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Fogoite-(Y), Na₃Ca₂Y₂Ti(Si₂O₇)₂OF₃, a Group I TS-block mineral from the Lagoa do Fogo, the Fogo volcano, São Miguel Island, the Azores: Description and crystal structure

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ABSTRACT

Fogoite-(Y), Na₃Ca₂Y₂Ti(Si₂O₇)₂OF₃, is a new mineral from the Lagoa do Fogo, São Miguel Island, the Azores. It occurs in cavities as highly elongated (on [001]) prisms, up to 2000 μm long and 50 μm × 50 μm in cross-section, associated with sanidine, astrophyllite, fluomatopryochlore, ferrokentbrooksit, quartz and ferrokatophorit. Crystals are generally transparent and colourless, with vitreous lustre, occasionally creamy white. Fogoite-(Y) has a white streak, splintery fracture and very good {100} cleavage. Mohs hardness is ~5. $D_{\text{calc.}} = 3.523 \text{ g/cm}^3$. It is biaxial (+) with refractive indices ($\lambda = 590 \text{ nm}$) $\alpha = 1.686(2)$, $\beta = 1.690(2)$, $\gamma = 1.702(5)$; $2V_{\text{meas.}} = 57(1)^\circ$ and $2V_{\text{calc.}} = 60^\circ$. It is nonpleochroic. Fogoite-(Y) is triclinic, space group $P\bar{1}$, $a = 9.575(6)$, $b = 5.685(4)$, $c = 7.279(5) \text{ \AA}$, $\alpha = 89.985(6)$, $\beta = 100.933(4)$, $\gamma = 101.300(5)^\circ$, $V = 381.2(7) \text{ \AA}^3$. The six strongest reflections in the powder X-ray diffraction data [d (Å), I, ($h k l$)] 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, ($\bar{1} \bar{1} 1, \bar{2} 1 0$); 2.626, 21, ($\bar{2} 2 0$); 1.820, 20, ($\bar{1} 0 4$). Electron microprobe analysis gave the following empirical formula calculated on 18 (O + F) (Na_{2.74}Mn_{0.15})_{Σ2.89}Ca₂[Y_{1.21}(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}Mn_{0.16} Zr_{0.11}Na_{0.09}Fe_{0.07}Ca_{0.01}]_{Σ2}(Ti_{0.76}Nb_{0.23}Ta_{0.01})_{Σ1}(Si_{4.03}O₁₄)O_{1.12}F_{2.88}, $Z = 1$. The crystal structure was refined on a twinned crystal to $R_1 = 2.81\%$ on the basis of 2157 unique reflections ($F_o > 4\sigma F_o$) and is a framework of TS (Titanium Silicate) blocks, which consist of HOH sheets (H – heteropolyhedral, O – octahedral) parallel to (100). In 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 $^{[6]}M^O(2)$ 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 $\langle M^O(3)-\varphi \rangle = 2.378 \text{ \AA}$. In the H sheet, the two $^{[4]}Si$ sites are occupied by Si, with $\langle Si-O \rangle = 1.623 \text{ \AA}$; the $^{[6]}M^H$ site is occupied by Y and rare-earth elements ($Y > REE$), with minor Mn, Zr, Na, Fe²⁺ and Ca, $\langle M^H-\varphi \rangle = 2.271 \text{ \AA}$ 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 and Si₂O₇ groups constitute the H sheet. The ideal compositions of the O and two H sheets are Na₃Ti(OF)F₂ and Y₂Ca₂(Si₂O₇)₂ apfu. Fogoite-(Y) is isostructural with götzenite and hainite. The mineral is named after the type locality, the Fogo volcano in the Azores.

KEYWORDS: fogoite-(Y), crystal-structure refinement, electron microprobe analysis, chemical formula, TS-block minerals, götzenite, hainite, Group I, Fogo volcano, the Azores.

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Introduction

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 Sokolova (2006). The mineral is named after the type locality, the Fogo volcano in the Azores. TS-block (Titanium Silicate) minerals are divided into four groups, characterized by a different topology and stereochemistry of the TS block. The TS block consists of the central O (Octahedral) sheet and two H (Heteropolyhedral) sheets containing Si_2O_7 groups. In Group I, Ti (+ Nb + Zr) = 1 apfu and Ti (+ Nb + Zr) occurs in the O sheet: $1 \text{M}^{\text{O}} = \text{Ti}, \text{Nb}, \text{Zr}$; $3 \text{M}^{\text{O}} = \text{Na}, \text{Ca}$ and rarely Mn; $^{[6],[7]}\text{M}^{\text{H}} = \text{Zr}, \text{Y}, \text{Ca} + \text{REE}, \text{Ca} + \text{Y} + \text{REE}, \text{Ca}, \text{Mn}$; $\text{A}^{\text{P}} = \text{Na}, \text{Ca}, \text{Ca} + \text{REE}$; $\text{X}^{\text{O}} = \text{anions O, F, OH and H}_2\text{O}$ groups. Sokolova (2006) wrote the general formula for minerals of Group I as $\text{A}_2^{\text{P}}\text{M}_2^{\text{H}}\text{M}_4^{\text{O}}(\text{Si}_2\text{O}_7)_2\text{X}_4^{\text{O}}$. There are ten Group I minerals of known structure: fogoite-(Y), hainite, götzenite, kochite, rosenbuschite, seidozerite, grenmarite, rinkite, nacareniobsite-(Ce) and mosandrite (Table 1). The stacking order of TS blocks in Group I structures is of two types (for details, see Christiansen and Rønsbo, 2000): type 1 occurs in rinkite, nacareniobsite-(Ce) and mosandrite (space group $P2_1/c$) and type 2 occurs in fogoite-(Y), hainite, götzenite, kochite, rosenbuschite (space group $P\bar{1}$) and related seidozerite and grenmarite (space group $P2/c$).

The new mineral and its name have been approved by the Commission on New Minerals, Nomenclature and Classification, International Mineralogical Association (IMA 2014-98). The holotype material is deposited in the collections of the Museo Regionale di Scienze Naturali di Torino, Torino, Italy, catalogue numbers M/U 16800 and M/U 16801, and the Royal Ontario Museum, Toronto, Ontario, Canada, catalogue number M56826. A further sample from the same locality has been deposited at the Muséum National d'Histoire Naturelle of Paris, France, catalogue number MIN2015-003. The current paper reports the description and crystal structure of fogoite-(Y).

Occurrence

Fogoite-(Y) was found in a syenite xenolith, in the bed of the upper part of the Ribeira Grande river near the ruins of Lombadas, close to Lagoa do Fogo (Lake of fire), a crater lake in the Agua de Pau stratovolcano (also named Fogo volcano) in the centre of São Miguel Island in the Azores ($37^\circ 46' 26'' \text{N}$

$25^\circ 27' 29'' \text{W}$). Associated minerals are sanidine, astrophyllite, fluornatropyrochlore, ferrokentbrooksite, quartz and ferro-katophorite. Other minerals described from these syenite ejecta are dalyite, chevkinite-(Ce), britholite-(Ce), eudialyte and a lävenite-like mineral (Ridolfi *et al.*, 2003).

The Azores archipelago straddles the Mid-Atlantic Ridge and emerges from the Azores Platform, ($37\text{--}40^\circ \text{N}$ and $25\text{--}31^\circ \text{W}$) near the North American-African-Eurasian triple-plate junction. São Miguel is one of the eastern islands, and is divisible into six volcanic zones (Moore, 1990): three large and dominantly trachytic, Quaternary stratovolcanoes (Sete Cidades, Agua de Pau and Furnas; Moore, 1991) and the Pliocene-Pleistocene northeast shield volcano (extinct) with its associated Povoação caldera (Abdel-Monem *et al.*, 1975; Fernandez, 1980) separated by two Quaternary alkali basalt volcanic fields. The Agua de Pau products (starting from 180 ka) range from basaltic to trachytic, and alkaline to transitional basalt lavas erupted from the flank vents. The more recent products date from 5 ka with the eruption of the trachytic Fogo-A plinian fall deposit (Walker and Croasdale, 1970; Widom *et al.*, 1992), which contains abundant syenite clasts containing feldspar, arfvedsonite, augite and/or aegirine, Fe-Ti oxide, zircon, pyrochlore, rare biotite and a few modal percent of quartz. The youngest clasts are friable syenites with miarolitic cavities and homogeneous sanidine, those containing fogoite-(Y). The syenite clasts within the Agua de Pau plinian deposits are divisible into silica-undersaturated syenites and silica-saturated/oversaturated syenites. They are considered to be the slowly cooled equivalents of the less-evolved and more-evolved trachytes in the shallow sub-volcanic magmatic system of Agua de Pau. Interstitial liquids of both syenite groups, trapped within a feldspathic framework, became progressively enriched in volatiles, alkalis, high-field-strength elements and REE. In the silica-undersaturated syenites (assumed to be material grown on the side-walls of the magma chamber), late-stage fractionation resulted in highly peralkalic (agpaitic) residual melts from which the complex Zr-Ti silicates eudialyte and a lävenite-like mineral crystallized (Ridolfi *et al.*, 2003).

Physical properties

Fogoite-(Y) occurs in cavities as acicular [001] prisms with equant cross-sections, up to 2000 μm long and 50 $\mu\text{m} \times 50 \mu\text{m}$ in cross-section (Fig. 1). The main forms are {100} and {010}. Crystals are generally creamy white, transparent to translucent, with vitreous

TABLE 1. The Group I TS-block minerals*, Ti (+ Nb + Zr) = 1 apfu.

Mineral Formula	Str. type	Ideal structural formula				a (Å)	b (Å)	c (Å)	Sp. gr.	Ref.
						α (°)	β (°)	γ (°)	Z	
Fogoite-(Y)	B2(GI)	A_2^P	M_2^H	M_4^O						
$Na_3Ca_2Y_2Ti(Si_2O_7)_2OF_3$		Ca_2	Y_2	Na_3	Ti	$(Si_2O_7)_2$	$(X_M^O)_2$	$(X_A^O)_2$	F_2	
Hainite	B2(GI)	$\Sigma A_2^P + M_2^H =$	Ca_2Y_2	$Na(NaCa)$	Ti	$(Si_2O_7)_2$	(OF)	F_2		(1)
$Na_2Ca_4(Y,REE)Ti(Si_2O_7)_2OF_3$		$\Sigma A_2^P + M_2^H =$	$Ca_3(Y,REE)$							(2,3)
Götzenite	B2(GI)	Ca_2	Ca_2	$NaCa_2$	Ti	$(Si_2O_7)_2$	(OF)	F_2		(4,3)
$NaCa_6Ti(Si_2O_7)_2OF_3$		$\Sigma A_2^P + M_2^H =$	Ca_4							
Kochite	B2(GI)	Ca_2	$Mn Zr$	Na_3	Ti	$(Si_2O_7)_2$	(OF)	F_2		(5)
$Na_3Ca_2MnZrTi(Si_2O_7)_2OF_3$		$\Sigma A_2^P + M_2^H =$	Ca_2MnZr							
Rosenbuschite	B2(GI)	Ca_4	$Ca_2 Zr_2$	Na_6	Ti Zr	$(Si_2O_7)_4$	(OF)	F_4		(6,3)
$Na_6Ca_6Zr_2ZrTi(Si_2O_7)_4O_2F_6$		$\Sigma A_4^P + M_4^H =$	Ca_6Zr_2							
Seidozerite	B2(GI)	Na_2	Zr_2	Na_2Mn	Ti	$(Si_2O_7)_2$	O_2	F_2		(7,3)
$Na_4MnZr_2Ti(Si_2O_7)_2O_2F_2$		$\Sigma A_2^P + M_2^H =$	Na_2Zr_2							
Grenmarite	B2(GI)	Na_2	Zr_2	Na_2Mn	Zr	$(Si_2O_7)_2$	O_2	F_2		(8)
$Na_4MnZr_2Ti(Si_2O_7)_2O_2F_2$		$\Sigma A_2^P + M_2^H =$	Na_2Zr_2							
Rinkite	B1(GI)	Ca_2	(CaREE)	$Na(NaCa)$	Ti	$(Si_2O_7)_2$	(OF)	F_2		(9,10)
$Na_2Ca_4REETi(Si_2O_7)_2OF_3$		$\Sigma A_2^P + M_2^H =$	Ca_3REE							
Nacareniobsite-(Ce)	B1(GI)	$(Ca,REE)_2$	(Ca,REE)	Na_3	Nb	$(Si_2O_7)_2$	(OF)	F_2		(11,12)
$Na_3Ca_3REENb(Si_2O_7)_2OF_3$		$\Sigma A_2^P + M_2^H =$	Ca_3REE							
Mosandrite	B1(GI)	Ca_2	(CaREE)	$(H_2O)_2$	Ti	$(Si_2O_7)_2$	(OH)	$(H_2O)_2$		(13,14)
$[(H_2O)_2Ca_{0.5}\square_{0.5}]Ca_3REETi(Si_2O_7)_2(OH)_2(H_2O)_2$		$\Sigma A_2^P + M_2^H =$	Ca_3REE	$Ca_{0.5}\square_{0.5}$						

*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.* (2003b); (4) Sahama and Hytönen (1957); (5) Christiansen *et al.* (2003a); (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).

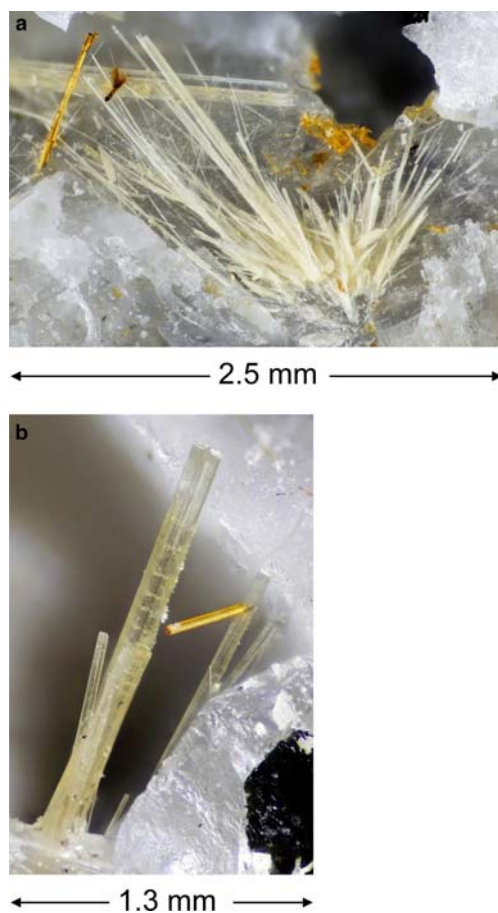


FIG. 1. Fogoite-(Y): (a) a radiating aggregate of fogoite-(Y) crystals (pale yellow) and astrophyllite crystals (orangy yellow) on sanidine; (b) an isolated crystal of astrophyllite intergrown with a fogoite-(Y) crystal, a fragment of an amphibole-super group mineral (black, possibly ferro-katophorite)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

lustre. Very thin crystals are colourless. Crystals are often parallel or grouped in radiating aggregates (Fig. 1a). They can also be isolated (Fig. 1b). Fogoite-(Y) has a white streak, splintery fracture and does not fluoresce under cathode or ultraviolet light. Cleavage is {100} very good, no parting was observed, Mohs hardness is ~5, and it is brittle, $D_{\text{calc.}} = 3.523 \text{ g/cm}^3$ (using the empirical formula and the single-crystal unit cell). Macroscopically, individual crystals do not show twinning. However, diffraction data show the presence of twinning by reticular merohedry (see later). Fogoite-(Y) is biaxial (+) with refractive indices ($\lambda = 590 \text{ nm}$) $\alpha = 1.686(2)$, $\beta = 1.690(2)$, $\gamma = 1.702(5)$.

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

The optic axial angle is $57(1)^\circ$ and $2V_{\text{calc.}} = 60^\circ$. It is nonpleochroic. The optical orientation is given in Table 2. The compatibility index $(1 - Kp/Kc) = 0.006$ (for $D_{\text{calc.}} = 3.523 \text{ g/cm}^3$) is rated as superior.

Fourier transform infrared (FTIR) spectroscopy

The IR spectrum of fogoite-(Y) was collected on a crystal fragment using a Bruker Hyperion 2000 IR microscope equipped with a liquid nitrogen cooled MCT detector (Fig. 2). Data over the range $4000\text{--}650 \text{ cm}^{-1}$ were obtained by averaging 100 scans with a resolution of 4 cm^{-1} . No bands were observed in the OH-stretching region ($3000\text{--}4000 \text{ cm}^{-1}$), in accord with the absence of OH and H_2O groups in the structure (Fig. 2). In the low-frequency region, peaks at 1088 , 1000 , 803 cm^{-1} are assigned to Si–O stretching vibrations of the Si_2O_7 groups, and a peak at 677 cm^{-1} is due to stretching vibrations of the Si–O–Si bridges of Si_2O_7 groups.

Chemical analysis

A single crystal of fogoite-(Y) was analysed with a Cameca SX-100 electron-microprobe operating in wavelength-dispersion mode with an accelerating voltage of 15 kV , a specimen current of 20 nA , a beam size of $5 \mu\text{m}$ and count times on peak and background of 20 and 10 s , respectively. The following standards were used: Si, Ca: diopside; F: fluorite; Na: albite; Nb: $\text{Ba}_2\text{NaNb}_5\text{O}_{15}$; Fe: fayalite; Mn: spessartine; Zr: zircon; Ti: titanite; Ta: $\text{Mn}(\text{Ta}_{1.7}\text{Nb}_{0.3})\text{O}_6$; Ce: CePO_4 ; La: LaPO_4 ; Nd: NdPO_4 ; Lu: LuPO_4 ; Sm: SmPO_4 ; Gd: GdPO_4 ; Dy: DyPO_4 ; Er: ErPO_4 ; Yb: YbPO_4 ; Y: $\text{Y}_3\text{Al}_5\text{O}_{12}$. Aluminium, Mg, Ba, Th, Pr and Ho were sought but not detected. Data were reduced using the $\varphi(\rho Z)$ procedure of Pouchou and Pichoir (1985). The chemical composition of fogoite-(Y) is the mean of ten determinations and is given in Table 3. The empirical formula of fogoite-(Y) calculated on the basis of 18 (O + F) is $(\text{Na}_{2.74}\text{Mn}_{0.15})_{\Sigma 2.89}\text{Ca}_2$

$[Y_{1.21}(La_{0.01}Ce_{0.03}Nd_{0.03}Sm_{0.02}Gd_{0.08}Dy_{0.08}Er_{0.05}Yb_{0.04}Lu_{0.01})_{\Sigma 0.35}Mn_{0.16}Zr_{0.11}Na_{0.09}Fe_{0.07}^{2+}Ca_{0.01}]_{\Sigma 2}(Ti_{0.76}Nb_{0.23}Ta_{0.01})_{\Sigma 1}(Si_{4.03}O_{14})O_{1.12}F_{2.88}, Z = 1$. The simplified formula is $Na_3Ca_2Y_2Ti(Si_2O_7)_2OF_3$.

X-ray data collection and structure refinement

X-ray data for fogoite-(Y) were collected from a twinned crystal with a single-crystal Bruker D8 three-circle diffractometer equipped with a rotating-anode generator (MoK α radiation), multilayer optics and an APEX-II detector. Powder X-ray diffraction data were obtained by collapsing experimental data from the single-crystal into two dimensions and are presented in Table 4. Details of data collection and structure refinement are given in Table 5. The intensities 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° and a frame time of 10 s, and an empirical absorption correction (*TWINABS*, Sheldrick, 2008) was applied. All tested crystals were twinned by reticular merohedry. The twin operation is a 180° rotation around [001] and twin index is 2 (see Fig. 3). The same twinning has reported by Bellezza *et al.* (2004b) in related minerals like götzenite. *CELL_NOW* (Sheldrick, 2004) was used to obtain an HKLF5 file, and with the Bruker *SHELXTL Version 5.1* refinement of the crystal structure was carried out in space group $P\bar{1}$ using the atom coordinates of götzenite

(Christiansen *et al.*, 2003b). The crystal structure of fogoite-(Y) was refined to $R_1 = 2.81\%$, the twin ratio being 0.534(4):0.466(4) (Table 5). The occupancies of five cation sites were refined with the following 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 observed disorder of Ti at the $M^O(1)$ site, with Ti–Ti = 0.366 Å. The refinement of the site-occupancy for the $M^O(2)$ site converged to 1.0 and was fixed. Scattering curves for neutral atoms were taken from the *International Tables for Crystallography* (Wilson, 1992). Final atom coordinates and equivalent displacement parameters are given in Table 6, selected interatomic distances and angles in Table 7, refined site-scattering values and assigned site-populations in Table 8, and bond-valence values for selected anions in Table 9. A list of observed and calculated structure factors, Crystallographic Information File (CIF) and anisotropic displacement parameters have been deposited with the Principal Editor of *Mineralogical Magazine* and are available from http://www.minersoc.org/pages/e_journals/dep_mat.html

Site-population assignment

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

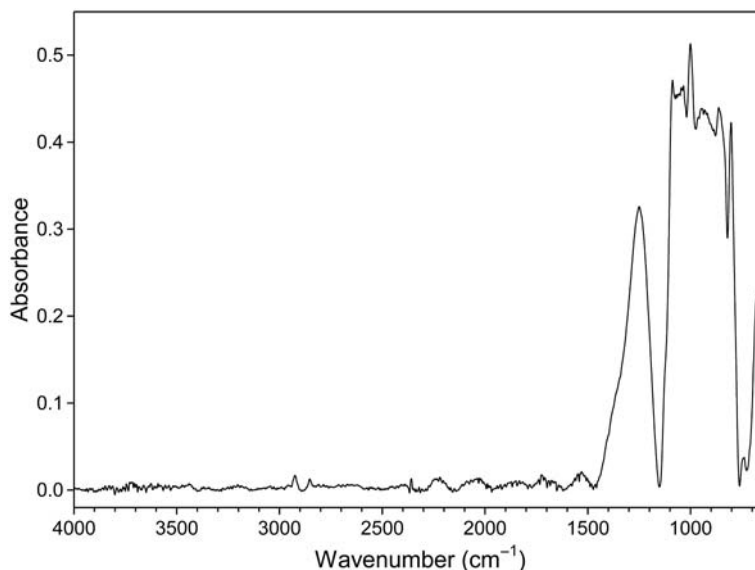


FIG. 2. The FTIR spectrum of fogoite-(Y).

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

Chemical composition				Unit formula* (apfu)	
	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	0.01
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	0.15
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	0.01
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	2.88
				Σanions	18.00

Esd – estimated standard deviation.

*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}

Consider first the two [6]-coordinated M^H and A^P sites in the H sheet. The <M^H–φ> distance of 2.271 Å is shorter than the <A^P–φ> distance of 2.416 Å (where φ = O, F) (Table 7) and the refined site-scattering at the M^H site, 81.2(2) electrons per formula unit (epfu), is higher than that at the A^P site, 41.8(2) epfu, and hence we assign all Y, REE³⁺, Zr and Fe²⁺ plus some Mn, Na and minor Ca to the M^H site, with an assigned site-scattering of 75.98 epfu, and the lighter Ca to the A^P site, with an assigned site-scattering of 40.00 epfu (Table 8).

In the O sheet, the bond lengths around the M^O(1) site in the O sheet vary from 1.809 to 2.174 Å (Table 7) and we assign all Ti, Nb and Ta to the M^O(1) site, with a calculated scattering of 26.88 epfu and a refined scattering of 26.0(2) epfu (Table 8). Consider next the [8]-coordinated

M^O(2) and [6]-coordinated M^O(3) sites in the O sheet. The refined site-scattering of 25.5 epfu at the M^O(3) site is higher than that at the M^O(2) site: 11.0 epfu; and the <M^O(3)–φ> distance of 2.378 Å is shorter than the <M^O(2)–φ> distance of 2.490 Å. Hence we assign 1.78 Na + 0.15 Mn to the M^O(3) site, with a calculated site-scattering of 23.33 epfu and all remaining 0.96 Na atoms per formula unit (apfu) to the M^O(2) site, with a calculated site-scattering of 10.56 epfu (Table 8).

Description of the structure

Cation and anion sites

Here we consider seven cation sites, three M^O sites of the O sheet and M^H, A^P and two Si sites of the H

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TABLE 4. Powder X-ray (2 dimensional) diffraction data for fogoite-(Y).

$I_{\text{obs.}}$	$d_{\text{obs.}}$ (Å)	h	k	l	$I_{\text{obs.}}$	$d_{\text{obs.}}$ (Å)	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			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			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			3	3	0
100	2.954	$\bar{1}$	$\bar{1}$	2	2	1.722	3	0	3
		$\bar{3}$	1	0			2	2	3
8	2.827	$\bar{1}$	2	0			2	1	4
11	2.786	2	1	1	3	1.701	2	$\bar{2}$	3
		0	2	0			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
		3	0	2			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			3	1	4
6	2.303	4	1	1	8	1.637	4	$\bar{2}$	1
		$\bar{3}$	2	0			4	2	3
		$\bar{2}$	0	3			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	5	1	3
2	2.109	1	$\bar{1}$	3			2	3	0
		4	1	2			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	4	0	4
		4	2	1			6	0	1
		4	2	0			6	1	0
23	1.893	$\bar{1}$	3	0	3	1.549	2	$\bar{1}$	4
		3	1	2					

sheet; and two anion sites: X_M^O = anion sites at the common vertices of $3M^O$ and M^H polyhedra; X_A^O = anion sites at the common vertices of $3M^O$ polyhedra that occur approximately under the A^P sites; labelling follows Sokolova (2006).

In the O sheet, the $M^O(1)$ site is occupied primarily by Ti with subordinate Nb and minor Ta (Table 8),

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 × 0.02 × 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	15,848
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 (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 $[\bar{1} 0 \frac{1}{2}, 0\bar{1} 0, 0 0 1]$.

and it is coordinated by four O atoms and two (O,F) anions at the X_M^O site (Fig. 4a), with $\langle M^O(1)-\varphi \rangle = 1.980$ Å (Table 7). Titanium is positionally disordered at the $M^O(1)$ site, with Ti–Ti = 0.366 Å (Fig. 4b). Similar positional disorder of Ti and Nb and Ti and Fe³⁺ has been reported for the Ti-silicate minerals vebenite, $K_2\text{Na}(\text{Fe}_5^{2+}\text{Fe}_4^{3+}\text{Mn}_7^{2+})\text{Nb}_3\text{Ti}(\text{Si}_2\text{O}_7)_2(\text{Si}_8\text{O}_{22})_2\text{O}_6(\text{OH})_{10}(\text{H}_2\text{O})_3$ (Cámara *et al.*, 2013) and narsarsukite, $\text{Na}_2(\text{Ti,Fe})\text{Si}_4(\text{O,F})_{11}$ (Mesto *et al.*, 2015). In fogoite-(Y), the four $M^O(1)$ –O bonds are approximately of the same length: 1.970–1.980 Å (Table 7). The longest and shortest bonds are from the $M^O(1)$ cation to the X_M^O anions, $M^O(1)$ – $X_M^O = 2.174$ Å and 1.809 Å, respectively (Table 7, Fig. 4b). The bond-valence sum at the X_M^O anion at a distance of 1.809 Å from the $M^O(1)$ cation is 1.90 vu (valence units) (Table 9) and 1.65 vu where it is calculated with the bond-valence parameters for cation–oxygen and

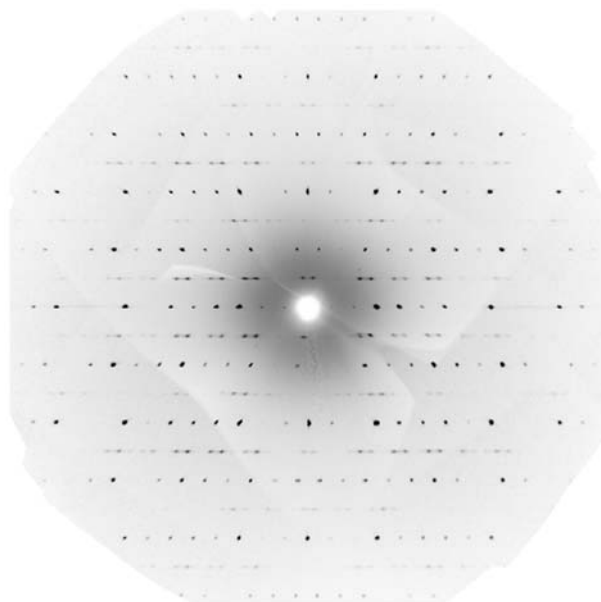


FIG. 3. Simulated precession slice of $h0l$ zone: $+h$ to right, $+l$ down. Imaged created with *APEX 2* software by Bruker (Bruker AXS Inc., Madison, Wisconsin, USA). Overlapping of reciprocal lattice nodes occurs on h even levels. Thus one node out of two is restored by the twin operation (twin index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

cation–fluorine bonds, respectively. The bond-valence sum of 1.90 vu is in accord with the 2^- charge of an O atom and the bond-valence sum of 1.65 vu is too high to compensate for the 1^- charge of

an F atom. Thus $X_M^O = O$ where $M^O(1) - X_M^O = 1.809 \text{ \AA}$. The bond-valence sum at the X_M^O anion at a distance of 2.174 \AA from the $M^O(1)$ cation is 0.69 vu (Table 9) and 1.29 vu where it is calculated with the

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	$\frac{1}{2}$	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_M^O	0.8787(2)	0.2498(4)	0.9673(6)	0.0163(4)
X_A^O	0.8806(2)	0.2988(4)	0.4721(7)	0.0221(4)

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

M ^H –O(5)a	2.198(4)	A ^P –X _A ^O	2.242(2)	M ^O (1)–X _M ^O e	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 _M ^O	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 _M ^O c	2.174(3)
<M ^H (1)–φ>	2.271	<A ^P –φ>	2.416	<M ^O (1)–φ>	1.980
M ^O (2)–X _A ^O j	2.215(2) x2	M ^O (3)–X _A ^O	2.326(5)	Short distance	
M ^O (2)–O(1)c	2.493(3) x2	M ^O (3)–X _A ^O k	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 _M ^O l	2.431(4)		
		M ^O (3)–X _M ^O k	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 (epfu)	Assigned site-population (apfu)	Calculated site-scattering (epfu)	<ct–φ> _{obs.} (Å)	Ideal composition (apfu)
Cations					
M ^H **	[M1]	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]	2.00 Ca	40.00	2.416	Ca ₂
M ^O (1)	[M5]	0.76 Ti + 0.23 Nb + 0.01 Ta	26.88	1.980	Ti
^[8] M ^O (2)	[M4]	0.96 Na + 0.04 □	10.56	2.490	Na
M ^O (3)	[M2]	1.78 Na + 0.15 Mn + 0.07 □	23.33	2.378	Na ₂
Anions					
X _M ^O	[X8]	1.12 O + 0.88 F			(OF)
X _A ^O	[F9]	2 F			F ₂

φ = O, F; ct = cation

*Coordination numbers are shown for non-[6]-coordinated cation sites; [] site labelling in accord with Christiansen *et al.* (2003b)

**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).

bond-valence parameters for cation–fluorine and cation–oxygen bonds, respectively. The bond-valence sum of 0.69 vu is in accord with the 1^- charge of an F atom and the bond-valence sum of 1.29 vu is too low to compensate for the 2^- charge of an O atom. Hence $X_M^O = F$ 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 disorder at the X_M^O site: the bond-valence sums at the X_M^O anions require a shorter Ti–O bond and a longer Ti–F bond (Table 7, Fig. 4b). The ideal composition of the $M^O(1)$ site is Ti apfu.

The Na-dominant $^{[8]}M^O(2)$ and $^{[6]}M^O(3)$ sites are coordinated by six O atoms plus two F 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 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 composition of the $M^O(2,3)$ sites is Na_3 apfu (Table 8).

In the H sheet, there are two tetrahedrally coordinated Si(1,2) sites occupied by Si and two [6]-coordinated sites, the Y-dominant M^H site and the A^P site occupied by Ca (Table 8). The 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 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. 4c). The ideal composition of the $A^P + M^H$ sites is Ca_2Y_2 apfu.

We write the cation part of the TS block, $A_2^P M_2^H M_4^O$, as the sum of cations of the O and H sheets: $Ca_2Y_2Na_3Ti$ apfu, with a total charge of 17^+ .

We assign O atoms to the O(1–7) sites that coordinate the Si(1) and Si(2) sites, giving $(Si_2O_7)_2$ pfu. Anions at the X_M^O and X_A^O sites

receive bond valences from four cations: X_M^O from $M^O(1)$, $2M^O(3)$ and M^H , and X_A^O from $M^O(2)$, $2M^O(3)$ and A^P , respectively (Tables 7, 9). We 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 the X_A^O atom, a lower bond-valence as it is bonded to Na at the $M^O(2)$ site. Above we showed 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, with an incident bond-valence sum of 0.68 vu (Table 9). Occurrence of O and F at the X_M^O site and F at the X_A^O site is common for Group I TS-block minerals (Table 1).

The anions sum as follows: $(Si_2O_7)_2 [O(1-7)] + [(OF)F_2] [(X_M^O)_2 \text{ and } (X_A^O)_2] = (Si_2O_7)_2(OF)F_2$ pfu, with a total charge of 17^- . We write ideal formula of fogoite-(Y) as the sum of cation and anion components: $Ca_2Y_2Na_3Ti + (Si_2O_7)_2(OF)F_2 = Ca_2Y_2Na_3Ti(Si_2O_7)_2(OF)F_2$, $Z = 1$, with a simplified formula $Na_3Ca_2Y_2Ti(Si_2O_7)_2OF_3$.

Structure topology of fogoite-(Y)

For the structure description, we use the terminology of Sokolova (2006). The main structural unit in the fogoite-(Y) structure is a TS block that consist of HOH sheets. The O sheet is composed of Ti-dominant $M^O(1)$ octahedra and Na-dominant $^{[8]}M^O(2)$ and $^{[6]}M^O(3)$ polyhedra (Fig. 4a). The H sheet is built of Si_2O_7 groups and [6]-coordinated M^H and A^P polyhedra occupied by Y and Ca, respectively (Fig. 4c). In fogoite-(Y), the topology of the TS block is as in Group I of the TS-block minerals where $Ti (+ Nb + Zr) = 1$ apfu per $(Si_2O_7)_2$: two H sheets connect to the O sheet such that two Si_2O_7 groups link to the *trans* edges of a Na [$M^O(2)$] polyhedron of the O sheet (Fig. 4d). The ideal compositions of the O and two H sheets are $Na_3Ti(OF)F_2$ and $Y_2Ca_2(Si_2O_7)_2$ apfu. In the crystal structure of fogoite-(Y), TS blocks parallel to (100) share corners and edges of the H-sheet polyhedra to form a framework (Fig. 4e).

Related minerals

Fogoite-(Y), $Na_3Ca_2Y_2Ti(Si_2O_7)_2OF_3$, is a new Group I TS-block mineral. It is isostructural with hainite, $Na_2Ca_4(Y,REE)Ti(Si_2O_7)_2OF_3$ (Blumrich, 1893; Christiansen *et al.*, 2003b) and götzenite, $NaCa_6Ti(Si_2O_7)_2OF_3$ (Sahama and Hytönen, 1957; Christiansen *et al.*, 2003b) [Table 1, mineral formulae are from Sokolova (2006)]. Fogoite-(Y) is an Y-dominant, Na-rich and Ca-poor analogue of

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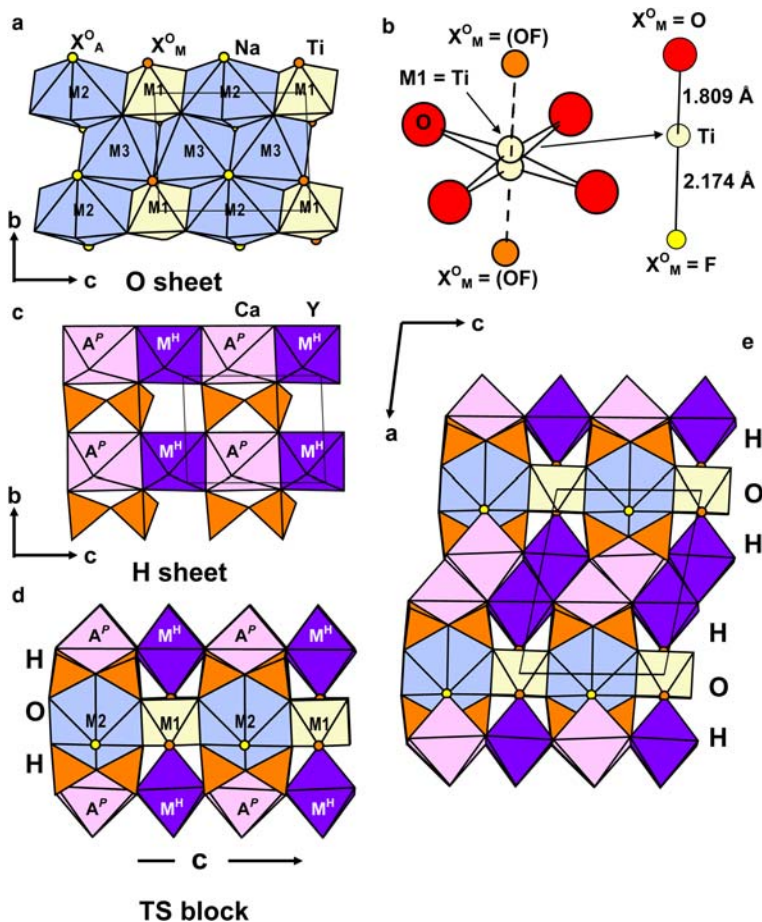


FIG. 4. The TS block in the crystal structure of fogoite-(Y): (a) the O sheet; (b) stereochemistry of Ti at the $M^O(1)$ site in the O sheet; (c) the H sheet; (d) the TS block; and (e) the general view of the crystal structure; Si tetrahedra are orange, Ti-dominant $M^O(1)$ octahedra are yellow, Na-dominant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

The letters H O H indicate the positions of H and O sheets in (d,e).

hainite and götzenite. Fogoite-(Y) and hainite are related by the substitution $^{[H]}Y_{\text{fog}}^{3+} + ^{[O]}Na_{\text{fog}}^+ \leftrightarrow ^{[H]}Ca_{\text{hai}}^{2+} + ^{[O]}Ca_{\text{hai}}^{2+}$, where [H] and [O] stand for H and O sheets in the TS block. Fogoite-(Y) and götzenite are related by the substitution $2^{[H]}Y_{\text{fog}}^{3+} + 2^{[O]}Na_{\text{fog}}^+ \leftrightarrow 2^{[H]}Ca_{\text{göt}}^{2+} + 2^{[O]}Ca_{\text{göt}}^{2+}$.

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