

# THE AMERICAN MINERALOGIST

JOURNAL OF THE MINERALOGICAL SOCIETY OF AMERICA

Vol. 46

MAY-JUNE, 1961

Nos. 5 and 6

## KIMZEYITE, A ZIRCONIUM GARNET FROM MAGNET COVE, ARKANSAS\*

CHARLES MILTON, BLANCHE L. INGRAM, AND LAWRENCE V. BLADE,  
*U. S. Geological Survey, Washington, D. C.*

### ABSTRACT

Kimzeyite,  $\text{Ca}_3(\text{Zr}, \text{Ti}, \text{Mg}, \text{Fe}''', \text{Nb})_2(\text{Al}, \text{Fe}''', \text{Si})_3\text{O}_{12}$ , 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 (dysanallyte), 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,  $\text{ZrO}_2$  29.9,  $\text{Ti}_2\text{O}_3$  5.0, MgO 0.5, FeO 0.8,  $\text{Nb}_2\text{O}_5$  1.0,  $\text{Al}_2\text{O}_3$  11.0,  $\text{Fe}_2\text{O}_3$  13.4,  $\text{SiO}_2$  9.6, sum 101.0 which computes to  $\text{Ca}_{3.11}(\text{Zr}_{1.42}{}^{+4}\text{Ti}_{0.40}{}^{+3}\text{Mg}_{0.07}{}^{+2}\text{Fe}_{0.07}{}^{+2}\text{Nb}_{0.05}{}^{+5})(\text{Al}_{1.26}{}^{+3}\text{Fe}_{0.98}{}^{+3}\text{Si}_{0.94}{}^{+4})\text{O}_{12.00}$ . Basically, this is  $\text{Ca}_3\text{Zr}_2(\text{Al}_2\text{Si})\text{O}_{12}$  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%  $\text{TiO}_2$ , 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%  $\text{ZrO}_2$  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  $\text{SiO}_2$  content is only 9.6%; most garnets contain 30 to 40%, and even the least siliceous types (titanian) contain over 25%  $\text{SiO}_2$ .

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  $\text{Gd}_3\text{Fe}_2\text{Fe}_3\text{O}_{12}$  or  $\text{Y}_3\text{Al}_2\text{Al}_3\text{O}_{12}$  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,

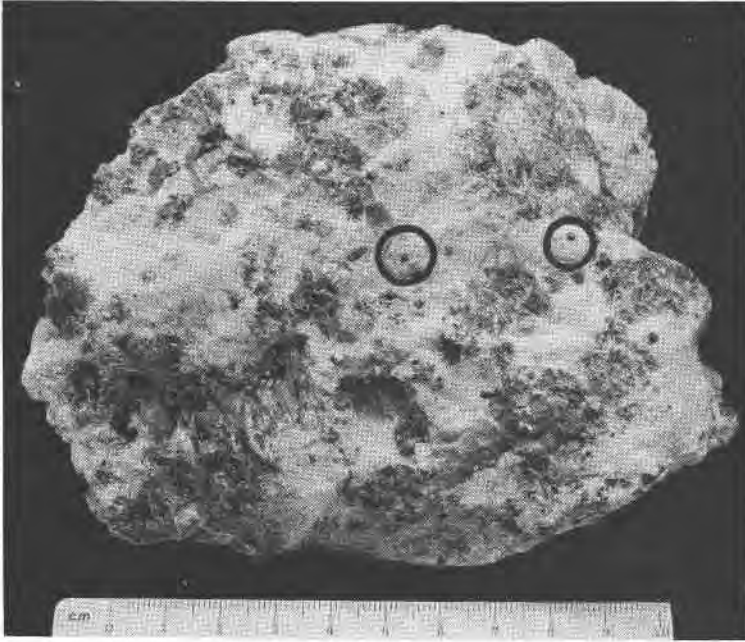


FIG. 1. Kimzeyite-bearing limestone, Magnet Cove, Ark. Two crystals of kimzeyite are present, indicated by circles. These are about average size. The white areas are fibrous apatite and calcite, the slightly darker glossy pale brownish monticellite. Rather coarse black magnetite (lower left) and disseminated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

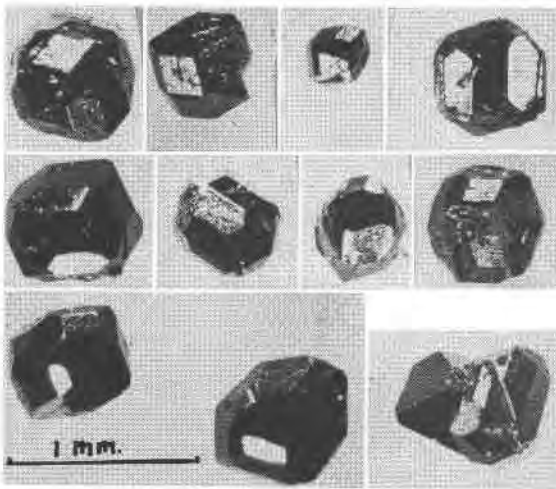


FIG. 2. Kimzeyite crystals isolated from carbonatite matrix. At the lower right is a kimzeyite crystal intergrown with a perovskite crystal.

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-

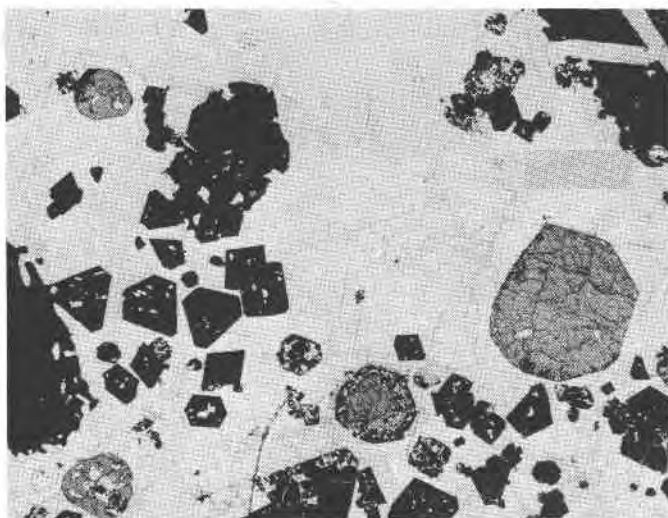


FIG. 3. Thin section of carbonatite, showing four rounded kimzeyite crystals (gray), and numerous smaller angular perovskite crystals (black) in calcitic matrix. The large black masses are magnetite; at the upper right two apatite crystals cut the magnetite.

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.

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  $110^\circ C.$  to determine  $H_2O(-)$ . It was then sintered with  $Na_2O_2$  at  $460^\circ C.$  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   | <i>alternate values * used in<br/>Table 3</i> |
| $FeO$     | 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,  $Ag$ ,  $Au$ ,  $Hg$ ,  $Ru$ ,  $Rh$ ,  $Pd$ ,  $Ce$ ,  $Ir$ ,  $Pt$ ,  $Mo$ ,  $W$ ,  $Re$ ,  $Ge$ ,  $Pb$ ,  $As$ ,  $Sb$ ,  $Bi$ ,  $Zn$ ,  $Cd$ ,  $Te$ ,  $In$ ,  $Co$ ,  $Ni$ ,  $Ga$ ,  $Cr$ ,  $V$ ,  $Y$ ,  $La$ ,  $Hf$ ,  $Th$ ,  $Ta$ ,  $Be$ ,  $Li$ ,  $Na$ ,  $K$ . 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.  $\text{Al}_2\text{O}_3$  was considered the difference between the total  $\text{R}_2\text{O}_3$  and the sum of  $\text{Fe}_2\text{O}_3$ ,  $\text{ZrO}_2$ ,  $\text{TiO}_2$  and  $\text{Nb}_2\text{O}_5$ .

Calcium was precipitated with  $(\text{NH}_4)_2\text{C}_2\text{O}_4$  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  $110^\circ\text{C}$ . and weighed. It was then ignited at  $800^\circ\text{C}$ . and the oxides dissolved. Mn was determined colorimetrically by oxidation to permanganate.

Total reducing capacity was determined by fusing the sample with sodium fluoroborate in a tube furnace at approximately  $900^\circ\text{C}$ . in an atmosphere of  $\text{N}_2$ . The fused sample was dissolved in an atmosphere of  $\text{N}_2$  with 10%  $\text{H}_2\text{SO}_4$  containing  $\text{H}_3\text{BO}_3$ , and titrated with standard  $\text{K}_2\text{Cr}_2\text{O}_7$  using sodium diphenylamine sulfonate as indicator. A fusion technique was necessary; the mineral is insoluble in the usual HF- $\text{H}_2\text{SO}_4$  mixture.

Total  $\text{H}_2\text{O}$  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% | $\frac{\text{Cation}\%}{\text{At. Wt.}}$ | $\frac{\text{Equiv.}}{\text{Oxygen}}$ | $\frac{\text{Cation}\%}{\text{At. Wt.} \times 171}$ |
|--------------------------------|---------|---------|--|---------------------------------------|---|
| CaO                            | 29.8    | 21.3    | 8.5                                      | .532                                  | 3.11 ( $\times 10^{-3}$ )                           |
| MgO                            | 0.5     | 0.3     | 0.2                                      | .012                                  | .07 ( $\times 10^{-3}$ )                            |
| FeO                            | 0.8     | 0.6     | 0.2                                      | .011                                  | .07 ( $\times 10^{-3}$ )                            |
| Fe <sub>2</sub> O <sub>3</sub> | 13.4    | 9.4     | 4.0                                      | .168                                  | .98 ( $\times 10^{-3}$ )                            |
| Ti <sub>2</sub> O <sub>3</sub> | 5.0     | 3.3     | 1.7                                      | .069                                  | .40 ( $\times 10^{-3}$ )                            |
| Al <sub>2</sub> O <sub>3</sub> | 11.0    | 5.8     | 5.2                                      | .215                                  | 1.26 ( $\times 10^{-3}$ )                           |
| ZrO <sub>2</sub>               | 29.9    | 22.1    | 7.8                                      | .242                                  | 1.42 ( $\times 10^{-3}$ )                           |
| Nb <sub>2</sub> O <sub>5</sub> | 1.0     | 0.7     | 0.3                                      | .008                                  | .05 ( $\times 10^{-3}$ )                            |
| SiO <sub>2</sub>               | 9.6     | 4.5     | 5.1                                      | .160                                  | .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 |
|----------------------|---------------|--------------|----------------------|
| $A = Ca_{3.11}^{+2}$ | 8             | 1.03 Å       | 6.22                 |
| $B = Mg_{.07}^{+2}$  | 6             | .66          | .14                  |
| $Nb_{.05}^{+5}$      | 6             | .69          | .25                  |
| $Ti_{.40}^{+3}$      | 6             | .76          | 1.20                 |
| $Fe_{.07}^{+2}$      | 6             | .74          | .14                  |
| $Zr_{1.42}^{+4}$     | 6             | .79          | 5.68                 |
| $X = Si_{.94}^{+4}$  | 4             | .40          | 3.76                 |
| $Fe_{.98}^{+3}$      | 4             | < .64        | 2.94                 |
| $Al_{1.26}^{+3}$     | 4             | .49          | 3.78                 |
|                      |               |              | 24.11 (cationic)     |
| $O_{12}^{-2}$        |               |              | 24.00 (anionic)      |

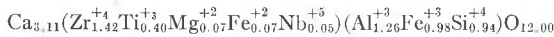
must exist in the garnet  $Gd_3Fe_5O_{12}$  ( $Gd_3Fe_2Fe_3O_{12}$ ) synthesized by Bertaut and Forrat (1956); and tetrahedral aluminum in the yttrio-garnet  $Y_3Al_5O_{12}$  ( $Y_3Al_2Al_3O_{12}$ ) synthesized by Yoder and Keith (1951). In many silicates, such as feldspars and zeolites, aluminum replaces silicon in



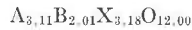
tetrahedral co-ordination. As to the ionic radius of such tetrahedrally co-ordinated iron, Green (1959) lists no value; but from geometrical considerations it must be less than the ionic radius he does list for octahedral trivalent iron, 0.64.

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.

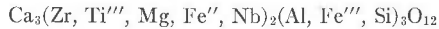
The formula of kimzeyite is therefore



with



or, more simply



and derives from a basic formula  $\text{Ca}_3\text{Zr}_2(\text{Al}_2\text{Si})\text{O}_{12}$  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  $\text{RO}_2$  and  $\text{RO}$ , and low for  $\text{R}_2\text{O}_3$ , which makes plausible the suggestion of Zedlitz that part of the titanium is present in the trivalent state. (Any  $\text{Ti}_2\text{O}_3$  present would cause a corresponding amount of  $\text{Fe}_2\text{O}_3$  to be reported as  $\text{FeO}$ .)"

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  $17.3 \pm 0.5\%$   $\text{TiO}_2$ , respectively. In computing their formulas he assigned in each case sufficient  $\text{TiO}_2$  to  $\text{SiO}_2$  to arrive at a close approximation to the type garnet ionic ratios of  $3\text{R}^{\text{VIII}}2\text{R}^{\text{VI}}3\text{R}^{\text{IV}}$ , grouping with the  $\text{SiO}_2$  the  $\text{Al}_2\text{O}_3$ , but not the equally available  $\text{Fe}_2\text{O}_3$ . His justification for grouping  $\text{TiO}_2$  with  $\text{SiO}_2$ , 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 Abkühlung des Oberflächenmuttergesteins"). 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<sub>2</sub> oder Ti<sub>2</sub>O<sub>3</sub> 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<br>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 fluorescence 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."

#### ACKNOWLEDGMENTS

Many people have materially assisted in this study, and we cannot name them all. Besides our numerous colleagues of the U. S. Geological Survey, and Michael Fleischer in particular, we are largely indebted to Mr. Norman T. Williams, State Geologist of Arkansas and to Mr. Joe W. Kimzey of Malvern, Arkansas, former State Geologist of Arkansas, for many kindnesses extended in a field study of the occurrence; we are also grateful to Professor Rustum Roy, of Pennsylvania State University, to Dr. Hatten S. Yoder, Jr. of the Geophysical Laboratory, to Professor Clifford Frondel, of Harvard University, and to Dr. P. Tarte, of the University of Liege, Belgium for their friendly interest and most helpful discussions of the problems encountered in this investigation; needless to say they are not responsible for any erroneous statements or conclusions of this report. Dr. J. A. Gower of the Northwestern Explorations,

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.

## REFERENCES

- BERTAUT, FELIX, and FORRAT, FRANCIS (1956), Structure des ferrites ferrimagnétiques des terres rares: *Acad. Sci. Paris comptes rendus*, **242**, 382-384.
- CHRISTOPHE-MICHEL-LEVY, M. (1956), Reproduction artificielle des grenats calciques: grossulaire et andradite: *Bull. Soc. française Mineral. Crist.*, **70**, 124-128.
- EITEL, WILHELM (1954), *The Physical Chemistry of the Silicates*: University of Chicago Press, p. 20.
- ERICKSON, R. L., and BLADE, L. V. (1956), Map of bedrock geology of Magnet Cove igneous area, Hot Spring County, Arkansas: *U. S. Geol. Survey Mineral Inv. Field Studies Map MF 53*.
- FLEISCHER, M. (1937), Relation between chemical composition and physical properties in the garnet group: *Am. Mineral.*, **22**, 751-759.
- FLEISCHER, M. (1955), Hafnium content and hafnium-zirconium ratio in minerals and rocks: *U. S. Geol. Survey Bull.*, **1021-A**, 9.
- FRONDEL, CLIFFORD (1957), Zirconium: Mineralogy and Geochemistry: *2d Nuclear Engineering and Science Conference Paper No. 57-NESC-32 Am. Soc. Mech. Engineers*.
- FRYKLUND, V. C., JR., HARNER, R. S., and KAISER, E. P. (1954), Niobium (columbium) and titanium at Magnet Cove and Potash Sulphur Springs, Arkansas: *U. S. Geol. Survey Bull.*, **1015 B**, 48.
- GELLER, S., and MILLER, C. E. with an appendix by TRUETING, R. G. (1960), New synthetic garnets: *Acta Cryst.*, **13**, 179-186.
- GOSSNER, B., and REINDL, E. (1934), Über die chemische Zusammensetzung titanhaltiger Silikate, insbesondere von Astrophyllite: *Centralblatt f. Mineralogie., etc. Abt. A* 161-167.
- GOWER, J. A. (1959), personal communication to L. G. Berry.
- GREEN, JACK (1959), Geochemical Table of the elements for 1959: *Geol. Soc. America Bull.*, **70**, 1127-1184.
- HENDRICKS, STERLING B. (1939), Random structures of layer minerals as illustrated by cronstedite ( $2\text{FeO} \cdot \text{Fe}_2\text{O}_3 \cdot \text{SiO}_2 \cdot 2\text{H}_2\text{O}$ ). Possible iron content of kaolin: *Am. Mineral.*, **24**, 529-539.
- JAFFE, HOWARD W. (1956), Application of the rule of Gladstone and Dale to minerals: *Am. Mineral.*, **41**, 757-777.
- LARSEN, ESPER S., and BERMAN, HARRY (1934), The microscopic determination of the non-opaque minerals, 2d ed: *U. S. Geol. Survey Bull.*, **848**, 30-31.
- MILTON, CHARLES, and BLADE, LAWRENCE V. (1958), Preliminary note on kimzeyite, a new zirconium garnet: *Science*, **127**, 1343.
- NICKEL, E. H. (1956), A mineralogical study of diamond drill core NX-6 from the Oka. P. Q. property of the Molybdenum Corporation of America: *Investigation No. MD-3116 Canada Dept. of Mines and Technical Surveys, Mines Branch*.

- NICKEL, E. H. (1960), A zirconium-bearing garnet from Oka, Quebec: *Canadian Mineral.*, **6**, 549-550.
- RAMDOHR, R. (1936), Ein Zinnvorkommen im Marmor bei Arandis, Deutsch Sudwestafrika: *Neues Jahrb. Min. Geol. B.B.*, **70**, A, 1 (cited in Rankama and Sahama, 1950 p. 732).
- RANKAMA, KALERVO AND SAHAMA, TH. G. (1950), *Geochemistry*: The University of Chicago Press.
- WILLIAMS, J. FRANCIS (1891), The igneous rock of Arkansas: Vol. II, Annual Report, Geological Survey of Arkansas.
- YODER, H. S., AND KEITH, M. C. (1951), Complete substitution of aluminum for silicon—the system  $3\text{MnO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2 \cdot 3\text{Y}_2\text{O}_3 \cdot 5\text{Al}_2\text{O}_3$ : *Am. Mineral.*, **36**, 519-533.
- ZEDLITZ, OTTO (1933), Über titanreichen Kalkeisengranat I: *Centralblatt f. Mineralogie, etc., Abt. A* 225-239.
- ZEDLITZ, OTTO (1935), Über titanreichen Kalkeisengranat II: *Centralblatt f. Mineralogie, etc., Abt. A* 68-78.

*Manuscript received July 11, 1960.*