedure—it was impossible to find a homogeneous fragment large enough to hold in a platinum forceps in a blowpipe flame. Therefore reasonably clean microscopic fragments were wrapped in platinum foil, and the packet heated in an air-gas blast to bright red heat for fifteen minutes. The kimzeyite showed no sign of fusion.

Kimzeyite is heavier than most other garnets, only those with 8-coordinated iron or manganese being heavier (almandite and calderite); only some strongly titanian garnets have higher index of refraction;

* The value of $k_{TiO_2} = .397$ given by Jaffe is used also for $k_{Ti_2O_3}$ for which he gives no data. The error thus introduced is unknown but probably small.

and the cell constant a_0 appears to be larger than that of any known natural garnet.

Marie L. Lindberg of the U. S. Geological Survey has kindly measured the film (11944) of the sample whose analysis is given in Table 2. Her data are given in Table 1.

TABLE 1. POWDER PATTERN DATA OF KIMZEYITE

Intensity	$d(\text{Å})$ meas.	hkl	$d(\text{Å})$ calc.
4	4.42	220	4.406
6	3.12	400	3.115
8	2.79	420	2.786
1	2.656	332	2.657
9	2.539	422	2.543
1	2.439	510, 431	2.444
1	2.273	521	2.275
2	2.019	532, 611	2.021
3	1.969	620	1.970
4	1.728	640	1.728
10	1.667	642	1.675
2	1.558	800	1.558
1	1.469	660	1.468
4	1.395	840	1.393
2	1.360	842	1.360
3	1.328	664	1.328
2	1.157		
4	1.137		
1	1.110		
2	1.011		
1 Broad	0.930		
2	0.848		
2	0.791		

The lower cut-off is at 10 Å. The film was corrected for shrinkage; the radiation nickel-filtered copper with $K_\alpha = 1.5418$ Å. The published lattice constant $a_0 = 12.46$ Å obtained by J. M. Axelrod (Milton and Blade, 1958) was used to index the pattern; the agreement of measured and calculated d-spacings is good.

COMPOSITION

Table 2 gives the chemical and spectrographic (of trace elements) analyses of kimzeyite. (Spectrographic analyses for major constituents were also made by the same analysts, with results concordant with Ingram's quantitative analysis.)

CHEMICAL ANALYSIS (METHODS)

One portion (50 mg.) of sample was used for $H_2O(-)$, SiO_2, Fe_2O_3, Al_2O_3, ZrO_2, Nb_2O_5, TiO_2, CaO, MgO, and MnO determinations. An-

other portion (13 mg.) was used to determine the total reducing capacity, and a third portion (25 mg.) was used to determine total H_2O.

The 50-mg. sample was dried to constant weight at 110° C. to determine $H_2O(-)$. It was then sintered with Na_2O_2 at 460° C. The sinter was dissolved in HCl. SiO_2 was determined gravimetrically by double dehydration of the solution and volatilization of the SiO_2 with HF and excess H_2SO_4.

The filtrate from the SiO_2 determination was treated with NH_4OH to precipitate the R_2O_3 group. The precipitate was ignited and weighed, and the filtrate was reserved for Ca, Mg, and Mn determinations. The R_2O_3 was fused with $K_2S_2O_7$ and dissolved in HCl and tartaric acid. Iron was separated from the group by making the solution ammoniacal and gassing with H_2S. FeS was dissolved and, after oxidation, the Fe was precipitated with NH_4OH. The precipitate was ignited and weighed as Fe_2O_3.

The solution remaining after H_2S precipitation of Fe contained Al, Zr, Nb, and Ti. Zr, Nb, and Ti were removed from solution by precipita-

TABLE 2. CHEMICAL ANALYSIS OF KIMZEYITE, MAGNET COVE, ARKANSAS
Analyst, Blanche L. Ingram

SiO_2	9.6	*alternate values * used in Table 3*
FeO	5.8	0.8
Fe_2O_3	7.8	13.4
TiO_2	5.6	Ti_2O_3 5.0
ZrO_2	29.9	
Nb_2O_5	1.0	
Al_2O_3	11.0	
CaO	29.8	
MgO	0.5	
	———	
	101.0	

also MnO <0.1
      H_2O^- <0.1
total H_2O <0.1
also Na 0.1–0.5 (spectrographic on 1 milligram; Helen Worthing and Katherine Hazel, U. S. Geol. Survey, analysts).
On a different but equally purified sample, Harry Bastron, U. S. Geol. Survey, found spectrographically Mn 0.1, Sn 0.07, Sc 0.06, Cu, Ba, and Sr, traces; and looked for but not found, Ag, Au, Hg, Ru, Rh, Pd, Ce, Ir, Pt, Mo, W, Re, Ge, Pb, As, Sb, Bi, Zn, Cd, Te, In, Co, Ni, Ga, Cr, V, Y, La, Hf, Th, Ta, Be, Li, Na, K, B. High Fe precludes determination of low P.

* No differentiation of Fe^{+2} and Ti^{+3} can be made in the chemical analysis. Values for FeO and Fe_2O_3 are therefore given with all of the Ti as Ti^{+4}, and, alternately, with all the Ti as Ti^{+3}.

tion with cupferron. This precipitate was ignited and weighed. The oxides were dissolved and Ti was determined colorimetrically with "Tiron"; Nb was determined colorimetrically using thiocyanate and Zr was determined gravimetrically as the oxide after precipitation with mandelic acid. Corrections were applied for the effect of Ti on the Nb determination and of Nb on the Zr determination. Al_2O_3 was considered the difference between the total R_2O_3 and the sum of Fe_2O_3, ZrO_2, TiO_2 and Nb_2O_5.

Calcium was precipitated with $(NH_4)_2C_2O_4$ from the reserved filtrate. The precipitate was ignited and weighed as CaO. Ammonium salts were destroyed in the filtrate from the calcium determination and Mg and Mn were precipitated with 8-hydroxyquinoline in an ammoniacal medium. The precipitate was dried at 110° C. and weighed. It was then ignited at 800° C. and the oxides dissolved. Mn was determined colorimetrically by oxidation to permanganate.

Total reducing capacity was determined by fusing the sample with sodium fluoborate in a tube furnace at approximately 900° C. in an atmosphere of N_2. The fused sample was dissolved in an atmosphere of N_2 with 10% H_2SO_4 containing H_3BO_3, and titrated with standard $K_2Cr_2O_7$ using sodium diphenylamine sulfonate as indicator. A fusion technique was necessary; the mineral is insoluble in the usual $HF-H_2SO_4$ mixture.

Total H_2O was determined by the Penfield method.

COMMENTS ON ANALYSIS

Because of the abundant perovskite, containing $5.6 \pm 0.3\%$ Nb, associated with kimzeyite in the Kimzey calcite quarry, and as much as 8.8% Nb in perovskite from the adjoining "perovskite hill" (Fryklund, Harner, and Kaiser, 1954), the possibility that the analyzed kimzeyite was contaminated with perovskite must be considered. However, because of the care used in selecting the particles for analysis, serious contamination is unlikely. Further if the Nb were indeed present in perovskite containing as much Nb as 8.8%, then there should have been about 11% of this mineral in the sample—but no lines of perovskite appeared on the x-ray powder pattern of the analyzed sample. With reference to perovskite with *less* Nb as possible contaminant (Fryklund et al., also cite 3.1% Nb in perovskite from Magnet Cove) the argument is even stronger: there would be correspondingly more perovskite to show up on the powder pattern if it were present. It may therefore be accepted that the Nb found in the kimzeyite is in the structure. Finally, as noted by Rankama and Sahama (1950), Nb is commonly associated with both Zr and Ti, both major elements in kimzeyite.

Bastron did not find Hf, which because of the high Zr could be ex-

pected in detectable amount. In zirconium silicates of alkalic rocks and carbonatites, the Hf/Zr ratio varies from 0.007 (in catapleite) to 0.069 (in eudialyte) as listed by Fleischer (1955). These values would correspond to 0.15% and 1.5% respectively of Hf. It is probable that any hafnium in kimzeyite is less than 0.1% (Bastron, oral communication).

Bastron also reports Sn 0.07% with a trace of Cu. Conceivably these may represent contamination from the brass sieves used in processing the sample. On the other hand, Ramdohr (1936) has found Sn replacing Ti, to the extent of 10% Sn in sphene.

The 0.06% Sc reported by Bastron is noteworthy.

Rankama and Sahama (1950) observe that scandium is virtually absent in calcium garnets (page 513) and likewise in zirconium minerals, notwithstanding the similar ionic radii of scandium and zirconium (page 515).

COMPUTATION OF FORMULA

Anticipating what follows, the formula proposed for kimzeyite, as a garnet, derived from the normal garnet type formula $R_3^{+2}R_2^{+3}Si_3O_{12}$, is $Ca_3(Zr,^{+4}, Ti^{+3}, Mg^{+2}, Fe^{+2}, Nb^{+5})_2(Al^{+3}Fe^{+3}Si^{+4})_3O_{12}$ or basically $Ca_3Zr_2(Al_2Si)O_{12}$. Essentially, the normal two trivalent ions (i.e., Al and Fe) in common garnet are here replaced by two zirconiums, with a minor further replacement of the latter by titanium, etc; and two of the normal three silicons are replaced by aluminum and iron.

The basic data for establishing the formula of kimzeyite are presented in Table 3, with the simple calculations leading to the formula.

A recent paper by Geller, Miller, and Treuting (1960) describes a remarkably extensive series of synthetic garnets, among them, garnets containing much zirconium (and also, niobium), but with germanium instead of silicon in tetrahedral position. The compound $Ca_3ZrFe^{+2.9}Ge_{2.8}O_{12}$ (defect structure) was made, whose similarity to kimzeyite $Ca_3(Zr, Ti^{+3})_2(Al, Fe, Si)O_{12}$ is apparent. They were unable to substitute Zr^4 for Ge^4 (*i.e.*, in tetrahedral co-ordination) observing that it is "very probable that the Zr^{4+} ion would go only into octahedral sites." As is well known, Ge^4 (ionic radius 0.50 Å) and Si^4 (ionic radius 0.40 Å) are generally replaceable for each other in silicate structures, so their work with germanium garnets may reasonably be extrapolated to silicon garnets. Because in kimzeyite zirconium with titanium virtually fills all the octahedral (6-co-ordinated) positions (calcium similarly pre-occupying all the 8-co-ordinated locations), ferric iron and aluminum have only the tetrahedral silicon positions available. As is well known, such tetrahedrally co-ordinated ferric iron exists in biotite (Eitel, 1954) and cronstedtite (Hendricks, 1939). Even more to the point, tetrahedral iron

TABLE 3. COMPUTATION OF FORMULA OF KIMZEYITE

Analysis		Cation%	Oxygen%	$\dfrac{\text{Cation}\%}{\text{At. Wt.}}$	Equiv. Oxygen	$\dfrac{\text{Cation}\%}{\text{At. Wt.} \times 171}$
CaO	29.8	21.3	8.5	.532	.532	3.11 ($\times 10^{-3}$)
MgO	0.5	0.3	0.2	.012	.012	.07 ($\times 10^{-3}$)
FeO	0.8	0.6	0.2	.011	.011	.07 ($\times 10^{-3}$)
Fe_2O_3	13.4	9.4	4.0	.168	.252	.98 ($\times 10^{-3}$)
Ti_2O_3	5.0	3.3	1.7	.069	.104	.40 ($\times 10^{-3}$)
Al_2O_3	11.0	5.8	5.2	.215	.322	1.26 ($\times 10^{-3}$)
ZrO_2	29.9	22.1	7.8	.242	.484	1.42 ($\times 10^{-3}$)
Nb_2O_5	1.0	0.7	0.3	.008	.020	.05 ($\times 10^{-3}$)
SiO_2	9.6	4.5	5.1	.160	.320	.94 ($\times 10^{-3}$)
	101.0%	68.0%	33.0%		2057($=12 \times 171.4$)	

Assuming the general garnet structural formula $A_3^{VIII}B_2^{VI}X_3^{IV}O_{12}$, the cations may be grouped as follows according to their respective co-ordinations, 8, 6, and 4, which corresponds well with their ionic radii.
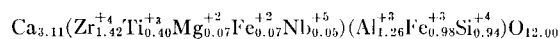
	Co-ordination	Ionic radius	Electrostatic charge
$A = Ca_{3.11}^{+2} \dfrac{}{3.11}$	8	1.03 Å	6.22
$B = Mg_{.07}^{+2}$	6	.66	.14
$Nb_{.05}^{+5}$	6	.69	.25
$Ti_{1.40}^{+3}$	6	.76	1.20
$Fe_{.07}^{+2}$	6	.74	.14
$Zr_{1.42}^{+4} \dfrac{}{2.01}$	6	.79	5.68
$X = Si_{.94}^{+4}$	4	.40	3.76
$Fe_{.98}^{+3}$	4	$< .64$	2.94
$Al_{1.26}^{+3} \dfrac{}{3.18}$	4	.49	$\dfrac{3.78}{24.11 \text{ (cationic)}}$
O_{12}^{-2}			24.00 (anionic)

must exist in the garnet $Gd_3Fe_5O_{12}$ ($Gd_3Fe_2Fe_3O_{12}$) synthesized by Bertaut and Forrat (1956); and tetrahedral aluminum in the yttro-garnet $Y_3Al_5O_{12}$ ($Y_3Al_2Al_3O_{12}$) synthesized by Yoder and Keith (1951). In many silicates, such as feldspars and zeolites, aluminum replaces silicon in
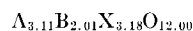
tetrahedral co-ordination. As to the ionic radius of such tetrahedrally co-ordinated iron, Green (1959) lists no value; but from geometrical considerations it must be less than the ionic radius he does list for octahedral trivalent iron, 0.64.

The slight excess of cationic over anionic charge, 0.11 (0.5%) must be considered a numerical error arising from rounding off decimals, and may be disregarded.
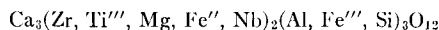
The formula of kimzeyite is therefore

$$Ca_{3.11}(Zr^{+4}_{1.42}Ti^{+3}_{0.40}Mg^{+2}_{0.07}Fe^{+2}_{0.07}Nb^{+5}_{0.05})(Al^{+3}_{1.26}Fe^{+3}_{0.98}Si^{+4}_{0.94})O_{12.00}$$

with

$$A_{3.11}B_{2.01}X_{3.18}O_{12.00}$$

or, more simply

$$Ca_3(Zr, Ti''', Mg, Fe'', Nb)_2(Al, Fe''', Si)_3O_{12}$$

and derives from a basic formula $Ca_3Zr_2(Al_2Si)O_{12}$ by substitution of Ti, etc. for Zr and Fe for Al.

It is evident from co-ordination and ionic radius considerations, that zirconium can not occupy a Si position in the structure, but only that of a trivalent octahedrally co-ordinated ion; and that titanium must be similarly located—together with the magnesium, ferrous iron, and niobium. The assignment of Ti in the garnet structure—whether octahedrally replacing trivalent iron or aluminum, or tetrahedrally replacing silicon, has long been an open question. Fleischer (1937) stated the problem concisely as follows: "There is considerable uncertainty at present as to the role of titanium in garnets. The problem has been discussed by Kunitz, who came to the conclusion that Ti replaces Si in these garnets. In nearly all the recent analyses, however, the molecular ratios are high for RO_2 and RO, and low for R_2O_3, which makes plausible the suggestion of Zedlitz that part of the titanium is present in the trivalent state. (Any Ti_2O_3 present would cause a corresponding amount of Fe_2O_3 to be reported as FeO.)"

Zedlitz (1933, 1935) analysed three titanium garnets, melanite from Kaiserstuhl, melanite from Magnet Cove, and a garnet from Ivaara, Finland, with 12.10%, 4.60% and 17.3±0.5% TiO_2, respectively. In computing their formulas he assigned in each case sufficient TiO_2 to SiO_2 to arrive at a close approximation to the type garnet ionic ratios of $3R^{VIII}2R^{VI}3R^{IV}$, grouping with the SiO_2 the Al_2O_3, but not the equally available Fe_2O_3. His justification for grouping TiO_2 with SiO_2, with the implication that Ti ions replace Si ions in the structure, is a hypothetical isomorphous replacement of Si by Ti at high temperatures (he admits that at ordinary temperatures no stable 4-co-ordinated structures are

known) and that this replacement is somehow preserved through rapid cooling ("rasche Abkuhlung des Oberflachenmuttergesteins"). We think his disregarding the possibility (if not probability) of Fe, as well as Al, ions replacing silicon is unjustified. It may also be noted that although Zedlitz's analysis of the Finnish garnet shows neither FeO nor Ti_2O_3, in computing the formula he assigns the bulk of the titanium to R^{VI} as TiO_2 *or* Ti_2O_3 ("TiO_2 oder Ti_2O_3 Rest"). In so doing he may have been influenced by the work of Gossner and Reindl (1934) who, discussing their analysis of a melanite from Magnet Cove (TiO_2 4.39%), observed that it was unlikely that titanium and silicon were isomorphously replaceable to any significant degree. These same authors, further in the same publication, discussing their analysis of astrophylite, have Ti (TiO_2 8.02%) and Zr (ZrO_2 5.34%) grouped isomorphously, but do not have silicon replaced by Ti.

Zedlitz (1935) attempted synthesis of $Ca_3Fe_2(SiO_4)_3$, $Ca_3Fe_2[(Si, Ti)O_4]_3$ with Si, Ti $= 1:1$, and $Ca_3Fe_2(TiO_4)_3$ in order to elucidate silicon-titanium replacement; but could not make these garnets. Recently Christophe-Michel-Levy (1956) has made both $Ca_3Fe_2(SiO_4)_3$ with $a_0 = 12.014 \pm .005$ and a titanium melanite $a_0 = 12.064 \pm .005$ but did not study these further.

P. Tarte (written communication, 1959) has recently investigated the co-ordination of titanium in garnets by their infrared absorption spectra, and kindly permitted us to mention here some of his unpublished results. He finds evidence that tetrahedrally co-ordinated titanium does replace silicon at least in part; and that whereas all common garnets have a consistent absorption spectrum, the presence of titanium causes marked divergence; and the spectrum of kimzeyite is even more markedly different from that of common garnets.

In summary, then, while we have considered the titanium in kimzeyite to be present as Ti_2O_3 and the titanium ions to be in octahedral co-ordination in the normal trivalent ionic position, other workers view at least part of the titanium (in titanium garnets) as TiO_2 and in tetrahedral co-ordination in the normal silicon position. The general question, whether Ti replaces Si, or octahedral Al, or both, is still open; but in kimzeyite, the weight of evidence favors replacement of aluminum in octahedral co-ordination.

ZIRCONIUM IN OTHER GARNETS

A crystal of Magnet Cove schorlomite from the Harvard Holden collection (85491) was reported to show appreciable (3.5–4%) zirconia by *x*-ray fluorescence (Milton, D. J., personal communication, 1958). A

spectrographic determination by N. Sheffey of the U. S. Geological Survey on the same material gave 2.7% ZrO_2.

Titanian andradite from the Oka, Quebec, carbonatite, found associated with niocalite, perovskite, and pyrochlore, contains 3.7% ZrO_2 (Nickel, 1960). Through the courtesy of Dr. J. A. Gower, the following data may be quoted from a report by E. H. Nickel (1956).

"*Andradite garnet*, a calcium-iron silicate, was found as a minor constituent. A spectrographic analysis of the andradite reveals that in addition to the iron and calcium, it contains 3% titanium and 2% manganese. The andradite varies in color from clear yellow, through brown, to black. The yellow garnet has a normal cell edge for andradite (12.03 Å) as determined by x-ray diffraction analysis, while the cell edge of the black garnet is abnormally high (12.15 Å). The only significant chemical difference between the two garnets is in zirconium content. The yellow garnet contains no appreciable zirconium . . . "

Dr. Gower (1959) further notes that the black garnet contains 0.25% Nb_2O_5, at least, and probably somewhat more.

It is of interest to note that at Oka, as in the Magnet Cove carbonatite, two garnets occur closely associated in similar paragenesis but only one contains zirconium.

Zedlitz, as already mentioned, found 0.19% ZrO_2 in the Kaiserstuhl melanite (TiO_2 12.10%). He cites an earlier analysis by R. Soltmann in 1890 who found 1.28% ZrO_2 in Kaiserstuhl melanite.

Because of these three instances of melanite (or andradite, schorlomite) containing substantial zirconia, it would be desirable to ascertain its presence or absence in all such analyzed garnets. Harry J. Rose, Jr., of the U. S. Geological Survey examined a small collection of schorlomites from the Yale University Brush collection, with the following results:

Specimen	Source	Zirconium found by x-ray fluorescence
2599	Magnet Cove	>1%
2596	Magnet Cove	>1%
2598	Magnet Cove	>1%
2597	Magnet Cove	.5–1%
907	Magnet Cove	.05–.1%
4333	Magnet Cove	<.05%
2600	Magnet Cove	<.05%
2591	Kaiserstuhl	.05–0.1%

Kimzeyite run at the same time showed far greater zirconia than any of these.

The four schorlomites containing more than a tenth of a per cent zir-

conia are coarsely crystallized (a centimeter or more across) and do not differ noticeably from those with least zirconia.

It follows that many though not all schorlomites from carbonatites contain zirconia from traces up to several per cent, and the presence or absence of this element should be established spectrographically or by x-ray fluoresence in analyses of such garnets; and if zirconia is present in more than tenths of a per cent it should be determined chemically.

The Name Kimzeyite

Kimzeyite has been named to honor the members of the Kimzey family who for almost a century have been instrumental in obtaining and preserving many of the remarkable mineral specimens for which the Magnet Cove area is famous. Williams (1891) refers to William T. Kimzey repeatedly, and the family since have continued to play an active part in the economic and mineralogical development of the Magnet Cove area. Mr. Joe W. Kimzey has kindly given us the following information concerning the Kimzey family (personal letter, October 16, 1958). "Wm. J. Kimzey came to the Magnet Cove area during the early 1870's and engaged in prospecting the area and collecting fine specimens of the numerous rare minerals for the leading dealers and some English, French, and German scientists, some of whom visited the 'Cove' from time to time. After the death of Wm. J. in 1906, his sons, John, Lawton, and Joe W., have spent much time seeking out specimens of the unusual and rare minerals of the area, that now enrich the finer mineral collections throughout the world. It was Joe W. who called the new zirconium garnet to the attention of Mr. Blade and Mr. Erickson in 1953 and who served as State Geologist for Arkansas during 1943 to 1945."

Ltd., Vancouver, B. C., and Dr. E. H. Nickel, of the Mines Branch, Department of Mines and Technical Survey, Ottawa, Canada, have furnished us specimens and data of the Oka, Quebec, zirconium garnet. Mr. Daniel J. Milton called our attention to the previously unrecognized considerable zirconium content of Magnet Cove schorlomite. Professor Horace Winchell of Yale University generously placed at our disposal the small reference collection of titanian garnets from the Brush collection.

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