Mineralogical Magazine, August 2013, Vol. 77(6), pp. 2753–2771

From structure topology to chemical composition. XIV. Titanium silicates: refinement of the crystal structure and revision of the chemical formula of mosandrite, $(Ca_3\mathit{REE})[(H_2O)_2Ca_{0.5}\square_{0.5}]Ti(Si_2O_7)_2(OH)_2(H_2O)_2$, a Group-I mineral from the Saga mine, Morje, Porsgrunn, Norway

E. SOKOLOVA* AND F. C. HAWTHORNE

Department of Geological Sciences, University of Manitoba, Winnipeg, Manitoba R3T 2N2, Canada

[*Received 25 March 2013; Accepted 28 June 2013; Associate Editor: S. Mills*]

ABSTRACT

The crystal structure of mosandrite, ideally $(Ca_3\mathit{REE})[(H_2O)_2Ca_{0.5}\square_{0.5}]Ti(Si_2O_7)_2(OH)_2(H_2O)_2$, from the Saga mine, Morje, Porsgrunn, Norway, has been refined as two components related by the TWIN matrix ($\bar{1}$ 0 0, 0 $\bar{1}$ 0, 1 0 1): *a* 7.4222(3), *b* 5.6178(2), *c* 18.7232(7) Å, β 101.4226(6)°, $V = 765.23(9)$ Å^3, space group $P2_1/c$, $D_{\text{calc.}} = 3.361$ g.cm^{-3}, $R_1 = 3.69\%$ using 1347 observed ($F_o > 4\sigma F$) reflections. The empirical formula of mosandrite (EMPA) was calculated on the basis of 4 Si a.p.f.u., with H_2O determined from structure refinement: $[(Ca_{2.89}Ba_{0.01})_{\Sigma 2.90}\,(Ce_{0.39}La_{0.18}Nd_{0.14}Sm_{0.02}Gd_{0.03}Y_{0.16}Th_{0.03})_{\Sigma 1.01}Zr_{0.09}]_{\Sigma 4}[(H_2O)_{2.00}Ca_{0.32}Na_{0.17}Al_{0.10}Mn_{0.04}Fe^{2+}_{0.02}\square_{0.35}]_{\Sigma 3}(Ti_{0.87}Nb_{0.09}Zr_{0.04})_{\Sigma 1}(Si_2O_7)_2[(OH)_{1.54}F_{0.46}]_{\Sigma 2}[(H_2O)_{1.50}F_{0.50}]_{\Sigma 2}$, $Z = 2$. The crystal structure of mosandrite is a framework of TS (titanium silicate) blocks; each TS block consists of HOH sheets (H-heteropolyhedral, O-octahedral). In the TS block, there are five fully occupied cation sites, two [4]-coordinated *Si* sites with <Si–O> 1.623 Å, [7]-coordinated M^{H} and A^{P} sites occupied by Ca and *REE* in the ratio ~ 3:1, and one [6]-coordinated Ti-dominant $M^{\text{O}}(1)$ site. There are two H_2O-dominant H_2O-alkali-cation sites. The partly occupied $M^{\text{O}}(2)$ site has composition $[(H_2O)_{0.5}\square_{0.33}Na_{0.17}]$, ideally $[(H_2O)_{0.5}\square_{0.5}]$ p.f.u. The $M^{\text{O}}(3)$ site has ideal composition $[(H_2O)_{1.5}Ca_{0.5}]$ p.f.u. In the O sheet, the X^{O}_{M} and X^{O}_{A} anion sites have compositions $[(OH)_{1.54}F_{0.46}]$ (X^{O}_{M}) and $[(H_2O)_{1.50}F_{0.50}]$ (X^{O}_{A}), ideally $(OH)_2$ and $(H_2O)_2$ p.f.u. The M^{H} and A^{P} polyhedra and Si_2O_7 groups constitute the H sheet that is completely ordered. In the O sheet, $\text{M}^{\text{O}}(1)$ octahedra are long-range ordered whereas H_2O and OH groups and alkali cations Na and Ca are long-range disordered. Two SRO (short-range ordered) arrangements have been proposed for the O sheet: (1) Na $[M^{\text{O}}(2)]$, Ca_2 $[M^{\text{O}}(3)]$ and F_4 [X^{O}_{M} and X^{O}_{A} anion sites]; (2) 2 H_2O $[M^{\text{O}}(2)]$ and $M^{\text{O}}(3)]$ and $(OH)_2$ and $(H_2O)_2$ [X^{O}_{M} and X^{O}_{A}]. Linkage of H and O sheets occurs mainly *via* common vertices of M^{H} polyhedra and Si_2O_7 groups and $\text{M}^{\text{O}}(1)$ octahedra. Two adjacent TS blocks are related by the glide plane c_y. Mosandrite is an H_2O- and OH-bearing Na- and Ca-depleted analogue of rinkite, ideally $(Ca_3\mathit{REE})Na(NaCa)\,Ti(Si_2O_7)_2(OF)F_2$. Mosandrite and rinkite are related by the following substitution at the $M^{\text{O}}(2,3)$ and $X^{\text{O}}_{(\text{M,A})}$ sites in the O sheet: $^{M}[(H_2O)_2 + \square_{0.5}] + {}^{X}[(OH)_2^{-} + (H_2O)_2] \leftrightarrow {}^{M}[Na_2^{+} + Ca_{0.5}^{2+}] + {}^{X}[(OF)^{3-} + (F_2)^{2-}]$.

KEYWORDS: mosandrite, crystal-structure refinement, EMP analysis, chemical formula, Ti-disilicate minerals, rinkite, Group I.

* E-mail: elena_sokolova@umanitoba.ca
DOI: 10.1180/minmag.2013.077.6.05

Introduction

THE name mosandrite was proposed by Erdman in 1841 (reported by Brögger, 1890) for a mineral from Låven (Skådön), Langesundsfjorden, Larvik, Vestfold, Norway. The name rinkite was proposed by Lorenzen (1884) for a mineral found at Kangerdluarssuk, Greenland. For a long time, it was not clear if mosandrite and rinkite were both valid mineral species. Slepnev (1957, in Russian) reviewed the minerals of the "rinkite group" and stated that mosandrite and rinkite were two valid mineral species, mosandrite being a product of alteration of rinkite. Fleischer (1958) misinterpreted the conclusions of Slepnev (1957), saying that Slepnev had suggested discreditation of the name rinkite in favour of mosandrite. Rinkite was not discredited but acquired the status of a questionable species. Sokolova and Cámara (2008) studied rinkite, ideally $Na_2Ca_4REETi(Si_2O_7)_2OF_3$, under the name mosandrite, as it was a museum specimen labelled mosandrite from the type locality of mosandrite: Låven, Norway. Fleisher's glossary of mineral species 2008 (Back and Mandarino, 2008) listed mosandrite with the formula $(H_3O^+,Na,Ca)_3Ca_3REE(Ti,Zr)(Si_2O_7)_2(O,OH,F)_4$. Bellezza *et al.* (2009) studied the crystal structure and chemical composition of mosandrite, $Ti(\square,Ca,Na)_3(Ca,REE)_4(Si_2O_7)_2[H_2O,OH,F]_4{\cdot}{\sim}1H_2O$, Z = 2, from the type locality, Låven (Skådön), Langesundsfjorden, Larvik, Vestfold, Norway, and confirmed it as a valid mineral species. They reported "a rinkite-type structure, characterized by a low occupancy of the $M^O(2)$ and $M^O(3)$ sites and chemical composition characterized by a lower Ca content, very low Na and F contents and a very high amount of H_2O with respect to the chemical composition of rinkite." Cámara *et al.* (2011) studied rinkite from several localities and confirmed its validity as a distinct mineral species. Hence in the official IMA list of minerals (http://pubsites.uws.edu.au/ima-cnmnc/), rinkite, $Na_2Ca_4CeTi(Si_2O_7)_2OF_3$, is a valid mineral species.

However the work of Bellezza *et al*. (2009) left some problems unresolved: (1) their empirical formula of mosandrite, $(Ti_{0.93}Nb_{0.08})_{\Sigma1.01}(\square_{1.65}Ca_{0.90}Na_{0.29}Mn_{0.07}Al_{0.06}Fe_{0.03})_{\Sigma3}(Ca_{2.80}REE_{0.85}Y_{0.21}Zr_{0.10}Th_{0.04})_{\Sigma4}(Si_2O_7)_2[(OH)_{3.01}F_{0.92}]_{\Sigma3.93}{\cdot}2H_2O$ [H_2O = 2 a.p.f.u., OH = 3.01 p.f.u. (with H_2O measured by TG-DSC) and Σanions = 20 a.p.f.u.], differs from its simplified formula $Ti(\square,Ca,Na)_3(Ca,REE)_4(Si_2O_7)_2[H_2O,OH,F]_4{\cdot}{\sim}1H_2O$, Z = 2 [$H_2O$ ~ 2 p.f.u.; OH ~2 p.f.u., Σanions = 19 a.p.f.u.] in the number of anions, 20 *vs.* 19 a.p.f.u.; (2) the simplified formula $Ti(\square,Ca,Na)_3(Ca,REE)_4(Si_2O_7)_2[H_2O,OH,F]_4{\cdot}{\sim}1H_2O$, which was written in accord with structure-refinement results, does not agree with those structure-refinement results: the structure refinement does not account for the ~1 H_2O p.f.u. in the mineral formula; hence there is disagreement between the chemical analysis and the structure-refinement results (for more details see *Previous work* below); and (3) mosandrite has not been redefined as a mineral species: cf. formulae $(H_3O^+,Na,Ca)_3Ca_3REE(Ti,Zr)(Si_2O_7)_2(O,OH,F)_4$[$H_3O^+$ is a dominant species at the three alkali-cation sites: $(H_3O^+,Na,Ca)_3$, Back and Mandarino (2008)] and $Ti(\square,Ca,Na)_3(Ca,REE)_4(Si_2O_7)_2[H_2O,OH,F]_4{\cdot}{\sim}1H_2O$ [□ is a dominant species at the three alkali-cation sites: $(\square,Ca,Na)_3$, Bellezza *et al.* (2009)]. In making these comments about the results of Bellezza *et al.* (2009), we wish to state that we have no intention of being critical. Mosandrite is extremely difficult to deal with, and Bellezza *et al.* (2009) made major progress with this mineral. Here, we try to resolve these residual problems and reach an adequate understanding of mosandrite.

Mosandrite is a Group-I TS-block mineral in accord with Sokolova (2006) who divided Ti-disilicate minerals into four groups, characterized by a different topology and stereochemistry of the titanium silicate (TS) block. The TS block consists of the central O (trioctahedral) sheet and two H (heteropolyhedral) sheets containing Si_2O_7 groups. In Group I, Ti = 1 a.p.f.u. and Ti (= Nb, Zr) occurs in the O sheet: 1 M^O = Ti, Nb, Zr; 3 M^O = Na, Ca and rarely Mn; $^{[6],[7]}M^H$ = Zr, Ca + *REE*, Ca, Mn; A^P = Na, Ca, Ca + *REE* ; X^O = anions = O, F. Sokolova (2006) wrote the general formula for minerals of Group I as $A^P_2M^H_2M^O_4(Si_2O_7)_2X^O_4$.

There are eight Group-I minerals of known structure: götzenite, hainite, seidozerite, grenmarite, rinkite, nacareniobsite-(Ce), kochite and rosenbuschite (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 and nacareniobsite-(Ce) (space group $P2_1/c$) and type 2 occurs in seidozerite, grenmarite, gotzenite, hainite, kochite and rosenbuschite (space groups $P\bar{1}$ and $P2/c$). Mosandrite is isostructural with rinkite (Cámara *et al.* 2011) and nacareniobsite-(Ce) (Sokolova and Hawthorne, 2008). Here we report refinement of the crystal structure and a revised chemical formula of mosandrite.

TABLE 1. Ideal structural formulae* and unit-cell parameters for TS-block minerals of Group I.

Mineral	Ideal structural formula						a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)	Sp. gr.	Z	Ref.
	$2A^P$ $2M^H$	$4M^O$		$(Si_2O_7)_2$	$4X^O$										
					$2X^O_M$	$2X^O_A$									
Mosandrite	$(Ca_3$*REE*$)$	$[(H_2O)_2Ca_{0.5}\square_{0.5}]$	Ti	$(Si_2O_7)_2$	$(OH)_2$	$(H_2O)_2$	7.4222	5.6178	18.7232		101.423		*P*2$_1$/*c*	2	(1)
Mosandrite**	$(Ca,$*REE*$)_4$	$(\square,Ca,Na)_3$	Ti	$(Si_2O_7)_2$	$[H_2O,OH,F]_4{\cdot}{\sim}1H_2O$		7.398	5.595	18.662		101.37		*P*2$_1$/*c*	2	(2)
Rinkite	$(Ca_3$*REE*$)$	Na(NaCa)	Ti	$(Si_2O_7)_2$	(OF)	F_2	7.4328	5.6595	18.818		101.353		*P*2$_1$/*c*	2	(3)
Nacareniobsite-(Ce)	$(Ca_3$*REE*$)$	Na_3	Nb	$(Si_2O_7)_2$	(OF)	F_2	7.468	5.689	18.891		101.37		*P*2$_1$/*c*	2	(4)
Seidozerite	Na_2Zr_2	Na_2Mn	Ti	$(Si_2O_7)_2$	O_2	F_2	5.5558	7.0752	18.406		102.713		*P*2/*c*	2	(5)
Grenmarite	Na_2Zr_2	Na_2Mn	Zr	$(Si_2O_7)_2$	O_2	F_2	5.608	7.139	18.575		102.60		*P*2/*c*	2	(6)
Götzenite	Ca_2 Ca_2	$NaCa_2$	Ti	$(Si_2O_7)_2$	(OF)	F_2	9.6192	5.7249	7.3307	89.981	101.132	100.639	$P\bar{1}$	1	(5)
Hainite	$[Ca_3(Y,$*REE*$)]$	Na(NaCa)	Ti	$(Si_2O_7)_2$	(OF)	F_2	9.6079	5.7135	7.3198	89.916	101.077	100.828	$P\bar{1}$	1	(5)
Kochite	Ca_2 MnZr	Na_3	Ti	$(Si_2O_7)_2$	OF	F_2	10.032	11.333	7.202	90.192	100.334	111.551	$P\bar{1}$	2	(7)
Rosenbuschite	Ca_4 Ca_2Zr_2	Na_2Na_4	TiZr	$(Si_2O_7)_4$	O_2F_2	F_4	10.137	11.398	7.2717	90.216	100.308	111.868	$P\bar{1}$	1	(5)

* The ideal structural formulae are written in the form $A^P{}_2M^H_2M^O_4(Si_2O_7)_2X^O_4$ in accord with Sokolova (2006): M^H = cations of the H sheet; M^O = cations of the O sheet; A^P = cations at the peripheral (*P*) sites, X^O_4 = anions of the O sheet not shared with Si_2O_7 groups: $X^O_4 = (X^O_M)_2 + (X^O_A)_2$;

** simplified formula.

References (the latest reference on the structure): (1) This work; (2) Bellezza *et al*. (2009); (3) Cámara *et al*. (2011, sample 1991C); (4) Sokolova and Hawthorne (2008); (5) Christiansen *et al*. (2003*a*); (6) Bellezza *et al*. (2004); (7) Christiansen *et al*. (2003*b*).

Previous work

Here we describe the general topology of the crystal structure of rinkite, the pseudomerohedral twinning characteristic of rinkite and nacareniobsite-(Ce), and unresolved problems with mosandrite.

The general topology of the TS block in the crystal structure of rinkite

For the structure description, we use the terminology of Sokolova (2006). The topology of the crystal structure of rinkite is in accord with the work of Galli and Alberti (1971). The crystal structure of rinkite is a framework of TS (titanium silicate) blocks that consist of HOH sheets. The O sheet is composed of Ti-dominant $M^O(1)$ octahedra, [8]-coordinated $M^O(2)$ polyhedra occupied by Na, and $M^O(3)$ octahedra occupied mainly by Na and Ca in the ratio ~1:1, Na > Ca (Fig. 1*a*). The H sheet is built of Si_2O_7 groups and [7]-coordinated M^H and A^P polyhedra occupied by Ca and *REE* in the ratio ~ 3:1 (Fig. 1*b*). In rinkite, the TS block exhibits linkage and stereochemistry typical of Group I (Ti = 1 a.p.f.u.) of the 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 (Fig. 1*c*).

Pseudomerohedral twinning

Structure work on rinkite, mosandrite and nacareniobsite-(Ce) is almost always complicated by pseudomerohedral twinning of their crystals. Sokolova and Cámara (2008) suggested that epitactic intergrowth of crystals of this structure type is possible, with the result that in a "crystal" of rinkite, layers of rinkite in a different orientation (relative to that required by the space-group symmetry and unit-cell orientation of the primary crystal) may occur owing to matching of the unit cells in two different orientations. As they noted, such an intergrowth will result in apparent violation of *c*-glide symmetry due to the layers in the second orientation. Cámara *et al*. (2011) suggested that this was the origin of the *h*0*l* reflections with $h + l = 2n + 1$ that seemed to violate the c_y glide of the structure. They dealt with this situation by incorporating a second component of the crystal into the refinement, a component that was related to the first by the transformation matrix ($\bar{1}$ 0 0, 0 $\bar{1}$ 0, 1 0 1). There are two settings for the space group No. 14, which correspond to space groups $P2_1/c$ and $P2_1/n$, and the pseudomerohedral twins correspond to two different cell choices for space group No. 14. Cámara *et al*. (2011) showed that in rinkite the volume of the second component varied from 1 to 85%. They also reported TEM studies of rinkite: sample 2909 was pervasively twinned on (001), which is in accord with the twin ratio of 0.58 defined from structure refinement of this sample. The size of every lamella was <200 nm, too small to resolve by optical microscopy, which explains the milky and badly behaved optical character of these crystals.

Mosandrite: problems

Previous work on mosandrite, rinkite and nacareniobsite-(Ce) [prior to (Bellezza *et al*., 2009)] was summarized by Bellezza *et al*. (2009) and Cámara *et al*. (2011). The work of Bellezza *et al*. (2009) was a breakthrough in the crystal chemistry of rinkite and mosandrite: this was the first determination of the crystal structure of mosandrite which made clear that mosandrite and rinkite are two distinct mineral species. They stated that the chemical composition of mosandrite differs from that of rinkite in "low Ca, Na and F contents and high amount of H_2O." However, there are some unresolved problems with the crystal structure and chemical formula of mosandrite which we outline here.

Problem 1: Lack of agreement between the mineral formula and the chemical analysis

The chemical analysis and the empirical formula for mosandrite of Bellezza *et al*. (2009) are given in Table 2. With variable amounts of H_2O (7.50−8.00 wt.% determined by TG-DSC analysis), the number of H^+ varies from 6.99 to 7.45 a.p.f.u. and the number of anions varies from 19.95 to 20.18 a.p.f.u., giving a mean H^+ of 7.22 a.p.f.u. and an average number of anions equal to 20.07 a.p.f.u. Bellezza *et al*. (2009) gave empirical and crystal-chemical formulae of mosandrite which differ in content of H_2O and number of anions (Table 3). They also gave a simplified formula (1) $Ti(\square,Ca,Na)_3(Ca,REE)_4(Si_2O_7)_2(OH,F)_4{\cdot}{\sim}2H_2O$ corresponding to the empirical formula and a simplified formula (2) $Ti(\square,Ca,Na)_3(Ca,REE)_4(Si_2O_7)_2[H_2O,OH,F]_4{\cdot}{\sim}1H_2O$ corresponding to the crystal-chemical formula. The simplified formula (2) is in accord with structure-refinement results and has been given as the formula of mosandrite [see

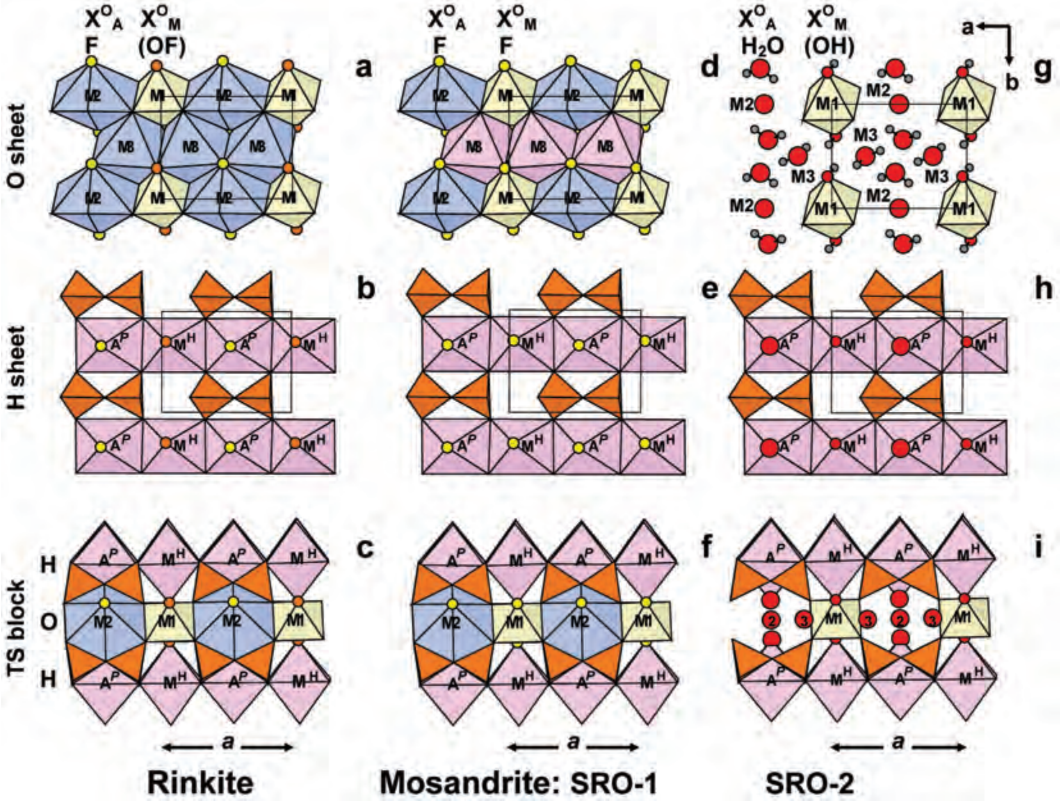

FIG. 1. The TS block in the crystal structures of rinkite and mosandrite. Rinkite [the $M^O(2)$ and $M^O(3)$ sites are occupied by Na and (Na,Ca), respectively; the X^O_M and X^O_A sites are occupied by (O,F) and F]: (*a*) the O sheet, (*b*) the H sheet, (*c*) the TS block; Short-range order (SRO) arrangements in mosandrite, SRO-1 [the $M^O(2)$ and $M^O(3)$ sites are occupied by Na and Ca, respectively; the X^O_M and X^O_A sites are occupied by F): (*d*) the O sheet, (*e*) the H sheet, (*f*) the TS block; SRO-2 [the $M^O(2)$ and $M^O(3)$ sites are occupied by H_2O groups and the X^O_M and X^O_A sites are occupied by OH and H_2O: (*g*) the O sheet, (*h*) the H sheet, (*i*) the TS block; Si tetrahedra are orange, Ti-dominant $M^O(1)$ octahedra are yellow, Na [8]-coordinated $M^O(2)$ polyhedra and (Na,Ca) $M^O(3)$ octahedra are blue, Ca-dominant [7]-coordinated M^H and A^P polyhedra and $M^O(3)$ octahedra are pink, (O,F) and F anions are shown as medium orange and yellow spheres, respectively; OH and H_2O groups are shown as small and large red spheres, respectively; H atoms are shown as small grey spheres; H_2O groups at the $M^O(2)$ and $M^O(3)$ sites are labelled 2 and 3 in (*f*). The unit cell is shown by thin black lines in (*a,b,d,e,g,h*). The letters H O H indicate the positions of H and O sheets in (*c,f,i*).

Bellezza *et al*. (2009) and IMA list of minerals]. The crystal-chemical formula contains 5.44 H^+ a.p.f.u. and 19 anions p.f.u. (Table 3), which contradicts the chemical analysis (H^+ = 6.99–7.45 a.p.f.u., Σanions = 19.95–20.18 a.p.f.u., Table 2).

Problem 2: Lack of agreement between the mineral formula and the structure-refinement results

Bellezza *et al*. (2009) reported the following site-occupancies for mosandrite: the $M^O(1)$ site is Ti-dominant and gives Ti a.p.f.u.; the $M^H + A^P$ sites are occupied by Ca and *REE* in the ratio ~3:1 and give (Ca,*REE*)$_4$ a.p.f.u.; the $M^O(2)$ and $M^O(3)$ sites are mainly vacant: $M^O(2)$ = $(\square_{0.70}\text{Ca}_{0.16}\text{Na}_{0.14})$ p.f.u. (70%-vacancy); $M^O(3)$ = $(\square_{1.30}\text{Ca}_{0.46}\text{Ce}_{0.14}\text{Na}_{0.10})$ p.f.u. (65%-vacancy), with simplified composition $(\square,\text{Ca,Na})_3$; the X^O_M [= OF(1), Bellezza *et al*., 2009)] and X^O_A [= OF(2), Bellezza *et al*. (2009)] anion sites are occupied by $[(\text{OH})_{1.30}\text{F}_{0.70}]$ and $[(\text{H}_2\text{O})_{0.92}(\text{OH})_{0.88}\text{F}_{0.20}]$ p.f.u., respectively [table 9, Bellezza *et al*. (2009)], with simplified composition

TABLE 2. Chemical composition and unit formula* of mosandrite.

Oxide (wt.%)	(1)	(2)**	(3)	(4)	Formula unit (a.p.f.u.)	(1)	(2)**	(3)	(4)
Nb_2O_5	n.a.	n.a.	1.40	1.57	Nb	n.a.	n.a.	0.08	0.09
ThO_2	0.34	0.34	1.04	0.95	Th	0.01	0.01	0.04	0.03
ZrO_2	7.43	7.43	1.45	2.04	Zr	0.47	0.47	0.10	0.13
TiO_2	5.33	5.33	8.89	9.03	Ti	0.52	0.52	0.93	0.87
SiO_2	30.71	30.71	28.64	31.13	Si	4.00	4.00	4.00	4.00
CeO_2	6.34	n.d.	n.d.	n.d.	Ce^{4+}	0.29	n.d.	n.d.	n.d.
Ce_2O_3	10.45	16.50	8.22	8.35	Ce^{3+}	0.50	0.79	0.42	0.39
Yb_2O_3	n.a.	n.a.	0.19	n.d.	Yb^{3+}	n.a.	n.a.	0.01	n.d.
Er_2O_3	n.d.	n.d.	0.39	n.d.	Er^{3+}	n.d.	n.d.	0.02	n.d.
Dy_2O_3	n.a.	n.a.	0.32	0.38	Dy^{3+}	n.a.	n.a.	0.01	n.d.
Gd_2O_3	n.a.	n.a.	0.31	0.60	Gd^{3+}	n.a.	n.a.	0.01	0.03
Sm_2O_3	n.a.	n.a.	0.28	0.50	Sm^{3+}	n.a.	n.a.	0.01	0.02
Nd_2O_3	n.a.	n.a.	2.13	3.05	Pr^{3+}	n.a.	n.a.	0.06	n.d.
Pr_2O_3	n.a.	n.a.	1.19	0.93	Nd^{3+}	n.a.	n.a.	0.11	0.14
La_2O_3	n.a.	n.a.	3.81	3.82	La^{3+}	n.a.	n.a.	0.20	0.18
Y_2O_3	3.52	3.52	2.82	2.34	Y	0.24	0.24	0.21	0.16
Al_2O_3	n.d.	n.d.	0.40	0.66	Al	n.d.	n.d.	0.06	0.10
Fe_2O_3	0.56	n.d.	n.d.	n.d.	Fe^{3+}	0.06	n.d.	n.d.	n.d.
FeO	n.d.	0.50	0.25	0.16	Fe^{2+}	n.d.	0.05	0.03	0.02
BaO	n.d.	n.d.	n.a.	0.15	Ba	n.d.	n.d.	n.a.	0.01
SrO	n.d.	n.d.	n.a.	n.d.	Sr	n.d.	n.d.	n.a.	n.d.
MnO	0.45	0.45	0.60	0.32	Mn^{2+}	0.05	0.05	0.07	0.04
CaO	22.53	22.53	24.74	23.28	Ca	3.14	3.14	3.70	3.21
MgO	0.63	0.63	n.d.	n.d.	Mg	0.12	0.12	n.d.	n.d.
K_2O	0.38	0.38	0.05	n.d.	K	0.06	0.06	0.01	n.d.
Na_2O	2.44	2.44	1.06	0.67	Na	0.62	0.62	0.29	0.17
Cl	n.d.	n.d.	0.04	n.d.	Cl	n.d.	n.d.	n.d.	n.d.
F	2.06	2.06	2.08	2.35	F	0.85	0.85	0.92	0.96
H_2O***	7.70	8.05	7.50–8.00	9.96	H^+	6.69	6.69	6.99–7.45	8.54
–O=Cl	n.d.	n.d.	0.01	n.d.					
–O=F	0.87	0.87	0.88	0.99	Σcations	10.09	10.09	10.38	9.63
Total	100.00	100.00	96.92–97.42	101.25	Σanions	19.21	19.19	19.95–20.18	20.00

References: wet chemistry: (1) Brögger (1890); electron-microprobe analysis: (3) Bellezza *et al*. (2009); (4) This work.

* Unit formulae were calculated on Si 4 a.p.f.u.

** (2) recalculated from (1): (a) Ce_2O_3 from {CeO_2 = 6.34 wt.% + Ce_2O_3 [= $(Ce,La,Dy)_2O_3$] = 10.45 wt.%} and (b) FeO from Fe2O3 = 0.56 wt.% in (1).

*** added as difference to 100% (1,2), measured with TG-DSC (3) and calculated from structure refinement (4).

4 $[H_2O,OH,F]$ p.f.u. However they gave an ideal composition of two anion OF(1) + OF(2) [= $X^O_M + X^O_A$] sites (4 a.p.f.u., see above) as {$[(OH)_2F(H_2O)]\cdot1H_2O$} (5 a.p.f.u.) [table 11, Bellezza *et al*. (2009)].

We sum cation and anion sites in accord with Bellezza *et al*. (2009)]: Ti [$M^O(1)$] + $(\square,Ca,Na)_3$ [$M^O(2)+M^O(3)$] + $(Ca,REE)_4$ [M^H+A^P] +$(Si_2O_7)_2$ + $[H_2O,OH,F]_4$ [$X^O_M + X^O_A$] = $Ti(\square,Ca,Na)_3(Ca,REE)_4(Si_2O_7)_2[H_2O,OH,F]_4$, and this sum corresponds to the simplified formula (2): $Ti(\square,Ca,Na)_3(Ca,REE)_4(Si_2O_7)_2[H_2O,OH,F]_4\cdot{\sim}1H_2O$, except for ~$1H_2O$. Although Bellezza *et al*. (2009) suggested that an H_2O group could occur at the $M^O(2)$ site, they did not include an H_2O group in the refinement. Hence there is disagreement between the chemical formula written in accord with structure-refinement results and the structure-refinement results.

TABLE 3. Empirical and crystal-chemical formulae of mosandrite calculated on Si = 4 a.p.f.u.; after Bellezza *et al.* (2009).

	Empirical formula	Crystal-chemical formula*
Cations	$(Ti_{0.93}Nb_{0.08})_{\Sigma 1.01}$ $(\square_{1.65}Ca_{0.90}Na_{0.29}Mn_{0.07}Al_{0.06}Fe_{0.03})_{\Sigma 3}$ $(Ca_{2.80}\mathit{REE}_{0.85}Y_{0.21}Zr_{0.10}Th_{0.04})_{\Sigma 4}$	$(Ti_{0.96}Nb_{0.04})_{\Sigma 1}$ $(\square_{2.00}Ca_{0.62}Na_{0.24}\mathit{REE}_{0.14})_{\Sigma 3}$ $(Ca_{2.96}\mathit{REE}_{0.96}Zr_{0.08})_{\Sigma 4}$
Complex oxy-anions	$(Si_2O_7)_2$	$(Si_2O_7)_2$
Anions	$[(OH)_{3.01}F_{0.92}]_{\Sigma 3.93}\cdot 2H_2O$	$[(H_2O)_{0.92}(OH)_{2.18}F_{0.90}]_{\Sigma 4}\cdot 0.71H_2O$
H_2O (p.f.u.)	2	1.63
OH (p.f.u.)	3.01	2.18
H^+ (a.p.f.u.)	7.01	5.44
Σanions (a.p.f.u.)	20	19

* in accord with structure-refinement results.

Bellezza *et al.* (2009) described mosandrite as having "a rinkite-type structure, characterized by a low occupancy of the $M^O(2)$ and $M^O(3)$ sites and chemical composition characterized by a lower Ca content, very low Na and F contents and a very high amount of H_2O with respect to the chemical composition of rinkite." Hence vacancy is a dominant species in the O sheet in the mosandrite formula, $Ti(\square,Ca,Na)_3(Ca,\mathit{REE})_4(Si_2O_7)_2[H_2O,OH,F]_4\cdot{\sim}1H_2O$. However ~2 H_2O p.f.u. (chemical analysis, Table 2) were left unaccounted for. Consequently, mosandrite must be re-defined as a mineral species.

So with regard to mosandrite, there are three questions that need to be answered:

(1) Do H_2O groups occur at the alkali-cation sites with partial occupancy, and what is a dominant species in the O sheet?

(2) What is the chemical formula of mosandrite and how many anions does it contain?

(3) What is the relation between mosandrite and rinkite?

Experimental details

Description of a sample

We studied sample 3859 of mosandrite from the Saga mine, Morje, Porsgrunn, Norway which was on loan from the Mineralogical Collection of Renato and Adriana Pagano. We first analysed a large grain which was honey brown in colour, with a dark core and a light edge. The EMP analysis of the central part (0.600 mm × 0.220 mm × 0.020 mm) of the grain is in good agreement with the chemical analyses of Brögger (1890) and Bellezza *et al.* (2009), and we concluded that it is mosandrite. After the EMP analysis, a smaller crystal (0.100 mm × 0.100 mm × 0.020 mm) was cut from the central part of the grain for the X-ray data collection. The honey-brown crystal of mosandrite used in this work is of good optical quality.

Chemical analysis

A single crystal of mosandrite was analysed using 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 10 μm and count times on peak and background of 20 and 10 s, respectively. The following standards, spectral lines and analysing crystals were used: Si, F: rinkite (sample YuksFe, Cámara *et al.*, 2011) (Si*K*α, TAP; F*K*α; LTAP); Na: albite (Na*K*α, TAP); Al: andalusite (Al*K*α, LTAP); Ca: diopside (Ca*K*α, LPET); Nb: $Ba_2NaNb_5O_{15}$ (Nb*L*α, LPET); Fe: fayalite (Fe*K*α, LLIF); Mn: spessartine (Mn*K*α, LLIF); Zr: zircon (Zr*L*α, LPET); Ce: $CePO_4$ (Ce*L*α, LLIF); La: $LaPO_4$ (La*L*α, LLIF); Nd: $NdPO_4$ (Nd*L*β, LLIF); Pr: $PrPO_4$ (Pr*M*β, LLIF); Sm: $SmPO_4$ (Sm*M*β, LLIF); Gd: $GdPO_4$ (Gd*M*β, LLIF); Dy: $DyPO_4$ (Dy*M*β, LLIF); Ti: titanite (Ti*K*α, LPET); Ba: baryte (Ba*L*α, LPET); Y: $Y_3Al_5O_{12}$ (Y*L*α, LPET); Th: ThO_2 (Th*M*α, LPET). Data were reduced using the $\varphi(\rho Z)$ procedure of Pouchou and Pichoir (1985). The chemical composition of the mosandrite is the mean of 10 determinations and is given in Table 2 [analysis (4)]. The empirical formula of mosandrite was calculated on the basis of 4 Si a.p.f.u.:

$[(Ca_{2.89}Ba_{0.01})_{\Sigma 2.90}(Ce_{0.39}La_{0.18}Nd_{0.14}Sm_{0.02}Gd_{0.03}Y_{0.16}Th_{0.03})_{\Sigma 1.01}Zr_{0.09}]_{\Sigma 4}[(H_2O)_{2.00}Ca_{0.32}Na_{0.17}Al_{0.10}Mn_{0.04}Fe^{2+}_{0.02}\square_{0.35}]_{\Sigma 3}(Ti_{0.87}Nb_{0.09}Zr_{0.04})_{\Sigma 1}(Si_2O_7)_2[(OH)_{1.54}F_{0.46}]_{\Sigma 2}[(H_2O)_{1.50}F_{0.50}]_{\Sigma 2}$, $Z = 2$, $D_{calc.} = 3.361$ g.cm^{-3}, with H_2O determined from structure refinement. Table 2 also includes chemical analyses (1,2) of Brögger (1890) and (3) of Bellezza *et al.* (2009). Comparison of analyses (4) (sample 3859, this work) and (3) (Bellezza *et al.*, 2009) shows that sample 3859 has (a) approximately the same F content: 2.35 (4) *vs*. 2.08 wt.% (3); (b) a smaller CaO content: 23.28 (4) *vs*. 24.74 wt.% (3); (b) a smaller Na_2O content: 0.67 (4) *vs*. 1.06 wt.% (3); and (d) a larger H_2O content: 9.96 (4) *vs*. 7.50−8.00 wt.% (3).

X-ray data collection and structure refinement

X-ray data for mosandrite were collected with a single-crystal Bruker D8 three-circle diffractometer equipped with a rotating-anode generator (Mo*K*α radiation), multilayer optics and an APEX-II detector. Details of data collection and structure refinement are given in Table 4. The intensities of reflections with $-10 \leqslant h \leqslant 10$, $-7 \leqslant k \leqslant 7$, $-26 \leqslant l \leqslant 26$ were collected for $2\theta \leqslant 60.14°$ with a frame width of 0.3° and a frame time of 2 s, and an empirical absorption correction (*SADABS*, Sheldrick, 2008) was applied. The unit-cell parameters were refined from 9897 reflections with $I > 10\sigma I$. Refinement of the crystal structure was done in monoclinic

TABLE 4. Miscellaneous refinement data for mosandrite.

a (Å)	7.4222(3)
b (Å)	5.6178(2)
c (Å)	18.7232(7)
β (°)	101.4226(6)
V (Å^3)	765.23(9)
Refl. ($I_o > 10\sigma I$)	9897
Space group	$P2_1/c$
Z	2
Absorption coefficient (mm^{-1})	5.42
F(000)	752.70
$D_{calc.}$ (g/cm^3)	3.361
Second component (%)*	17.6(4)
Reflections violating	
c glide plain (I > 3σI)	151
n glide plain (I > 3σI)	205
Crystal size (mm)	0.100 × 0.100 × 0.020
Radiation/filter	Mo-*K*α/graphite
$2\theta_{max}$ for structure refinement (°)	50.00
R(int) (%)	1.27
Reflections collected**	8948
Independent reflections	1412
$F_o > 4\sigma F$	1347
Refinement method	Full-matrix least squares on F^2, fixed weights proportional to $1/\sigma F_o^2$
No. of refined parameters	174
Final R $_{(obs)}$ (%)	
R_1 [$F_o > 4\sigma F$]	3.69
R_1 [all data]	3.84
wR_2	11.28
Highest peak, deepest hole (e Å^{-3})	1.04 −0.58
Goodness of fit on F^2	1.164

* Second component of the crystal is compatible with *n*-glide symmetry and is related to the first component, compatible with *c*-glide symmetry, by the matrix ($\bar{1}$00, 0$\bar{1}$0, 101);

** in accord with 2θ range for structure refinement.

symmetry using the atom coordinates of Sokolova and Cámara (2008). The crystal structure of mosandrite was refined with the Bruker *SHELXTL* Version 5.1 system of programs (Sheldrick, 2008) to R_1 = 3.69% (Table 4). We observed 151 violations of the *c*-glide extinction criterion and refined the structure as two components related by the TWIN matrix ($\bar{1}$ 0 0, 0 $\bar{1}$ 0, 1 0 1) (see discussion above), the second component being 17.6(4)% (equivalent to the batch scale factor in *SHELX*, "BASF"). There were few observed reflections at high 2θ, and those that do occur show splitting due to pseudomerohedral twinning, and refinement of the structure was done for $2\theta \leqslant 50^{\circ}$, $-8 \leqslant h \leqslant 8$, $-6 \leqslant k \leqslant 6$, $-22 \leqslant l \leqslant 22$. The occupancies of five cation sites were refined with the following scattering curves: M^{H} and A^{P} sites: Y; $M^{\mathrm{O}}(1)$ site: Ti; $M^{\mathrm{O}}(2)$ and $M^{\mathrm{O}}(3)$ sites: Na and Ca, respectively. The occupancies of the M^{H}, A^{P} and $M^{\mathrm{O}}(1)$ sites were in good agreement with occupancies of these sites in rinkite (Cámara *et al*., 2011) and with the cations available from EMP analysis (Table 2). Refinement of the $M^{\mathrm{O}}(2)$ and $M^{\mathrm{O}}(3)$ site occupancies converged to 6.2(2) and 20.6(3) e.p.f.u. (electron per formula unit), giving in total 26.8 e.p.f.u. The $M^{\mathrm{O}}(2)$ and $M^{\mathrm{O}}(3)$ sites give 3 a.p.f.u. The cation content to assign to these two sites (available from chemical analysis), equals 0.64 a.p.f.u. and comprises 0.32 Ca + 0.17 Na + 0.10 Al + 0.04 Mn + 0.02 Fe^{2+}, with a total calculated scattering of 11.09 e.p.f.u. We were left with 26.8 − 11.09 = 15.71 e.p.f.u., which corresponds to the scattering of ~2 O atoms, i.e., ~2 H_2O a.p.f.u.

Note that Bellezza *et al.* (2009) measured the content of H_2O in mosandrite [Table 2, analysis (3)] and gave the empirical formula $(\mathrm{Ti}_{0.93}\mathrm{Nb}_{0.08})_{\Sigma 1.01}(\square_{1.65}\mathrm{Ca}_{0.90}\mathrm{Na}_{0.29}\mathrm{Mn}_{0.07}\mathrm{Al}_{0.06}\mathrm{Fe}_{0.03})_{\Sigma 3}(\mathrm{Ca}_{2.80}\mathit{REE}_{0.85}\mathrm{Y}_{0.21}\mathrm{Zr}_{0.10}\mathrm{Th}_{0.04})_{\Sigma 4}(\mathrm{Si}_2\mathrm{O}_7)_2[(\mathrm{OH})_{3.01}\mathrm{F}_{0.92}]_{\Sigma 3.93}\cdot 2\mathrm{H}_2\mathrm{O}$, where H_2O = 2 p.f.u.; OH = 3 p.f.u., Σanions = 20 a.p.f.u.; the latter formula does not agree with their structure-refinement results. However, both the H_2O content determined by Bellezza *et al.* (2009) and their suggestion that an H_2O group could occur at the $M^{\mathrm{O}}(2)$ site are in accord with our structure-refinement results. We conclude that H_2O groups occur at both $M^{\mathrm{O}}(2)$ and $M^{\mathrm{O}}(3)$ sites. In accord with the refined site-scattering values (see above), we assigned available cations and H_2O groups to the $M^{\mathrm{O}}(2,3)$ sites and refined the atom coordinates and displacement parameters of atoms at these sites with fixed occupancies and with the following scattering curves: $M^{\mathrm{O}}(2)$ site, with Na and O; and $M^{\mathrm{O}}(3)$ site, with Ca and O. The occupancies of the $X^{\mathrm{O}}_{\mathrm{M}}$ and $X^{\mathrm{O}}_{\mathrm{A}}$ anion sites were refined using the scattering curves of F and O. At the final stages of the refinement, hydrogen atoms were located in the difference-Fourier map; they belong to the OH group at the $X^{\mathrm{O}}_{\mathrm{M}}$ site and the H_2O groups at the $M^{\mathrm{O}}(3)$ and $X^{\mathrm{O}}_{\mathrm{A}}$ sites. Hydrogen atoms with fixed occupancies equal to those of the corresponding O atoms of the OH and H_2O groups were included in the refinement, and all H(1−5) positions were softly constrained by setting the O−H distances equal to 0.98 and the H−H distances equal to 1.50 Å. Scattering curves for neutral atoms were taken from the *International Tables for Crystallography* (Wilson, 1992). Details of data collection and structure refinement are given in Table 4, final atom coordinates and displacement parameters are given in Table 5, selected interatomic distances and angles in Table 6, refined site-scattering values and assigned populations for selected sites in Table 7, and bond-valence values in Table 8. A list of observed and calculated structure factors has been deposited with the Principal Editor of *Mineralogical Magazine* and is available from www.minersoc.org/pages/e_journals/dep_mat_mm.html.

Site-population assignment

There are seven cation sites in the crystal structure of mosandrite: three M^{O} sites of the O sheet and the M^{H}, A^{P} and two *Si* sites of the H sheet; site labelling follows Sokolova (2006). Consider first the Ti-dominant $M^{\mathrm{O}}(1)$ site. The bond lengths around the $M^{\mathrm{O}}(1)$ site vary from 1.963 to 2.053 Å (Table 6). We assign cations to this site based on our previous work on rinkite (Cámara *et al*., 2011): Ti(+Nb)-dominant sites are always fully occupied. In mosandrite, the $M^{\mathrm{O}}(1)$ site is occupied mainly by Ti and minor Nb and Zr, with the calculated scattering of 24.43 e.p.f.u. and the refined scattering of 22.5(3) e.p.f.u. (Table 7).

Consider next the two [7]-coordinated M^{H} and A^{P} sites in the H sheet. In rinkite, these sites are fully occupied by Ca and REE^{3+} in the ratio ~ 3:1 (Cámara *et al*., 2011). The cations to be assigned to the M^{H} and A^{P} sites are Ca, REE^{3+}, Y, Th and Ba (Table 2). By analogy with (Cámara *et al*., 2011), let us decide if we should assign any Na to these sites. First, we assign all REE^{3+}, Y and Th, with a total of 1.01 a.p.f.u. (Tables 2, 7). Next, we assign Zr ($^{[7]}r$ = 0.78 Å, Shannon, 1976) which substitutes for REE^{3+}, Y and Th; and Ba, a large

TABLE 5. Final atom coordinates and displacement parameters (Å^2) for mosandrite.

Atom	Site occ. (%)	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	U_{eq}*
M^H	100	0.09437(13)	0.66265(15)	0.19228(4)	0.0113(5)	0.0145(5)	0.0250(6)	0.0011(3)	0.0044(5)	-0.0001(4)	0.0168(4)
A^P	100	0.5973(2)	0.6620(3)	0.19120(6)	0.0121(7)	0.0181(7)	0.0210(8)	0.0015(7)	0.0046(8)	0.0001(5)	0.0169(5)
$M^O(1)$	100	0	0	0	0.0111(10)	0.0402(14)	0.0207(11)	-0.0172(9)	0.0043(10)	-0.0039(12)	0.0238(7)
**$M^O(2)(H_2O)_{0.5}Na_{0.17}$	67	½	0	0	0.023(5)	0.055(7)	0.014(4)	-0.008(5)	0.003(5)	-0.011(7)	0.031(2)
**$M^O(3)(H_2O)_{0.75}Ca_{0.24}$	99	0.7501(4)	0.5012(6)	0.0001(2)	0.0089(17)	0.0073(18)	0.026(2)	0.0008(14)	0.005(2)	-0.003(2)	0.0138(9)
Si(1)	100	0.3507(3)	0.1572(4)	0.13863(12)	0.0168(14)	0.0136(11)	0.0184(11)	-0.0036(8)	0.0017(9)	-0.0006(10)	0.0165(7)
Si(2)	100	0.7839(3)	0.1566(4)	0.13679(12)	0.0149(15)	0.0154(12)	0.0186(11)	-0.0028(8)	0.0054(8)	-0.0007(10)	0.0160(6)
O(1)	100	0.2142(9)	0.1550(13)	0.0605(3)	0.032(4)	0.041(4)	0.028(3)	-0.001(3)	-0.009(3)	-0.012(3)	0.0358(17)
O(2)	100	0.8390(10)	0.1507(13)	0.0585(3)	0.044(4)	0.042(4)	0.026(3)	0.002(3)	0.018(3)	0.010(3)	0.0359(17)
O(3)	100	0.3374(9)	0.3969(11)	0.1853(3)	0.021(3)	0.015(3)	0.039(3)	-0.009(2)	0.011(3)	-0.002(3)	0.0240(14)
O(4)	100	0.8454(9)	0.3963(11)	0.1823(3)	0.020(3)	0.016(3)	0.045(4)	-0.014(3)	0.006(3)	-0.004(3)	0.0268(14)
O(5)	100	0.3381(9)	0.9276(10)	0.1904(3)	0.024(3)	0.015(3)	0.022(3)	-0.000(2)	0.001(3)	-0.002(3)	0.0207(13)
O(6)	100	0.8518(9)	0.9301(10)	0.1895(3)	0.024(3)	0.014(3)	0.022(3)	0.000(2)	0.005(3)	0.001(3)	0.0201(13)
O(7)	100	0.5574(9)	0.1518(15)	0.1193(4)	0.018(3)	0.067(5)	0.052(4)	-0.005(4)	0.010(3)	0.001(4)	0.0451(18)
**$X^O_M(OH)_{0.77}F_{0.23}$	100	0.0307(12)	0.6954(12)	0.0618(3)	0.034(4)	0.049(4)	0.023(3)	-0.004(3)	0.004(3)	-0.001(4)	0.0354(16)
**$X^O_A(H_2O)_{0.75}F_{0.25}$	100	0.5290(14)	0.6581(13)	0.0616(4)	0.064(5)	0.051(4)	0.031(3)	-0.016(3)	0.005(4)	-0.000(5)	0.0494(19)
H(1)	77	–0.016(8)	0.62(2)	0.015(3)	0.04248						
H(2)	75	0.429(5)	0.755(17)	0.034(6)	0.05929						
H(3)	75	0.629(6)	0.703(7)	0.037(3)	0.05929						
H(4)	75	0.812(4)	0.584(9)	0.0442(17)	0.01659						
H(5)	75	0.640(4)	0.446(8)	0.016(2)	0.01659						
Subsidiary peaks											
1	<1	–0.017(6)	0.654(8)	–0.031(2)	0.02						
2	2	0.606(5)	0.661(7)	0.2139(17)	0.02						
3	<1	0.890(12)	0.158(12)	0.135(4)	0.02						

* U_{iso} for H atoms; U_{iso} = 0.02 Å^2 (fixed) for subsidiary peaks;

** $M^O(2)$ and $M^O(3)$ refined as O + Na and O + Ca, respectively; $Ca_{0.24} = Ca_{0.16}Al_{0.05}Mn_{0.02}Fe^{2+}_{0.01}$; X^O_M and X^O_A refined as O + F.

TABLE 6. Interatomic distances (Å) and angles (°) for mosandrite.

Si(1)–O(5)a	1.607(6)		Si(2)–O(4)	1.597(6)
Si(1)–O(1)	1.619(6)		Si(2)–O(2)	1.610(6)
Si(1)–O(3)	1.627(6)		Si(2)–O(6)a	1.628(6)
Si(1)–O(7)	1.646(7)		Si(2)–O(7)	1.648(7)
<Si(1)–O>	1.625		<Si(2)–O>	1.621
Si(1)–O(7)–Si(2)	156.2(5)			
Si(1)–O(7)–Si(2)*	203.8(5)			
M$^{\mathrm{H}}$–O(6)b	2.337(6)		A^{P}–X$^{\mathrm{O}}_{\mathrm{A}}$	2.379(7)
M$^{\mathrm{H}}$–O(5)	2.348(6)		A^{P}–O(4)	2.402(7)
M$^{\mathrm{H}}$–O(4)b	2.356(7)		A^{P}–O(6)	2.421(6)
M$^{\mathrm{H}}$–O(3)	2.365(6)		A^{P}–O(3)	2.422(7)
M$^{\mathrm{H}}$-X$^{\mathrm{O}}_{\mathrm{M}}$	2.401(6)		A^{P}–O(5)	2.432(7)
M$^{\mathrm{H}}$–O(6)c	2.533(5)		A^{P}–O(5)c	2.542(5)
M$^{\mathrm{H}}$–O(4)d	2.651(7)		A^{P}–O(3)d	2.624(6)
<M$^{\mathrm{H}}$–φ**>	2.427		<A^{P}-φ>	2.460
M$^{\mathrm{O}}$(1)–O(1)	1.963(6)	×2	M$^{\mathrm{O}}$(3)–O(1)e	2.282(8)
M$^{\mathrm{O}}$(1)–O(2)b	1.966(6)	×2	M$^{\mathrm{O}}$(3)–O(2)	2.285(8)
M$^{\mathrm{O}}$(1)–X$^{\mathrm{O}}_{\mathrm{M}}$	2.053(7)	×2	M$^{\mathrm{O}}$(3)–X$^{\mathrm{O}}_{\mathrm{A}}$	2.341(10)
<M$^{\mathrm{O}}$(1)–φ>	1.994		M$^{\mathrm{O}}$(3)–X$^{\mathrm{O}}_{\mathrm{A}}$ e	2.355(10)
			M$^{\mathrm{O}}$(3)–X$^{\mathrm{O}}_{\mathrm{M}}$ f	2.431(8)
M$^{\mathrm{O}}$(2)–X$^{\mathrm{O}}_{\mathrm{A}}$	2.229(7)	×2	M$^{\mathrm{O}}$(3)–X$^{\mathrm{O}}_{\mathrm{M}}$ e	2.441(9)
M$^{\mathrm{O}}$(2)–O(7)	2.349(7)	×2	<M$^{\mathrm{O}}$(3)–φ>	2.355
M$^{\mathrm{O}}$(2)–O(2)	2.675(7)	×2		
M$^{\mathrm{O}}$(2)–O(1)	2.737(7)	×2		
<M$^{\mathrm{O}}$(2)–φ>	2.498			

* 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*.

cation ($^{[7]}$r = 1.38 Å) which substitutes for Ca. The <M$^{\mathrm{H}}$–φ> distance of 2.427 Å is shorter than the <A^{P}–φ> distance of 2.460 Å (where φ = unspecified anion) (Table 6) and the scattering at the A^{P} site is lower than that at the M^{H} site, and hence we assign the smaller (compared to REE^{3+} and Ca) Zr to the M^{H} site and the larger ($^{[7]}$r = 1.38 Å) and lighter (compared to REE^{3+}) Ba to the A^{P} site. We are now left with 2.89 a.p.f.u. to assign to the M^{H} and A^{P} sites. The total refined site-scattering for these sites is 121.4 e.p.f.u. (Table 7). The aggregate site-scattering value calculated from EMPA for (REE^{3+} + Y + Th + Ba + Zr) is 62.99 e.p.f.u. Therefore we must assign 2.89 a.p.f.u. with a scattering curve (s.c.) of (121.4−62.99)/2.89 = 20.21 el. The scattering curve for the cation species to be assigned is ⩾20 el; therefore we must assign Ca (not Na) to the M^{H} and A^{P} sites (Tables 2, 7).

Consider next the [8]-coordinated M^{O}(2) and [6]-coordinated M^{O}(3) sites in the O sheet. In rinkite, these sites are occupied by Na and (NaCa), respectively. In sample 3859, the refined site-scattering at the M^{O}(2) site equals 6.2 e.p.f.u. In accord with the crystal chemistry of rinkite, we assign all available 0.17 Na a.p.f.u. to the M^{O}(2) site, with a calculated site-scattering of 1.87 e.p.f.u. We are left with the site-scattering of 6.2 − 1.87 = 4.33 e.p.f.u. which corresponds to ~0.5 H_2O a.p.f.u. Hence we assign 0.5 H_2O + 0.33 □ + 0.17 Na to the M^{O}(2) site, with a calculated site-scattering of 5.87 e.p.f.u. (Table 7). The refined site-scattering at the M^{O}(3) site is 20.6 e.p.f.u. We assign all Ca [remaining after the (M^{H} + A^{P}) site assignments] and minor Al, Mn and Fe^{2+} to this site, giving 0.47 a.p.f.u., with calculated site-scattering of 9.22 e.p.f.u. (Table 7). The remaining site-scattering of 20.6 − 9.22 = 11.38 e.p.f.u. corresponds to ~1.5 H_2O a.p.f.u. Hence we assign 1.5 H_2O + 0.32 Ca + 0.10 Al + 0.04 Mn + 0.02 Fe^{2+} + 0.02 □ to the M^{O}(3) site, with a

TABLE 7. Refined site-scattering values and assigned site-populations for mosandrite: samples 3589 (this work) and B (Bellezza *et al.*, 2009).

Sample	Site-scattering (e.p.f.u.)	Assigned site-population (a.p.f.u.)	Calculated site-scattering (e.p.f.u.)	<X-φ>*$_{calc.}$ (Å)	<X-φ>$_{obs}$ (Å)
		$^{[6]}M^O(1)$			
3859	22.5(3)	0.87 Ti + 0.09 Nb + 0.04 Zr	24.43	1.993	1.994
B		0.96 Ti + 0.04 Nb	22.76		1.991
		$^{[6]}M^O(2)$			
3859	6.2(2)	0.5 (H_2O) + 0.34 □ + 0.17 Na	5.87	2.551†	2.498
B		0.70 □ + 0.16 Ca + 0.14 Na	6.50		2.480
		$^{[6]}M^O(3)$			
3859	20.6(3)	1.50 (H_2O) + 0.32 Ca + 0.10 Al + 0.04 Mn + 0.02 Fe^{2+} + 0.02 □	21.22	2.372†	2.355
B		1.30 □ + 0.46 Ca + 0.14 Ce + 0.10 Na	18.42		2.352
		$\Sigma[M^O(2) + M^O(3)]$ 3 a.p.f.u.			
3859	26.8	2.00 (H_2O) + 0.36 □ + 0.32 Ca + 0.17 Na + 0.10 Al + 0.04 Mn + 0.02 Fe^{2+}	27.09		
B		2.00 □ + 0.62 Ca + 0.24 Na + 0.14 Ce	24.92		
		$^{[7]}M^H$			
3859	68.4(6)	1.22 Ca + 0.69 *REE*** + 0.09 Zr	68.19	2.424	2.427
B		1.30 Ca + 0.62 Ce + 0.08 Zr	65.16		2.419
		$^{[7]}A^P$			
3859	53.0(4)	1.67 Ca + 0.32 *REE* + 0.01 Ba	52.70	2.437	2.460
B		1.66 Ca + 0.34 Ce	52.92		2.457
		$\Sigma(M^H + A^P)$ 4 a.p.f.u.			
3859	121.4	2.89 Ca + 1.01 *REE* + 0.09 Zr + 0.01 Ba	120.89		
B		2.96 Ca + 0.96 Ce + 0.08 Zr	118.08		
Bond-valence sum (vu)***		**X^O_M**			
3859	0.85	1.54 (OH) + 0.46 F			
B	1.04	1.30 (OH) + 0.70 F			
		X^O_A			
3859	0.50	1.50 (H_2O) + 0.50 F			
B	0.57	0.92 (H_2O) + 0.88 (OH) + 0.20 F			

* ionic radii from Shannon (1976); X = cation; φ = unspecified anion;
** *REE* = 0.02 Dy + 0.03 Gd + 0.02 Sm + 0.14 Nd + 0.04 Pr + 0.39 Ce + 0.18 La + 0.16 Y + 0.03 Th; Σ*REE* = 1.01 a.p.f.u.; scattering curve for REE^{3+} = 58.25 el;
*** bond-valence parameters are from Brown (1981);
† <X–φ>$_{calc.}$: $M^O(2)$ = Na; $M^O(3)$ = Ca.

calculated site-scattering of 21.22 e.p.f.u. (Table 7). Occurrence of H_2O groups at partly occupied alkali-cation sites in the O sheet has been reported for delindeite, ideally $Na_2\square Ba_2Ti_3(Si_2O_7)O_2(OH)_2(H_2O)_2$, a TS-block mineral of Group III (Ti = 3 a.p.f.u.) (Sokolova and Cámara, 2007).

Description of the structure

Fully occupied cation sites

In the O sheet, the $M^O(1)$ site is occupied primarily by Ti with subordinate Nb and minor Zr, and it is coordinated by four O atoms and two (OH,F) anions at the X^O_M site (Fig. 1*d*). The ideal

TABLE 8. Bond-valence values* for mosandrite.

Atom Site occ. (%)	Si(1) 100	Si(2) 100	M^H 100	A^P 100	$M^O(1)$ 100	$M^O(2)$ 17	$M^O(3)$ 24	Σ	$M^O(2)$ 100	$M^O(3)$ 100
O(1)	1.05				$0.64^{\times 2}\downarrow$	$0.02^{\times 2}\downarrow$	0.09	1.80	$0.12^{\times 2}\downarrow$	0.38
O(2)		1.07			$0.64^{\times 2}\downarrow$	$0.02^{\times 2}\downarrow$	0.09	1.82	$0.13^{\times 2}\downarrow$	0.38
O(3)	1.01		0.38	0.33 0.21				1.93		
O(4)		1.03	0.38 0.20	0.35				1.96		
O(5)	0.99		0.40	0.32 0.25				1.96		
O(6)		0.98	0.40 0.25	0.33				1.96		
O(7)	0.94	0.93				$0.04^{\times 2}\downarrow$		1.91	$0.26^{\times 2}\downarrow$	
X^O_M			0.35 $\underline{0.27}$		$0.51^{\times 2}\downarrow$ $\underline{0.38^{\times 2}\downarrow}$		0.06 0.06 $\underline{0.05}$ $\underline{0.05}$	0.98 $\underline{0.75}$		0.27 0.26 $\underline{0.22}$ $\underline{0.22}$
X^O_A				0.35 $\underline{0.28}$		$0.05^{\times 2}\downarrow$ $\underline{0.03^{\times 2}\downarrow}$	0.07 0.07 $\underline{0.08}$ $\underline{0.06}$	0.54 $\underline{0.45}$	$0.29^{\times 2}\downarrow$ $\underline{0.19^{\times 2}\downarrow}$	0.33 0.32 $\underline{0.28}$ $\underline{0.27}$
Total	3.99	4.01	2.36 $\underline{2.28}$	2.14 $\underline{2.07}$	3.58 $\underline{3.32}$	0.26 $\underline{0.22}$	0.44 $\underline{0.42}$		1.60 $\underline{1.40}$	1.94 $\underline{1.75}$
Aggregate charge	4.00	4.00	2.25	2.25	4.09	0.16	0.42		1.00	2.00

* bond-valence parameters (vu) are from Brown (1981); bond-valence values for cations at the M^H, A^P, $M^O(1)$, $M^O(2)$ and $M^O(3)$ sites calculated for the following composition: $M^H = A^P = Ca_{0.75}REE_{0.25}$; $M^O(1)$ = Ti, $M^O(2)$ = Na (17%-occupancy) and $M^O(3)$ = Ca (24%-occupancy); underlined values calculated using cation-F parameters.

composition of the $M^O(1)$ site is Ti a.p.f.u. The longest bond is from the $M^O(1)$ cation to the X^O_M anion, $M^O(1)–X^O_M$ = 2.053 Å. The mean observed bond-length $< M^O(1)–\varphi>$ of 1.994 Å (Table 6) is in good agreement with the calculated value of 1.993 Å (Table 7).

In the H sheet, there are two tetrahedrally coordinated *Si*(1,2) sites occupied by Si and two [7]-coordinated sites, M^H and A^P, occupied by Ca and *REE* (from here on *REE* include REE^{3+} + Y + Th) approximately in the ratio 3:1 (Tables 5, 7). 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 an X^O_A anion (Table 6, Fig. 1*e*). The shortest A^P-anion bond-length $A^P–X^O_A$ equals 2.379 Å (Table 6). The total of the M^H and A^P cations is 2.89 Ca + 1.01 *REE* + 0.09 Zr + 0.01 Ba (Table 7), and the two H sheets give $(Ca_3REE)Si_4$ (8 a.p.f.u.).

Mixed H_2O-alkali-cation sites

In the O sheet, there are two $M^O(2)$ and $M^O(3)$ sites occupied by H_2O groups, alkali cations, mainly Na and Ca, and vacancy (□). The $M^O(2)$ site is occupied mainly by an H_2O group (50%), vacancy (33%) and minor Na (17%) (Table 7), ideally $[(H_2O)_{0.5}\square_{0.5}]$ p.f.u. Where the $M^O(2)$ site is occupied by Na, it is [8]-coordinated by six O and two F (= X^O_A) atoms, with $<M^O(2)–\varphi>$ = 2.498 Å (Table 6, Fig. 1*d*). The $M^O(3)$ site is occupied mainly by H_2O (75%), cations: Ca, Al, Mn, Fe^{2+} (24%) and minor □ (1%) (Table 7), ideally $[(H_2O)_{1.5}Ca_{0.5}]$ p.f.u. Where the $M^O(2)$ site is occupied by cations (mainly Ca), it is coordinated by two O atoms, two F atoms at the X^O_A site and two F atoms at the X^O_M site, with $<M^O(3)–\varphi>$ = 2.355 Å (Table 6). The H_2O-dominant $M^O(2)$ and $M^O(3)$ sites of the O sheet ideally sum to $[(H_2O)_{0.5}\square_{0.5}] + [(H_2O)_{1.5}Ca_{0.5}] = [(H_2O)_2Ca_{0.5}\square_{0.5}]$ p.f.u. with a total charge of 1^+.

Further details for the $M^{O}(2,3)$ sites will be given in the section on *Short-range order*.

The $M^{O}(1-3)$ sites of the O sheet give $[(H_2O)_2Ca_{0.5}\square_{0.5}]Ti$ (4 a.p.f.u.). We sum five fully occupied cation sites and two mixed H_2O-alkali-cation sites to give $[(H_2O)_2Ca_{0.5}\square_{0.5}]Ti$ (O sheet) + $(Ca_3\mathit{REE})Si_4$ (2H sheets) = $(Ca_3\mathit{REE})[(H_2O)_2Ca_{0.5}\square_{0.5}]TiSi_4$ p.f.u., with a total charge of 30^+ and a total number of cations of 9.5 a.p.f.u. In rinkite, the total number of cations is ideally 12 a.p.f.u.: $(Ca_3\mathit{REE})Na(NaCa)TiSi_4$, with a total charge of 33^+.

Anion considerations: long-range order

We assign O atoms to the O(1−7) sites that constitute tetrahedral coordination of the *Si*(1) and *Si*(2) sites; for the O(1−7) atoms, bond-valence values vary from 1.79 to 1.96 vu (Table 8). Anions at the X^{O}_{M} and X^{O}_{A} sites receive bond valences from four cations: X^{O}_{M} from $M^{O}(1)$ (100%-occupancy), $2M^{O}(3)$ (24%-occupancy), and M^{H} (100%-occupancy), and X^{O}_{A} from $M^{O}(2)$ (17%-occupancy), $2M^{O}(3)$ (24%-occupancy), and A^{P} (100%-occupancy), respectively (Tables 7, 8). We expect the X^{O}_{M} atom to receive a higher bond-valence as it is bonded to Ti at the $M^{O}(1)$ site, and the X^{O}_{A} atom, a lower bond-valence as it is bonded to Na at the $M^{O}(2)$ site. Calculation of bond-valence sums at the X^{O}_{M} and X^{O}_{A} anions using cation-oxygen and cation-fluorine parameters gave 0.98 and 0.75 vu for the X^{O}_{M} anion and 0.54 and 0.45 vu for the X^{O}_{A} anion (Table 8). We conclude that the X^{O}_{M} and X^{O}_{A} sites are mainly occupied by monovalent anions (OH and F) and H_2O groups, respectively. For final assignment of anion species to the X^{O}_{M} and X^{O}_{A} sites, we need to consider bond-valence contributions from the two $M^{O}(2,3)$ mixed H_2O-alkali-cation sites. Table 8 gives bond-valence contributions from Na and Ca at the $M^{O}(2,3)$ sites where they are 100% occupied. There is a better agreement between total and aggregate charges for the $M^{O}(2)$ site where the Na−F bond-valence parameters are used, and it seems reasonable to assume that where the $M^{O}(2)$ site is occupied by Na, the adjacent X^{O}_{A} site must be occupied by F. Final assignment of anions to the $X^{O}_{(A,M)}$ sites will be considered in the section *Anion considerations: short-range order*

Short-range order

For a better understanding of the role of the mixed H_2O-alkali-cation sites in the O sheet, we need to consider two short-range order (SRO) models for the $M^{O}(2,3)$ and $X^{O}_{(A,M)}$ sites.

SRO-1

Consider the $M^{O}(2)$ and $M^{O}(3)$ sites where they are fully occupied by Na and Ca, respectively, and the $X^{O}_{(A,M)}$ sites are occupied by F (Fig. 1*d*–*f*). SRO-1 arrangement involves M^{H} and A^{P} atoms [100%], Na at the $M^{O}(2)$ site [17%] and Ca at the $M^{O}(3)$ site [24%]. Note that this SRO arrangement occurs when all constituent cation sites (next-nearest-neighbours) are fully occupied, i.e. at 17%. Table 9 gives bond-valence sums of 2.13−2.22 vu for the O atoms at the O(1,2,7) sites and 1.09 and 1.02 vu for F atoms at the X^{O}_{M} and X^{O}_{A} sites. The SRO-1 arrangement is in close agreement with the crystal structure of rinkite (Fig. 1*a*–*c*) except for different chemical composition of the $M^{O}(3)$ and X^{O}_{M} sites: $M^{O}(3)$ = Ca_2 (mosandrite) and (NaCa) (rinkite); X^{O}_{M} = F_2 (mosandrite) and (OF) (rinkite) (Table 1).

SRO-2

Consider the $M^{O}(2)$ and $M^{O}(3)$ sites where they are occupied by H_2O groups. The SRO-2 arrangement involves M^{H} and A^{P} atoms [100%] and H_2O at the $M^{O}(2)$ [50%] and $M^{O}(3)$ [75%] sites (Fig. 1*g*–*i*). We were able to locate H atoms of H_2O groups at the $M^{O}(3)$ [H(4,5)] and

TABLE 9. Bond-valence values* for the local arrangement of cations in mosandrite where $M^{O}(2)$ = Na, $M^{O}(3)$ = Ca, X^{O}_{M} = X^{O}_{A} = F.

Atom	Σ_1**	$M^{O}(2)$	$M^{O}(3)$	Σ_2***
O(1)	1.69	$0.12^{\times 2}\downarrow$	0.38	2.19
O(2)	1.71	$0.13^{\times 2}\downarrow$	0.38	2.22
O(7)	1.87	$0.26^{\times 2}\downarrow$		2.13
X^{O}_{M}	0.65		0.22 0.22	1.09
X^{O}_{A}	0.28	$0.19^{\times 2}\downarrow$	0.28 0.27	1.02
Total		1.40	1.75	
Aggregate charge		1.00	2.00	

* bond-valence parameters (vu) are from Brown (1981);
** Σ_1 = sum of bond-valences received from Si(1,2), M^{H}, A^{P} and $M^{O}(1)$;
*** $\Sigma_2 = \Sigma_1$ + bond valence from $M^{O}(2)$ and $M^{O}(3)$ (Fig. 1*d,e,f*).

TABLE 10. Hydrogen bonding in mosandrite.

D–H···A	D–H (Å)	H···A (Å)	D···A (Å)	ĞDHA (°)
X^O_M OH–H(1)···X^O_M a OH	0.983(2)	2.26(6)	3.16(1)	152(11)
X^O_M OH–H(1)···M^O(3)b H_2O	0.983(2)	1.82(3)	2.431(8)	117(3)
X^O_A H_2O–H(2)···O(2)c	0.981(2)	2.43(6)	3.35(1)	158(11)
X^O_A H_2O–H(2)···M^O(2)d H_2O	0.980(2)	1.65(6)	2.229(7)	114(5)
X^O_A H_2O–H(3)···M^O(3) H_2O	0.980(2)	1.68(3)	2.36(1)	122(3)
X^O_A H_2O–H(3)···O(1)c	0.980(2)	2.48(3)	3.42(1)	160(5)
M^O(3) H_2O–H(4)···X^O_M e OH	0.980(2)	1.71(3)	2.431(8)	128(3)
M^O(3) H_2O–H(5)···X^O_A H_2O	0.980(2)	1.75(4)	2.36(1)	116(3)
Possible hydrogen bonding				
M^O(3) H_2O–H(5)···X^O_A c H_2O	0.980(2)		2.34(1)	
M^O(2) H_2O···O(7) OH			2.349(7)	
M^O(2) H_2O···O(2) OH			2.675(7)	
M^O(2) H_2O···O(1) OH			2.737(7)	

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*.

X^O_A sites [H(2,3)] and an OH group at the X^O_M site [H(1)] (Table 5), and details of hydrogen bonding are given in Table 10. Figure 2 shows the net of hydrogen bonds in the O sheet of mosandrite; it involves H_2O groups at the M^O(2,3) and X^O_A sites, an OH group at the X^O_M site and O atoms at the O(1,2) sites which belong to the Ti-dominant M^O(1) octahedra and

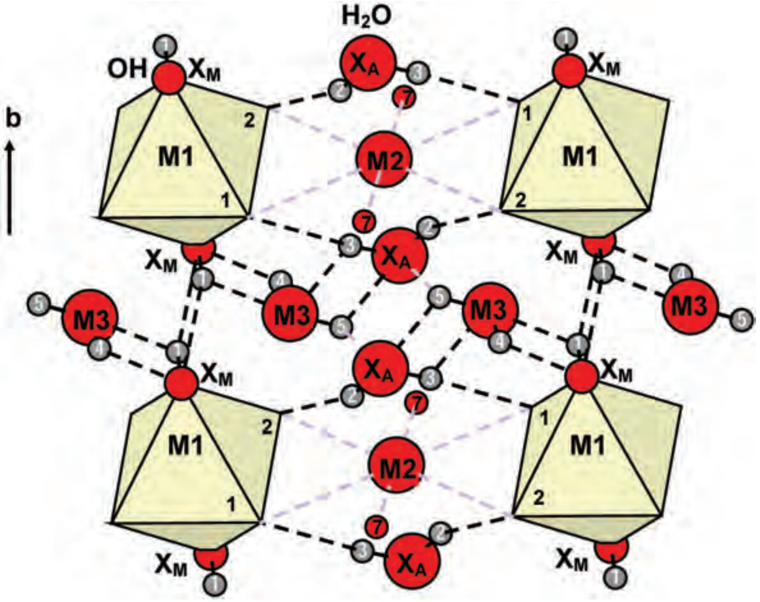

FIG. 2. A fragment of the SRO-2 arrangement in mosandrite. Ti-dominant M^O(1) octahedra are yellow; O atom of H_2O groups at the M^O(2), M^O(3) and X^O_A sites are shown as large red spheres; O atom of an OH group at the X^O_M site is shown as a medium red sphere; H atoms are shown as small grey spheres; bonds O (D)–H are shown as solid black lines; hydrogen bonds H···O (A) are shown as dashed black lines; dashed lilac lines show the positions of possible hydrogen bonds; the O(7) atom is shown as a small red sphere labelled 7, numbers 1 and 2 on yellow show the positions of the O(1) and O(2) atoms, acceptors of hydrogen bonds.

the O(7) atom. In the O sheet, the $\mathrm{M^O}(1)$ octahedra and H_2O groups connect *via* hydrogen bonds (Fig. 1*g*). The $\mathrm{M^H}$ atom is coordinated by six O atoms and an OH ($\mathrm{X_M^O}$) group, and the A^P atom is coordinated by six O atoms and an H_2O ($\mathrm{X_A^O}$) group (Fig. 1*h*). Hence the number of cations in the 2H and the O sheet is in the ratio 4:1 (Fig. 1*i*) (cf. 4:4 in rinkite). The SRO-2 arrangement occurs when all constituent sites (next-nearest-neighbours) are fully occupied, i.e. at 50%. Table 11 gives reasonable bond-valence sums of 1.75–1.87 vu for the O atoms at the O(1,2,7) sites; 1.69 and 1.89 vu for O atoms at the $X_{\mathrm{M}}^{\mathrm{O}}$ and $X_{\mathrm{A}}^{\mathrm{O}}$ sites; 1.98 vu for the O atom of an H_2O group at the $M^{\mathrm{O}}(3)$ site and 0.25 vu for the O atom of an H_2O group at the $M^{\mathrm{O}}(2)$ site. We were not able to locate H atoms (50% occupancy) of the H_2O group at the $M^{\mathrm{O}}(2)$ site and, hence, cannot account for possible bond-valence contributions from H atoms to the O atom at the $M^{\mathrm{O}}(2)$ site and the O(1,2,7) atoms [see Table 10 for three possible D–A (donor-acceptor) distances involving an O atom at the $M^{\mathrm{O}}(2)$ site].

Anion considerations: short-range order

In accord with their bond-valence sums (Table 8), the $X_{\mathrm{M}}^{\mathrm{O}}$ and $X_{\mathrm{A}}^{\mathrm{O}}$ sites are occupied mainly by monovalent anions (OH and F) and H_2O groups, respectively (Table 8). Hence the $X_{\mathrm{A}}^{\mathrm{O}}$ site must be occupied mainly by H_2O groups. Within the SRO-1 arrangement, the $\mathrm{X_A^O}$ anion receives 0.28 vu [A^P, 100%-occupancy] + 0.19 [$\mathrm{M^O}(2)$ = Na, 17%] + (0.28+ 0.27) [$\mathrm{M^O}(3) = \mathrm{Ca_2}$, 24%] = 1.02 vu (Table 9). What maximal amount of F shall we assign to the $X_{\mathrm{A}}^{\mathrm{O}}$ site, 17 or 24%? The two local arrangements: (17%) [A^P, $\mathrm{M^O}(2)$ = Na, $\mathrm{M^O}(3) = \mathrm{Ca_2}$] and (24%) [$\mathrm{A}^P$, $\mathrm{M^O}(2)$ = Na or □, $\mathrm{M^O}(3) = \mathrm{Ca_2}$] contribute 1.02 and 1.02–0.83 vu to the $\mathrm{X_A^O}$ anion (Table 9), sufficient for the F atom. Hence we assign ~25% F + 75% H_2O to the $X_{\mathrm{A}}^{\mathrm{O}}$ site: $[(H_2O)_{1.50}F_{0.50}]$, ideally $(H_2O)_2$ p.f.u.

The $X_{\mathrm{M}}^{\mathrm{O}}$ site must be occupied by monovalent anions (Table 8, see discussion above). Chemical analysis gives 0.96 F a.p.f.u. and we assign the remaining 0.46 F a.p.f.u. to the $X_{\mathrm{M}}^{\mathrm{O}}$ site: $[(OH)_{1.54}F_{0.46}]$, ideally $(OH)_2$ p.f.u. Ideally, the $X_{\mathrm{M}}^{\mathrm{O}}$ and $X_{\mathrm{A}}^{\mathrm{O}}$ sites sum to $[(OH)_2(H_2O)_2]$ p.f.u.

The anions sum as follows: O_{14} [O(1–7)] + $[(OH)_2(H_2O)_2]$ [$\mathrm{X_M^O}$ and $\mathrm{X_A^O}$] = $O_{14}(OH)_2(H_2O)_2$ p.f.u., with a total charge of 30^-. We write the ideal formula of mosandrite as the sum of cation and anion components: $(\mathrm{Ca_3}\mathit{REE})[(H_2O)_2\mathrm{Ca_{0.5}\square_{0.5}}]\mathrm{TiSi_4}$ + $O_{14}(OH)_2(H_2O)_2$ = $(\mathrm{Ca_3}\mathit{REE})[(H_2O)_2\mathrm{Ca_{0.5}\square_{0.5}}]\mathrm{Ti(Si_2O_7)_2(OH)_2(H_2O)_2}$, $Z = 2$, Σanions = 20 a.p.f.u., H_2O = 4 p.f.u., OH = 2 p.f.u.

Structure topology of mosandrite

The crystal structure of mosandrite is a framework of TS (titanium silicate) blocks that consist of HOH sheets. The $\mathrm{M^H}$ and A^P polyhedra and Si_2O_7 groups constitute the H sheet that is completely ordered. In the O sheet, $\mathrm{M^O}(1)$ octahedra are long-

TABLE 11. Bond-valence values* for the local arrangement of H_2O groups in mosandrite where $\mathrm{M^O}(2) = \mathrm{M^O}(3) = H_2O$, $\mathrm{X_M^O}$ = OH, $\mathrm{X_A^O} = H_2O$.

Atom	Σ_1**	H(1)	H(2)	H(3)	H(4)	H(5)	Σ_2***
O(1)	1.69			0.06			1.75
O(2)	1.71		0.06				1.77
O(7)	1.87						1.87
$\mathrm{X_M^O}$	0.65	0.74 0.08			0.22		1.69
$\mathrm{X_A^O}$	0.28		0.69	0.71		0.21	1.89
$\mathrm{M^O}(2)$			0.25				0.25
$\mathrm{M^O}(3)$		0.18		0.23	0.78	0.79	1.98
Total		1.00	1.00	1.00	1.00	1.00	

* bond-valence parameters (vu) are from Brown (1981) and, for hydrogen bonding, from Brown and Altermatt (1985);

** Σ_1 = sum of bond-valences received from Si(1,2), $\mathrm{M^H}$, A^P and $\mathrm{M^O}(1)$;

*** $\Sigma_2 = \Sigma_1$ + bond-valences from H(1–5) (Fig. 2).

range ordered whereas H_2O and OH groups and alkali cations Na and Ca are long-range disordered. Figure 3 shows general views of the crystal structure of mosandrite in accord with the short-range order arrangements of atoms at the $M^O(2)$, $M^O(3)$, X^O_M and X^O_A sites in the O sheet.

SRO-1 occurs where the $M^O(2)$ and $M^O(3)$ sites are fully occupied by Na and Ca, respectively, and the $X^O_{(A,M)}$ sites are occupied by F (Fig. 3*a*). The trioctahedral O sheet is composed of Ti-dominant $M^O(1)$ octahedra, [8]-coordinated $M^O(2)$ polyhedra occupied by Na, and $M^O(3)$ octahedra occupied mainly by Ca. The H sheet is built of Si_2O_7 groups and [7]-coordinated M^H and A^P polyhedra occupied by Ca and *REE* in the ratio ~ 3:1 Here, the TS block exhibits linkage and stereochemistry typical of Group I (Ti = 1 a.p.f.u.) of the 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.

SRO-2 occurs where the $M^O(2)$ and $M^O(3)$ sites are fully occupied by H_2O groups and the X^O_M and X^O_A sites are occupied by OH and H_2O groups, respectively (Fig. 3*b*). The O sheet is composed of Ti-dominant $M^O(1)$ octahedra connected by hydrogen bonding via H_2O groups. The H sheet is built of Si_2O_7 groups and [7]-coordinated M^H and A^P polyhedra occupied by Ca and *REE* in the ratio ~ 3:1 as with SRO-1. Linkage of H and O sheets occurs mainly *via* common vertices of M^H polyhedra and Si_2O_7 groups and $M^O(1)$ octahedra. We suggest that in the crystal structure of mosandrite (1) the SRO-2 atom arrangement is dominant as H_2O groups are the dominant species at the $M^O(2)$ and $M^O(3)$ sites in the O sheet and (2) SRO-1 atom arrangements occur as islands in a continuous matrix of SRO-2 atom arrangement.

Summary

Here, we give answers to three questions that we posed at the beginning of this paper.

(1) Do H_2O groups occur at the alkali-cation sites with partial occupancy and what is a dominant species in the O sheet?

Structure-refinement results testify to the occurrence of H_2O groups at the $M^O(2)$ and $M^O(3)$ sites; H_2O is the dominant species in the O sheet which has the ideal composition $[(H_2O)_2Ca_{0.5}\square_{0.5}]Ti$ p.f.u.

Mosandrite has a rinkite-type structure. The M^H and A^P polyhedra and Si_2O_7 groups constitute the H sheet that is completely ordered. In the O sheet, $M^O(1)$ octahedra are long-range ordered whereas H_2O and OH groups and alkali cations Na and Ca are long-range disordered. Two SRO

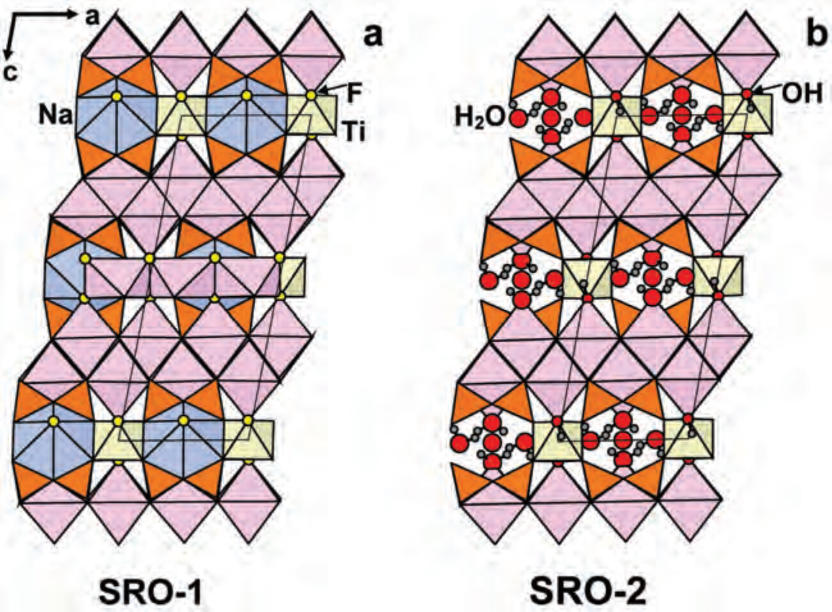

FIG. 3. General view of the crystal structure of mosandrite projected on (010): (*a*) SRO-1; (*b*) SRO-2. Legend as in Fig. 1.

(short-range order) arrangements have been considered for the O sheet.

(2) What is the chemical formula of mosandrite ($Z = 2$), and how many anions does it contain?

The empirical and ideal chemical formulae of mosandrite, $[(\mathrm{Ca}_{2.89}\mathrm{Ba}_{0.01})_{\Sigma 2.90}(\mathrm{Ce}_{0.39}\mathrm{La}_{0.18}\mathrm{Nd}_{0.14}\mathrm{Sm}_{0.02}\mathrm{Gd}_{0.03}\mathrm{Y}_{0.16}\mathrm{Th}_{0.03})_{\Sigma 1.01}\mathrm{Zr}_{0.09}]_{\Sigma 4}[(\mathrm{H_2O})_{2.00}\mathrm{Ca}_{0.32}\mathrm{Na}_{0.17}\mathrm{Al}_{0.10}\mathrm{Mn}_{0.04}\mathrm{Fe}^{2+}_{0.02}\square_{0.35}]_{\Sigma 3}(\mathrm{Ti}_{0.87}\mathrm{Nb}_{0.09}\mathrm{Zr}_{0.04})_{\Sigma 1}(\mathrm{Si_2O_7})_2[(\mathrm{OH})_{1.54}(\mathrm{H_2O})_{1.50}\mathrm{F}_{0.96}]_{\Sigma 4}$[3.50 H_2O, 1.54 OH, 8.54 H^+ p.f.u.] and $(\mathrm{Ca}_3\mathit{REE})[(\mathrm{H_2O})_2\mathrm{Ca}_{0.5}\square_{0.5}]\mathrm{Ti}(\mathrm{Si_2O_7})_2(\mathrm{OH})_2(\mathrm{H_2O})_2$[4 H_2O, 2 OH, 10 H^+ p.f.u.], contain 20 anions.

Comparison of the empirical formula of mosandrite from this work with those of Bellezza *et al.* (2009): $(\mathrm{Ca}_{2.80}\mathit{REE}_{0.85}\mathrm{Y}_{0.21}\mathrm{Zr}_{0.10}\mathrm{Th}_{0.04})_{\Sigma 4}(\square_{1.65}\mathrm{Ca}_{0.90}\mathrm{Na}_{0.29}\mathrm{Mn}_{0.07}\mathrm{Al}_{0.06}\mathrm{Fe}_{0.03})_{\Sigma 3}(\mathrm{Ti}_{0.93}\mathrm{Nb}_{0.08})_{\Sigma 1.01}(\mathrm{Si_2O_7})_2[(\mathrm{OH})_{3.01}\mathrm{F}_{0.92}]_{\Sigma 3.93}\cdot 2\mathrm{H_2O}$ [2 H_2O, 3.01OH, 7.01 H^+ p.f.u., Σanions = 20 a.p.f.u.] and Brögger (1890): $(\mathrm{Ca}_{2.90}\mathrm{Ce}^{3+}_{0.85}\mathrm{Y}_{0.24}\mathrm{Th}_{0.01})_{\Sigma 4}(\square_{2.04}\mathrm{Na}_{0.62}\mathrm{Ca}_{0.24}\mathrm{Mn}_{0.05}\mathrm{Fe}_{0.05})_{\Sigma 3}(\mathrm{Ti}_{0.52}\mathrm{Zr}_{0.47})_{\Sigma 1.01}(\mathrm{Si_2O_7})_2\mathrm{O}_{4.34}\mathrm{F}_{0.85}\mathrm{H}^+_{6.69}$ [2 H_2O, 3.01 OH, 6.69 H^+ p.f.u., Σanions = 19.19 a.p.f.u.] indicate that the sample 3859 (this work) has the smallest Na content and the largest H_2O content (Table 2).

(3) What is the relation between mosandrite and rinkite?

Mosandrite, ideally $(\mathrm{Ca}_3\mathit{REE})[(\mathrm{H_2O})_2\mathrm{Ca}_{0.5}\square_{0.5}]\mathrm{Ti}(\mathrm{Si_2O_7})_2(\mathrm{OH})_2(\mathrm{H_2O})_2$, is an H_2O- and OH-bearing Na- and Ca-depleted analogue of rinkite, ideally $(\mathrm{Ca}_3\mathit{REE})\mathrm{Na}(\mathrm{NaCa})\mathrm{Ti}(\mathrm{Si_2O_7})_2(\mathrm{OF})\mathrm{F}_2$.

Mosandrite and rinkite are related by the following substitution at the $M^{\mathrm{O}}(2,3)$ and $X^{\mathrm{O}}_{(\mathrm{M,A})}$ sites in the O sheet:

$$
{}^{M}[(\mathrm{H_2O})_2 + \square_{0.5}] + {}^{X}[(\mathrm{OH})_2^- + (\mathrm{H_2O})_2] \leftrightarrow
{}^{M}[\mathrm{Na}_2^+ + \mathrm{Ca}^{2+}_{0.5}] + {}^{X}[(\mathrm{OF})^{3-} + (\mathrm{F}_2)^{2-}].
$$

It seems likely that mosandrite is a product of alteration of rinkite, in accord with Slepnev (1957), but the rarity of mosandrite and lack of textural context do not allow elucidation of any detail of this process.

Acknowledgements

We thank reviewer Fernando Cámara and two anonymous reviewers for their comments that helped to improve the manuscript; we also thank Structures Editor Peter Leverett and Principal Editor Peter Williams for their input. We thank Renato and Adriana Pagano for mosandrite sample 3859 from their mineral collection (Collezione Mineralogica). This work was supported by a Canada Research Chair in Crystallography and Mineralogy and by a Discovery Grant from the Natural Sciences and Engineering Research Council of Canada to FCH, and by Innovation Grants from the Canada Foundation for Innovation to FCH.

References

Back, M.E. and Mandarino, J.A. (2008) *Fleischer's Glossary of Mineral Species 2008*. The Mineralogical Record Inc., Tucson.

Bellezza, M., Franzini, M., Larsen, A.O., Merlino, S. and Perchiazzi, N. (2004) Grenmarite, a new member of the götzenite-seidozerite-rosenbuschite group from the Langesundsfjord district, Norway: definition and crystal structure. *European Journal of Mineralogy*, **16**, 971−978.

Bellezza, M., Merlino, S. and Perchiazzi, N. (2009) Mozandrite, structural and crystal-chemical relationships with rinkite. *The Canadian Mineralogist*, **47**, 897−908.

Brögger, W.C. (1890) Die miniralien der syenitpegmatitgänge der südnorwegischen augit- und nephelinsienite. *Zeitschrift für Kristallographie und Mineralogie*, **16**, 74−94.

Brown, I.D. (1981) The bond-valence method: an empirical approach to chemical structure and bonding. Pp. 1−30 in: *Structure and Bonding in Crystals II* (M. O'Keeffe and A. Navrotsky, editors). Academic Press, New York.

Brown, I.D. and Altermatt, D. (1985) Bond-valence parameters obtained from a systematic analysis of the inorganic crystal structure database. *Acta Crystallographica*, **B41**, 244−247.

Cámara, F., Sokolova, E. and Hawthorne, F.C. (2011) From structure topology to chemical composition. XII. Titanium silicates: the crystal chemistry of rinkite, $\mathrm{Na_2Ca_4}\mathit{REE}\mathrm{Ti}\ (\mathrm{Si_2O_7})_2\mathrm{OF_3}$. *Mineralogical Magazine*, **75**, 2755−2774.

Christiansen, C.C. and Rønsbo, J.G. (2000) On the structural relationship between götzenite and rinkite. *Neues Jahrbuch für Mineralogie Monatshefte*, 496−506.

Christiansen, C.C., Johnsen, O. and Makovicky, E. (2003*a*) Crystal chemistry of the rosenbuschite group. *The Canadian Mineralogist*, **41**, 1203−1224.

Christiansen, C.C., Gault, R.A., Grice, J.D. and Johnsen, O. (2003*b*) Kochite, a new member of the rosenbuschite group from the Werner Bjerge alkaline complex, East Greenland. *European Journal of Mineralogy*, **15**, 551−554.

Fleischer, M. (1958) Rinkite, johnstrupite, lovchorrite and calcium rinkite (all = mosandrite). *American Mineralogist*, **43**, 795−796.

Galli, E. and Alberti, A. (1971) The crystal structure of rinkite. *Acta Crystallographica*, **B27**, 1277−1284.

Lorenzen, J. (1884) Untersuchung einiger Mineralien aus Kangerdluarsuk in Grönland. *Zeitschrift für Kristallographie*, **9**, 243−254.

Pouchou, J.L. and Pichoir, F. (1985) "PAP" φ(ρ) procedure for improved quantitative microanalysis. Pp. 104−106 in: *Microbeam Analysis* (J.T. Armstrong, editor). San Francisco Press, San Francisco, California, USA.

Shannon, R.D. (1976) Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta Crystallographica*, **A32**, 751−767.

Sheldrick, G.M. (2008) A short history of SHELX. *Acta Crystallographica*, **A64**, 112−122.

Slepnev, Yu.S. (1957) On the minerals of the rinkite group. *Izvestiya Akademii Nauk SSSR, Seriya Geologicheskaya*, **N3**, 63−75 (in Russian).

Sokolova, E. (2006) From structure topology to chemical composition. I. Structural hierarchy and stereochemistry in titanium disilicate minerals. *The Canadian Mineralogist*, **44**, 1273−1330.

Sokolova, E. and Cámara, F. (2007) From structure topology to chemical composition. II. Titanium silicates: revision of the crystal structure and chemical formula of delindeite. *The Canadian Mineralogist*, **45**, 1247−1261.

Sokolova, E. and Cámara, F. (2008) From structure topology to chemical composition. VIII. Titanium silicates: the crystal structure and crystal chemistry of mosandrite from type locality of Låven (Skådön), Langesundsfjorden, Larvik, Vestfold, Norway. *Mineralogical Magazine*, **72**, 887−897.

Sokolova, E. and Hawthorne, F.C. (2008) From structure topology to chemical composition. V. Titanium silicates: crystal chemistry of nacareniobsite-(Ce). *The Canadian Mineralogist*, **46**, 1333−1342.

Wilson, A.J.C. (editor) (1992) *International Tables for Crystallography. Volume C: Mathematical, Physical and Chemical Tables*. Kluwer Academic Publishers, Dordrecht, The Netherlands.