## Dedicated to the memory of Polina Zaitseva

# Kerimasite, $Ca_3Zr_2(Fe_2^{3+}Si)O_{12}$ , a new garnet from carbonatites of Kerimasi volcano and surrounding explosion craters, northern Tanzania

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### ABSTRACT

Kerimasite, ideally Ca<sub>3</sub>Zr<sub>2</sub>(Fe<sub>2</sub><sup>3+</sup>Si)O<sub>12</sub>, is a new calcium zirconium silicate-ferrite member of the garnet group from the extinct nephelinitic volcano Kerimasi and surrounding explosion craters in northern Tanzania. The mineral occurs as subhedral crystals up to 100 µm in size in calcite carbonatites, and as euhedral to subhedral crystals up to 180 µm in size in carbonatite eluvium. Kerimasite is light to darkbrown in colour and transparent with a vitreous lustre. No cleavage or parting was observed and the mineral is brittle. The calculated density is 4.105(1) g/cm<sup>3</sup>. The micro-indentation, VHN<sub>25</sub>, ranges from 1168 to 1288 kg/mm<sup>2</sup>. Kerimasite is isotropic with n = 1.945(5). The average chemical formula of the mineral derived from electron microprobe analyses (sample K 94-25) and calculated for O = 12 and all Fe as Fe<sub>2</sub>O<sub>3</sub> is (Ca<sub>3.00</sub>Mn<sub>0.01</sub>Ce<sub>0.01</sub>Nd<sub>0.01</sub>)<sub>5.0.3</sub>(Zr<sub>1.72</sub>Nb<sub>0.14</sub>Ti<sub>0.08</sub>Mg<sub>0.02</sub>Y<sub>0.02</sub>)<sub>5.1.98</sub>(Fe<sub>1.23</sub><sup>4</sup>Si<sub>0.86</sub>Al<sub>0.82</sub> Ti<sub>0.09</sub>)<sub>5.2.00</sub>O<sub>12</sub>. The largest Fe content determined in kerimasite is 21.6 wt.% Fe<sub>2</sub>O<sub>3</sub> and this value corresponds to 1.66 a.p.f.u. in the tetrahedral site. Kerimasite is cubic, space group  $Ia\bar{3}d$  with a = 12.549(1) Å, V = 1976.2(4) Å<sup>3</sup> and Z = 8. The five strongest powder-diffraction lines [*d* in Å, (*I/I*<sub>0</sub>), *hkI*] are: 4.441 (49) (220), 3.140 (91) (400), 2.808 (70) (420), 2.564 (93) (422) and 1.677 (100) (642). Single-crystal structure refinement revealed the typical structure of the garnet-group minerals. The name is given after the locality, Kerimasi volcano, Tanzania.

**Keywords:** kerimasite, kimzeyite, garnet, new mineral, carbonatite, chemical composition, crystal structure, Kerimasi, Loluni, Kisete, Loolmurwak, Tanzania.

#### Introduction

ZIRCONIUM is a common minor component in Ca-Fe<sup>3+</sup>-Ti<sup>4+</sup>garnets forming the andradite-melanite-schorlomite solid solution. Typically these minerals occur in ultrabasic, alkaline rocks and carbonatites: e.g. Oka, Québec, Canada (Nickel,

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1957), Vuorivarvi, Seblyavr and Afrikanda, Kola Peninsula, Russia (Borodin and Bykova, 1963; Lapin, 1979; Chakhmouradian and Zaitsev, 2002; Chakhmouradian and McCammon, 2005), Guly, Maimecha-Kotuy, Russia (Borodin and Bykova, 1963), Iron Hill, Colorado, USA (Dowty, 1971), Magnet Cove, Arkansas, USA (Chakhmouradian and McCammon 2005), Marathon, Ontario, Canada (Platt and Mitchell, 1979), Polino, Umbria, Italy (Lupini et al., 1992), Osečná, Bohemia, Czech Republic (Ulrych et al., 1994), Oldoinyo Lengai, Gregory rift, Tanzania (Dawson et al., 1995; Dawson and Hill, 1998), Tomgat, Québec and Labrador, Canada (Tappe et al., 2004) and Tikiusaaq, West Greenland (Tappe et al., 2009). Garnet can accommodate significant Zr contents, up to 19.5 wt.% ZrO<sub>2</sub>, and the incorporation of Zr is explained by the coupled substitution  ${}^{[6]}Fe^{3+} + {}^{[4]}Si^{4+} \rightleftharpoons {}^{[6]}Zr^{4+} +$ <sup>[4]</sup>(Al,Fe)<sup>3+</sup> (Platt and Mitchell, 1979). Zr-bearing garnet, with 1.2-7.3 wt.% ZrO2 has also been reported from skarns at Fuka, Okayama, Japan (Henmi et al., 1996) and Maronia, Rhodope, Greece (Katerinopoulou et al., 2009), and 3.2-16.9 wt.% ZrO<sub>2</sub> was recorded in garnet from rodingite-like aposkarn rocks from Wiluy, Sakha-Yakutia, Russia (Galuskina et al., 2005).

Garnet with Zr as a dominant octahedral cation was originally documented in carbonatites from Magnet Cove, Arkansas, USA and named kimzeyite, with a simplified chemical formula:  $Ca_3(Zr,Ti,Mg,Fe^{2+},Nb)_2(Al,Fe^{3+},Si)_3O_{12}$  and ideal formula:  $Ca_3Zr_2(Al_2Si)O_{12}$  (Milton and Blade, 1958; Milton *et al.*, 1961). Additional compositional data for kimzeyite from Magnet Cove are given by Lupini *et al.* (1992), Haynes *et al.* (2003) and Whittle *et al.* (2007) (the last paper gives a mineral formula only), and these data show some variations in the content of cations filling the tetrahedral Z site:  $(Si_{1.09}Fe_{1.08}^{3+}$  $Al_{0.82}Ti_{0.01}$ ),  $(Si_{1.19}Al_{0.92}Fe_{0.90}^{3+})$  and  $(Fe_{1.09}^{3+}Si_{0.94}^{-})$  $Al_{0.87}$ ), respectively.

Kimzeyite is also known from a shoshonitic basalt from Stromboli, Italy (Munno *et al.*, 1980) and from a holocrystalline ejectum in a pyroclastic flow near Anguillara Sabazia, Italy (Schingaro *et al.*, 2001). The *Z* site in kimzeyite from both Italian localities is relatively rich in Si, i.e.  $(Si_{1.51}Al_{1.00}Fe_{0.49}^{3+})$  and  $(Si_{1.34}Fe_{0.85}^{3+}Al_{0.81})$ , respectively. On the basis of the study by Munno *et al.* (1980), the kimzeyite formula was revised as Ca<sub>3</sub>(Zr,Ti)<sub>2</sub>(Si,Al,Fe<sup>3+</sup>)<sub>3</sub>O<sub>12</sub> (Anthony *et al.*, 1995; IMA list of minerals at http:// pubsites.uws.edu.au/ima-cnmnc/). Other known localities of kimzeyite are in metamorphic rocks from Flekkeren, Norway (Jamtveit *et al.*, 1997), and rodingite-like aposkarn rocks from Wiluy, Sakha-Yakutia, Russia (Galuskina *et al.*, 2005).

During recent years considerable attention has been given to the mineralogical and geochemical studies of carbonatites from Oldoinvo Lengai and Kerimasi volcanoes located in the Gregory rift in northern Tanzania (Keller and Zaitsev, 2006; Mitchell, 2006a,b; Zaitsev and Keller, 2006; Reguir et al., 2008; Zaitsev et al., 2008, 2009a,b; Zaitsev, 2009), and in this paper we describe a new zirconium mineral from the Kerimasi volcano and Loluni, Kisete and Loolmurwak explosion craters. The new mineral is a member of the garnet group, and has been named kerimasite, after its type locality, the Kerimasi volcano. Both the mineral and mineral name have been approved by the Commission on New Mineral and Minerals Names of the IMA, proposal 2009-029. The co-type specimens of two samples studied are part of the petrology collection at the Natural History Museum, London, UK [sample K 94-25 - catalogue number BM.1995, P6(47) and sample K 22 catalogue number BM.1995,P6(22)]. A polished block with heavy mineral fractions from eluvial deposits that contain kerimasite, samples KZ 2 and LL 4, is deposited at the Mineralogical Museum, Department of Mineralogy, Faculty of Geology, St. Petersburg State University, St. Petersburg, Russia (catalogue number 1/19363).

#### Geological setting

The Gregory rift in northern Tanzania is a well known volcanic province of Neogene-Quaternary phonolitic, nephelinitic and carbonatitic volcanism. Several large volcanoes, including Oldoinyo Lengai, Kerimasi and Mosonik, and numerous small volcanic cones and explosion craters occur within an area of  $\sim 1000 \text{ km}^2$  (Fig. 1) (Dawson, 1962, 1964, 2008; Dawson and Powell, 1969). Oldoinyo Lengai is a famous nephelinitephonolite volcano with recent eruptions of lavas and lapilli of gregoryite-nyerereite carbonatites (e.g. Keller and Krafft, 1990; Peterson, 1990; Zaitsev et al., 2009b). Kerimasi is an extinct volcano composed of nephelinitic pyroclastic rocks and lavas with carbonatite agglomerates and tuffs (Mariano and Roeder, 1983; Hay, 1983; Church, 1995; Reguir et al., 2008; Zaitsev, 2009).

There are  $\sim 100$  small volcanic features in this part of the Gregory rift represented by tuff cones,



FIG. 1. Panoramic view of Kerimasi volcano, Loolmurwak crater and Oldoinyo Lengai volcano. The direction of view is to the west (photo by S.V. Petrov).

ubehebe-type tuff rings and maar-type explosions craters (Dawson and Powell, 1969; Hay, 1983; Dawson and Smith, 1988; Johnson *et al.*, 1997; Tripoli, 2008). These features consist of silicate and carbonate pyroclastic rocks with small volumes of olivine melilitite and olivine-melilite nephelite lavas (Dawson *et al.*, 1985; Keller *et al.*, 2006, Wiedenmann *et al.*, 2010).

Carbonatites are represented by both intrusive and extrusive types. They occur as blocks up to 0.5 m in diameter. Intrusive carbonatites are calcitic in composition and contain forsterite pseudomorphs, magnetite or magnesioferrite and fluorapatite as minor mineral phases, and phlogopite, perovskite, pyrochlore, baddeleyite and calzirtite as accessory minerals (Dawson et al., 1996; Church, 1995; Reguir et al., 2008). A rare variety of calcite carbonatite with abundant periclase has been described from the crater of the Kerimasi volcano (Mariano and Roeder, 1983). Extrusive carbonatites, lava blocks and tuffs, are also calcitic in composition and consist of two morphological varieties of calcite (Mariano and Roeder, 1983; Hay, 1983; Church, 1995; Zaitsev, 2009). The first variety is tabular, single-crystal phenocrysts up to  $0.8 \text{ mm} \times 4 \text{ mm}$  in size. The second variety is also tabular but contains polycrystalline phenocrysts consisting of parallel layers of calcite and voids. Whereas the tabular calcite phenocrysts are a primary magmatic phase (Mariano and Roeder, 1983; Church, 1995; Zaitsev, 2009), the polycrystalline phenocrysts are considered to be pseudomorphs after nyerereite (Hay, 1983). Although this hypothesis has not been generally accepted (Bailey, 1993; Church, 1995; Mitchell, 2005; Woolley and Church, 2005), a recent finding of abundant nyerereite solid inclusions in magnesioferrite from Kerimasi carbonatite supports Hay's suggestion that Kerimasi carbonatites were originally alkalinerich and could have crystallized nyerereite phenocrysts (Zaitsev, 2009).

# Mineral occurrence, morphology and physical properties

Kerimasite has been identified in five samples of carbonatites collected from outcrops on the eastern slope of the volcano (samples K 94-25 and K 22) and from explosion craters at Kisete (sample KZ 2-4 and KZ 2-5) and Loolmurwak (sample TZ 41). Carbonatites occur as blocks in agglomerates and are typically intrusive rocks with calcite as the major mineral, with minor forsterite, now completely pseudomorphed, together with magnesioferrite and fluorapatite, and accessory baddeleyite and pyrochlore (Fig. 2a). All samples show signs of alteration which resulted in calcite recrystallization, forsterite alteration and development of latestage veinlets and nests of dolomite, baryte and an unidentified Ca-Ba-Mn hydroxide. Kerimasite occurs as single spherical, subhedral to euhedral crystals up to 100 µm in diameter enclosed in calcite and rarely in fluorapatite, and occasionally is associated with, and overgrows, magnesioferrite (Fig. 2b).

Large subhedral to euhedral crystals, up to 180  $\mu$ m in diameter (Fig. 2*c*), have been identified in samples of heavy mineral fractions from eluvial deposits on carbonatite agglomerates associated with the Loluni and Kisete explosion craters (samples LL 4 and KZ 2, respectively). Kerimasite occurs in a paramagnetic fraction with magnetic susceptibility of minerals between 40 and  $120 \times 10^{-6}$  cm<sup>3</sup>/g. In addition to kerimasite, heavy mineral fractions contain diopside, schorlomite, andradite, magnetic, magnetic, perovskite,



FIG. 2. (a) BSE image of sample K 94-25 showing calcite carbonatite with pseudomorphed forsterite, fluorapatite and magnesioferrite; (b) BSE image of sample K 94-25 showing subhedral crystal of kerimasite; (c) SE image of sample LL 4 of a typical kerimasite crystal from carbonatite eluvium; (d) BSE image of sample KZ 2 show kerimasite crystals intergrown with fluorapatite and cored by corroded relict baddelyite.

fluorapatite, pyrochlore, calzirtite, baddeleyite and cerianite-(Ce). Fluorapatite was observed as inclusions in kerimasite, and one of the kerimasite crystals studied has a corroded relict baddeleyite core (Fig. 2d).

On the basis of its microstructures, we conclude that kerimasite in the carbonatites is a magmatic mineral that crystallized after pyrochlore, baddeleyite, and magnesioferrite, but before calcite. Kerimasite also crystallized after fluorapatite, or in some cases, simultaneously with it.

Kerimasite typically occurs as isometric single crystals with well developed trapezohedron  $\{211\}$  faces (Fig. 2c). In a few cases, intergrowths of two or three crystals were observed. Macroscopically the mineral is light to dark brown in colour; it is transparent with a vitreous lustre, and brittle, but no cleavage or parting were observed. The micro-indentation (microhardness), VHN load 25 g,

ranges from 1168 to 1288 kg/mm<sup>2</sup> (three measurements were made on a single crystal mounted in a polished block) which is equivalent to a Mohs' hardness of ~7. The density of the kerimasite could not be measured because of the small grain size and abundant pores and inclusions, but the calculated density from average empirical formulae and refined unit-cell parameter is 4.104(1) g/cm<sup>3</sup>. Kerimasite has a refractive index *n* of 1.945(5) (Na light, 589 nm). In thin section, under transmitted light, kerimasite is characterized by a yellowish-greenish colour, and under crossed polars the mineral is optically heterogeneous – isotropic to anisotropic.

#### Raman spectroscopy

Raman spectra were obtained using a Renishaw RM 1000 microspectrometer with a 633 nm HeNe

laser (School of Earth Sciences and Geography, Kingston University, London) and the calibration of spectra was performed using a Si standard. Four Raman spectra of kerimasite were recorded from the crystal shown in Fig. 2b. All spectra have identical peak positions  $(\pm 1 \text{ cm}^{-1})$ , with minor variations in peak intensities. A spectrum from the crystal core is shown in Fig. 3.

The Raman spectrum of kerimasite between 100 and 1100 cm<sup>-1</sup> (Fig. 3*a*) is almost identical to those for kimzeyite from Anguillara, Italy and from Wiluy, Russia for which intense Raman bands occur at 298 and 500 cm<sup>-1</sup>. The bands are attributed to rotations  $[R(ZO_4)]$ /translations  $[T(ZO_4)]$  and a bending mode  $[(Z-O)_{bend.})$  of the ZO<sub>4</sub> group, respectively (Schingaro *et al.*, 2001; Galuskina *et al.*, 2005). A less intense Raman band is observed at 732 cm<sup>-1</sup> and is assigned to stretching vibrations of the ZO<sub>4</sub> tetrahedron  $[(Z-O)_{str.}]$ . Compared with kimzeyite, an additional low-intensity broad Raman band occurs at 573 cm<sup>-1</sup> in the kerimasite spectrum and no bands are present at 937–939 cm<sup>-1</sup>.

Low-intensity, broad and composite Raman bands occur in all recorded spectra between 3100 and 3700 cm<sup>-1</sup> with a maximum at 3420 cm<sup>-1</sup> in the kerimasite spectrum (Fig. 3*b*). The presence of

Raman bands at ~3600 cm<sup>-1</sup> indicates incorporation of an (OH)<sup>-</sup> group in the structure of garnet minerals (e.g. Arredondo and Rossman, 2002). The observed bands in the kerimasite spectra can also be attributed to internal O–H stretching vibrations of the O<sub>4</sub>H<sub>4</sub> group, but the explanation for a strong shift in bond position is unclear.

#### **Chemical composition**

Prior to acquiring quantitative microprobe analyses, kerimasite was studied using a JEOL 5900LV SEM equipped with an Oxford Instruments X-sight Si(Li) detector (The Natural History Museum, London). All kerimasite crystals exhibit oscillatory zoning with individual zones <10 µm wide. This zonation is interpreted as a primary crystal-growth feature as individual zones are parallel to crystal faces (Fig. 4). Additionally, many kerimasite crystals from eluvial deposits display both this internal structure, and the development of irregular patches and veinlet areas, possibly indicating some degree of secondary alteration (Fig. 4a,b). A few crystals have a distinctive core that has a smaller mean atomic number (Z), and display a multi-stage crystal growth formation (Fig. 4c,d).



FIG. 3. Raman spectra of kerimasite, sample K 94-25 (Fig. 2b, Table 1, analyses 1–4). The relative scaling factor for the band at 3420 cm<sup>-1</sup> is  $\times 6.3$  with respect to the band at 500 cm<sup>-1</sup>.



FIG. 4. BSE images of sample KZ 2 (a,b,c) and LL 4 (d) showing the internal structure of kerimasite from carbonatite eluvium.

Quantitative microprobe analyses of kerimasite were obtained using the wavelengthdispersive Cameca SX-50 and SX-100 electron microprobes at the Natural History Museum, London. The operating conditions were 15 kV accelerating voltage, 25 nA beam current and 1 µm beam diameter. The following standards were used for calibration: magnetite (Fe), corundum (Al), zircon (Si, Zr), rutile (Ti), NaNbO3 (Nb), MgO (Mg), Y and Ln-silicate glasses (Y, La, Ce, Nd, Sm, Eu, Gd), wollastonite (Ca), MnTiO<sub>3</sub> (Mn), Sc(PO<sub>4</sub>) (Sc), jadeite (Na), baryte (Ba), Hf metal (Hf). Corrections due to element peak overlaps were applied. The chemical composition of the garnet was determined in three carbonatite samples K 94-25, K 22 and TZ 41, and in seven separate crystals from eluvial deposits KZ 2 and LL 4. A total of 98 microprobe analyses was obtained and the data are plotted in Fig. 5. For classification purposes the so-called 'dominant-valency rule' was chosen. As shown in Fig. 5, all data from the crystal studied were plotted in the kerimasite field and two varieties of the mineral are present:



FIG. 5. Composition (Z site, at.%) of kerimasite. Data are from this study (red symbols for Fe<sup>3+</sup>-enriched kerimasite and green symbols for Si-enriched kerimasite). Black symbols are published data for kimzeyite (Milton *et al.*, 1961; Munno *et al.*, 1980; Lupini *et al.*, 1992; Schingaro *et al.*, 2001; Haynes *et al.*, 2003; Galuskina *et al.*, 2005; Whittle *et al.*, 2007).

one is a kerimasite with dominant  $Fe^{3+}$  in a tetrahedral site and another is a kerimasite enriched in Si. The latter variety corresponds to published data for kimzeyite and has a simplified mineral formula identical to the formula accepted by the International Mineralogical Association for kimzeyite. This is an example of a confusing situation in mineral nomenclature following introduction of the 'dominant-valency rule' (Bulakh, 2009; Wiedenmann *et al.*, 2009).

The garnet studied is characterized by large amounts of Zr (22.6–36.6 wt.% ZrO<sub>2</sub>), Ca (26.1–28.9 wt.% CaO), Fe (15.0–20.4 wt.% Fe<sub>2</sub>O<sub>3</sub>), Si (7.4–14.7 wt.% SiO<sub>2</sub>) and Al (5.0–7.4 wt.% Al<sub>2</sub>O<sub>3</sub>), and a relatively small amount of of Ti (1.4–5.7 wt.% TiO<sub>2</sub>) (Table 1). It also contains minor Ln (lanthanides) (0.1–1.6 wt.% Ln<sub>2</sub>O<sub>3</sub>), Mg ( $\leq 0.9$  wt.% MgO), Y (0.2–0.5 wt.% Y<sub>2</sub>O<sub>3</sub>), Mn (0.1–0.4 wt.% MnO) and traces of Ba and Hf ( $\leq 0.3$  wt.% BaO and HfO<sub>2</sub>). A particular feature is the high and variable content of Nb, which ranges between 1.9 and 6.7 wt.% Nb<sub>2</sub>O<sub>5</sub>.

Calculation of the mineral formulae was based on 12 oxygens and the assumption that all Fe is present as  $Fe^{3+}$  (Table 1). Unfortunately, there was insufficient material for direct determination of  $Fe_2O_3$ , FeO and for  $H_2O$ . However, the analytical totals, which range from 98.5 to 101.3, have an average value of 99.7 wt.%. Cation totals range from 7.94 to 8.05, possibly due to the presence of water and some Fe as  $Fe^{2+}$ . However, the average of 7.99 suggests that the  $H_2O$  contents are probably not significant.

Assignment of the cations to the individual sites in the garnet was based on available data for kimzeyite and schorlomite (Munno *et al.*, 1980; Schingaro *et al.*, 2001; Chakhmouradian and McCammon 2005; Galuskina *et al.*, 2005), and on the results of this study:

1: Z site: 
$$Si + Al + Fe^{3+} + Ti$$

2: Y site: 
$$Zr + Ti + Nb + Fe^{3+} + Mg$$

3: X site: Ca + Mn

Figures 6 and 7 show the relationships between the major cations of the garnet for the Z and Y sites. Data from 44 analyses indicate the presence of two mineral varieties within our samples. The first is kerimasite with  $Fe^{3+}$  as a dominant cation in the Z site (1.12–1.52 a.p.f.u.) with subordinate amounts of Si (0.76–1.16 a.p.f.u.) and Al



FIG. 6. Tetrahedral (Z site) composition of kerimasite (red colour: carbonatites, green colour: carbonatite eluvium, filled symbols:  $Fe^{3+}$ -enriched kerimasite; empty symbols: Si-enriched kerimasite).

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wt.% Fe <sub>2</sub> O <sub>3</sub> 17.84 16.52 16.23 16.40 16.41 15.54 16.01	0.72 0.33 0.88 1.20 0.43
Fe <sub>2</sub> O <sub>3</sub> 17.84 16.52 16.23 16.40 16.41 15.54 16.01	0.72 0.33 0.88 1.20 0.43
2-5	0.33 0.88 1.20 0.43
$A_{12}O_{3}$ 6.07 7.27 7.17 6.93 6.94 6.62 6.83	0.88 1.20 0.43
SiO <sub>2</sub> 7.97 7.43 7.75 7.75 8.09 9.97 8.37	1.20 0.43
ZrO <sub>2</sub> 34.10 33.55 32.60 35.80 34.56 32.97 34.42	0.43
TiO <sub>2</sub> 1.43 2.03 2.09 1.90 1.83 2.77 2.10	
Nb <sub>2</sub> O <sub>5</sub> 3.05 4.76 4.31 2.80 3.46 2.61 3.00	0.75
MgO 0.09 0.16 0.17 0.08 0.14 0.36 0.16	0.10
Y <sub>2</sub> O <sub>3</sub> 0.33 0.25 0.29 0.18 0.33 0.22 0.30	0.06
$La_2O_3$ 0.09 0.07 0.10 0.09 0.08 - 0.09	0.02
$Ce_2O_3$ 0.44 0.29 0.32 0.40 0.24 0.19 0.31	0.09
Nd <sub>2</sub> O <sub>3</sub> 0.21 0.23 0.20 0.24 0.24 0.20 0.24	0.06
$Sm_2O_3$ 0.10 0.12	
$Gd_2O_3 = 0.12 - 0.18$	
CaO 26.65 27.33 27.59 26.96 26.99 28.01 27.31	0.41
MnO – 0.12 0.14 – 0.10 0.15 0.11	0.03
Total         98.47         100.01         99.12         99.53         99.38         100.07 <sup>1</sup> 99.25	
Formulae calculated for 12 O	
$Fe^{3+}$ 140 1.27 1.25 1.27 1.26 1.17 1.23	
Si 0.83 0.76 0.80 0.80 0.83 1.00 0.86	
Al 0.75 0.87 0.87 0.84 0.84 0.78 0.82	
Ti 0.02 0.10 0.08 0.09 0.07 0.05 0.09	
Total Z 3.00 3.00 3.00 3.00 3.00 3.00 3.00	
Zr 1./3 1.6/ 1.63 1.80 1./3 1.61 1./2	
Nb $0.14$ $0.22$ $0.20$ $0.13$ $0.16$ $0.12$ $0.14$	
11 0.09 0.06 0.08 0.06 0.07 0.16 0.08	
Mg 0.01 0.02 0.02 0.01 0.02 0.05 0.02	
Y 0.02 0.01 0.02 0.01 0.02 0.01 0.02	
Gd 0.01	
Total Y         1.99         1.98         1.96         2.01         2.00         1.96 <sup>1</sup> 1.98	
Ca 2.98 2.99 3.03 2.97 2.96 3.01 3.00	
Mn 0.01 0.01 0.01 0.01 0.01	
Ce 0.02 0.01 0.01 0.02 0.01 0.01 0.01	
Nd 0.01 0.01 0.01 0.01 0.01 0.01 0.01	
Total X         3.01         3.02         3.06         3.00         2.99         3.04         3.03	

TABLE 1. Chemical composition of kerimasite and kimzeyite from carbonatites.

Sample K 94-25. All Fe calculated as Fe<sub>2</sub>O<sub>3</sub>.

<sup>1</sup> including Eu<sub>2</sub>O<sub>3</sub> 0.13 wt.%, Sc<sub>2</sub>O<sub>3</sub> 0.03 wt.% and BaO 0.18 wt.% (0.01 a.p.f.u.).

- below detection limit.

 $(0.62-0.89 \ a.p.f.u.)$  in samples K 94-25, K 22 and TZ 41 (Table 1, analyses 1–11, Fig. 6).

The second kerimasite variety has Si as a dominant cation in the Z site (1.11-1.40 a.p.f.u.) with subordinate Fe<sup>3+</sup> (1.0-1.14 a.p.f.u.) and Al (0.57-0.78 a.p.f.u.), and it occurs only in sample TZ 41 (Table 1, analyses 12–14, Fig. 6). Sienriched calcium-zirconium garnet has been

described previously as the mineral kimzeyite from Stromboli, Italy (Munno *et al.*, 1980) and Anguillara Sabazia, Italy (Schingaro *et al.*, 2001). Kimzeyite from Italian localities has the simplified formula  $Ca_3(Zr,Ti)_2(Si,Al,Fe^{3+})_3O_{12}$ (Anthony *et al.*, 1995) and is different from the original description of kimzeyite from the Magnet Cove carbonatite, for which the ideal

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Analysis	7	8	9	10	11	12	13	14
wt.%								
Fe <sub>2</sub> O <sub>3</sub>	18.44	15.87	15.95	18.15	17.72	16.37	16.98	15.10
Al <sub>2</sub> O <sub>3</sub>	5.85	6.94	7.33	6.00	6.01	5.37	5.12	6.66
SiO <sub>2</sub>	7.53	8.52	8.50	7.92	8.09	14.71	13.14	11.24
$ZrO_2$	33.50	32.94	33.21	31.45	32.27	25.90	29.83	32.36
TiO <sub>2</sub>	1.64	2.65	2.74	1.87	2.58	5.71	3.22	3.49
$Nb_2O_5$	4.17	3.74	3.98	5.14	3.87	1.91	3.24	2.01
MgO	0.15	0.23	0.16	0.24	0.23	0.92	0.74	0.36
$Y_2O_3$	0.45	0.36	0.34	0.46	0.38	0.28	_	0.19
$La_2O_3$	0.15	0.08	0.12	0.14	0.16	_	_	_
$Ce_2O_3$	0.50	0.32	0.25	0.61	0.51	0.13	0.19	0.22
Nd <sub>2</sub> O <sub>3</sub>	0.35	0.24	0.17	0.45	0.23	0.18	_	_
$Sm_2O_3$	_	0.11	_	0.16	0.11	_	_	0.09
$Gd_2O_3$	_	—	—	0.19	0.19	_	—	0.11
HfO <sub>2</sub>	—	—	—	0.20	—	0.21	0.14	—
CaO	26.94	27.36	27.31	26.17	26.85	28.50	27.78	27.82
MnO	0.15	0.18	0.14	0.20	0.18	0.27	0.37	0.13
Total	99.81	99.55	100.20	99.61 <sup>2</sup>	99.36	100.46	100.74	99.78
Formulae calcul	ated for 12 O							
Fe <sup>3+</sup>	1.43	1.21	1.21	1.41	1.37	1.00	1.14	1.11
Si	0.78	0.87	0.86	0.82	0.83	1.40	1.28	1.11
Al	0.71	0.83	0.87	0.73	0.73	0.60	0.58	0.78
Ti	0.08	0.09	0.06	0.04	0.07			
Total Z	3.00	3.00	3.00	3.00	3.00	3.00	3.00	3.00
Zr	1.67	1.63	1.63	1.58	1.62	1.20	1.41	1.56
Ti	0.05	0.11	0.15	0.10	0.13	0.41	0.24	0.26
Nb	0.20	0.17	0.18	0.24	0.18	0.08	0.14	0.09
Fe <sup>3+</sup>						0.18	0.10	0.02
Mg	0.02	0.04	0.02	0.04	0.04	0.13	0.11	0.05
Hf				0.01		0.01		
Y	0.03	0.02	0.02	0.03	0.02	0.01		0.01
Gd				0.01	0.01			
Total Y	1.97	1.97	2.00	$2.02^{2}$	2.00	2.02	2.00	1.99
Са	2.98	2.98	2.95	2.90	2.96	2.91	2.89	2.95
Mn	0.01	0.02	0.01	0.02	0.01	0.02	0.03	0.01
La	0.01				0.01			
Ce	0.02	0.01	0.01	0.02	0.02		0.01	0.01
Nd	0.01	0.01	0.01	0.02	0.01	0.01	5.01	
Sm				0.01				
Total X	3 03	3.02	2 98	2 97	3.01	2 94	2 03	2 97
10101 /1	5.05	5.02	2.70	2.71	5.01	2.74	2.75	2.91

Samples K 22 (analyses 7–9) and TZ 41 (analyses 10–14). All Fe calculated as  $Fe_2O_3$ . <sup>2</sup> including BaO 0.27 wt % (0.01 a p fu.)

including BaO 0.27 wt.% (0.01 a.p.f.u.).

- below detection limit.

formula derived from wet microchemical analysis was given as Ca3Zr2(Al2Si)O12 (Milton and Blade, 1958; Milton et al., 1961). Unfortunately, only a few microprobe data are available for kimzeyite from Magnet Cove, and these show that the Z site in the mineral is characterized by a slight dominance of Si compared with Al and  $Fe^{3+}$ :

 $\begin{array}{c}(Ca_{3.25}Mn_{0.01})_{\Sigma3.26}(Zr_{1.40}Ti_{0.42}Mg_{0.05}Y_{0.01})_{\Sigma1.88}\\(Si_{1.09}Fe_{1.88}^{3+}Al_{0.82}Ti_{0.01})_{\Sigma3.00}O_{12}\\(Lupini\ et\ al.,\ 1992)\\Ca_{3.05}(Zr_{1.38}Ti_{0.43}Fe_{0.10}^{3+}Mg_{0.07})_{\Sigma1.98}\\(Si_{1.19}\ Al_{0.92}Fe_{0.90}^{3+})_{\Sigma3.00}O_{12}\end{array}$ 

(Haynes *et al.*, 2003)

Calculated formulae of the kerimasite with dominant Fe<sup>3+</sup> in the *Z* site show that for many, but not all, the total of Fe<sup>3+</sup>+Si+Al at the *Z* site is <3 a.p.f.u. (the minimum value is 2.85), possibly indicating the presence of Ti in the *Z* site (Table 1, analyses 1–11). In contrast, the *Z* site in Si-enriched kerimasite is fully occupied by Si, Al and Fe<sup>3+</sup>, and some Fe<sup>3+</sup> is also present at the *Y* site (0.02–0.18 a.p.f.u.) (Table 1, analyses 12–14).

The *Y* site in kerimasite has Zr as the dominant cation, ranging between 1.86 and 1.23 a.p.f.u. (Fig. 7). These Zr contents are significantly greater than those of Si-enriched kerimasite from sample TZ 41, and also kimzeyite from Stromboli and Anguillara Sabazia, Italy (Munno *et al.*, 1980; Schingaro *et al.*, 2001) and Wiluy, Russia (Galuskina *et al.*, 2005). Ti and Nb are two

other important components in the *Y* site, where they amount to  $\leq 0.32$  Ti and 0.09-0.30 Nb a.p.f.u. Both elements display a negative correlation with Zr (Fig. 7). The *Y* site in Si-enriched kerimasite contains, in addition to Ti and Nb, a significant amount of Fe<sup>3+</sup> (up to 0.18 a.p.f.u.) and there is a positive correlation between <sup>[6]</sup>Fe<sup>3+</sup> and <sup>[4]</sup>Si<sup>4+</sup> (R = 0.70 for 20 analyses of mineral in TZ 41 sample). Data from Table 1 and Figs 6 and 7 suggest two major substitution mechanisms for kerimasite: (1) simple <sup>[6]</sup>Zr<sup>4+</sup>  $\rightleftharpoons$  <sup>[6]</sup>Ti<sup>4+</sup> and (2) coupled <sup>[6]</sup>(Zr,Ti)<sup>4+</sup> + <sup>[4]</sup>Si  $\rightleftharpoons$  <sup>[6]</sup>Nb<sup>5+</sup> + <sup>[4]</sup>(Fe,Al)<sup>3+</sup>. Enrichment of Si in kerimasite can be explained by the coupled substitution: <sup>[6]</sup>(Zr,Ti)<sup>4+</sup> + <sup>[4]</sup>(Fe,Al)<sup>3+</sup>  $\rightleftharpoons$  <sup>[6]</sup>Fe<sup>3+</sup> + <sup>[4]</sup>Si<sup>4+</sup>.

Both varieties of kerimasite also occur in the carbonatite eluvium of Loluni and Kiseta craters (Table 2, Figs 6, 7), where some of the crystals studied are characterized by complex chemical compositions and internal structure. They have Nb contents ranging from 0.7 to 10.1 wt.% Nb<sub>2</sub>O<sub>5</sub> (0.03-0.48 a.p.f.u.) (Table 2, analysis 7), the latter being the largest Nb content in all of the samples of kerimasite studied (Fig. 8). Nb-bearing kerimasite (>2 wt.% Nb<sub>2</sub>O<sub>5</sub>) is also



FIG. 7. Octahedral (Y site) composition of kerimasite (red colour – carbonatites, green colour – carbonatite eluvium, filled symbols –  $Fe^{3+}$ -enriched kerimasite, open symbols – Si-enriched kerimasite).

#### KERIMASITE, A NEW GARNET FROM TANZANIA



FIG. 8. X-ray element distribution maps for a zoned kerimasite crystal, sample LL 4.

enriched in rare earth elements (*REE*) with 0.7–4.6 wt.%  $Ln_2O_3$  and 0.4–1.6 wt.%  $Y_2O_3$  (e.g. Table 2, analysis 4). Kerimasite with the largest *REE* content also contains the most Fe, ranging from 18.3 and 21.6 wt.% Fe<sub>2</sub>O<sub>3</sub> (1.48–1.66 a.p.f.u. in the *Z* site) (Table 2, analyses 3–5).

The assignment of the *REE* in the kimzeyite structure was discussed by Schingaro *et al.* (2001). They showed, using classical crystalchemical principles (i.e. radius ratio rule and electrostatic requirements), that *REE* are located at the *Y* site; however, experimental data and bond-valence theory suggest the location of *REE* at the *X* site. Our results for kerimasite with small concentrations of Y and Ln, i.e. <1 wt.% Ln<sub>2</sub>O<sub>3</sub>+Y<sub>2</sub>O<sub>3</sub> (Tables 1 and 2) do not give a clear indication of how the *REE* are distributed between the *Y* and *X* sites, and relatively good site occupancies are obtained whether these elements are placed in either the *X* or the *Y* sites. Data from kerimasite with 1-3 wt.%  $REE_2O_3$  suggest that these elements can be located at both crystallographic sites, e.g. smaller Y and heavy *REE* at the Y site, and the larger light *REE* at the X site. However, kerimasite with >3 wt.%  $REE_2O_3$  is characterized by non-stoichiometric coefficients at X and Y sites with whatever distribution is assumed for REE between these sites: (1) all *REE* at X or (2) Y sites or (3) *LREE* at X sites and Y+HREE at Y sites. Nonetheless, assuming light *REE* at the X site and Y+HREE at the Y site gives a formula with the least deviation from stoichiometry (Table 2).

Several of the crystals studied from the carbonatite eluvium show well developed compositional zonation and have a distinct low-Z core (dark) which is overgrown by a high-Z (bright) rim (Fig. 4c,d). The zonation results from variations in Si, Al, Fe<sup>3+</sup>, Zr, Nb and Ti (Fig. 8), and microprobe analyses of different zones confirmed that, in some crystals, the low-Z

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Analysis	1	2	3	4	5	6	7	Average
wt.%								
Fe <sub>2</sub> O <sub>3</sub>	14.69	16.68	21.55	18.99	20.39	16.83	17.39	16.92
$Al_2O_3$	5.62	6.12	4.00	7.15	4.98	8.29	7.85	6.77
SiQ <sub>2</sub>	14.35	9.72	8.05	5.29	8.25	5.90	5.83	7.32
ZrO <sub>2</sub>	27.66	35.29	30.71	30.09	29.12	27.10	26.05	27.93
TiO <sub>2</sub>	5.70	1.30	1.02	1.50	1.45	1.33	1.36	1.04
Nb <sub>2</sub> O <sub>5</sub>	0.89	1.52	4.56	5.54	6.07	9.57	10.09	8.78
MgO	0.86	0.20	0.34	0.21	0.38	0.37	0.45	0.63
$Y_2O_3$	0.16	0.32	0.82	1.48	0.71	0.87	0.73	0.71
La <sub>2</sub> O <sub>3</sub>	_	0.06	0.30	0.42	0.28	0.28	0.25	0.18
Ce <sub>2</sub> O <sub>3</sub>	0.09	0.25	0.90	1.49	0.73	0.73	0.65	0.64
Pr <sub>2</sub> O <sub>3</sub>	_	_	0.15	0.24	0.08	0.15	0.11	0.10
Nd <sub>2</sub> O <sub>2</sub>	0.07	0.19	0.53	1.04	0.44	0.42	0.43	0.43
$Sm_2O_2$	_	_	0.13	0.30	0.13	0.11	0.08	0.13
Gd <sub>2</sub> O <sub>2</sub>	_	0.07	0.14	0.38	0.14	0.16	0.11	0.10
$Dv_2O_3$	_	_	0.14	0.26	0.11	0.14	0.10	0.11
$Er_2O_2$	0.08	0.10	0.18	0.20	0.14	0.12	0.12	0.06
$Yb_2O_2$	_	_	_	0.10	0.08	0.07	_	_
HfO <sub>2</sub>	0.16	_	0.08	_	_	_	_	0.16
CaO	28.76	27.23	25.62	24.33	26.21	26.21	26.39	25.86
MnO	0.16	0.09	0.16	0.15	0.20	0.28	0.35	0.33
Total	99.25	99.13	99.38	99.17	99.89	98.93	98.34	98.20
Formulae calci	ulated for 12 O							
Fe <sup>3+</sup>	0.98	1 27	1.66	1.52	1 54	1 32	1 36	1 33
Si	1 38	0.99	0.85	0.56	0.85	0.61	0.61	0.76
Al	0.64	0.74	0.49	0.90	0.61	1.02	0.01	0.83
Ti	0.01	0.71	0.19	0.02	0.01	0.05	0.06	0.05
Tatal 7	2 00	2 00	2.00	2.00	2.00	2.00	2.00	2.00
	3.00	3.00	3.00	3.00	3.00	3.00	5.00	3.00
Zr	1.30	1.76	1.57	1.56	1.4/	1.37	1.33	1.42
11	0.41	0.10	0.08	0.10	0.11	0.05	0.05	0.44
Nb	0.04	0.07	0.22	0.27	0.28	0.45	0.48	0.41
Fe	0.09	0.02	0.04	0.02	0.04	0.06	0.01	0.10
Mg	0.12	0.03	0.05	0.03	0.06	0.06	0.07	0.10
Y	0.01	0.02	0.05	0.08	0.04	0.05	0.04	0.04
Gd			0.04	0.01		0.01		
Er			0.01	0.01				
Total Y	1.98 <sup>1</sup>	2.00	2.02	2.06	2.00	1.99	1.98	1.98 <sup>1</sup>
Са	2.97	2.98	2.88	2.78	2.90	2.92	2.95	2.89
Mn	0.01	0.01	0.01	0.01	0.02	0.02	0.03	0.03
La			0.01	0.02	0.01	0.01	0.01	0.01
Ce		0.01	0.03	0.06	0.03	0.03	0.02	0.02
Pr			0.01	0.01		0.01		
Nd		0.01	0.02	0.04	0.02	0.02	0.02	0.02
Sm				0.01				0.01
Total X	2.98	3.01	2.96	2.94	2.98	3.01	3.03	2.98

TABLE 2. Chemical composition of kimzeyite and kerimasite from carbonatite eluvium.

Samples LL 4 (analyses 1–7) and KZ 2 (average – data from five analyses). All Fe calculated as  $Fe_2O_3$ . – below detection limit, <sup>1</sup> including 0.01 Hf (a.p.f.u.).

core corresponds to Si-enriched kerimasite, and the high-Z rim is  $Fe^{3+}$ -rich kerimasite.

Using the Gladstone-Dale constants and the average chemical composition of kerimasite (sample K 94-25), 1-(Kp/Kc) = -0.026: this value indicates excellent compatibility between the chemical and physical data.

#### Crystal structure and X-ray diffraction

Based on the results of our microprobe analyses, two crystals of kerimasite that had very different Nb contents were selected for study by X-ray diffraction (XRD): samples K 94-25 (Fig. 2b, Table 1, analyses 1-4), and KZ 2 (Fig. 2d, Table 2, average analysis).

#### X-ray powder diffraction

Powder XRD data for the two kerimasite samples (Table 3) were collected by the Gandolfi method ( $\phi$ - $\omega$  rotation) using a Stoe IPDS II image plate diffractometer located at St. Petersburg State University (Mo- $K\alpha$ , graphite monochromator,

TABLE 3. Powder XRD data and unit-cell parameters for kerimasite.

_	- Sample	е К 94-25	5 —		— Sam	ple KZ 2 -				
$I_{\rm obs}$	$d_{\rm obs}$	Icalc	$d_{\text{calc}}$	$I_{\rm obs}$	$d_{\rm obs}$	I I <sub>calc</sub>	$d_{\text{calc}}$	h	k	l
49	4.441	67	4.437	67	4.445	74	4.435	2	2	0
91	3.140	71	3.137	89	3.141	73	3.136	4	0	0
70	2.808	51	2.806	100	2.808	50	2.805	4	2	0
13	2.680	5	2.675	14	2.678	5	2.674	3	3	2
93	2.564	92	2.562	89	2.563	93	2.560	4	2	2
14	2.468	8	2.461	11	2.452	8	2.460	4	3	1
9	2.292	9	2.291	8	2.292	9	2.290	5	2	1
2	2.225	5	2.218	7	2.219	5	2.217	4	4	0
12	2.036	7	2.036	13	2.035	7	2.035	6	1	1
		6	2.036			6	2.035	5	3	2
21	1.985	28	1.984	17	1.984	29	1.983	6	2	0
3	1.810	1	1.811					4	4	4
26	1.741	21	1.740	25	1.741	22	1.739	6	4	0
		1	1.7076			1.	1.7069	5	5	2
100	1.677	100	1.6769	75	1.677	100	1.6761	6	4	2
16	1.568	16	1.5686	18	1.568	16	1.5679	8	0	0
		1	1.5446	6	1.542	1	1.5439	7	4	1
4	1.480	3	1.4789	10	1.477	3	1.4782	6	6	0
		9	1.4789			9	1.4782	8	2	2
17	1.403	25	1.4030	21	1.402	25	1.4024	8	4	0
12	1.369	10	1.3692	16	1.369	10	1.3686	8	4	2
12	1.337	19	1.3377	17	1.336	19	1.3371	6	6	4
		1	1.3227	7	1.320	1	1.3221	8	5	1
		1	1.3227			1	1.3221	7	5	4
3	1.279	5	1.2807	8	1.278	5	1.2802	8	4	4
		1	1.2676	8	1.266	1	2.2670	9	4	1
		1	1.2676			1	2.2670	8	5	3
1	1.231	1	1.2305			1	1.2299	10	2	0
		5	1.2305	7	1.230	5	1.2299	8	6	2
		1	1.1965			1	1.1959	7	6	5
8	1.165	4	1.1651	12	1.164	4	1.1646	10	4	0
		5	1.1651			5	1.1646	8	6	4
12	1.145	24	1.1455	15	1.145	23	1.1450	10	4	2
6	1.109	11	1.1091	10	1.109	11	1.1087	8	8	0
<i>a</i> =	= 12.549(	1) Å		а	= 12.54	43(2) Å				
V =	= 1976.2(	4) Å <sup>3</sup>		V	= 1973	.2(7) Å <sup>3</sup>				
	`	·				. /				

Entries in bold are the five most significant reflections.

TABLE 4. Crystallographic data and refinement parameters for kerimasite from single-crystal XRD.

Crystal system, space group	Cubic, Ia3d
a (Å)	12.5512 (15)
Z	8
Crystal size (mm)	$0.05 \times 0.06 \times 0.06$
$\mu (mm^{-1})$	6.66
Distance to detector (mm)	80
Total frames	90
Omega increment (°)	2
Exposure time (min)	9
Total reflections	11255
Unique reflections	290
Unique observed, $ F_0  \ge 4\sigma_F$	107
2θ min., max (°)	6.5, 64.4
h,k,l	$\pm 18, \pm 18, \pm 18$
R <sub>int</sub>	0.161
$R_{\sigma}$	0.158
$R_1 ( F_0  \ge 4\sigma_F)$	0.045
$R_1$ (all)	0.160
$wR_2$	0.093
S = GoF	0.912

40 kV, 50 mA), a 200 mm detector-to-crystal distance and 60 min exposure time.

The *a* cell parameters of the two kerimasites (12.549 and 12.543 Å) are significantly larger than that of kimzeyite (a = 12.46, 12.365 and 12.397 Å – Milton *et al.*, 1961; Munno *et al.*, 1980; Schingaro *et al.*, 2001, respectively). This difference can be explained by the greater contents of small-radius cations <sup>[6]</sup>Ti (0.605 Å) and <sup>[4]</sup>Si (0.26 Å) in kimzeyite (ionic radii are from Henderson, 1982). Synthetic Ca-Zr garnets with variable Fe<sup>3+</sup>/Al ratios and constant Si in the tetrahedral site show an increase in parameter *a* 

from 12.512 Å for the Z site of [FeAlSi] to 12.616 Å for the Z site of [Fe<sub>2</sub>Si] (Whittle *et al.*, 2007).

#### Single-crystal XRD

Single-crystal data were collected using same Stoe IPDS II image plate diffractometer as used for the collection of powder diffraction data (Mo-Kα, graphite monochromator, 40 kV, 50 mA). Corrections for Lorentz, polarization and absorption effects were made using the Stoe X-Area 1.42 software package. In order to minimize the effects of zoning upon diffraction data we selected two small crystals for structure refinement. However, the refinement for the crystal from sample K-94-25 was poor (large  $R_{int}$  and very high R indices), no doubt due to zoning and its small size (0.04 mm diameter) compared with the crystal from sample KZ 2 (0.06 mm diameter). As a result, we report only the structure refinement of crystal KZ 2, for which a satisfactory result was obtained.

Analysis of reciprocal space did not reveal deviations from the suggested space group  $Ia\bar{3}d$ which was employed for subsequent integrations. The structure of crystal KZ 2 was solved by Direct Methods and refined using the SHELX-97 program (Sheldrick, 2008). Details of the refinements are given in Table 4. Atom coordinates, equivalent isotropic displacement parameters and interatomic distances are given in Table 5. A crystallographic information file has been deposited and can be downloaded from the journal's website at www.minersoc.org/pages/e journals/ dep mat.html. The crystal structure of kerimasite is typical of grandite garnets (e.g. Yakovlevskaya, 1972), consisting of three types of polyhedra: an eight-fold coordinated X site occupied by  $Ca^{2+}$ , octahedral Y position (Zr,Nb) and  $[(Fe,Al,Si)O_4]$ 

TABLE 5. Atomic coordinates, isotropic displacement parameters and cation–oxygen interatomic distances for kerimasite crystal KZ 2.

Site	Occupancy	x	У	Ζ	$U_{\rm iso}$	Interatomic distances (Å)
Х	$Ca_{0.96}La_{0.03}Mn_{0.01}$	1/8	0	1/4	0.0048(4)	$2 \times 2.558(4),$ $2 \times 2.420(4)$
Y	$Zr_{0.73}Nb_{0.22}Mg_{0.05}$	0	0	0	0.0093(2)	$6 \times 2.053(4)$
Ζ	Fe <sub>0.44</sub> Al <sub>0.28</sub> Si <sub>0.25</sub> Ti <sub>0.03</sub>	3/8	0	1/4	0.013(2)	$4 \times 1.803(4)$
0	O <sub>1</sub>	0.0330(3)	0.0509(3)	0.6519(3)	0.0116(8)	

Reference	Occupancy	BVS	Charge
KZ 2 (this study)	Fe <sub>0.44</sub> Al <sub>0.28</sub> Si <sub>0.25</sub> Ti <sub>0.03</sub>	3.01	3.28
Munno et al. (1980)	$Si_{0.54}Al_{0.33}Fe_{0.13}$	3.28	3.54
Schingaro et al. (2001)	$Si_{0.45}Fe_{0.28}Al_{0.27}$	3.35	3.45
Whittle et al. (2007)	Fe <sub>0.33</sub> Al <sub>0.33</sub> Si <sub>0.33</sub>	3.19	3.33
Whittle et al. (2007)	$Fe_{0.50}Si_{0.33}Al_{0.67}$	3.19	3.33
Whittle et al. (2007)	$Fe_{0.67}Si_{0.33}$	3.25	3.33

TABLE 6. Bond-valence sums (BVS) and formal charges for Z-position cations in zirconian garnets.

tetrahedron. A notable feature of kerimasite is its large Nb content, with Nb substituting for Zr.

Zirconium-rich garnets are rare in Nature, and only two kimzeyite structures are available for comparison (Munno et al., 1980; Schingaro et al., 2001), both of which are relatively Ti-rich, and so a comparison of bond-valence relationships for the octahedral position is not appropriate. Comparative bond-valence analysis for the tetrahedral site (Table 6) has been carried out for kerimasite, kimzevite and synthetic Zr-ferrite garnets, with their structures refined using the Rietveld method (Whittle et al., 2007). The general result of bond-valence analysis is that in all five ferrite garnets, bond-valence sums calculated using conventionally accepted coefficients (O'Keeffe and Brese, 1991) are less than the sums of formal calculated charges of Zcations. In this respect we believe that the bondvalence parameter for Fe<sup>3+</sup> cannot be applied directly for the tetrahedrally coordinated Z site in the garnet structure.

#### Discussion

Kerimasite is a calcium zirconium silicate-ferrite member of the garnet group. There is a continuous solid solution between  $[Fe^{3+} + Al]$ and Si in mineral ranging from  $((Fe^{3+},Al)_{\Sigma 2.23}$ Si<sub>0.62</sub>Ti<sub>0.15</sub>O<sub>12</sub>) to  $((Fe^{3+},Al)_{\Sigma 1.52}Si_{1.48}O_{12})$  and no solid solution between  $(Fe_2SiO_{12})$  and  $(Al_2SiO_{12})$ (Fig. 5). The simplified chemical formulae of kerimasite are Ca<sub>3</sub>(Zr,Nb,Ti,)<sub>2</sub>(Fe<sup>3+</sup>,Si,Al)<sub>3</sub>O<sub>12</sub> and Ca<sub>3</sub>(Zr,Ti,Nb)<sub>2</sub>(Si,Fe<sup>3+</sup>,Al)<sub>3</sub>O<sub>12</sub>, and the ideal, end-member formula, according to the 'dominant-valency rule' is Ca<sub>3</sub>Zr<sub>2</sub>(Fe<sup>3+</sup><sub>2</sub>Si)O<sub>12</sub>. Previously, this formula had been suggested for a theoretical end-member of Zr-bearing garnets and termed as "ferric-kimzeyite" by Rickwood (1968) or "kimzeyite-Fe" by Locock (2008). Strunz and Nickel (2001) gave an incorrect reference to the term "ferric-kimzeyite" being introduced by Brandenberger (1933).

Several Zr-Al-Fe<sup>3+</sup> synthetic garnets are known, including Ca<sub>3</sub>Zr<sub>2</sub>(Al<sub>2</sub>Si)O<sub>12</sub>, Ca<sub>3</sub>Zr<sub>2</sub>  $(Al_{1.5}Fe_{0.5}^{3+}Si)O_{12}, Ca_3Zr_2(AlFe^{3+}Si)O_{12},$  $Ca_3Zr_2(Al_{0.5}Fe_{1.5}^{3+}Si)O_{12}$  and  $Ca_3Zr_2(Fe_2^{3+}Si)O_{12}$ . There is also a solid solution between Al and  $Fe^{3+}$ end-members (Ito and Frondel, 1967; Yamakawa et al., 1993; Whittle et al., 2007). A noteworthy feature of kerimasite from the Kerimasi volcano and the explosion craters is the presence of Nb, which ranges from 0.7 to 10.1 wt.% Nb2O5 (0.03-0.48 a.p.f.u.). Nb is a relatively uncommon component of natural garnets, and typically the concentration of Nb<sub>2</sub>O<sub>5</sub> in garnet-group minerals does not exceed 0.1 wt.%, e.g. Guly, Maimecha-Kotuy, Russia (Borodin and Bykova, 1963), Seblyavr, Kola Peninsula, Russia (Lapin, 1979), Polino, Umbria, Italy (Lupini et al., 1992), Afrikanda, Kola Peninsula, Russia and Magnet Cove, Arkansas, USA (Chakhmouradian and McCammon, 2005). Values from 0.1 to 0.7 wt.% Nb<sub>2</sub>O<sub>5</sub> were recorded in a melaniteschorlomite garnet from Oldoinyo Lengai, Gregory rift, Tanzania (Dawson et al., 1995; Dawson and Hill, 1998), and kimzevite from Magnet Cove contains between 0.1 and 1.0 wt.% niobium oxide (Milton and Blade, 1958; Milton et al., 1961; Ledger et al., 1988; Lupini et al., 1992). There are several known synthetic garnets which contain Nb in the Y site, e.g.  $Mn_3(NbZn)$  $(FeGe_2)O_{12}$  (Geller *et al.*, 1960), Ca<sub>3</sub>(ZrNb)Ga<sub>3</sub>O<sub>12</sub>, Ca<sub>3</sub>(HfNb)Ga<sub>3</sub>O<sub>12</sub> (Mill et al., 1966), Ca<sub>3</sub>(Nb,Ga)Ga<sub>3</sub>O<sub>12</sub> (Sarkisov and Kaminskii, 1988). We can expect in natural samples that the substitutions  ${}^{[6]}Zr^{4+} + {}^{[4]}Si \rightarrow$  ${}^{[6]}Nb^{5+} + {}^{[4]}Fe^{3+} \text{ and } {}^{[6]}Zr^{4+} + {}^{[4]}Si \rightarrow {}^{[6]}Nb^{5+} +$ <sup>[4]</sup>Al may lead to the formation of Si-free garnets such as  $Ca_3(ZrNb)Fe_3^{3+}O_{12}$  or  $Ca_3(ZrNb)Al_3O_{12}$ .

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