MOSANDRITE: STRUCTURAL AND CRYSTAL-CHEMICAL RELATIONSHIPS WITH RINKITE

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ABSTRACT

Mosandrite, $Ti(\square,Ca,Na)_3(Ca,REE)_4(Si_2O_7)_2[H_2O,OH,F]_4 \bullet \sim 1 \ H_2O$, is a distinct mineral species in the rinkite group. Chemical (EPM data), TG–DSC studies and structural investigations indicate that mosandrite presents a particular chemical composition (low Ca, Na and F contents, high amount of H_2O), unit-cell parameters (a 7.398, b 5.595, c 18.662 Å, β 101.37°, V 757.29 Å^3; space-group symmetry $P2_1/c$; Z = 2), and a rinkite-type structure characterized by a low occupancy of the $M(2)$ and $M(3)$ sites.

Keywords: mosandrite, rinkite group, Låven Island, Norway.

SOMMAIRE

La mosandrite, $Ti(\square,Ca,Na)_3(Ca,REE)_4(Si_2O_7)_2[H_2O,OH,F]_4 \bullet \sim 1 \ H_2O$, est une espèce minérale distincte dans le groupe de la rinkite. Les données chimiques (analyses avec une microsonde électronique), des études par thermogravimétrie et calorimérie différentielle à balayage, et une caractérisation de sa structure démontrent que la mosandrite présente une composition chimique particulière (faibles teneurs en Ca, Na et F, teneur élevée en H_2O), des paramètres réticulaires distincts (a 7.398, b 5.595, c 18.662 Å, β 101.37°, V 757.29 Å^3; groupe spatial $P2_1/c$; Z = 2), et une structure de type rinkite ayant un faible taux d'occupation des sites $M(2)$ et $M(3)$.

(Traduit par la Rédaction)

Mots-clés: mosandrite, groupe de la rinkite, île de Låven, Norvège.

INTRODUCTION

Mosandrite was introduced as a new mineral species from Låven, Langesundfjord, Norway, by Axel Joakim Erdmann, as reported by Berzelius (1841); Erdmann had found lanthanum in it and therefore gave that name to the mineral species to honor Carl Gustaf Mosander (1797–1858), who had discovered the new element in 1839. A very thorough description was given by Brøgger (1890), together with the results of a wet-chemical analysis performed by H. Bäckström, an analysis carried out, as was stressed by Brøgger himself, on fresh and translucent material, carefully selected and purified (Brøgger 1890). It seems proper to recall that in the same paper, Brøgger (1890) described also the related mineral "johnstrupite" from Barkevik, Langesundfjord, Norway.

Mosandrite, rinkite (Lorenzen 1884, Galli & Alberti 1971) and nacareniobsite-(Ce) (Petersen *et al.* 1989,

Sokolova & Hawthorne 2008) are closely related Na–Ca–REE–Ti–Nb silicates, originally described from the nepheline syenites in Langesundsfjord (Norway), Ilímaussaq (Greenland), and Khibina (Russia).

Slepnev (1957) placed the earlier-described minerals rinkite, "johnstrupite", rinkolite and lovchorrite (Bonshtedt 1926) into one mineral group, the rinkite group: mosandrite, having a distinctly higher H_2O and lower Na content than the other minerals, was described as a Na-leached, hydrated product of alteration of the minerals belonging to the rinkite group. This definition has also been used by Semenov (1969), whereas Fleischer (1958, 1987), reviewing Slepnev's study, suggested to drop the names rinkite, rinkolite, lovchorrite and "johnstrupite" in favor of mosandrite. Petersen *et al.* (1989) also used the distinction made by Slepnev (1957), and their observation on the alteration of nacareniobsite-(Ce) supported this point of view. In the latest edition of Fleischer's Glossary of Mineral Species

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(Back & Mandarino 2008), mosandrite and rinkite are listed as separate species. Strunz & Nickel (2001) in the *Mineralogical Tables* and Gaines *et al.* (1997) in *Dana's New Mineralogy* have dropped rinkite in favor of mosandrite, whereas Anthony *et al.* (1995) in the *Handbook of Mineralogy* include rinkite but not mosandrite. The official list of the Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association (IMA–CNMNC) presents mosandrite as a valid, "grandfathered" (G) species, with the same composition, $Na_2Ca_4REETi(Si_2O_7)_2OF_3$, as rinkite, listed as a questionable (Q) species.

The previous structural studies on the minerals of the rinkite group have been listed and thoroughly compared and discussed by Sokolova & Cámara (2008) in their study of a specimen of "mosandrite" from Låven (on loan from the American Museum of Natural History, New York, USA). The chemical and structural data presented by Sokolova & Cámara (2008) point to the identity of "mosandrite" and rinkite.

The mosandrite crystals examined in the present study, obtained through the kindness of G. Raade, Museum of Natural History of the University of Oslo, also come from the nepheline syenite pegmatites on Låven Island, in Langesundsfjord district, the type locality. There, mosandrite occurs as lath-shaped, translucent crystals, in association with aegirine, nepheline, sodalite, annite, catapleiite, astrophyllite, rosenbuschite, låvenite, leucophanite, analcime and fluorite. However, in our case, the results are quite different from those of Sokolova & Cámara (2008). The aim of the present work is actually to definitively show that mosandrite is a separate species, to indicate what makes it unique, and to discuss its relationships with rinkite (and related minerals), through combined powder and single-crystal X-ray diffraction (XRD) studies, SEM–EDAX observations and electron-probe micro-analyses.

Experimental

Chemical analyses

A large crystal of mosandrite was selected for qualitative chemical analyses, performed using SEM–EDS

equipment, in order to verify the homogeneity of the material and to find out the components to be determined in the subsequent quantitative chemical investigation. Images obtained with back-scattered electrons showed that the crystal of mosandrite is strikingly homogeneous (Fig. 1): thus there is no indication of mosandrite being derived by hydrothermal leaching of Na and Ca at the expense of a primary rinkite phase, as maintained by Slepnev (1957) and Petersen *et al.* (1989). It is proper to recall that in addition to fresh and unaltered specimens of mosandrite, heavily altered specimens do occur, as was first noticed by Brøgger (1890) and confirmed by Raade (1967), who found "ramsayite" (the presently accepted correct name is lorenzenite) among the products of alteration.

Quantitative chemical analyses were done on a large fragment of mosandrite in wavelength-dispersive (WDS) mode by means of a JEOL JXA–8600 electron microprobe. The operating voltage was 15 kV, the beam current was 20 nA, and the beam diameter was 20 μm. We used the standards kaersutite (Si$K\alpha$, Ca$K\alpha$, Fe$K\alpha$, Al$K\alpha$), albite (Na$K\alpha$), ilmenite (Ti$K\alpha$), monazite (Ce$L\alpha$, La$L\alpha$, Pr$L\beta$, Nd$L\beta$), REE1 [glasses of Drake & Weill (1972); Gd$L\beta$], REE2 [glasses of Drake & Weill (1972); Sm$L\beta$, Yb$L\alpha$], REE4 [glasses of Drake & Weill (1972); Dy$L\beta$, Er$L\beta$], bustamite (Mn$K\alpha$), cubic zirconia (Zr$K\alpha$, Y$K\alpha$), sanidine (K$K\alpha$), metal Nb (Nb$K\alpha$), metal Th (Th$K\alpha$), tugtupite (Cl$K\alpha$) and fluorite (F$K\alpha$).

Notwithstanding the high number of measured components, the analyses show a low total, close to 90 wt.%; in view of the indications from the literature [H. Bäckström in Brøgger (1890)], we hypothesized a high content of H_2O. We therefore carried out a simultaneous TG–DSC run on Netzsch 449C thermoanalyzer (inert atmosphere with N_2 flow of 30 mL/min, heating rate 10 °C/min, analysis range 20–1000°C) connected to a mass spectrometer: the weight loss of H_2O was found to be in the range 7.5–8.0 wt.%. The electron-microprobe data and the H_2O content determined by TG–DSC are reported in Table 1, together with the crystal-chemical content recalculated on the basis of four Si atoms. In Table 1, the analytical data are compared with those reported in Brøgger (1890): apart from a noteworthy
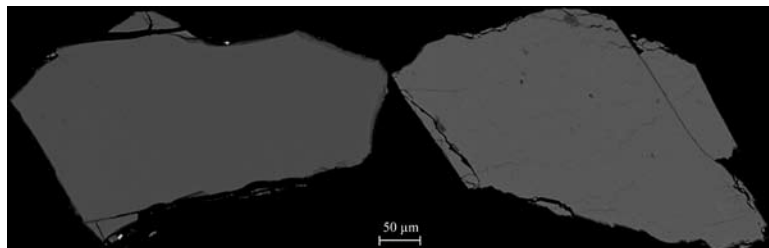

Fig. 1. Back-scattered electron images of mosandrite from Langesundsfjord, collected with SEM–EDAX equipment.

difference in the ZrO_2 content, there is a substantial agreement between the two sets of data, in particular with regards to the very low sodium and fluorine contents, the relatively low calcium content and the high amount of H_2O, which seem to be characteristic features of the composition of mosandrite. The total obtained in the present work is relatively low, as commonly is the case for minerals belonging to this group (Petersen *et al.* 1989) and to the related götzenite – seidozerite – rosenbushite group (Christiansen *et al.* 2003, Bellezza *et al.* 2004). The empirical formula obtained from these data, assuming a content of ~3.5 molecules of H_2O in the unit formula, corresponds to the lower value in the range indicated in the present work but higher than that resulting from the analysis of Bäckström (Brøgger 1890), is $(Ti_{0.93}Nb_{0.08})_{\Sigma1.01}$ $(\square_{1.65}Ca_{0.90}Na_{0.29}$ $Mn_{0.07}Al_{0.06}Fe_{0.03})_{\Sigma3.00}$ $(Ca_{2.80}REE_{0.85}Y_{0.21}Zr_{0.10}$ $Th_{0.04})_{\Sigma4.0}$ $(Si_2O_7)_2[(OH)_{3.01}F_{0.92}]_{\Sigma3.93}\bullet2H_2O$, which may be expressed in a simplified form as $Ti(\square,Ca,Na)_3(Ca,REE)_4$ $(Si_2O_7)_2(OH,F)_4\bullet\sim2H_2O$, where REE includes not only the rare-earth elements but also Y.

X-ray crystallography

Single-crystal rotation and Weissenberg photographs of mosandrite show that the mineral is monoclinic, space group $P2_1/c$, with cell parameters corresponding to those of rinkite (Galli & Alberti 1971).

An X-ray powder diffraction pattern made on the type material was published by Sahama & Hytönen (1957) [*cf.* PDF 12–540]. It shows ten reflections; two of the weakest (3.248, 2.611 Å) cannot be indexed on a mosandrite cell and are due to admixed titanite. The remaining reflections have been indexed by G. Raade (pers. commun.), assuming a $P2_1/a$ space-group symmetry, and give the unit cell *a* 18.71, *b* 5.62, *c* 7.43 Å, β 100.9°; the reflections [*d* in Å(I)(*hkl*)] are: 3.561(15)(410), 3.053(100)(21$\overline{2}$), 2.931(15)(31$\overline{2}$), 2.778(10)(120), 2.687(20)(220), 2.296(10)(800), 2.010(15)(52$\overline{2}$), and 1.849(10)(712). The assigned indices correspond to the strongest reflections calculated on the basis of the structural results of Galli & Alberti (1971) for rinkite from Greenland. Other powder data for alleged mosandrite are PDF 31–313 (= PDF 12–582) (actually for rinkite from Greenland) and PDF 45–1422 (sample from Saima, China); both patterns are poorly indexed on triclinic cells.

For the sake of completeness, we collected an X-ray powder-diffraction pattern on mosandrite (Table 2), using a Philips PW1710 diffractometer with a secondary graphite monochromator (Cu*K*α radiation). Data were collected from 5 to 60° 2θ, with steps of 0.02° 2θ and 10 s counting time for each step. The pattern, which was indexed taking into account the single-crystal intensity data (see next paragraphs), is in good agreement with that published by Sahama & Hytönen (1957) and

indexed by G. Raade (pers. commun.), and shows no presence of admixed titanite.

TABLE 1. CHEMICAL COMPOSITION OF MOSANDRITE

	(1) Bäckström in Brøgger (1890)	(2) mean n = 13	(2) range	(2) crystal-chemical content	
SiO_2 wt.%	30.71	28.64	28.10 - 29.03	Si *apfu*	4.00
TiO_2	5.33	8.89	8.42 - 9.53	Ti	0.93
ZrO_2	7.43	1.45	1.05 - 1.78	Zr	0.10
Nb_2O_5	-	1.40	1.32 - 1.52	Nb	0.08
ThO_2	0.34	1.04	0.86 - 1.16	Th	0.04
Al_2O_3	-	0.40	0.22 - 0.68	Al	0.06
CaO	22.53	24.74	23.89 - 25.86	Ca	3.70
MnO	0.45	0.60	0.52 - 0.71	Mn	0.07
MgO	0.63	-	-	Mg	-
FeO	-	0.25	0.19 - 0.35	Fe^{2+}	0.03
Fe_2O_3	0.56	-	-	Fe^{3+}	-
Na_2O	2.44	1.06	0.92 - 1.22	Na	0.29
K_2O	0.38	0.05	0.04 - 0.07	K	0.01
Y_2O_3	3.52	2.82	2.46 - 3.25	Y	0.21
CeO_2	6.34	-	-	Ce^{4+}	-
Ce_2O_3	10.45(*)	8.22	7.91 - 8.56	Ce^{3+}	0.42
La_2O_3	-	3.81	3.52 - 4.39	La	0.20
Pr_2O_3	-	1.19	0.97 - 1.49	Pr	0.06
Nd_2O_3	-	2.13	1.88 - 2.42	Nd	0.11
Sm_2O_3	-	0.28	0.14 - 0.40	Sm	0.01
Gd_2O_3	-	0.31	0.21 - 0.45	Gd	0.01
Dy_2O_3	-	0.32	0.18 - 0.45	Dy	0.01
Er_2O_3	-	0.39	0.19 - 0.56	Er	0.02
Yb_2O_3	-	0.19	0.06 - 0.36	Yb	0.01
F	2.06	2.08	1.69 - 2.40	F	0.92
Cl	-	0.04	0.00 - 0.06	Cl	0.00
Sum	93.17	90.30	88.70 - 90.60		
O = F, Cl	-0.86	- 0.88			
Total	92.31	89.42			
H_2O	7.70	7.50–8.00		H	6.99–7.45
Total incl. H_2O	100.01	96.92 – 97.42			

The H_2O content was measured by means of TG–DSC analysis. The crystal-chemical content, expressed in atoms per formula unit (*apfu*), is recalculated on the basis of 4 Si *apfu*. (*) $(Ce,La,Dy)_2O_3$. (1) Bäckström's analytical data reported in Brøgger (1890); (2) this work.

TABLE 2. X-RAY POWDER-DIFFRACTION DATA FOR MOSANDRITE

I	d_{meas} (Å)	d_{calc} (Å)	h	k	l	I	d_{meas} (Å)	d_{calc} (Å)	h	k	l
25	9.107	9.148	0	0	2	13	2.167	2.168	2	2	1
8	7.220	7.253	1	0	0			2.167	$\overline{2}$	2	3
8	5.343	5.350	0	1	1	10	2.133	2.136	$\overline{2}$	0	6
8	5.182	5.206	1	0	2			2.133	2	0	6
9	4.264	4.267	$\overline{1}$	0	4	8	2.115	2.117	0	1	8
11	4.185	4.190	$\overline{1}$	1	2	10	2.096	2.096	2	2	2
11	4.120	4.123	0	1	3			2.095	$\overline{2}$	2	4
10	3.806	3.809	$\overline{1}$	1	3	7	2.061	2.061	2	0	6
28	3.538	3.541	0	1	4			2.057	1	2	5
11	3.390	3.395	1	1	3	21	2.005	2.006	$\overline{2}$	2	5
19	3.083	3.086	$\overline{2}$	1	1			2.005	2	2	3
100	3.041	3.043	$\overline{2}$	1	2	16	1.994	1.995	2	1	6
30	2.920	2.925	$\overline{2}$	1	3			1.993	$\overline{2}$	1	8
		2.923	2	1	1	10	1.905	1.906	2	2	4
29	2.765	2.765	0	2	1			1.904	$\overline{2}$	2	6
39	2.675	2.675	0	1	6	14	1.848	1.850	$\overline{4}$	0	2
14	2.598	2.603	$\overline{2}$	0	6	15	1.837	1.838	2	1	7
		2.600	2	0	4			1.837	$\overline{2}$	1	9
11	2.555	2.557	2	1	5	18	1.801	1.801	2	2	5
9	2.386	2.387	0	2	4			1.800	$\overline{2}$	2	7
8	2.366	2.368	0	1	7	10	1.698	1.698	2	1	8
12	2.287	2.287	0	0	8			1.697	$\overline{2}$	1	10

A crystal with dimension of $0.25 \times 0.12 \times 0.10$ mm^3 was chosen for the collection of X-ray single-crystal data. The intensity data were collected with a Bruker P4 four-circle diffractometer using MoKα radiation (λ = 0.71073 Å). The measured reflections were corrected for Lorentz, polarization and absorption factors. This last correction was made according to the method of North *et al.* (1968) using 12 reflections automatically selected. The unit-cell parameters were determined by the least-squares method based on the angular parameters of 24 reflections in the range 18° ≤ 2θ ≤ 30°. The structure was refined in space group $P2_1/c$ starting from the atom coordinates reported by Galli & Alberti (1971) for rinkite. Details of the data collection and structure refinement are given in Table 3.

The refinement of the structure was carried out using the SHELXL97 program package (Sheldrick 1997). Initially, the structure was refined assuming isotropic thermal parameters to R = 0.118, thus validating the starting structural model. The distribution of the cations over the five non-equivalent "octahedral" sites, $M(1)$ to $M(5)$, and that of the anions over the two sites, OF(1) and OF(2), not linked to the Si atoms, were established, taking into account the corresponding electron-densities and the bond-valence balance. In assessing the cationic

distribution in the polyhedra, Ce was taken to represent all the rare-earth elements. The occupancies of the cation sites were subsequently refined, whereas those of the two anion sites OF(1) and OF(2) were kept fixed at $F_{0.5}O_{0.5}$ and $O_{1.0}$, respectively. After introduction of the anisotropic thermal parameters, the final cycles of refinement gave a reliability index R = 0.0515 for 1326 reflections with $F_o > 4\sigma(F_o)$. In Table 4, we report the occupancies of the "mixed" cation sites in mosandrite, compared with the corresponding sites in rinkite as given by Galli & Alberti (1971): as can be seen, the $M(2)$ and $M(3)$ sites are mainly vacant in mosandrite, whereas in rinkite, these sites are almost completely occupied by sodium and calcium.

Final positional coordinates of the atoms and their displacement parameters are given in Table 5 and Table 6, respectively. A table of structure factors may be obtained from the Depository of Unpublished Data, on the MAC website [document Mosandrite CM47_897].

DESCRIPTION OF THE STRUCTURE

Mosandrite is a member of the rinkite group, together with rinkite (Galli & Alberti 1971) and nacareniobsite-(Ce) (Sokolova & Hawthorne 2008). Mosandrite displays the same structure-type as rinkite, with vacancies largely dominant at both the $M(2)$ and $M(3)$ sites. The structure type of rinkite has been described by Sokolova & Cámara (2008) in terms of TS (titanium silicate) blocks presenting "a three-layered structure consisting of a central sheet of octahedra (O sheet) and two adjacent heteropolyhedral sheets (H sheets). The O and H sheets link together through common vertices of constituent polyhedra" (Sokolova 2006). Whereas this description is convenient in Sokolova's approach aimed at establishing the general relationships between structure topology and chemical composition in a wide group of titanium disilicate minerals, we do prefer to emphasize the presence, in the compounds with the structure-type of rinkite, besides "octahedral layers"

TABLE 3. CRYSTAL DATA AND REFINEMENT DETAILS FOR MOSANDRITE

Space group	$P2_1/c$	Radiation type (λ)	MoKα (0.71073 Å)
a	7.398(1) Å	Crystal size	0.25 × 0.12 × 0.10 mm^3
b	5.595(1) Å	Scan mode	θ–2θ
c	18.662(2) Å	Scan width	±0.57° (in θ)
β	101.37(1)°	Scan speed	2°/min
V	757.29 Å^3	Range, data coll.	4 – 60.04° (in 2θ)
Z	2		
Reflection ranges		$-10 \le h \le 1, -7 \le k \le 1, -26 \le l \le 26$	
Reflections collected / unique		3404 / 2202	
Reflections observed		1326 with $F_o > 4\sigma F_o$	
Absorption correction		Ψ-scan on 12 reflections	
Absorption coefficient		5.60 mm^{-1}	
Data / restraints / parameters		1326 / 0 / 149	
$R(F)$ [a], $wR(F^2)$ [b], GooF [c]		R_1 = 0.0515; 0.130; 1.009	
Largest residues		1.81, –0.84 e/Å^3	

(a) $R_1 = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$. (b) $wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]]^{1/2}; w = 1/[\sigma^2(F_o^2) + (0.0567Q)^2 + 4.00Q]$, where $Q = [\text{Max }(F_o^2,0) + 2F_c^2]/3$. (c) Goodness of fit = $[\Sigma[w(F_o^2 - F_c^2)^2] / (N - P)]^{1/2}$, where N, P are the numbers of data and parameters.

TABLE 4. WYCKOFF MULTIPLICITY AND OCCUPANCY
FOR THE "MIXED" SITES IN MOSANDRITE AND RINKITE

Site	Wyckoff multiplicity	mosandrite this work	rinkite Galli & Alberti (1971)
$M(1)$	2	$Ti_{0.96}Nb_{0.04}$	$Ti_{0.51}Nb_{0.33}Al_{0.09}Zr_{0.07}$
$M(2)$	2	$\square_{0.70}Na_{0.14}Ca_{0.16}$	$Na_{0.66}Ca_{0.19}\square_{0.13}K_{0.02}$
$M(3)$	4	$\square_{0.65}Na_{0.05}Ca_{0.23}Ce_{0.07}$	$Na_{0.76}Ca_{0.22}K_{0.02}$
$M(4)$	4	$Ca_{0.65}Ce_{0.31}Zr_{0.04}$	$Ca_{0.68}Ce_{0.26}Fe_{0.03}Mg_{0.02}Th_{0.01}$
$M(5)$	4	$Ca_{0.83}Ce_{0.17}$	$Ca_{0.68}Ce_{0.26}Fe_{0.03}Mg_{0.02}Th_{0.01}$

The estimated standard deviations for occupancies in mosandrite are ~0.01 *apfu* for cation sites.

TABLE 5. COORDINATES OF THE BASIS ATOMS IN MOSANDRITE

Site	x	y	z
$M(1)$	0	0	0
$M(2)$	0.5	0	0
$M(3)$	0.7507(4)	0.5013(7)	0.0004(2)
$M(4)$	0.0944(1)	0.6658(2)	0.1925(1)
$M(5)$	0.5973(1)	0.6646(2)	0.1918(1)
Si(1)	0.3504(2)	0.1605(4)	0.1385(1)
Si(2)	0.7837(2)	0.1595(4)	0.1365(1)
O(1)	0.2135(7)	0.1579(12)	0.0611(3)
O(2)	0.8379(7)	0.1504(12)	0.0581(3)
O(3)	0.3369(6)	0.3991(9)	0.1850(3)
O(4)	0.8464(6)	0.3984(9)	0.1817(3)
O(5)	0.3366(6)	0.9326(9)	0.1903(3)
O(6)	0.8521(6)	0.9337(9)	0.1886(3)
O(7)	0.5569(6)	0.1543(14)	0.1189(3)
OF(1)	0.0311(7)	0.6958(11)	0.0623(3)
OF(2)	0.5295(9)	0.6659(13)	0.0611(3)

TABLE 6. DISPLACEMENT PARAMETERS (IN Å^2) FOR MOSANDRITE

Site	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	U_{eq}
M(1)	0.014(1)	0.040(1)	0.015(1)	-0.018(1)	0.004(1)	-0.003(1)	0.023(1)
M(2)	0.024(4)	0.044(6)	0.013(4)	-0.008(5)	0.001(3)	-0.002(5)	0.027(2)
M(3)	0.028(1)	0.021(1)	0.035(2)	0.005(1)	0.007(1)	-0.001(1)	0.028(1)
M(4)	0.015(1)	0.014(1)	0.018(1)	0.001(1)	0.003(1)	0.000(1)	0.016(1)
M(5)	0.015(1)	0.016(1)	0.019(1)	0.002(1)	0.004(1)	0.000(1)	0.016(1)
Si(1)	0.017(1)	0.013(1)	0.012(1)	-0.002(1)	0.001(1)	-0.001(1)	0.014(1)
Si(2)	0.019(1)	0.014(1)	0.010(1)	0.000(1)	0.003(1)	0.000(1)	0.014(1)
O(1)	0.032(2)	0.041(3)	0.017(3)	-0.002(3)	-0.009(2)	-0.011(3)	0.032(1)
O(2)	0.038(3)	0.039(3)	0.017(3)	-0.004(3)	0.0145(2)	0.008(3)	0.030(1)
O(3)	0.027(2)	0.014(3)	0.023(3)	-0.005(2)	0.008(2)	-0.002(2)	0.021(1)
O(4)	0.023(2)	0.018(3)	0.030(3)	-0.009(3)	0.004(2)	0.000(2)	0.024(1)
O(5)	0.027(2)	0.019(3)	0.021(3)	0.002(2)	0.006(2)	-0.001(2)	0.022(1)
O(6)	0.026(2)	0.012(3)	0.020(3)	0.001(2)	0.004(2)	0.002(2)	0.019(1)
O(7)	0.015 (2)	0.065(4)	0.043(3)	-0.006(4)	0.011(2)	-0.003(3)	0.040(2)
OF(1)	0.037(2)	0.050(4)	0.020(3)	0.000(3)	0.006(2)	0.000(3)	0.036(1)
OF(2)	0.069(4)	0.044(4)	0.017(3)	-0.006(3)	0.001(3)	-0.004(4)	0.043(2)

TABLE 7. SELECTED INTERATOMIC DISTANCES (IN Å) FOR THE DIORTHOSILICATE GROUPS IN MOSANDRITE

Si(1)	–	O(1)	1.592(5)	Si(2)	–	O(2)	1.593(5)
	–	O(3)	1.606(6)		–	O(4)	1.600(5)
	–	O(5)	1.616(5)		–	O(6)	1.613(5)
	–	O(7)	1.639(5)		–	O(7)	1.646(5)
<Si(1)	–	O>	1.613	<Si(2)	–	O>	1.613

parallel to (001) with attached disilicate groups, of tobermorite-like layers, a presence already noticed and discussed by Kadiyski *et al.* (2008) in their description of dovyrenite and comparison to rinkite. As represented in Figure 2, drawn with the program ATOMS (Dowty 1995), both types of layers consist of edge-sharing polyhedra, characterized by six-fold to eight-fold coordination, interconnected through corner-sharing to form a framework of polyhedra. A further connection between the two layers is afforded by the disilicate groups.

The main geometrical features of the disilicate groups are given in Table 7. As in rinkite and nacareniobsite-(Ce), the lengths of the bonds between the Si atoms and the bridging oxygen atom, O(7), 1.639 and 1.646 Å, are greater than the other Si–O bonds (from 1.592 up to 1.616 Å). Bond-valence calculations (to be discussed in the following), indicate that in mosandrite, the bridging oxygen atom is overbonded by 0.15 valence units: as is explained in the following, this overbonding is due to the contribution of hydrogen bonds in which the bridging oxygen atom represents the acceptor oxygen.

Bond distances for the five independent cationic sites M(1) to M(5) are given in Table 8. The arrangement of the cationic sites in the two kinds of layer is shown in Figure 3.

The "octahedral layer" [M(1), M(2), M(3) *polyhedra*]

The layers consist of two distinct columns, running along **a**: the first column is composed of regularly alternating M(1) octahedra and eight-fold-coordinated M(2) polyhedra, which are located on inversion centers; the second column contains only M(3) octahedra mutually related by an inversion center. Octahedron M(1), which hosts Ti almost completely (96%), is the smallest one present in the structure, with an average cation–anion distance of 1.991 Å. It is geometrically similar to the corresponding site in the structure of rinkite. Polyhedron M(2) is the largest one in the structure of mosandrite, with an average cation–anion distance of 2.480 Å. It can be described as a hexagonal bipyramid; it is mainly vacant (70%), with minor presence of Ca and Na. Octahedron M(3) is distorted, mainly vacant (65%) with minor presence of Ca, REE and Na (23, 7 and 5%, respectively). The M(2) and M(3) sites are largely occupied by Na and Ca in rinkite (Galli & Alberti 1971), as reported in Table 4.

The tobermorite-like layer [M(4), M(5)]

In the tobermorite-like layer, calcium, with admixed minor REE and very minor Zr, is found to have the sevenfold coordination already described by Hoffmann & Armbruster (1997) and Merlino *et al.* (2000) in their papers on the family and real structures of clinotobermorite, respectively, as consisting of "a pyramidal part on one side and a dome part on the other side joining the equatorial oxygen atoms". Polyhedra M(4) and M(5) alternate along **a**, forming columns of edge-sharing polyhedra. These columns are connected to each other, once more through edge-sharing, along **b**: adjacent columns present the pyramidal apical ligands
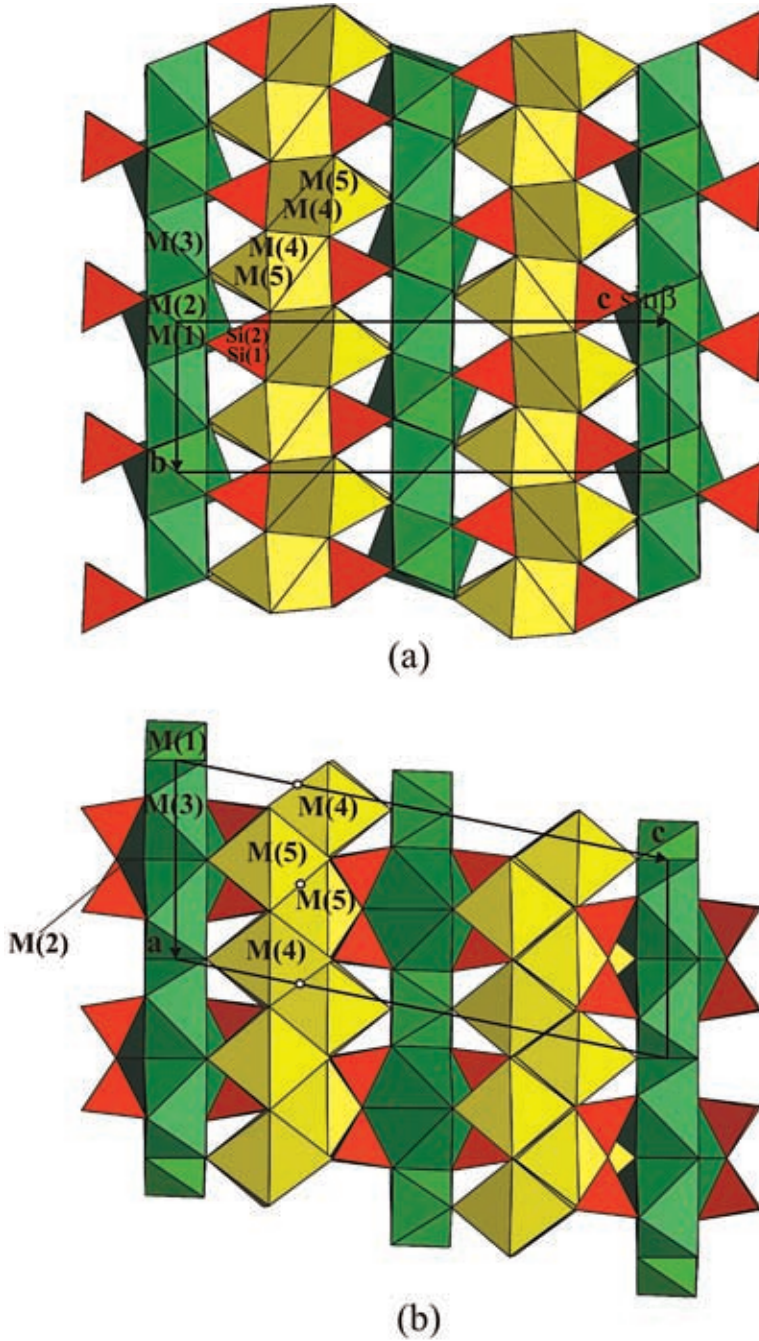
FIG. 2.   Crystal structure of mosandrite: (a) [100] projection; (b) [010] projection.

on opposite sides of the resulting infinite layers parallel to (001). Those apical ligands, OF(1) and OF(2) for M(4) and M(5) polyhedra respectively, are the common corners between the tobermorite-like "layers" and the layers of "octahedra"; unlike the other anionic sites, they present mixed occupancy, which will be evaluated
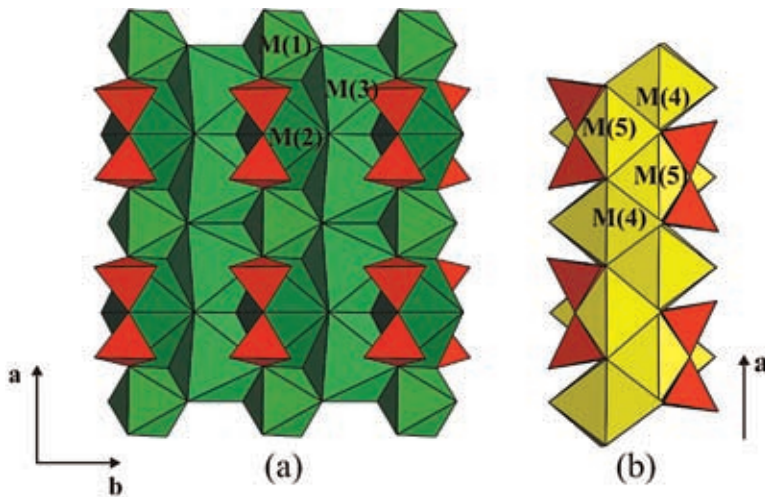
FIG. 3.   (a) The "octahedral layer" of mosandrite, as seen along [001]; (b) the "tober-morite-like layer" as seen along [010].

TABLE 8. SELECTED INTERATOMIC DISTANCES (Å) FOR THE NON-TETRAHEDRAL COORDINATION POLYHEDRA IN THE STRUCTURE OF MOSANDRITE

$M(1)$			$M(2)$		
$(Ti_{0.96}Nb_{0.04})$	$- O(2)^{II}$	1.958(5)	$(\square_{0.70}Na_{0.14}Ca_{0.16})$	$- OF(2)^{V}$	2.178(7)
	$- O(2)^{IV}$	1.958(5)		$- OF(2)^{III}$	2.178(7)
	$- O(1)^{IX}$	1.966(5)		$- O(7)^{IV}$	2.341(6)
	$- O(1)$	1.966(5)		$- O(7)$	2.341(6)
	$- OF(1)^{VI}$	2.049(6)		$- O(2)$	2.658(5)
	$- OF(1)^{III}$	2.049(6)		$- O(2)^{IV}$	2.658(5)
	$<M(1)–O>$	1.991		$- O(1)$	2.743(6)
				$- O(1)^{IV}$	2.743(6)
$M(3)$	$- O(1)^{V}$	2.268(7)		$<M(2)–O>$	2.480
$(\square_{0.65}Na_{0.05}Ca_{0.23}Ce_{0.07})$	$- O(2)$	2.271(7)			
	$- OF(2)$	2.354(7)	$M(4)$		
	$- OF(2)^{V}$	2.356(7)	$(Ca_{0.65}Ce_{0.31}Zr_{0.04})$	$- O(6)^{II}$	2.327(5)
	$- OF(1)^{I}$	2.425(6)		$- O(5)$	2.339(5)
	$- OF(1)^{V}$	2.437(6)		$- O(4)^{II}$	2.345(5)
	$<M(3)–O>$	2.352		$- O(3)$	2.359(5)
				$- OF(1)$	2.387(5)
				$- O(6)^{VII}$	2.535(5)
$M(5)$	$- OF(2)$	2.392(6)		$- O(4)^{VIII}$	2.644(6)
$(Ca_{0.83}Ce_{0.17})$	$- O(4)$	2.406(5)		$<M(4)–O>$	2.419
	$- O(3)$	2.416(5)			
	$- O(6)$	2.422(5)			
	$- O(5)$	2.438(5)			
	$- O(5)^{VIII}$	2.519(5)			
	$- O(3)^{VIII}$	2.608(5)			
	$<M(5)–O>$	2.457			

Operations for generating equivalent atoms are:

I.	$x + 1, y, z$	IV.	$-x + 1, -y, -z$	VII.	$-x + 1, y - ½, -z + ½$
II.	$x - 1, y, z$	V.	$-x + 1, -y + 1, -z$	VIII.	$-x + 1, y + ½, -z + ½$
III.	$x, y - 1, z$	VI.	$-x, -y + 1, -z$	IX.	$-x, -y, -z$

by means of the crystal-chemical modeling discussed in what follows.

The tobermorite-like layer has been found not only in the various minerals of the tobermorite group, clinotobermorite (Merlino *et al.* 2000), tobermorite 11 Å (Merlino *et al.* 2001), tobermorite 14Å (Bonaccorsi

et al. 2005), and in the minerals of the rinkite group, as was first pointed out by Kadiyski *et al.* (2008), but also in dovyrenite (Kadiyski *et al.* 2008), in fukalite (Rastsvetaeva *et al.* 2005; Merlino *et al.* 2009), and in a new mineral from Rouma island, Los Archipelago, Guinea, $(Ca,Na,REE,)_7(Nb,Ti)[Si_2O_7]_2OF_3$ (Biagioni *et*

al., in prep.). This module is quite flexible and allows the entrance in the sevenfold coordinated sites, not only of calcium cations but also trivalent REE cations, as in minerals of the rinkite group and in the synthetic compounds $KNa_2REE_2[Si_6O_{16}(OH)]•3H_2O$ (REE: Eu, Tb, Sm, Ce) (Ferreira *et al.* 2003), as well as Bi^{3+} cations, as in the compound $KNa_3Bi_2Si_6O_{17}•3H_2O$ (Zanardi *et al.* 2006).

Modeling the occupancies in OF(1) and OF(2) sites

Whereas the cationic distribution has been directly derived through the structural refinement, the distribution of H_2O, OH^- and F^- on the "anionic" sites OF(1) and OF(2) has been indirectly derived by means of the following crystal-chemical considerations, based on local charge-balance, coordination of the "anion site" (a four-fold coordination prevents the presence of hydroxyl and H_2O molecules), as well as analytical chemical data for H_2O and fluorine contents.

• Where both $M(2)$ and $M(3)$ sites are vacant (frequency of occurrence ~46%), OF(2) hosts the oxygen atom of a H_2O molecule; the bridging oxygen atoms O(7) of the two Si_2O_7 groups are the very probable acceptors for the hydrogen bonds, with O…O distances of 2.93 and 3.05 Å. At the same time, OF(1) can be occupied by a hydroxyl group, as it does not belong to the Si_2O_7 group, and it is two-fold coordinated.

• Where the $M(2)$ site is vacant and $M(3)$ site is occupied (frequency of occurrence ~25%), OF(2) is occupied by a hydroxyl group; at the same time, the four-fold coordinated OF(1) hosts fluorine anions.

• Where the $M(2)$ site is occupied and $M(3)$ site is vacant (frequency of occurrence ~19%), both OF(1) and OF(2) host hydroxyl groups, as they do not belong to the Si_2O_7 group and present two-fold coordination.

• Where both $M(2)$ and $M(3)$ sites are occupied (frequency of occurrence ~10%), both four-fold coordinated OF(1) and OF(2) sites host fluorine anions.

According to these considerations, the OF(1) site is occupied by $OH_{0.65}F_{0.35}$ [*i.e.,* 0.46 (OH) + 0.25 F + 0.19 (OH) + 0.10 F], and the OF(2) site is occupied by $(H_2O)_{0.46}OH_{0.44}F_{0.10}$ [*i.e.,* 0.46 (H_2O) + 0.25 (OH) + 0.19 (OH) + 0.10 F]. Moreover, for every vacant $M(2)$ site (frequency of occurrence ~71%), the resulting cavity can be occupied by an additional H_2O molecule. The average distance from the center of the cavity is nearly 2.48 Å; however, it is reasonable to hypothesize

that the H_2O molecule is not placed precisely at the cavity center but moved away from it and distributed over a region of space with appropriate distances to the "anion" sites delimiting the cavity.

As regards the atomic quantities indicated in the above cases, it is not our intention to defend the exactness of the proposed values, but it is our belief that the proposed pattern of distribution properly describes the structural setting of mosandrite and convincingly explains the considerable quantity of H_2O molecules present in the structure.

The crystal-chemical formula that results from the structural study is $(Ti_{0.96}Nb_{0.04})_{\Sigma 1}(\square_{2.00}Ca_{0.62}Na_{0.24}REE_{0.14})_{\Sigma 3.0}(Ca_{2.96}REE_{0.96}Zr_{0.08})_{\Sigma 4.0}(Si_2O_7)_2 [(H_2O)_{0.46}(OH)_{1.09}F_{0.45}]_2•0.71 H_2O$ and can be simplified to $Ti(\square,Ca,Na)_3(Ca,REE)_4(Si_2O_7)_2[H_2O,OH,F]_4•~1 H_2O$. The resulting H_2O content, 2.72 molecules per unit formula, is in agreement with that indicated by the wet-chemical analysis of H. Bäckström (Brøgger 1890), although substantially lower than that obtained in the present study.

The significantly lower number of total cations in mosandrite with respect to rinkite, ideally $Ti(Na,Ca)_3(Ca,REE)_4(Si_2O_7)_2OF_3$, is due to a large deficit in Na (and a minor amount of Ca). This deficit and the simultaneous entrance of H_2O molecules correspond to the replacement of Na^+ by H^+ and space-filling H_2O, as demonstrated in steenstrupine by Makovicky & Karup-Møller (1981) and in delindeite by Sokolova & Cámara (2007). This replacement is here accompanied by substitution of fluoride by hydroxyl anions.

The bond-valence summation is presented in Table 9. Bond-valence parameters are taken from Brese & O'Keeffe (1991), whereas the hydrogen-bond contributions [donor OF(2), acceptor O(7)] have been calculated according to Ferraris & Ivaldi (1988), taking into account the distribution of H_2O and OH^- at the OF(2) site. The results are in accordance with the cation distribution determined by the structure refinement, as well as with the "anion" distribution over the two OF(1) and OF(2) sites defined in the crystal-chemical model that we propose.
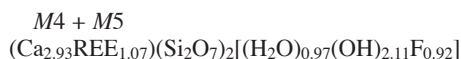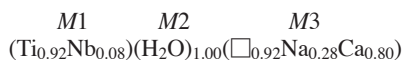
A structural model for mosandrite

The results of the structural study suggest a reliable model for mosandrite. It seems probable that the scattering power at $M(2)$ site may be due to the H_2O molecules that are hosted into the cavity in a relatively disordered way, more than to calcium and sodium cations partially occupying that site. The species distribution on $M(1)$ to $M(5)$ sites in agreement with such a hypothesis and in keeping with the analytical results [omitting the minor components, with the exception of Nb substituting for Ti at the $M(1)$ site], is indicated in the following:

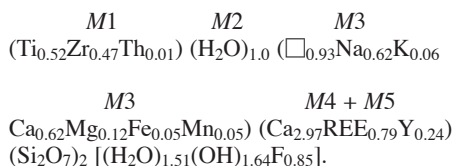TABLE 9. BOND-VALENCE SUMS (IN VALENCE UNITS, *vu*) FOR MOSANDRITE

	O(1)	O(2)	O(3)	O(4)	O(5)	O(6)	O(7)	OF(1)	OF(2)	Σv_a
$M(1)$ $(Ti_{0.96}Nb_{0.04})$	$0.67^{\times 2}$	$0.69^{\times 2}$						$0.51^{\times 2}$		3.74 (4.04)
$M(2)$ $(Na_{0.14}Ca_{0.16}\square_{0.70})$	$0.03^{\times 2}$	$0.03^{\times 2}$					$0.07^{\times 2}$		$0.14^{\times 2}$	0.54 (0.46)
$M(3)$ $(Na_{0.05}Ca_{0.23}Ce_{0.07}\square_{0.65})$	0.17	0.17						0.09 0.09	0.13 0.13	0.78 (0.72)
$M(4)$ $(Ca_{0.65}Ce_{0.31}Zr_{0.04})$			0.42	0.43 0.19	0.44	0.45 0.26		0.35		2.54 (2.39)
$M(5)$ $(Ca_{0.83}Ce_{0.17})$			0.33 0.20	0.34	0.31 0.23	0.32			0.35	2.08 (2.17)
Si(1)	1.09		1.05		1.02		0.96			4.12 (4.00)
Si(2)		1.09		1.07		1.03	0.94			4.13 (4.00)
Σv_H								+0.18	-0.18	
Σv_c	1.97	1.98	2.00	2.03	2.01	2.06	2.15	1.04 0.65 (OH) 0.35 F 0.10 F	0.57 0.46 (H_2O) 0.44 (OH)	

The bond-valence parameters are taken from Brese & O'Keeffe (1991) and from Ferraris & Ivaldi (1988). Right "×2" superscript means that the corresponding bond-valences have been considered twice in the horizontal sums, in keeping with the special positions of the atoms involved. The sums Σv_c and Σv_a give the sum of charges reaching each anion and cation, respectively, together with the values calculated from the occupancies (in parentheses). The sum Σv_H represents the contribution of hydrogen bonds. The last row presents the species distribution in the two OF(1) and OF(2) sites as obtained by the crystal-chemical modeling.

$$M1 \qquad M2 \qquad M3$$
$$(Ti_{0.92}Nb_{0.08})(H_2O)_{1.00}(\square_{0.92}Na_{0.28}Ca_{0.80})$$

$$M4 + M5$$
$$(Ca_{2.93}REE_{1.07})(Si_2O_7)_2[(H_2O)_{0.97}(OH)_{2.11}F_{0.92}]$$

A constrained structural refinement based on this distribution resulted in a reliability index of 0.0522, only slightly higher than that obtained in the unconstrained refinement (0.0515).

With this model, not only a substantially higher amount of H_2O can be hosted in the structural framework, but also the results of the wet-chemical analysis by H. Bäckström (Brøgger 1890) may be perfectly accounted for, as indicated by the following distribution scheme:

$$M1 \qquad M2 \qquad M3$$
$$(Ti_{0.52}Zr_{0.47}Th_{0.01})\ (H_2O)_{1.0}\ (\square_{0.93}Na_{0.62}K_{0.06}$$

$$M3 \qquad\qquad M4 + M5$$
$$Ca_{0.62}Mg_{0.12}Fe_{0.05}Mn_{0.05})\ (Ca_{2.97}REE_{0.79}Y_{0.24})$$
$$(Si_2O_7)_2\ [(H_2O)_{1.51}(OH)_{1.64}F_{0.85}].$$

CONCLUSIONS

Mosandrite, $Ti(\square,Ca,Na)_3(Ca,REE)_4(Si_2O_7)_2$ $[H_2O,OH,F]_4 \cdot 1\ H_2O$, is a mineral species belonging to the rinkite group and differing from rinkite in its chemical, crystallographic and structural features. The chemical composition we have determined is in keeping with that reported by Brøgger (1890) and characterized by a lower Ca content, very low Na and F contents with respect to the chemical composition of rinkite, as well

TABLE 10. CRYSTALLOGRAPHIC PARAMETERS FOR MOSANDRITE, COMPARED WITH THOSE DETERMINED FOR RINKITE, NACARENIOBSITE-(Ce) AND THE "MOSANDRITE" SPECIMEN STUDIED BY SOKOLOVA & CÁMARA

Mineral	a (Å)	b (Å)	c (Å)	β (°)	V (Å³)	Ref.
Rinkite	7.437	5.664	18.843	101.38	778.12	(1)
Nacareniobsite-(Ce)	7.468	5.689	18.891	101.37	786.90	(2)
"Mosandrite"	7.4184	5.6789	18.873	101.41	779.37	(3)
Mosandrite	7.398	5.595	18.662	101.37	757.29	(4)

(1) Galli & Alberti (1971), (2) Sokolova & Hawthorne (2008), (3) Sokolova & Cámara (2008), (4) this paper.

TABLE 11. DISTRIBUTIONS OF CATIONS AND "ANIONS" AMONG THE VARIOUS SITES
IN THE MINERALS OF THE RINKITE GROUP

	$M(1)$	$M(2) + M(3)$	$M(4) + M(5)$	OF(1) + OF(2)	
Ti	$\square_2$(Ca,Na)	Ca$_3$REE	[Si$_2$O$_7$]$_2$	[(OH)$_2$F(H$_2$O)]•1H$_2$O	mosandrite[1]
(Ti,Nb)	Na$_2$(Na,Ca)	Ca$_3$REE	[Si$_2$O$_7$]$_2$	[F$_3$O]	rinkite[2]
Ti	Na$_2$Ca	Ca$_3$REE	[Si$_2$O$_7$]$_2$	[F$_3$O]	"mosandrite" = rinkite[3]
Nb	Na$_3$	Ca$_3$REE	[Si$_2$O$_7$]$_2$	[F$_3$O]	nacareniobsite-(Ce)[4]

[1] This work, [2] Galli & Alberti (1971), [3] Sokolova & Cámara (2008), [4] Sokolova & Hawthorne (2007).

as by a very high amount of H_2O. The unit-cell parameters of mosandrite are here compared (Table 10) with those of rinkite, nacareniobsite-(Ce), the "mosandrite" specimen studied by Sokolova & Cámara (2008): they present significantly lower values with respect to those of the other listed natural phases. The crystal-chemical relationships among the various minerals of the rinkite group are best summarized in Table 11.

All these minerals present a closely similar distribution of cations in the tobermorite-like layer [sites $M(4)$ + $M(5)$]; rinkite and nacareniobsite-(Ce) have filled "octahedral layers" [sites $M(1) + M(2) + M(3)$], the first presenting dominant Ti, the other, dominant Nb at the $M(1)$ site. On the contrary, mosandrite presents largely vacant $M(2)$ and $M(3)$ sites. These cationic vacancies are balanced by the low total charge of the "anions" in the sites OF(1) and OF(2): these sites, which have F_3O stoichiometry in rinkite and nacareniobsite-(Ce), are largely occupied by hydroxyl anions and H_2O molecules, in addition to F^- anions. Finally, in agreement with the high H_2O content revealed by TG analyses, mosandrite contains an additional H_2O molecule, which is placed, according to our model, at the empty $M(2)$ site.

An interesting question is raised by the contrasting results obtained by us and by Sokolova & Cámara (2008). The intricate history of definition, discreditation, and redefinition of mosandrite, recalled in the introduction, as well as its close relationships with the other natural phases of the rinkite group, may possibly explain those contrasting results as due to an erroneously identical labeling of actually different compounds. In any case, the evidence presented in the present work indicates that mosandrite has distinct crystallographic parameters and structural arrangement, and a specific composition, characterized by low Na, F and a high H_2O contents. Those chemical features are not the result of hydrothermal alteration, *i.e.,* of hydration and leaching of Na from a rinkite phase, as there is no evidence of alteration in the material examined.

As a consequence of the results obtained in the present study, rinkite need no longer be considered a questionable (Q) species, but a fully valid member of the rinkite group of minerals, together with mosandrite and nacareniobsite-(Ce).

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