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From structure topology to chemical composition. VIII. Titanium silicates: the crystal chemistry of mosandrite from type locality of Låven (Skådön), Langesundsfjorden, Larvik, Vestfold, Norway

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ABSTRACT

The crystal structure of mosandrite, ideally $Na_2Ca_4REETi(Si_2O_7)_2OF_3$, a = 7.4184(8), b = 5.6789(6), c = 18.873(2) Å, ß = 101.410(2)º, V = 779.35(5) Å^3, space group $P2_1/c$, Z = 2, D_{calc} = 3.363 g.cm^{-3}, from the type locality, Låven (Skådön), Langesundsfjorden, Larvik, Vestfold, Norway, has been refined to R_1 = 6.33% on the basis of 1113 unique reflections $|F_o \geqslant 4\sigma F|$. Electron microprobe analysis gave the empirical formula $Na_{1.99}(Ca_{3.93}Sr_{0.02})_{\Sigma 3.95}(Ce_{0.41}La_{0.16}Nd_{0.13}Pr_{0.04}Sm_{0.02}Dy_{0.01}Y_{0.13})_{\Sigma 0.90}(Ti^{4+}_{0.86}Nb_{0.08}Zr_{0.05})_{\Sigma 0.99}(Si_2O_7)_2(F_{1.20}O_{0.80})_{\Sigma 2.00}F_2$, Z = 2, calculated on the basis of 18 (O + F) a.p.f.u.. The crystal structure of mosandrite is a framework of TS (titanium silicate) blocks. The TS block consists of HOH sheets (H-heteropolyhedral, O-octahedral). The TS block in mosandrite exhibits linkage and stereochemistry typical for Group I (Ti = 1 a.p.f.u.) Ti-disilicate minerals: two H sheets connect to the O sheet such that two (Si_2O_7) groups link to the *trans* edges of a Na polyhedron of the O sheet. The O sheet cations give Na(NaCa)Ti (4 a.p.f.u.). The TS blocks link *via* common vertices of (Si_2O_7) groups and common vertices and edges of Ca-dominant M^H and A^P polyhedra. Two adjacent TS blocks are related by the glide plane c_y. Composition and topology of the TS block in mosandrite and rinkite are identical. The crystal structure of mosandrite from the type locality is topologically and chemically identical to that of rinkite from the type locality of Kangerdluarssuk, Greenland.

Keywords: mosandrite, rinkite, crystal structure, EMP analysis, chemical formula, Ti disilicate minerals, Group I, type locality.

Introduction

The name mosandrite, ideally $Na_2Ca_4REETi(Si_2O_7)_2OF_3$, was proposed by Erdman in 1841 (reported by Brögger 1890) for a mineral from Låven (Skådön), Langesundsfjorden, Larvik, Vestfold, Norway. The name rinkite, ideally $Na_2Ca_4REETi(Si_2O_7)_2OF_3$, was proposed by Lorenzen (1884) for a mineral found at Kangerdluarssuk, Greenland. The ideal formulae for mosandrite and rinkite given above are in accord with Sokolova (2006). Taking into account the temporal precedence of mosandrite (1841) over rinkite (1884), Fleischer (1958) and Sahama (1960) recommended discreditation of the name rinkite. However, it is still listed as questionable/doubtful in the official IMA list of minerals and all structural crystallography (1963–1991) has been done on samples designated rinkite (see section 'Previous work' below). The crystal structure of mosandrite from the type locality in Norway has never been studied. Petersen *et al.* (1989) described nacareniobsite-(Ce), ideally $Na_3Ca_3REENb(Si_2O_7)_2OF_3$, from the Ilímaussaq alkaline complex in south Greenland and related

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nacareniobsite-(Ce) to rinkite through the substitution $Nb^{5+} + Na^{+} \rightleftharpoons Ti^{4+} + Ca^{2+}$. The crystal structure of nacareniobsite-(Ce) has not yet been reported.

Sokolova (2006) established the relationship between structure topology and chemical composition for 24 Ti disilicate minerals and divided them into four groups, characterized by different topology and stereochemistry of the titanium silicate (TS) block. Each group of structures has a different linkage of H (heteropolyhedral) and O (octahedral) sheets in the TS block and a different arrangement of Ti (= Ti+Nb) polyhedra. In Groups I, II, III and IV, Ti equals 1, 2, 3 and 4 a.p.f.u., respectively. Note that the amount of Ti is very important for the hierarchy of structures of Ti disilicates and each group is defined by its topology, chemical composition and stereochemistry; none of these factors can be ignored. Sokolova (2006) listed seven minerals with known structures in Group I: götzenite, hainite, seidozerite, grenmarite, rinkite, kochite and rosenbuschite (Table 1), and wrote the general formula for minerals of Group I as $A_2^P M_2^H M_4^O (Si_2O_7)_2 X_4^O$ (see Table 1). In Group I, Ti = 1 a.p.f.u. and Ti (or Zr+Ti in grenmarite) occurs in the O sheet: $1M^O$ = Ti, $3M^O$ = Na, Ca and rarely Mn^{2+}; $^{[6],[7]}M^H = Zr^{4+}$,Ca + *REE*,Ca,Mn^{2+}; A^P = Na, Ca, Ca + *REE*. Sokolova (2006) considered the topology of rinkite based on the latest structure work of Rastvetaeva *et al*. (1991). However, mosandrite from the type locality has not been characterized from a structural perspective, and this prompted the present work. Following Sokolova (2006), further work on the Ti disilicate minerals includes revision of the crystal structure and chemical formula of delindeite (Sokolova and Cámara, 2007), determination of the crystal structure of bornemanite (Cámara and Sokolova, 2007), revision of the chemical formula and crystal chemistry of barytolamprophyllite (Sokolova and Cámara, 2008), structure work on nacareniobsite-(Ce) (Sokolova and Hawthorne, 2008*a*), an orthorhombic polytype of nabalamprophyllite (Sokolova and Hawthorne, 2008*b*), jinshajiangite (Sokolova *et al*., 2008), and the present work on mosandrite from the type locality, Låven, Norway.

Previous work

The crystal structure of rinkite has been described in both triclinic and monoclinic symmetries. The first structure determination of the type rinkite from Kangerdluarssuk, Greenland, was done in triclinic symmetry, *a* 18.9, *b* 7.47, *c* 5.68 Å, $\alpha \approx \gamma \approx 90$, $\beta = 101.3^{o}$, space grroup $P\bar{1}$, by Kheirov *et al*. (1963) who reported a reasonable basic structure and discussed its similarity to seidozerite (for ideal formula and references of the Group-I structures, see Table 1). Tê-yü *et al.* (1965) described the structure of type rinkite from Kangerdluarssuk, Greenland, as monoclinic based on the cell parameters of Kheirov *et al*. (1963) but with $\beta = 90^{o}$, space group $P2_1$, and emphasized the similarity of the topology of the rinkite structure to the structures of seidozerite and rosenbushite (Table 1). Simonov and Belov (1968) used the atom coordinates of Tê-yü *et al.* (1965) to refine the crystal structure of rinkite with the monoclinic unit-cell parameters a = 18.60, b = 7.421, c = 5.636 Å, $\gamma = 101.3^{o}$, V = 762.9 $Å^3$, space group $P2_1$. They gave the formula of rinkite as $Na_2Ca(Ca,Ce)_4(Ti,Nb)(Si_2O_7)_2(O,F)_2F_2$, discussed the crystal chemistry of rinkite, compared it to seidozerite and defined a *seidozerite-rinkite group* (compare Group I of Sokolova (2006), Table 1). The latest structure refinements were done by Galli and Alberti (1971) for rinkite from Kangerdluarssuk, Greenland: a = 7.437, b = 5.664, c = 18.843 Å, ß = 101.38º, V = 778.11 $Å^3$, space group $P2_1/c$, Z = 2, $D_{calc.}$ = 3.45 g cm^{-3}, with an approximate formula $(Ti,Nb,Al,Zr)(Na,Ca)_3(Ca,Ce)_4(Si_2O_7)_2(O,F)_4$, and by Rastsvetaeva *et al.* (1991) for rinkite from Khibina massif, Kola Peninsula, Russia: a = 5.679, b = 7.412, c = 18.835 Å, $\alpha = 101.26^{o}$, V = 777.6 $Å^3$, space group $P2_1$, Z = 2, $D_{calc.}$ = 3.36 g cm^{-3}, with the structural formula: $\{TiF(O,F)[Si_2O_7]_2\}\{Na(Na,Ca)_2F(O,F)\}\{(Ca,TR)_4\}$ (Table 1). Note that these two formulae are more complicated than the formula of Simonov and Belov (1968).

Galli and Alberti (1971) stated that their results were in good agreement with the structure of Simonov and Belov (1968). Rastsvetaeva *et al.* (1991) stated that the lower symmetry of rinkite from Khibina is due to the order of *REE*s and Ca and concluded that their model is in good agreement with all previous work. Christiansen *et al*. (1999) and Christiansen and Rønsbo (2000) analysed the structural relation between götzenite and rinkite and stated that the models of Rastsvetaeva *et al.* (1991) and Galli and Alberti (1971) are the same except for the lower symmetry of the first "due to minor ordering of some cations".

TABLE 1. Structural formulae* and unit-cell parameters for Group-I minerals with the TS block.

Mineral	Structural formula			a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)	Space group	Z	Ref.
	$A_2^P M_2^H$	M_4^O	$(Si_2O_7)_2X_4^O$									
Mosandrite	(Ca_3*REE*)	Na(NaCa)Ti	$(Si_2O_7)_2OF_3$	7.4184	5.6789	18.873		101.410		$P2_1/c$	2	(1)
Rinkite	(Ca_3*REE*)	Na(NaCa)Ti	$(Si_2O_7)_2OF_3$	7.437	5.664	18.843		101.38		$P2_1/c$	2	(2)
Rinkite	(Ca_3*REE*)	Na(NaCa)Ti	$(Si_2O_7)_2OF_3$	5.679	7.412	18.835	101.26			$P2_1$	2	(3)
Götzenite	Ca_2Ca_2	$NaCa_2Ti$	$(Si_2O_7)_2OF_3$	9.6192	5.7249	7.3307	89.981	101.132	100.639	$P\bar{1}$	1	(4)
Hainite	Ca_3(Y,*REE*)	Na(NaCa)Ti	$(Si_2O_7)_2OF_3$	9.6079	5.7135	7.3198	89.916	101.077	100.828	$P\bar{1}$	1	(5)
Seidozerite	Na_2Zr_2	Na_2 MnTi	$(Si_2O_7)_2O_2F_2$	5.5558	7.0752	18.406		102.713		$P2/c$	1	(6)
Grenmarite	Na_2 Zr_2	Na_2MnZr	$(Si_2O_7)_2O_2F_2$	5.608	7.139	18.575		102.60		$P2/c$	1	(7)
Kochite	Ca_2MnZr	Na_3Ti	$(Si_2O_7)_2OF_3$	10.032	11.333	7.202	90.192	100.334	111.551	$P\bar{1}$	1	(8)
Rosenbuschite	$Ca_4Ca_2Zr_2$	Na_2Na_4TiZr	$(Si_2O_7)_4O_2F_6$	10.137	11.398	7.2717	90.216	100.308	111.868	$P\bar{1}$	1	(9)

* The structural formulae are written in the form $A_2^P M_2^H M_4^O (Si_2O_7)_2 X_4^O$ in accordance with Sokolova (2006);
References (the latest reference on the structure is the first entry in the numbered list of references): (1) this work; (2) Galli and Alberti (1971); (3) Rastsvetaeva *et al.* (1991), Simonov and Belov (1968), Tê-yü *et al.* (1965), Kheirov *et al.* (1963); (4) Christiansen *et al.* (2003*a*), Cannillo *et al.* (1972); (5) Christiansen *et al.* (2003*a*), Rastsvetaeva *et al.* (1995); (6) Christiansen *et al.* (2003*a*), Simonov and Belov (1960), Skszat and Simonov (1966), Puscharovskii *et al.* (2002); (7) Bellezza *et al.* (2004); (8) Christiansen *et al.* (2003*b*); (9) Christiansen *et al.* (2003*a*), Shibaeva *et al.* (1964).

Experimental

The sample of mosandrite used in this work is from Låven (Skådön), Langesundsfjorden, Larvik, Vestfold, Norway, and was on loan from the American Museum of Natural History, New York, USA.

Electron microprobe analysis

A single crystal of mosandrite previously used for the structure solution was analysed using a Cameca SX100 electron microprobe operating in wavelength-dispersion mode with an accelerating voltage of 15 kV, a beam current of 20 nA, a beam size of 20 μm and count times on peak and background of 20 and 10 s, respectively. The following standards were used for *K* or *L* X-ray lines: F: topaz; Na: jadeite; Si, Ca: diopside; Nb: $Ba_2NaNb_5O_{15}$; Ce: $CePO_4$; La: $LaPO_4$; Nd: $NdPO_4$; Pr: $PrPO_4$; Sm: $SmPO_4$; Gd: $GdPO_4$; Ti: titanite; Sr: $SrTiO_3$; Y: YPO_4; Ta: $MnNb_2Ta_2O_9$. Data were reduced using the φ(ρZ) procedure of Pouchou and Pichoir (1985). The chemical composition of mosandrite is given in Table 2 and is the mean of 10 determinations. The empirical formula (Table 2) was calculated on the basis of 18 (O+F) anions: $Na_{1.99}(Ca_{3.93}Sr_{0.02})_{\Sigma 3.95}(Ce_{0.41}La_{0.16}Nd_{0.13}Pr_{0.04}Sm_{0.02}Dy_{0.01}Y_{0.13})_{\Sigma 0.90}(Ti^{4+}_{0.86}Nb_{0.08}Zr_{0.05})_{\Sigma 0.99}(Si_2O_7)_2(F_{1.20}O_{0.80})_{\Sigma 2.00}F_2$, $Z=2$, and the end-member composition is $Na_2Ca_4REETi(Si_2O_7)_2OF_3$. The end-member formula corresponds to that written for rinkite by Sokolova (2006).

Crystal structure

A single crystal of mosandrite was mounted on a Bruker AXS SMART APEX diffractometer with a CCD detector and Mo-*K*α radiation. The intensities of 11768 reflections with $-10 \leqslant h \leqslant 10$, $-8 \leqslant k \leqslant 8$, $-26 \leqslant l \leqslant 26$ were collected to 60.18º2θ with a frame width of 0.2º and a frame time of 5 s, and an empirical absorption correction (SADABS, Sheldrick, 1998) was applied. The unit-cell parameters were refined from 2419 reflections with $I > 10\ \sigma I$. Refinement of the crystal structure was done in monoclinic symmetry using atom coordinates of Galli and Alberti (1971). As there were hardly any observed reflections at high 2θ, refinement of the structure was done for $2\theta \leqslant 50$º. On the basis of 1113 unique observed reflections ($F_o > 4\sigma F$), the crystal structure of mosandrite was

TABLE 2. Chemical composition* (wt.%) and unit formula (a.p.f.u.) for mosandrite.

	Wt.%		a.p.f.u.
SiO_2	29.78	Si	4.03
ZrO_2	0.79	Σ	4.03
TiO_2	8.47		
Nb_2O_5	1.34	Zr	0.05
Ta_2O_5	0.07	Ti^{4+}	0.86
Ce_2O_3	8.36	Nb	0.08
La_2O_3	3.14	$\Sigma M^O(1)$	0.99
Nd_2O_3	2.58		
Pr_2O_3	0.85	Na	1.99
Sm_2O_3	0.40	Ca	0.85
Dy_2O_3	0.30	$\Sigma[M^O(2)+M^O(3)]$	2.84
Y_2O_3	1.79		
CaO	27.06	Ca	3.08
SrO	0.26	REE^{3+}, Y**	0.90
Na_2O	7.59	Sr	0.02
F	7.48	$\Sigma(M^H+A^P)$	4.00
O≡F	−3.15	F	3.20
Total	97.11		

* Al_2O_3 – not detected
** REE^{3+}, Y = 0.41 Ce + 0.16 La + 0.13 Nd +0.04 Pr + 0.02 Sm + 0.01 Dy + 0.13 Y

refined with the Bruker SHELXTL Version 5.1 system of programs (Sheldrick, 1997) to R_1 = 6.33% and a GoF of 1.19 in space group $P2_1/c$. We observed three violations of the *c*-glide extinction criterion ($I > 3\sigma I$). These violations are possibly due to epitactic intergrowth of mosandrite domains within one crystal where layers of mosandrite are oriented in a different orientation due to matching of the unit-cells in two different orientations (see text below). However, our attempt to refine the structure as two components was not successful probably due to an extremely small size of the second domain. The occupancies of five cation sites were refined with the following curves: M^H and A^P sites: Y; $M^O(1)$ site: Ti; M^O (2) and M^O (3) sites: Na and Ca, respectively. Scattering curves for neutral atoms were taken from the International Tables for X-ray Crystallography (1992). Details of the data collection and structure refinement are given in Table 3, final atom parameters are given in Table 4, selected interatomic distances and angles in Table 5, refined site-scattering values and assigned populations for selected sites in Table 6, and bond-valence values in Table 7. A list of observed and calculated structure factors has been deposited with the Principal Editor of *Mineralogical Magazine* and are available from www.minersoc.org/pages/e_journals/dep_mat.html

Description of the structure

Mosandrite belongs to the Group I titanium disilicate minerals with a TS block Sokolova (2006). We will describe mosandrite from the type locality and compare it to the structure of rinkite by Galli and Alberti (1971), space group $P2_1/c$.

Cation sites

The O sheet

In the O sheet, there are two octahedrally coordinated sites, $M^O(1)$ and $M^O(3)$, and one [8]-coordinated $M^O(2)$ site. The $M^O(1)$ site is coordinated by four O atoms and two (O,F) anions [= X^O_M in the terminology of Sokolova (2006)], with $\langle M^O(1)-\varphi \rangle$ = 1.994 Å (φ = unspecified anion, Table 5) and is primarily occupied by Ti

TABLE 3. Miscellaneous refinement data for mosandrite.

a (Å)	7.4184(8)
b	5.6789(6)
c	18.873(2)
β (º)	101.410(2)
V (Å^3)	779.35(5)
Space group	$P2_1/c$
Z	2
Absorption coefficient (mm^{-1})	5.14
F(000)	758.1
$D_{calc.}$ (g/cm^3)	3.363
Crystal size (mm)	0.33 × 0.21 × 0.18
Radiation/filter	Mo-*K*α/graphite
2θ-range for data collection (º)	50.00 (60.00)*
R(int) (%)	3.6
Reflections collected	7604 (11768)*
Independent reflections	1371
$F_o > 4\sigma F$	1113
Refinement method	Full-matrix least squares on F^2, fixed weights proportional to $1/\sigma F_o^2$
Goodness of fit on F^2	1.190
Final $R_{(obs)}$ (%) [$F_o > 4\sigma F$]	6.33
R indices (all data) (%)	R_1 = 7.55 wR_2 = 16.56 Go*F* = 1.190

* full resolution (see text)

TABLE 4. Final atom coordinates and displacement parameters (Å^2) for mosandrite.

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	U_{eq}
M^H	0.09361(12)	0.66173(17)	0.19146(5)	0.0129(6)	0.0191(6)	0.0311(7)	0.0025(4)	0.0058(4)	−0.0003(4)	0.0208(4)
A^P	0.59716(15)	0.6643(2)	0.19102(6)	0.0164(7)	0.0253(8)	0.0322(8)	0.0014(5)	0.0075(5)	0.0004(5)	0.0243(5)
$M^O(1)$	0	0	0	0.0115(10)	0.0403(15)	0.0306(13)	−0.0189(10)	0.0071(8)	−0.0035(9)	0.0271(8)
$M^O(2)$	½	0	0	0.0377(3)	0.037(3)	0.020(3)	−0.002(2)	0.000(2)	−0.002(3)	0.032(2)
$M^O(3)$	0.7542(3)	0.5013(5)	0.00097(15)	0.0293(16)	0.0266(17)	0.062(2)	0.0099(14)	0.0141(14)	0.0008(12)	0.0384(12)
Si(1)	0.3509(3)	0.1556(4)	0.13991(12)	0.0149(11)	0.0171(12)	0.0213(12	−0.0016(10)	0.0038(9)	0.0007(9)	0.0178(6)
Si(2)	0.7841(3)	0.1552(4)	0.13788(12)	0.0159(12)	0.0177(12)	0.0201(12	−0.0011(9)	0.0056(9)	−0.0006(9)	0.0176(6)
O(1)	0.2160(8)	0.1509(12)	0.0608(3)	0.027(3)	0.040(4)	0.032(4)	0.001(3)	−0.008(3)	−0.012(3)	0.0346(17)
O(2)	0.8333(9)	0.1417(12)	0.0582(3)	0.037(4)	0.041(4)	0.023(3)	−0.000(3)	0.018(3)	0.009(3)	0.0321(16)
O(3)	0.3387(8)	0.3990(12)	0.1837(4)	0.024(3)	0.025(4)	0.047(4)	−0.014(3)	0.012(3)	−0.001(3)	0.0312(16)
O(4)	0.8427(8)	0.3987(13)	0.1790(4)	0.021(3)	0.032(4)	0.061(5)	−0.025(3)	0.009(3)	−0.003(3)	0.0376(18)
O(5)	0.3341(8)	0.9316(12)	0.1910(3)	0.029(3)	0.024(4)	0.025(3)	0.005(3)	0.006(3)	−0.004(3)	0.0262(15)
O(6)	0.8557(8)	0.9342(12)	0.1902(3)	0.028(3)	0.024(4)	0.024(3)	0.007(3)	0.004(3)	0.006(3)	0.0257(15)
O(7)	0.5582(8)	0.1441(14)	0.1206(4)	0.017(3)	0.063(5)	0.049(4)	−0.014(4)	0.010(3)	−0.006(3)	0.0428(19)
X_M^O	0.0312(8)	0.7011(11)	0.0602(3)	0.031(4)	0.038(4)	0.031(4)	0.003(3)	0.006(3)	0.001(3)	0.033(2)
F	0.5280(10)	0.6573(10)	0.0612(3)	0.063(5)	0.033(4)	0.032(4)	−0.002(3)	0.005(3)	0.002(3)	0.043(2)

TABLE 5. Interatomic distances (Å) and angles (º) for mosandrite.

Si(1)−O(5)a	1.616(6)	Si(2)−O(4)	1.603(7)
Si(1)−O(3)	1.622(7)	Si(2)−O(2)	1.618(6)
Si(1)−O(1)	1.625(6)	Si(2)−O(6)a	1.621(6)
Si(1)−O(7)	1.650(6)	Si(2)−O(7)	1.641(6)
<Si(1)−O>	1.628	<Si(2)−O>	1.621
Si(1)−O(7)−Si(2) 155.9(5) [204.1(5)]*			
$^{[7]}M^{H}$−O(6)b	2.344(6)	$^{[7]}A^{P}$−F	2.403(6)
$^{[7]}M^{H}$−O(5)	2.353(6)	$^{[7]}A^{P}$−O(4)	2.410(6)
$^{[7]}M^{H}$−O(4)b	2.362(7)	$^{[7]}A^{P}$−O(3)	2.421(6)
$^{[7]}M^{H}$−O(3)	2.379(6)	$^{[7]}A^{P}$−O(6)	2.457(6)
$^{[7]}M^{H}$−X^{O}_{M}	2.438(6)	$^{[7]}A^{P}$−O(5)	2.472(6)
$^{[7]}M^{H}$−O(6)c	2.542(6)	$^{[7]}A^{P}$−O(5)c	2.553(6)
$^{[7]}M^{H}$−O(4)d	2.749(8)	$^{[7]}A^{P}$−O(3)d	2.674(7)
<M^{H}− φ**>	2.452	<A^{P}−φ>	2.484
$^{[6]}M^{O}$(1)−O(1)	1.973(6) ×2	$^{[6]}M^{O}$(3)−O(1)e	2.327(7)
$^{[6]}M^{O}$(1)−O(2)b	1.980(6) ×2	$^{[6]}M^{O}$(3)−O(2)	2.330(7)
$^{[6]}M^{O}$(1)−X^{O}_{M}a	2.030(6) ×2	$^{[6]}M^{O}$(3)−Fe	2.366(7)
<M^{O}(1)−φ>	1.994	$^{[6]}M^{O}$(3)−F	2.377(7)
		$^{[6]}M^{O}$(3)−X^{O}_{M}f	2.419(7)
$^{[8]}M^{O}$(2)−Fa	2.251(6) ×2	$^{[6]}M^{O}$(3)−X^{O}_{M}e	2.432(7)
$^{[8]}M^{O}$(2)−O(7)	2.377(7) ×2	<M^{O}(3)−φ>	2.375
$^{[8]}M^{O}$(2)−O(2)	2.626(7) ×2		
$^{[8]}M^{O}$(2)−O(1)	2.729(7) ×2		
<M^{O}(2)−φ>	2.496		

* a reflex angle toward the O sheet
** φ − unspecified anion
a: $x, y-1, z$; b: $x-1, y, z$; c: $-x+1, y-½, -z+½$; d: $-x+1, y+½, -z+½$; e: $-x+1, -y+1, -z$; f: $x+1, y, z$.

with minor Nb and Zr (Table 6), i.e. ideally Ti^{4+} as in rinkite (Galli and Alberti, 1971). The $M^{O}(3)$ site is coordinated by four O and two F atoms [= X^{O}_{A} in the terminology of Sokolova (2006)] and is 92% occupied by Na and Ca (Table 6), giving ideally (NaCa) a.p.f.u., and <$M^{O}(3)$−φ> = 2.375 Å (Table 5). The $M^{O}(2)$ site is coordinated by six O and two F atoms and is occupied by Na

TABLE 6. Refined site-scattering values (e.p.f.u.) and assigned site-populations (a.p.f.u.) for mosandrite.

Site	Site-scattering	Site population	Calculated site-scattering	<X−φ>$_{calc.}$ (Å)	<X−φ>$_{obs.}$ (Å)
$^{[6]}M^{O}(1)$	23.8(2)	0.87 Ti + 0.08 Nb + 0.05 Zr	24.4	1.99	1.994
$^{[8]}M^{O}(2)$	10.7(2)	1.00 Na	11.0	2.54	2.496
$^{[6]}M^{O}(3)$	30.2(2)	0.99 Na + 0.85 Ca + 0.16 □	27.9	2.36	2.375
$^{[7]}M^{H}$	66.7(5)	1.35 Ca + 0.65 REE^{3+} **	63.2	2.44	2.452
$^{[7]}A^{P}$	55.6(5)	1.63 Ca + 0.35 REE^{3+} + 0.02 Sr	52.09	2.43	2.484

* ionic radii from Shannon (1976); φ = unspecified anion
** REE^{3+} (total 0.90 a.p.f.u. with 0.41Ce + 0.16La + 0.13Nd + 0.04Pr + 0.02Sm + 0.01 Dy + 0.13 Y): mean scattering curve of 55.68 e^{-1} and ionic radius of $^{[7]}Ce^{3+}$.

TABLE 7. Bond-valence* (vu) table for mosandrite.

Atom	Si(1)	Si(2)	M^H	A^P	$M^O(1)$	$M^O(2)$	$M^O(3)$	Σ
O(1)	1.02		0.38	0.31 0.18				1.89
O(2)	1.03		0.41	0.28 0.23				1.95
O(3)		1.02	0.42 0.26	0.29				1.99
O(4)	1.00				$0.67^{x2}\downarrow$	$0.12^{x2}\downarrow$	0.26	2.05
O(5)		1.02			$0.66^{x2}\downarrow$	$0.14^{x2}\downarrow$	0.26	2.08
O(6)		1.07	0.40 0.16	0.32				1.95
O(7)	0.95	0.97				$0.21^{x2}\downarrow$		2.13
X^O_M			0.33		$0.58^{x2}\downarrow$		0.22 0.21	1.34
F				0.26		$0.19^{x2}\downarrow$	0.19 0.18	0.82
Total	4.00	4.08	2.36	1.87	3.82	1.32	1.32	
Aggregate charge	4.00	4.00	2.33	2.15	4.08	1.00	1.35	

* bond-valence parameters from Brown (1981)

with $<M^O(2)-\varphi>$ = 2.496 Å (Table 6). In mosandrite, the alkali sites of the O sheet, $M^O(2)$ and $M^O(3)$, sum to $Na_{1.99}Ca_{0.85}\square_{0.16}$, i.e. ideally Na_2Ca with a total charge of +4. Similarly, in rinkite (Galli and Albert, 1971), the corresponding sites sum to $(Na_{2.18}K_{0.06}Ca_{0.63}\square_{0.13})$, i.e. ideally Na_2Ca with a total charge of +4.

The H sheet

In the H sheet, there are two tetrahedrally coordinated sites occupied by Si with a <Si–O> distance of 1.625 Å. There are two [7]-coordinated sites, M^H and A^P, occupied by Ca and REE^{3+} approximately in the ratio 3:1 (Table 6). The scattering at the A^P site is slightly lower than at the M^H site, and consequently less REE^{3+} and all minor Sr was assigned to the A^P site. The M^H site is coordinated by six O atoms and an X^O_M anion, and the A^P site is coordinated by six O atoms and one F atom, with $<M^H-\varphi>$ and $<A^P-\varphi>$ = 2.452 and 2.484 Å, respectively. In rinkite, the M^H and A^P sites are also [7]-coordinated and are occupied by Ca and REE^{3+} approximately in the ratio 3:1 (Galli and Alberti, 1971).

Anion considerations

In the structure of mosandrite, there are nine anion sites. Analysis of incident bond-valence sums at these anions (Table 7) indicates that seven sites are occupied by O atoms [O(1)–O(7)], the *F* site (= X^O_A) is occupied by F (<1 v.u.), and the X^O_M site is statistically occupied by O and F with a bond-valence sum of 1.32 v.u. We can calculate the content of F at the X^O_M site as the difference between the total F content, 3.20 a.p.f.u. (chemical analysis, Table 2), and the F content at the X^O_A site, 2 a.p.f.u.: 1.20 a.p.f.u.. Therefore, the X^O_M site is occupied by $(O_{0.80}F_{1.20})$ a.p.f.u.. The two sites, X^O_M and X^O_A, sum to $(O_{0.80}F_{1.20}) + F_2$, ideally OF_3. In rinkite, the two corresponding anion sites are occupied by $(O_{0.25}F_{0.75})$(Galli and Alberti, 1971), also ideally OF_3.

Structure topology

The M^O polyhedra each share six common edges to form a close-packed octahedral O sheet, the central part of the TS block. Two outer parts of the block are H sheets of (Si_2O_7) groups and [7]-coordinated M^H and A^P polyhedra. Two H sheets are connected to the sheet of octahedra *via* common vertices of (SiO_4) tetrahedra and M^H and A^P polyhedra. Within the TS block in mosandrite, two (Si_2O_7) groups, one from each H sheet, link to the $M^O(2)$ polyhedron of the O sheet occupied by Na, and two H sheets are related approximately by a pseudo mirror-plane, m_z (Fig. 1*a*) as in rinkite (Galli and Alberti, 1971). We conclude

that the TS blocks in mosandrite and the rinkite structure of Galli and Alberti (1971) are stereochemically and topologically identical (see the sections 'Cation sites' and 'Anion considerations' above). In the structure of mosandrite, TS blocks are connected through common vertices of (Si_2O_7) groups and M^H and A^P polyhedra (Fig. 1*a*). The TS blocks repeat along the **c** direction. There are two unique TS blocks per unit cell in the crystal structure of mosandrite and they are related by the c_y glide plane as in the rinkite structure of Galli and Alberti (1971). Therefore

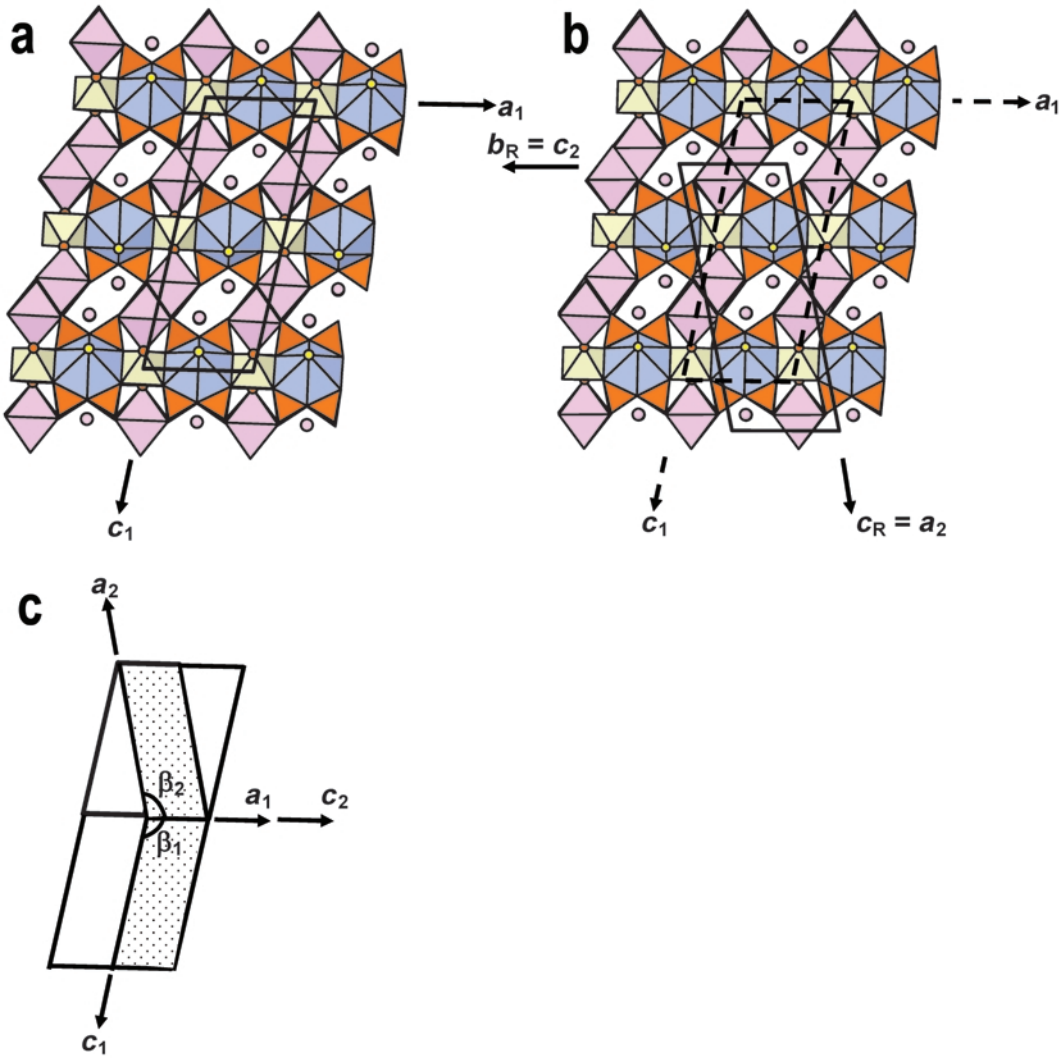

FIG. 1. General view of the crystal structure: (*a*) mosandrite, cell choice 1 (unit cell is shown by black solid lines) corresponding to space group $P2_1/c$ (#14) and the rinkite model of Galli and Alberti (1971); (*b*) mosandrite, cell choice 2 (unit cell is shown by black solid lines) corresponding to space group $P2_1/n$ (#14) which coincides with the unit cell chosen by Rastsvetaeva *et al*. (1991) with space group $P2_1$; (unit cell of the choice 1 is shown by black dashed lines). (*c*) Relation between unit cells of choice 1 (labelled a_1, c_1, β_1) and choice 2 (labelled a_2, c_2, β_2). Two axes of the unit cell of Rastsvetaeva *et al*. (1991) (*b*) are labelled b_R and c_R. [8]-coordinated Na-dominant polyhedra blue, Ti-dominant octahedra in yellow, Si tetrahedra in red, Ca-dominant M^H polyhedra in pink, Ca-dominant A^P sites are shown as pink spheres, F atoms and X^O_M anions are shown as small yellow and orange spheres.

the crystal structure of mosandrite from the type locality is topologically and chemically identical to that of rinkite from type locality of Kangerdluarssuk, Greenland. Table 1 shows the identity of the unit cells of mosandrite and rinkite with $\beta \approx 101.4^{o}$ and space group $P2_1/c$.

Rastsvetaeva *et al*. (1991) refined the structure of rinkite in space group $P2_1$, the same space group as used by Simonov and Belov (1968). Note that the rinkite structure of Rastsvetaeva *et al.* (1991) has $\alpha \approx 101.26^{o}$. Figure 1*b* shows that Rastvetaeva *et al.* (1991) determined the structure of rinkite in the setting that corresponds to the second choice of cell for space group No. 14, i.e. $P2_1/n$, whereas space group $P2_1/c$ (Galli and Alberti, 1971; this work) corresponds to the first choice of the cell. The two cells are related *via* the transformation matrix [0 1 0, $\bar{1}$ 0 0, 1 0 1] (Galli and Alberti, 1971 → Rastsvetaeva *et al.*, 1991).

We do not find any additional order of cations in the structure of rinkite of Rastsvetaeva *et al.* (1991) if compared to the structure of rinkite (Galli and Alberti, 1971) and mosandrite (this work). We suggest that epitactic intergrowth of mosandrite crystals reflecting two different cell choices for space group No. 14 results in the apparent loss of the glide plane and apparent reduction of symmetry to space group $P2_1$.

Summary

The crystal structure of mosandrite, ideally $Na_2Ca_4REETi(Si_2O_7)_2OF_3$, from the type locality of Låven (Skådön), Langesundsfjorden, Larvik, Vestfold, Norway, has been refined in space group $P2_1/c$. The crystal structure of mosandrite is a framework of TS (titanium silicate) blocks. The chemical composition and topology of the TS block in mosandrite and rinkite, ideally $Na_2Ca_4REETi(Si_2O_7)_2OF_3$, space group $P2_1/c$ (Galli and Alberti, 1971), are identical.

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