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This is the author's manuscript

Original Citation:

Availability:

This version is available <http://hdl.handle.net/2318/1564833> since 2016-06-08T11:40:05Z

Published version:

DOI:DOI: <http://dx.doi.org/10.1180/minmag.2016.080.103>

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Fogoite-(Y), $\text{Na}_3\text{Ca}_2\text{Y}_2\text{Ti}(\text{Si}_2\text{O}_7)_2\text{OF}_3$, a Group-I TS-block mineral from the Lagoa do Fogo, the Fogo volcano, the São Miguel Island, the Azores: Description and crystal structure

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34 **Abstract**

35 Fogoite-(Y), $\text{Na}_3\text{Ca}_2\text{Y}_2\text{Ti}(\text{Si}_2\text{O}_7)_2\text{OF}_3$, is a new mineral from the Lagoa do Fogo, the São Miguel
36 Island, the Azores. It occurs in cavities as highly elongated (on [001]) prisms, up to 2000 μm
37 long and 50 x 50 μm in cross-section, associated to sanidine, astrophyllite, fluornatropyrochlore,
38 ferrokentbrooksite, quartz and ferro-katophorite. Crystals are generally transparent and
39 colourless, with vitreous luster, occasionally creamy white. Fogoite-(Y) has a white streak,
40 splintery fracture and very good {100} cleavage. Mohs hardness is ~5. $D_{\text{calc.}} = 3.523 \text{ g/cm}^3$. It is
41 biaxial (+) with refractive indices ($\lambda = 590 \text{ nm}$) $\alpha = 1.686(2)$, $\beta = 1.690(2)$, $\gamma = 1.702(5)$; $2V_{\text{meas.}} =$
42 $57(1)^\circ$ and $2V_{\text{calc.}} = 60^\circ$. It is nonpleochroic. Fogoite-(Y) is triclinic, space group $P\bar{1}$, $a =$
43 $9.575(6)$, $b = 5.685(4)$, $c = 7.279(5) \text{ \AA}$, $\alpha = 89.985(6)$, $\beta = 100.933(4)$, $\gamma = 101.300(5)^\circ$, $V =$
44 $381.2(7) \text{ \AA}^3$. The six strongest reflections in the X-ray powder diffraction data [d (\AA), I , ($h k l$)]
45 are: 2.954, 100, ($\bar{1} \bar{1} 2$, $\bar{3} 1 0$); 3.069, 42, ($3 0 0$, $0 \bar{1} 2$); 2.486, 24, ($3 1 0$, $2 \bar{1} 2$); 3.960, 23,
46 ($\bar{1} \bar{1} 1$, $\bar{2} 1 0$); 2.626, 21, ($\bar{2} 2 0$); 1.820, 20, ($\bar{1} 0 4$). Electron microprobe analysis gave the
47 following empirical formula calculated on 18 (O + F) $(\text{Na}_{2.74}\text{Mn}_{0.15})_{\Sigma 2.89}\text{Ca}_2[\text{Y}_{1.21}(\text{La}_{0.01}\text{Ce}_{0.03}$
48 $\text{Nd}_{0.03}\text{Sm}_{0.02}\text{Gd}_{0.08}\text{Dy}_{0.08}\text{Er}_{0.05}\text{Yb}_{0.04}\text{Lu}_{0.01})_{\Sigma 0.35}\text{Mn}_{0.16}\text{Zr}_{0.11}\text{Na}_{0.09}\text{Fe}^{2+}_{0.07}\text{Ca}_{0.01}]_{\Sigma 2}(\text{Ti}_{0.76}\text{Nb}_{0.23}\text{Ta}_{0.01})_{\Sigma 1}(\text{Si}_{4.03}\text{O}_{14})\text{O}_{1.12}\text{F}_{2.88}$, $Z = 1$. The crystal structure was refined on a twinned crystal to $R_1 = 2.81\%$
49 on the basis of 2157 unique reflections ($F_o > 4\sigma F_o$) and is a framework of TS (Titanium Silicate)
50 blocks, which consists of HOH sheets (H-heteropolyhedral, O-octahedral) parallel to (100). In
51 the O sheet, the the $^{[6]}M^O(1)$ site is occupied mainly by Ti, $\langle M^O(1)-\varphi \rangle = 1.980 \text{ \AA}$ and the $^{[6]}M^O(2)$
52 and $^{[6]}M^O(3)$ sites are occupied by Na and Na plus minor Mn, $\langle M^O(2)-\varphi \rangle = 2.490 \text{ \AA}$ and
53 $\langle M^O(3)-\varphi \rangle = 2.378 \text{ \AA}$. In the H sheet, the two $^{[4]}Si$ sites are occupied by Si, with $\langle \text{Si}-\text{O} \rangle = 1.623$
54 \AA ; the $^{[6]}M^H$ site is occupied by Y and REE ($Y > \text{REE}$), with minor Mn, Zr, Na, Fe^{2+} and Ca, $\langle M^H-$
55 $\varphi \rangle = 2.271 \text{ \AA}$ and the $^{[6]}A^P$ site is occupied by Ca, $\langle A^P-\varphi \rangle = 2.416 \text{ \AA}$. The M^H and A^P octahedra
56 and Si_2O_7 groups constitute the H sheet. The ideal compositions of the O and two H sheets are
57 $\text{Na}_3\text{Ti}(\text{OF})\text{F}_2$ and $\text{Y}_2\text{Ca}_2(\text{Si}_2\text{O}_7)_2$ a.p.f.u. Fogoite-(Y) is isostructural with götzenite. The mineral is
58

59 named after the type locality, the Fogo volcano in the Azores.

60

61 **Keywords:** fogoite-(Y), crystal-structure refinement, EMP analysis, chemical formula, TS-block
62 minerals, rinkite, hainite, Group I, the Fogo volcano, the Azores

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64

65 Introduction

66 Fogoite-(Y), $\text{Na}_3\text{Ca}_2\text{Y}_2\text{Ti}(\text{Si}_2\text{O}_7)_2\text{OF}_3$, is a Group-I TS-block mineral in accord with
67 Sokolova (2006). The mineral is named after the type locality, the Fogo volcano in the Azores.
68 TS-block (Titanium Silicate) minerals are divided into four groups, characterized by a different
69 topology and stereochemistry of the TS block. The TS block consists of the central O
70 (Octahedral) sheet and two H (Heteropolyhedral) sheets containing Si_2O_7 groups. In Group I, Ti
71 (+ Nb + Zr) = 1 a.p.f.u. and Ti (+ Nb + Zr) occurs in the O sheet: $1 M^O = \text{Ti, Nb, Zr}$; $3 M^O = \text{Na,}$
72 Ca and rarely Mn; $^{[6],[7]}M^H = \text{Zr, Y, Ca} + \text{REE, Ca} + \text{Y} + \text{REE, Ca, Mn}$; $A^P = \text{Na, Ca, Ca} + \text{REE}$;
73 $X^O = \text{anions O, F, OH and H}_2\text{O groups}$. Sokolova (2006) wrote the general formula for minerals
74 of Group I as $A^P_2M^H_2M^O_4(\text{Si}_2\text{O}_7)_2X^O_4$. There are ten Group-I minerals of known structure: fogoite-
75 (Y), hainite, götzenite, kochite, rosenbuschite, seidozerite, grenmarite, rinkite, nacareniobsite-
76 (Ce) and mosandrite (Table 1). The stacking order of TS blocks in Group-I structures is of two
77 types (for details, see Christiansen and Rønso, 2000): type 1 occurs in rinkite, nacareniobsite-
78 (Ce) and mosandrite (space group $P2_1/c$) and type 2 occurs in fogoite-(Y), hainite, götzenite,
79 kochite, rosenbuschite (space group $P\bar{1}$) and related seidozerite and grenmarite (space group
80 $P2/c$).

81 The new mineral and its name have been approved by the Commission on New
82 Minerals, Nomenclature and Classification, International Mineralogical Association (IMA 2014-
83 98). The holotype material is deposited in the collections of the Museo Regionale di Scienze
84 Naturali di Torino, Torino, Italy, catalogue numbers M/U 16800 and M/U 16801, and the Royal

85 Ontario Museum, Toronto, Ontario, Canada, catalogue number M56826. The current paper
86 reports the description and crystal structure of fogoite-(Y).

87

88 **Occurrence**

89 Fogoite-(Y) was found in a syenite xenolith, in the bed of the upper part of the Ribeira Grande
90 river near the ruins of Lombadas, close to Lagoa do Fogo (Lake of fire), a crater lake in the
91 Agua de Pau stratovolcano (also named Fogo volcano) in the centre of the São Miguel Island in
92 the Azores (37°46'26"N 25°27'29"W). Associated minerals are sanidine, astrophyllite,
93 fluornatropyrochlore, ferrokentbrooksite, quartz and ferro-katophorite. Other minerals described
94 from these syenite ejecta are dalyite, chevkinite-(Ce), britholite-(Ce), eudialyte and a lãvenite-
95 like mineral (Ridolfi *et al.*, 2003).

96 The Azores archipelago straddles the Mid-Atlantic Ridge and emerges from the Azores
97 Platform, (37-40°N and 25-31°W) near the North American-African-Eurasian triple-plate junction.
98 São Miguel is one of the eastern islands, and is divisible into six volcanic zones (Moore, 1990):
99 three large and dominantly trachytic, Quaternary stratovolcanoes (Sete Cidades, Agua de Pau
100 and Furnas; Moore, 1991) and the Pliocene-Pleistocene northeast shield volcano (extinct) with
101 its associated Povoação caldera (Abdel-Monem *et al.*, 1975; Fernandez, 1980) separated by
102 two Quaternary alkali basalt volcanic fields. The Agua de Pau products (starting from 180 ka)
103 range from basaltic to trachytic, and alkaline to transitional basalt lavas erupted from the flank
104 vents. The more recent products date from 5 ka with the eruption of the trachytic Fogo-A plinian
105 fall deposit (Walker and Croasdale, 1970; Widom *et al.*, 1992), which contains abundant syenite
106 clasts containing feldspar, arfvedsonite, augite and/or aegirine, Fe-Ti oxide, zircon, pyrochlore,
107 rare biotite and a few modal percent of quartz. The youngest clasts are friable syenites with
108 miarolitic cavities and homogeneous sanidine, those containing fogoite-(Y). The syenite clasts
109 within the Agua de Pau plinian deposits are divisible into silica-undersaturated syenites and
110 silica-saturated/oversaturated syenites. They are considered to be the slowly cooled equivalents

111 of the less evolved and more evolved trachytes in the shallow sub-volcanic magmatic system of
112 Agua de Pau. Interstitial liquids of both syenite groups, trapped within a feldspathic framework,
113 became progressively enriched in volatiles, alkalis, HFSE and *REE*. In the silica-undersaturated
114 syenites (assumed to be material grown on the side-walls of the magma chamber), late-stage
115 fractionation resulted in highly peralkalic (agpaitic) residual melts from which the complex Zr-Ti
116 silicates eudialyte and a lâvenite-like mineral crystallized (Ridolfi *et al.*, 2003).

117

118 **Physical properties**

119 Fogoite-(Y) occurs in cavities as acicular [001] prisms with equant cross-sections, up to 2000
120 μm long and $50 \times 50 \mu\text{m}$ in cross-section (Fig. 1). The main forms are {100} and {010}. Crystals
121 are generally creamy white, transparent to translucent, with vitreous luster. Very thin crystals
122 are colourless. Crystals are often parallel or grouped in radiating aggregates (Fig. 1a). They can
123 also be isolated (Fig. 1b). Fogoite-(Y) has a white streak, splintery fracture and does not
124 fluoresce under cathode or ultraviolet light. Cleavage is {100} very good, no parting was
125 observed, Mohs hardness is ~ 5 , and it is brittle, $D_{\text{calc.}} = 3.523 \text{ g/cm}^3$ (using the empirical formula
126 and the single-crystal unit cell). Macroscopically, individual crystals do not show twinning.
127 However, diffraction data show the presence of twinning by reticular merohedry (see later).
128 Fogoite-(Y) is biaxial (+) with refractive indices ($\lambda = 590 \text{ nm}$) $\alpha = 1.686(2)$, $\beta = 1.690(2)$, $\gamma =$
129 $1.702(5)$. The optic axial angle is $57(1)^\circ$, and $2V_{\text{calc.}} = 60^\circ$. It is nonpleochroic. The optical
130 orientation is given in Table 2. The compatibility index $(1 - Kp/Kc) = 0.006$ (for $D_{\text{calc.}} = 3.523$
131 g/cm^3) is rated as superior.

132

133 **FTIR spectroscopy**

134 The IR spectrum of fogoite-(Y) was collected on a crystal fragment using a Bruker Hyperion
135 2000 IR microscope equipped with a liquid nitrogen cooled MCT detector (Fig. 2). Data over the
136 range $4000\text{--}650 \text{ cm}^{-1}$ were obtained by averaging 100 scans with a resolution of 4 cm^{-1} . No

137 bands were observed in the OH-stretching region (3000-4000 cm^{-1}), in accord with the absence
138 of OH and H₂O groups in the structure (Fig. 2). In the low-frequency region, peaks at 1088,
139 1000, 803 cm^{-1} are assigned to Si-O stretching vibrations of the Si₂O₇ groups, and a peak at 677
140 cm^{-1} is due to stretching vibrations of the Si-O-Si bridges of Si₂O₇ groups.

141 **Chemical analysis**

143 A single crystal of fogoite-(Y) was analyzed with a Cameca SX-100 electron-microprobe
144 operating in wavelength-dispersion mode with an accelerating voltage of 15 kV, a specimen
145 current of 20 nA, a beam size of 5 μm and count times on peak and background of 20 and 10 s,
146 respectively. The following standards were used: Si, Ca: diopside; F: fluorite; Na: albite; Nb:
147 Ba₂NaNb₅O₁₅; Fe: fayalite; Mn: spessartine; Zr: zircon; Ti: titanite; Ta: Mn(Ta_{1.7}Nb_{0.3})O₆; Ce:
148 CePO₄; La: LaPO₄; Nd: NdPO₄; Lu: LuPO₄; Sm: SmPO₄; Gd: GdPO₄; Dy: DyPO₄; Er: ErPO₄;
149 Yb: YbPO₄; Y: Y₃Al₅O₁₂. Al, Mg, Ba, Th, Pr and Ho were sought but not detected. Data were
150 reduced using the $\phi(\rho Z)$ procedure of Pouchou and Pichoir (1985). The chemical composition of
151 the fogoite-(Y) is the mean of 10 determinations and is given in Table 3. The empirical formula
152 of fogoite-(Y) calculated on the basis of 18 (O + F) is (Na_{2.74}Mn_{0.15})_{Σ2.89}Ca₂[Y_{1.21}(La_{0.01}Ce_{0.03}
153 Nd_{0.03}Sm_{0.02}Gd_{0.08}Dy_{0.08}Er_{0.05}Yb_{0.04}Lu_{0.01})_{Σ0.35}Mn_{0.16}Zr_{0.11}Na_{0.09}Fe²⁺_{0.07}Ca_{0.01}]_{Σ2}
154 (Ti_{0.76}Nb_{0.23}Ta_{0.01})_{Σ1}(Si_{4.03}O₁₄)O_{1.12}F_{2.88}, Z = 1. The simplified formula is Na₃Ca₂Y₂Ti(Si₂O₇)₂OF₃.

156 **X-ray data collection and structure refinement**

157 X-ray data for fogoite-(Y) were collected from a twinned crystal with a single-crystal Bruker D8
158 three-circle diffractometer equipped with a rotating-anode generator (Mo-K α radiation),
159 multilayer optics and an APEX-II detector. X-ray powder-diffraction data were obtained by
160 collapsing experimental data from the single-crystal into two dimensions and are presented in
161 Table 4. Details of data collection and structure refinement are given in Table 5. The intensities
162 of reflections with $-13 \leq h \leq 13$, $-7 \leq k \leq 7$, $0 \leq l \leq 10$ were collected with a frame width of 0.3°

163 and a frame time of 10 s, and an empirical absorption correction (TWINABS, Sheldrick, 2008)
164 was applied. All tested crystals were twinned by reticular merohedry. Twin operation is a 180°
165 rotation around [001] and twin index is 2 (see Fig. 3). Same twinning has reported by Bellezza
166 et al. (2004b) in related minerals like götzenite. CELL_NOW (Sheldrick, 2004) was used to
167 obtain an HKLF5 file, and with the Bruker SHELXTL Version 5.1 refinement of the crystal
168 structure was done in space group $P\bar{1}$ using the atom coordinates of götzenite (Christiansen *et*
169 *al.*, 2003a). The crystal structure of fogoite-(Y) was refined to $R_1 = 2.81\%$, the twin ratio being
170 0.534(4):0.466(4) (Table 5). The occupancies of five cation sites were refined with the following
171 scattering curves: M^H and A^P sites: Y and Ca; $M^O(1)$ site: Ti; $M^O(2)$ and $M^O(3)$ sites: Na. We
172 observed disorder of Ti at the $M^O(1)$ site, with Ti-Ti = 0.366 Å. The refinement of the site-
173 occupancy for the $M^O(2)$ site converged to 1.0 and was fixed. Scattering curves for neutral
174 atoms were taken from the International Tables for Crystallography (Wilson, 1992). Final atom
175 coordinates and equivalent displacement parameters are given in Table 6, selected interatomic
176 distances and angles in Table 7, refined site-scattering values and assigned site-populations in
177 Table 8, and bond-valence values for selected anions in Table 9. A list of observed and
178 calculated structure factors, Crystallography Information File (CIF) and anisotropic displacement
179 parameters have been deposited with the Principal Editor of *Mineralogical Magazine* and are
180 available from www.minersoc.org/pages/e_journals/dep_mat.html.

181

182 **Site-population assignment**

183 There are seven cation sites in the crystal structure of fogoite-(Y): the M^H , A^P and two *Si* sites of
184 the H sheet and three M^O sites of the O sheet; site labelling follows Sokolova (2006).

185 Consider first the two [6]-coordinated M^H and A^P sites in the H sheet. The $\langle M^H-\phi \rangle$
186 distance of 2.271 Å is shorter than the $\langle A^P-\phi \rangle$ distance of 2.416 Å (where $\phi = O, F$) (Table 7)
187 and the refined site-scattering at the M^H site, 81.2(2) e.p.f.u., is higher than that at the A^P site,

188 41.8(2) e.p.f.u., and hence we assign all Y, REE^{3+} , Zr and Fe^{2+} plus some Mn, Na and minor Ca
189 to the M^H site, with an assigned site-scattering of 75.98 e.p.f.u., and the lighter Ca to the A^P site,
190 with an assigned site-scattering of 40.00 e.p.f.u. (Table 8).

191 In the O sheet, the bonds-lengths around the $M^O(1)$ site in the O sheet vary from 1.809
192 to 2.174 Å (Table 7) and we assign all Ti, Nb and Ta to the $M^O(1)$ site, with a calculated
193 scattering of 26.88 e.p.f.u. and a refined scattering of 26.0(2) e.p.f.u. (Table 8). Consider next
194 the [8]-coordinated $M^O(2)$ and [6]-coordinated $M^O(3)$ sites in the O sheet. The refined site-
195 scattering of 25.5 e.p.f.u. at the $M^O(3)$ site is higher than that at the $M^O(2)$ site: 11.0 e.p.f.u.; and
196 the $\langle M^O(3)-\varphi \rangle$ distance of 2.378 Å is shorter than the $\langle M^O(2)-\varphi \rangle$ distance of 2.490 Å. Hence we
197 assign 1.78 Na + 0.15 Mn to the $M^O(3)$ site, with a calculated site-scattering of 23.33 e.p.f.u. and
198 all remaining 0.96 Na a.p.f.u. to the $M^O(2)$ site, with a calculated site-scattering of 10.56 e.p.f.u.
199 (Table 8).

200

201 **Description of the structure**

202 *Cation and anion sites*

203 Here we consider seven cation sites, three M^O sites of the O sheet and M^H , A^P and two Si sites
204 of the H sheet; and two anion sites: X^O_M = anion sites at the common vertices of $3M^O$ and M^H
205 polyhedra; X^O_A = anion sites at the common vertices of $3M^O$ polyhedra that occur approximately
206 under the A^P sites; labelling follows Sokolova (2006).

207 In the O sheet, the $M^O(1)$ site is occupied primarily by Ti with subordinate Nb and minor
208 Ta (Table 8), and it is coordinated by four O atoms and two (O,F) anions at the X^O_M site (Fig.
209 4a), with $\langle M^O(1)-\varphi \rangle = 1.980$ Å (Table 7). Ti is positionally disordered at the $M^O(1)$ site, with Ti-Ti
210 = 0.366 Å (Fig. 4b). Similar positional disorder of Ti and Nb and Ti and Fe^{3+} has been reported
211 for the Ti-silicate minerals veblenite, $K_2\Box_2Na(Fe^{2+}_5Fe^{3+}_4Mn^{2+}_7\Box)Nb_3Ti(Si_2O_7)_2(Si_8O_{22})_2O_6(OH)_{10}$
212 $(H_2O)_3$ (Cámara *et al.*, 2013) and narsarsukite, $Na_2(Ti,Fe)Si_4(O,F)_{11}$ (Mesto *et al.*, 2015). In
213 fogoite-(Y), the four $M^O(1)-O$ bonds are approximately of the same length: 1.970-1.980 Å (Table

214 7). The longest and shortest bonds are from the $M^O(1)$ cation to the X_M^O anions, $M^O(1)-X_M^O =$
215 2.174 Å and 1.809 Å, respectively (Table 7, Fig. 4b). The bond-valence sum at the X_M^O anion at
216 a distance of 1.809 Å from the $M^O(1)$ cation is 1.90 vu (valence units) (Table 9) and 1.65 vu
217 where it is calculated with the bond-valence parameters for cation-oxygen and cation-fluorine
218 bonds, respectively. The bond-valence sum of 1.90 vu is in accord with the 2^- charge of an O
219 atom and the bond-valence sum of 1.65 vu is too high to compensate for the 1^- charge of an F
220 atom. Thus $X_M^O = O$ where $M^O(1)-X_M^O = 1.809$ Å. The bond-valence sum at the X_M^O anion at a
221 distance of 2.174 Å from the $M^O(1)$ cation is 0.69 vu (Table 9) and 1.29 vu where it is calculated
222 with the bond-valence parameters for cation-fluorine and cation-oxygen bonds, respectively.
223 The bond-valence sum of 0.69 vu is in accord with the 1^- charge of an F atom and the bond-
224 valence sum of 1.29 vu is too low to compensate for the 2^- charge of an O atom. Hence $X_M^O = F$
225 where $M^O(1)-X_M^O = 2.174$ Å. We suggest that the disorder of Ti at the $M^O(1)$ site is due to O-F
226 disorder at the X_M^O site: the bond-valence sums at the X_M^O anions require a shorter Ti-O bond
227 and a longer Ti-F bond (Table 7, Fig. 4b). The ideal composition of the $M^O(1)$ site is Ti a.p.f.u.

228 The Na-dominant $^{[8]}M^O(2)$ and $^{[6]}M^O(3)$ sites are coordinated by six O atoms plus two F
229 atoms at the X_A^O site, with $\langle M^O(2)-\varphi \rangle = 2.490$ Å, and two O atoms plus two F atoms at the X_A^O
230 and two (OF) anions at the X_M^O site, with $\langle M^O(3)-\varphi \rangle = 2.378$ Å (Tables 7,8). The ideal
231 composition of the $M^O(2,3)$ sites is Na_3 a.p.f.u. (Table 8).

232 In the H sheet, there are two tetrahedrally coordinated Si(1,2) sites occupied by Si and
233 two [6]-coordinated sites, the Y-dominant M^H site and the A^P site occupied by Ca (Table 8). The
234 M^H site is coordinated by five O atoms and an X_M^O anion, with $\langle M^H-\varphi \rangle = 2.271$ Å, and the A^P
235 site is coordinated by five O atoms and an X_A^O anion, with $\langle A^P-\varphi \rangle = 2.416$ Å (Tables 7, 8, Fig.
236 4c). The ideal composition of the $A^P + M^H$ sites is Ca_2Y_2 a.p.f.u.

237 We write the cation part of the TS block, $A^P_2M^H_2M^O_4$, as the sum of cations of the O and
238 H sheets: $Ca_2Y_2Na_3Ti$ a.p.f.u., with a total charge of 17^+ .

239 We assign O atoms to the O(1–7) sites that coordinate the Si(1) and Si(2) sites, giving
240 $(\text{Si}_2\text{O}_7)_2$ p.f.u. Anions at the X_M^O and X_A^O sites receive bond valences from four cations: X_M^O from
241 $M^O(1)$, $2M^O(3)$ and M^H , and X_A^O from $M^O(2)$, $2M^O(3)$, and A^P , respectively (Tables 7, 9). We
242 expect the X_M^O atom to receive a higher bond-valence as it is bonded to Ti at the $M^O(1)$ site, and
243 the X_A^O atom, a lower bond-valence as it is bonded to Na at the $M^O(2)$ site. Above we showed
244 that the X_M^O site is occupied by O and F atoms in the ratio 1 : 1. The X_A^O anion is occupied by F,
245 with an incident bond-valence sum of 0.68 vu (Table 9). Occurrence of O and F at the X_M^O site
246 and F at the X_A^O site is common for Group-I TS-block minerals (Table 1).

247 The anions sum as follows: $(\text{Si}_2\text{O}_7)_2 [\text{O}(1-7)] + [(\text{OF})\text{F}_2] [(X_M^O)_2 \text{ and } (X_A^O)_2] =$
248 $(\text{Si}_2\text{O}_7)_2(\text{OF})\text{F}_2$ p.f.u., with a total charge of 17^- . We write ideal formula of fogoite-(Y) as the sum
249 of cation and anion components: $\text{Ca}_2\text{Y}_2\text{Na}_3\text{Ti} + (\text{Si}_2\text{O}_7)_2(\text{OF})\text{F}_2 = \text{Ca}_2\text{Y}_2\text{Na}_3\text{Ti}(\text{Si}_2\text{O}_7)_2(\text{OF})\text{F}_2$, $Z =$
250 1, with a simplified formula $\text{Na}_3\text{Ca}_2\text{Y}_2\text{Ti}(\text{Si}_2\text{O}_7)_2\text{OF}_3$.

251

252 *Structure topology of fogoite-(Y)*

253 For the structure description, we use the terminology of Sokolova (2006). The main structural
254 unit in the fogoite-(Y) structure is a TS block that consist of HOH sheets. The O sheet is
255 composed of Ti-dominant $M^O(1)$ octahedra and Na-dominant $^{[8]}M^O(2)$ and $^{[6]}M^O(3)$ polyhedra
256 (Fig. 4a). The H sheet is built of Si_2O_7 groups and [6]-coordinated M^H and A^P polyhedra
257 occupied by Y and Ca, respectively (Fig. 4c). In fogoite-(Y), the topology of the TS block is as in
258 Group I of the TS-block minerals where $\text{Ti} (+ \text{Nb} + \text{Zr}) = 1$ a.p.f.u. per $(\text{Si}_2\text{O}_7)_2$: two H sheets
259 connect to the O sheet such that two Si_2O_7 groups link to the *trans* edges of a Na $[M^O(2)]$
260 polyhedron of the O sheet (Fig. 4d). The ideal compositions of the O and two H sheets are
261 $\text{Na}_3\text{Ti}(\text{OF})\text{F}_2$ and $\text{Y}_2\text{Ca}_2(\text{Si}_2\text{O}_7)_2$ a.p.f.u. In the crystal structure of fogoite-(Y), TS blocks parallel
262 to (100) share corners and edges of the H-sheet polyhedra to form a framework (Fig. 4e).

263

264

265 **Related Minerals**

266 Fogoite-(Y), $\text{Na}_3\text{Ca}_2\text{Y}_2\text{Ti}(\text{Si}_2\text{O}_7)_2\text{OF}_3$, is a new Group-I TS-block mineral. It is isostructural
267 with hainite, $\text{Na}_2\text{Ca}_4(\text{Y}, \text{REE})\text{Ti}(\text{Si}_2\text{O}_7)_2\text{OF}_3$ (Blumrich, 1893; Christiansen *et al.*, 2003a) and
268 götzenite, $\text{NaCa}_6\text{Ti}(\text{Si}_2\text{O}_7)_2\text{OF}_3$ (Sahama and Hytonen, 1957; Christiansen *et al.*, 2003a) [Table
269 1, mineral formulae are from Sokolova (2006)]. Fogoite-(Y) is a Y-dominant, Na-rich and Ca-
270 poor analogue of hainite and götzenite. Fogoite-(Y) and hainite are related by the substitution
271 ${}^{[\text{H}]}\text{Y}^{3+}_{\text{fog}} + {}^{[\text{O}]}\text{Na}^{+}_{\text{fog}} \leftrightarrow {}^{[\text{H}]}\text{Ca}^{2+}_{\text{hai}} + {}^{[\text{O}]}\text{Ca}^{2+}_{\text{hai}}$, where [H] and [O] stand for H and O sheets in the TS
272 block. Fogoite-(Y) and götzenite are related by the substitution $2{}^{[\text{H}]}\text{Y}^{3+}_{\text{fog}} + 2{}^{[\text{O}]}\text{Na}^{+}_{\text{fog}} \leftrightarrow 2{}^{[\text{H}]}\text{Ca}^{2+}_{\text{göt}}$
273 $+ 2{}^{[\text{O}]}\text{Ca}^{2+}_{\text{göt}}$.

274

275

276 **Acknowledgements**

277

278 We thank Mark A. Cooper for collection of single-crystal X-ray data and Jean-Marc Johannet for
279 high-definition photographs of fogoite-(Y). FC acknowledges support by the University
280 of Torino "Progetti di ricerca finanziati dall'Università degli Studi di Torino (ex 60 %)"- year 2014.
281 This work was supported by a Canada Research Chair in Crystallography and Mineralogy and
282 by a Discovery Grant from the Natural Sciences and Engineering Research Council of Canada
283 to FCH, and by Innovation Grants from the Canada Foundation for Innovation to FCH.

284

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357 formula of mosandrite, $(\text{Ca}_3\text{REE})[(\text{H}_2\text{O})_2\text{Ca}_{0.5}\square_{0.5}]\text{Ti}(\text{Si}_2\text{O}_7)_2(\text{OH})_2(\text{H}_2\text{O})_2$, a Group-I
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- 367

368 **Figure captions**

369 Fig. 1. Fogoite-(Y): (a) a radiating aggregate of fogoite-(Y) crystals (pale yellow) and
370 astrophyllite crystals (orangy yellow) on sanidine; (b) an isolated crystal of astrophyllite
371 intergrown with a fogoite-(Y) crystal, a fragment of an amphibole-supergroup mineral (black,
372 possibly ferro-katophorite) is in the lower right corner. Photo by Jean-Marc Johannet.

373

374 Fig. 2. The FTIR spectrum of fogoite-(Y).

375

376 Fig. 3. Simulated precession slice of $h0l$ zone: $+h$ to right, $+l$ down. Imaged created with APEX 2
377 software by Bruker. Overlapping of reciprocal lattice nodes occurs on h even levels. Thus one
378 node out of two is restored by the twin operation (twin index 2).

379

380 Fig. 4. The TS block in the crystal structure of fogoite-(Y): (a) the O sheet, (b) stereochemistry of
381 Ti at the $M^O(1)$ site in the O sheet; (c) the H sheet; (d) the TS block, and (e) the general view of
382 the crystal structure; Si tetrahedra are orange, Ti-dominant $M^O(1)$ octahedra are yellow, Na-
383 dominant [8]-coordinated $M^O(2)$ polyhedra and $M^O(3)$ octahedra are navy blue, [6]-coordinated
384 Y-dominant M^H and Ca A^P polyhedra are purple and pink, (O,F) and F anions at the X^O_M and
385 X^O_A sites are shown as medium orange and yellow spheres, respectively. The unit cell is shown
386 by thin black lines in (a,c,e). The letters H O H indicate the positions of H and O sheets in (d,e).

387

Table 1. The Group-I TS-block minerals*, Ti (+ Nb + Zr) = 1 a.p.f.u.

Mineral Formula	Str. type	Ideal structural formula	a (Å) α (°)	b (Å) β (°)	c (Å) γ (°)	Sp. gr. Z	Ref.
		A_2^P M_2^H M_4^O $(Si_2O_7)_2$ $(X_M^O)_2$ $(X_A^O)_2$					
Fogoite-(Y) $Na_3Ca_2Y_2Ti(Si_2O_7)_2OF_3$	B2(GI)	Ca_2 Y_2 Na_3 Ti $(Si_2O_7)_2$ (OF) F_2 $\Sigma A_2^P + M_2^H = Ca_2Y_2$	9.575 89.985	5.685 100.933	7.279 101.300	$P\bar{1}$ 1	(1)
Hainite $Na_2Ca_4(Y,REE)Ti(Si_2O_7)_2OF_3$	B2(GI)	Ca_2 Ca(Y,REE) Na(NaCa) Ti $(Si_2O_7)_2$ (OF) F_2 $\Sigma A_2^P + M_2^H = Ca_3(Y,REE)$	9.6079 89.916	5.7135 101.077	7.3198 100.828	$P\bar{1}$ 1	(2,3)
Götzenite $NaCa_6Ti(Si_2O_7)_2OF_3$	B2(GI)	Ca_2 Ca NaCa Ti $(Si_2O_7)_2$ (OF) F_2 $\Sigma A_2^P + M_2^H = Ca_4$	9.6192 89.981	5.7249 101.132	7.3307 100.639	$P\bar{1}$ 1	(4,3)
Kochite $Na_3Ca_2MnZrTi(Si_2O_7)_2OF_3$	B2(GI)	Ca_2 Mn Zr Na_3 Ti $(Si_2O_7)_2$ (OF) F_2 $\Sigma A_2^P + M_2^H = Ca_2MnZr$	10.032 90.192	11.333 100.334	7.202 111.551	$P\bar{1}$ 2	(5)
Rosenbuschite $Na_6Ca_6Zr_2ZrTi(Si_2O_7)_4O_2F_6$	B2(GI)	Ca_4 Ca Zr Na_6 Ti Zr $(Si_2O_7)_4$ (OF) $_2$ F_4 $\Sigma A_4^P + M_4^H = Ca_6Zr_2$	10.137 90.216	11.398 100.308	7.2717 111.868	$P\bar{1}$ 1	(6,3)
Seidozerite $Na_4MnZr_2Ti(Si_2O_7)_2O_2F_2$	B2(GI)	Na_2 Zr Na_2Mn Ti $(Si_2O_7)_2$ O_2 F_2 $\Sigma A_2^P + M_2^H = Na_2Zr_2$	5.5558	7.0752 102.713	18.406	$P2_1/c$ 2	(7,3)
Grenmarite $Na_4MnZr_2Ti(Si_2O_7)_2O_2F_2$	B2(GI)	Na_2 Zr Na_2Mn Zr $(Si_2O_7)_2$ O_2 F_2 $\Sigma A_2^P + M_2^H = Na_2Zr_2$	5.608	7.139 102.60	18.575	$P2_1/c$ 2	(8)
Rinkite $Na_2Ca_4REETi(Si_2O_7)_2OF_3$	B1(GI)	Ca_2 (CaREE) Na(NaCa) Ti $(Si_2O_7)_2$ (OF) F_2 $\Sigma A_2^P + M_2^H = Ca_3REE$	7.4414	5.6628 101.383	18.8315	$P2_1/c$ 2	(9,10)
Nacareniobsite-(Ce) $Na_3Ca_3REENb(Si_2O_7)_2OF_3$	B1(GI)	$(Ca,REE)_2$ (Ca,REE) Na_3 Nb $(Si_2O_7)_2$ (OF) F_2 $\Sigma A_2^P + M_2^H = Ca_3REE$	7.468	5.689 101.37	18.891	$P2_1/c$ 2	(11,12)
Mosandrite $[(H_2O)_2Ca_{0.5}\square_{0.5}]Ca_3REETi(Si_2O_7)_2(OH)_2(H_2O)_2$	B1(GI)	Ca_2 (CaREE) $(H_2O)_2$ Ti $(Si_2O_7)_2$ (OH) $_2$ $(H_2O)_2$ $\Sigma A_2^P + M_2^H = Ca_3REE$ Ca $_{0.5}$ $_{0.5}$	7.4222	5.6178 101.4226	18.7232	$P2_1/c$ 2	(13,14)

* Structure types, B (basic), and structural formula are from Sokolova and Cámara (2013); formulae are per $(Si_2O_7)_2$, except per $(Si_2O_7)_4$ for rosenbuschite. The invariant core of the TS block, $M_2^H M_4^O (Si_2O_7)_2 X_4^O$, is shown in bold: M^O and M^H = cations of the O and H sheets, A^P = cations at the peripheral (P) sites, X_4^O = anions of the O sheet not bonded to Si; X_M^O = anions at the common vertices of $3M^O$ and M^H polyhedra; X_A^O = anions at the common vertices of $3M^O$ polyhedra that occur approximately under the A^P sites (Sokolova, 2006); Ti (+ Nb + Zr) at the $M^O(1)$ site is shown in red.

References (discovery of a mineral, the most recent structure work): (1) This work; (2) Blumrich (1893); (3) Christiansen *et al.* (2003a); (4) Sahama and Hytönen (1957); (5) Christiansen *et al.* (2003b); (6) Brögger (1887); (7) Semenov *et al.* (1958); (8) Bellezza *et al.* (2004a); (9) Lorenzen (1884); (10) Sample 1991C, Cámara *et al.* (2011); (11) Petersen *et al.* (1989); (12) Sokolova and Hawthorne (2008); (13) Brögger (1890); (14) Sokolova and Hawthorne (2013).

Table 2. Optical orientation ($^{\circ}$) for fogoite-(Y).

	a	b	c
X	100.5	92.0	2.1
Y	100.8	2.1	88.0
Z	164.9	89.1	89.9

Table 3. Chemical composition and unit formula for fogoite-(Y).

Chemical composition				Unit formula* (a.p.f.u.)	
	wt. %	Range	Esd		
Ta ₂ O ₅	0.24	0.23-0.25	0.01	Si	4.03
Nb ₂ O ₅	3.73	3.50-3.89	0.15		
ZrO ₂	1.72	1.51-1.89	0.11	Ti	0.76
TiO ₂	7.48	7.35-7.60	0.09	Nb	0.23
SiO ₂	29.81	29.40-29.85	0.14	Ta	<u>0.01</u>
Lu ₂ O ₃	0.29	0.14-0.43	0.15	M ^O (1)	1.00
Yb ₂ O ₃	0.87	0.72-0.98	0.10		
Er ₂ O ₃	1.17	1.17-1.18	0.01	Na	2.74
Dy ₂ O ₃	1.78	1.64-1.97	0.12	Mn	<u>0.15</u>
Gd ₂ O ₃	1.74	1.43-1.90	0.17	M ^O (2,3)	2.89
Sm ₂ O ₃	0.41	0.32-0.50	0.09		
Nd ₂ O ₃	0.72	0.52-0.85	0.10	Y	1.21
Ce ₂ O ₃	0.62	0.57-0.66	0.05	REE**	0.35
La ₂ O ₃	0.18	0.19-0.17	0.01	Mn	0.16
Y ₂ O ₃	16.74	16.53-16.95	0.21	Zr	0.11
FeO	0.64	0.61-0.67	0.02	Na	0.09
MnO	2.74	2.71-2.77	0.03	Fe ²⁺	0.07
CaO	13.89	13.75-13.96	0.07	Ca	<u>0.01</u>
Na ₂ O	10.80	10.72-10.95	0.05	M ^H	2.00
F	6.74	6.31-7.04	0.10		
O = F	-2.84			Ca	2.00
Total	99.47			A ^P	2.00
				Σcations	11.92
				O	15.12
				F	<u>2.88</u>
				Σanions	18.00

*formula calculated on 18 (O + F);

** REE = (La_{0.01}Ce_{0.03}Nd_{0.03}Sm_{0.02}Gd_{0.08}Dy_{0.08}Er_{0.05}Yb_{0.04}Lu_{0.01})_{Σ0.35}

Table 4. X-ray powder (2 dimensional) diffraction data for fogoite-(Y).

$l_{\text{obs.}}$	$d_{\text{obs.}} (\text{\AA})$	h	k	l	$l_{\text{obs.}}$	$d_{\text{obs.}} (\text{\AA})$	h	k	l
3	9.212	1	0	0	7	1.863	$\bar{5}$	1	0
3	7.142	0	0	1	3	1.842	3	$\bar{2}$	2
7	5.571	0	1	0			$\bar{4}$	0	3
2	4.392	1	1	0			4	$\bar{2}$	1
		$\bar{1}$	1	0			5	0	0
4	4.313	0	1	1			$\bar{1}$	2	3
23	3.960	$\bar{1}$	$\bar{1}$	1	20	1.820	$\bar{1}$	0	4
		$\bar{2}$	1	0	6	1.792	4	$\bar{1}$	2
2	3.686	$\bar{2}$	1	1			$\bar{5}$	1	2
5	3.569	0	0	2			2	1	3
		$\bar{1}$	0	2	7	1.777	0	3	1
		2	0	1			2	$\bar{3}$	1
4	3.274	2	$\bar{1}$	1			2	2	2
4	3.247	2	1	0			0	2	3
42	3.069	3	0	0	2	1.751	1	3	0
		0	$\bar{1}$	2			$\bar{3}$	3	0
100	2.954	$\bar{1}$	$\bar{1}$	2	2	1.722	3	0	3
		$\bar{3}$	1	0			$\bar{2}$	$\bar{2}$	3
8	2.827	$\bar{1}$	2	0			$\bar{2}$	1	4
11	2.786	2	1	1	3	1.701	2	$\bar{2}$	3
		0	2	0			$\bar{5}$	2	0
21	2.626	$\bar{2}$	2	0	15	1.674	$\bar{1}$	3	2
5	2.590	2	0	2			0	$\bar{3}$	2
		$\bar{3}$	0	2			$\bar{2}$	3	2
3	2.530	1	2	0	4	1.654	5	1	0
24	2.486	3	1	0			1	$\bar{1}$	4
		2	$\bar{1}$	2			$\bar{3}$	1	4
6	2.303	$\bar{4}$	1	1	8	1.637	$\bar{4}$	$\bar{2}$	1
		$\bar{3}$	2	0			$\bar{4}$	2	3
		$\bar{2}$	0	3			$\bar{5}$	2	2
		4	0	0	4	1.622	4	2	0
10	2.239	$\bar{1}$	2	2			0	3	2
		2	1	2			2	$\bar{3}$	2
17	2.195	2	2	0			4	1	2
		$\bar{2}$	2	2	2	1.615	$\bar{5}$	1	3
2	2.109	1	$\bar{1}$	3			2	3	0
		$\bar{4}$	1	2			$\bar{4}$	3	0
6	2.045	$\bar{3}$	2	2	6	1.575	3	2	2
7	1.983	1	2	2	10	1.565	$\bar{4}$	0	4
		$\bar{4}$	2	1			$\bar{6}$	0	1
		$\bar{4}$	2	0			$\bar{6}$	1	0
23	1.893	$\bar{1}$	3	0	3	1.549	2	$\bar{1}$	4
		3	1	2					

Table 5. Miscellaneous refinement data for fogoite-(Y).

a (Å)	9.575(6)
b	5.685(4)
c	7.279(5)
α (°)	89.985(6)
β	100.933(4)
γ	101.300(5)
V (Å ³)	381.2(7)
Refl. ($I_o > 10\sigma I$)	9985
Space group	$P\bar{1}$
Z	1
Absorption coefficient (mm ⁻¹)	8.39
$F(000)$	385.3
$D_{\text{calc.}}$ (g/cm ³)	3.523
Crystal size (mm)	0.10 x 0.02 x 0.02
Radiation/monochromator	MoK α / graphite
$2\theta_{\text{max}}$ (°)	60.27
$R(\text{int})$ (%)	5.69
Second component (%)*	46.6(4)
Reflections collected	15848
Independent reflections	2225
$F_o > 4\sigma F$	2157
Refinement method	Full-matrix least squares on F^2 , fixed weights proportional to $1/\sigma F_o^2$
Final $R_{(\text{obs})}$ (%)	
R_1 [$F_o > 4\sigma F$]	2.81
R_1 (all data)	2.89
wR_2	7.71
Goodness of fit on F^2	1.124

* Second component of the crystal is related to the first component by the twin matrix [1 0 1/2, 0 1 0, 0 0 1].

Table 6. Atom coordinates and equivalent displacement parameters for fogoite-(Y).

Atom	x/a	y/b	z/c	$U_{eq}(\text{\AA}^2)$
M ^H	0.63631(2)	0.22040(4)	0.90986(7)	0.00776(9)
A ^P	0.63726(6)	0.22484(10)	0.41070(16)	0.0159(2)
M ^O (1)	0.0117(4)	0.0221(6)	-0.0037(9)	0.0036(4)
M ^O (2)	0	0	½	0.0090(3)
M ^O (3)	0.99700(11)	0.49783(17)	0.24679(14)	0.0133(3)
Si(1)	0.71363(8)	0.74517(14)	0.65351(15)	0.0071(2)
Si(2)	0.72015(9)	0.74442(15)	0.21150(12)	0.0075(2)
O(1)	0.7446(3)	0.7708(5)	0.4393(4)	0.0206(5)
O(2)	0.6138(3)	0.9385(4)	0.6769(6)	0.0141(7)
O(3)	0.6131(2)	0.9248(4)	0.1324(7)	0.0151(7)
O(4)	0.6374(3)	0.4697(4)	0.6756(7)	0.0177(6)
O(5)	0.6552(3)	0.4686(4)	0.1488(7)	0.0183(6)
O(6)	0.8746(3)	0.8111(4)	0.7826(3)	0.0144(5)
O(7)	0.8824(2)	0.8285(5)	0.1703(3)	0.0142(5)
X ^O _M	0.8787(2)	0.2498(4)	0.9673(6)	0.0163(4)
X ^O _A	0.8806(2)	0.2988(4)	0.4721(7)	0.0221(4)

Table 7. Selected interatomic distances (Å) and angles (°) in fogoite-(Y).

M ^H –O(5)a	2.198(4)	A ^P –X ^O _A	2.242(2)	M ^O (1)–X ^O _{Me}	1.809(3)
M ^H –O(4)	2.217(5)	A ^P –O(2)c	2.364(3)	M ^O (1)–O(7)f	1.970(6)
M ^H –X ^O _M	2.251(2)	A ^P –O(5)	2.370(5)	M ^O (1)–O(7)g	1.973(6)
M ^H –O(2)b	2.285(4)	A ^P –O(4)	2.378(5)	M ^O (1)–O(6)h	1.972(6)
M ^H –O(3)c	2.330(3)	A ^P –O(2)b	2.545(4)	M ^O (1)–O(6)c	1.981(6)
M ^H –O(3)d	2.343(4)	A ^P –O(3)b	2.595(4)	M ^O (1)–X ^O _{Mc}	2.174(3)
<M ^H (1)–φ>	2.271	<A ^P –φ>	2.416	<M ^O (1)–φ>	1.980
M ^O (2)–X ^O _{Aj}	2.215(2) x2	M ^O (3)–X ^O _A	2.326(5)	Short distance	
M ^O (2)–O(1)c	2.493(3) x2	M ^O (3)–X ^O _{Ak}	2.337(5)	M ^O (1)–M ^O (1)m	0.366(3)
M ^O (2)–O(7)c	2.555(4) x2	M ^O (3)–O(6)k	2.365(3)		
M ^O (2)–O(6)c	2.694(3) x2	M ^O (3)–O(7)	2.371(3)		
<M ^O (2)–φ>	2.490	M ^O (3)–X ^O _{Ml}	2.431(4)		
		M ^O (3)–X ^O _{Mk}	2.437(4)		
		<M ^O (3)–φ>	2.378		
Si(1)–O(4)	1.615(3)	Si(2)–O(5)	1.602(3)	Si(1)–O(1)–Si(2)	160.9(2)
Si(1)–O(6)	1.619(3)	Si(2)–O(7)	1.618(3)		
Si(1)–O(2)	1.620(3)	Si(2)–O(3)	1.619(3)		
Si(1)–O(1)	1.643(3)	Si(2)–O(1)	1.643(3)		
<Si(1)–O>	1.624	<Si(2)–O>	1.621		

φ = O, F;

Symmetry operators: a: x, y, z+1; b: x, y-1, z; c: -x+1, -y+1, -z+1; d: x, y-1, z+1; e: x-1, y, z-1; f: -x+1, -y+1, -z; g: x-1, y-1, z; h: x-1, y-1, z-1; i: -x+1, -y, -z+1; j: x-1, y, z; k: -x+2, -y+1, -z+1; l: x, y, z-1; m: -x, -y, -z.

Table 8. Refined site-scattering and assigned site-populations for fogoite-(Y).

Site*	Refined site-scattering (e.p.f.u.)	Assigned site-population (a.p.f.u.)	Calculated site-scattering (e.p.f.u.)	<cation- φ > _{obs.} (Å)	Ideal composition (a.p.f.u.)
Cations					
M^{H**}	[M1]	81.2(2)	1.21Y + 0.35REE + 0.16Mn + 0.11Zr + 0.09 Na + 0.07 Fe ²⁺ + 0.01 Ca	75.98	2.271 Y ₂
A^P	[M3]	41.8(2)	2.00 Ca	40.00	2.416 Ca ₂
$M^O(1)$	[M5]	26.0(2)	0.76 Ti + 0.23 Nb + 0.01 Ta	26.88	1.980 Ti
^[8] $M^O(2)$	[M4]	11.0	0.96 Na + 0.04 □	10.56	2.490 Na
$M^O(3)$	[M2]	25.5(1)	1.78 Na + 0.15 Mn + 0.07 □	23.33	2.378 Na ₂
Anions					
X^O_M	[X8]		1.12 O + 0.88 F		(OF)
X^O_A	[F9]		2 F		F ₂

*Coordination numbers are shown for non-[6]-coordinated cation sites; [] site labelling in accord with Christiansen *et al.* (2003a); φ = O, F;

**0.35REE = La_{0.01}Ce_{0.03}Nd_{0.03}Sm_{0.02}Gd_{0.08}Dy_{0.08}Er_{0.05}Yb_{0.04}Lu_{0.01}.

Table 9. Bond-valence values* for selected anions in fogoite-(Y).

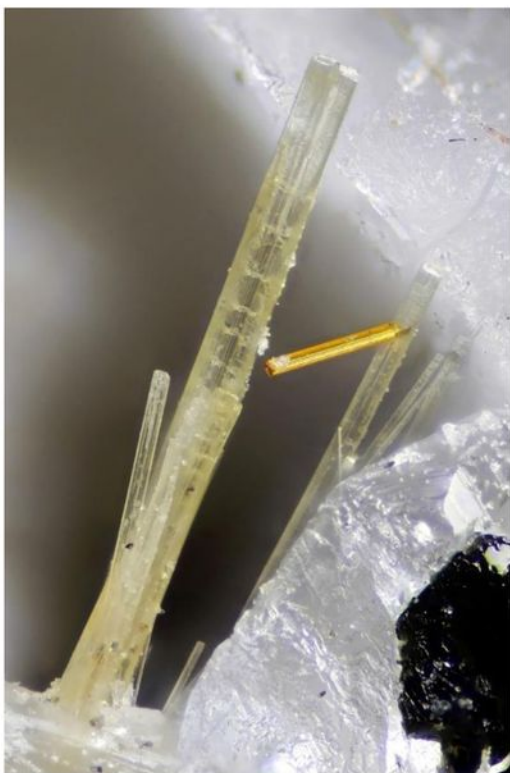
Cation	Anion		
	$X_M^O(O)^{**}$	$X_M^O(F)^{**}$	$X_A^O(F)$
M^H (Y)	0.56	0.15	
A^P (Ca)			0.14
$M^O(1)$ (Ti)	0.99	0.26	
$M^O(2)$ (Na)			0.21
$M^O(3)$ (Na)	0.18	0.14	0.17
	0.17	0.14	0.16
Σ	1.90	0.69	0.68

*bond-valence parameters are from Brown (1981);

** $X_M^O = (OF)$: for $X_M^O = O$, $M^O(1)-X_M^O = 1.809(3)$ Å
and for $X_M^O = F$, $M^O(1)-X_M^O = 2.174(3)$ Å (see text).

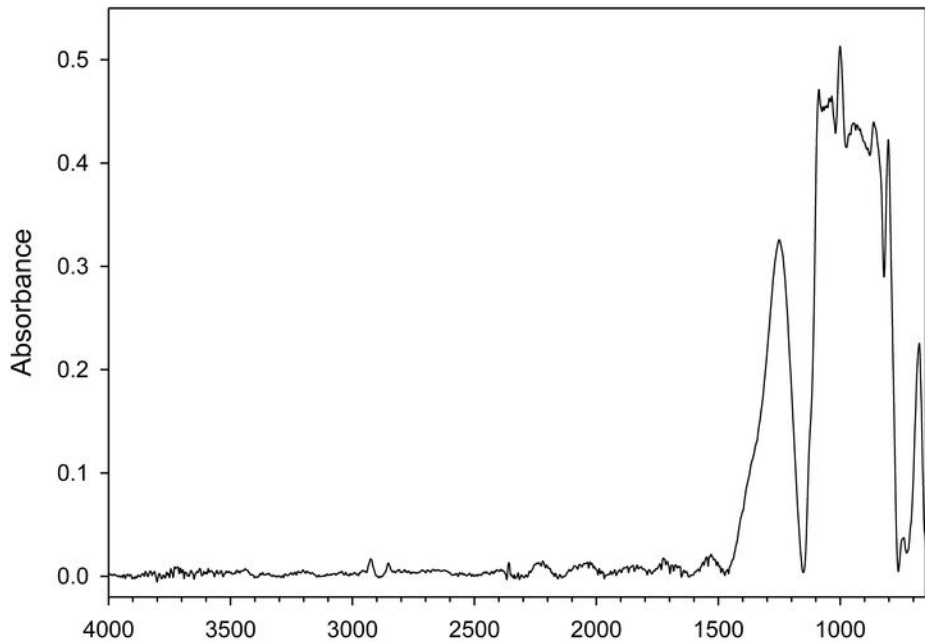
a

← 2.5 mm →

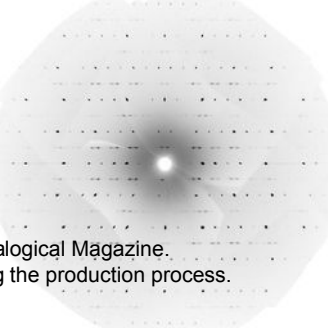
b

← 1.3 mm →

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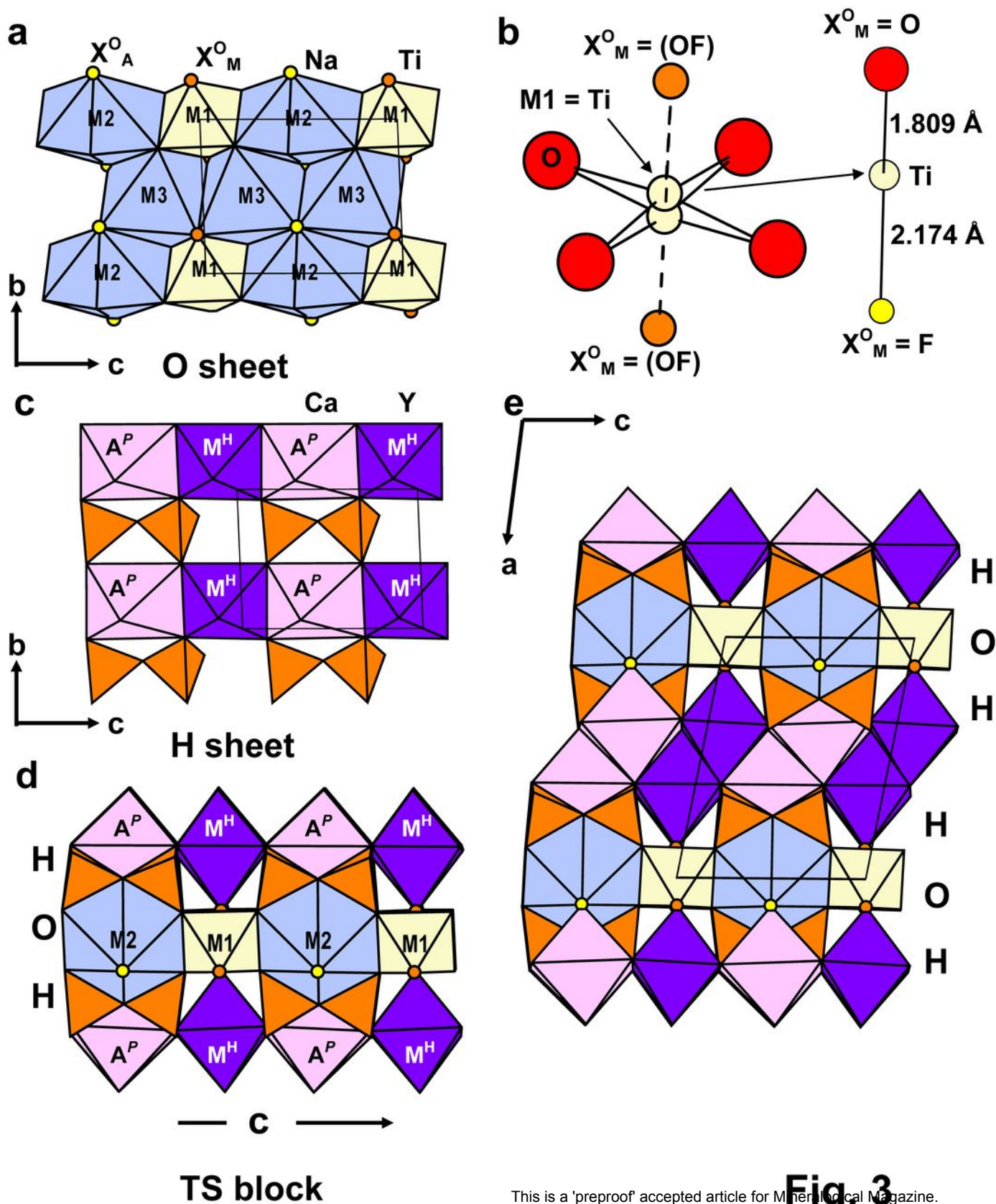


Table D. Anisotropic displacement parameters (\AA^2) for fogoite-(Y)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	U_{eq}
M ^H	0.00929(13)	0.00837(13)	0.00623(18)	-0.0002(3)	0.0022(3)	0.00114(8)	0.00796(9)
A ^P	0.0148(3)	0.0216(3)	0.0119(4)	-0.0010(8)	0.0045(8)	-0.0006(2)	0.0164(2)
M ^O (1)	0.0036(10)	0.0055(11)	0.0031(5)	0.0011(10)	0.0003(9)	0.0022(5)	0.0039(4)
M ^O (2)	0.0062(6)	0.0098(7)	0.0124(9)	-0.0004(16)	0.0005(14)	0.0038(5)	0.0093(3)
M ^O (3)	0.0184(5)	0.0107(5)	0.0142(7)	0.0003(14)	0.0037(12)	0.0081(4)	0.0136(3)
Si(1)	0.0081(3)	0.0085(3)	0.0056(6)	-0.0002(3)	0.0006(3)	0.0028(2)	0.0073(2)
Si(2)	0.0077(3)	0.0092(3)	0.0070(6)	0.0006(3)	0.0012(3)	0.0032(3)	0.0078(2)
O(1)	0.0194(10)	0.0357(13)	0.0064(9)	0.0004(11)	0.0036(10)	0.0019(9)	0.0208(5)
O(2)	0.0129(9)	0.0142(9)	0.017(2)	-0.0041(10)	0.0014(10)	0.0069(7)	0.0144(7)
O(3)	0.0114(9)	0.0159(10)	0.020(2)	0.0073(11)	0.0028(10)	0.0068(7)	0.0153(7)
O(4)	0.0199(10)	0.0113(9)	0.0207(16)	0.0010(12)	0.0040(13)	-0.0013(8)	0.0179(6)
O(5)	0.0238(11)	0.0118(9)	0.0192(16)	-0.0057(13)	0.0058(13)	-0.0004(8)	0.0186(6)
O(6)	0.0125(10)	0.0169(11)	0.0123(10)	-0.0042(8)	-0.0041(8)	0.0042(9)	0.0146(5)
O(7)	0.0095(10)	0.0200(11)	0.0159(12)	0.0056(8)	0.0070(8)	0.0038(8)	0.0144(5)
X _M ^O	0.0129(8)	0.0210(9)	0.0161(10)	-0.0004(13)	0.0021(12)	0.0049(7)	0.0166(4)
X _A ^O	0.0177(9)	0.0208(9)	0.0290(11)	0.0028(13)	0.0026(13)	0.0068(7)	0.0224(4)