

From structure topology to chemical composition. XII. Titanium silicates: the crystal chemistry of rinkite, $\text{Na}_2\text{Ca}_4\text{REETi}(\text{Si}_2\text{O}_7)_2\text{OF}_3$

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ABSTRACT

Rinkite, ideally $\text{Na}_2\text{Ca}_4\text{REETi}(\text{Si}_2\text{O}_7)_2\text{OF}_3$, is a common mineral in alkaline and peralkaline rocks. The crystal structures of five rinkite crystals from three alkaline massifs: Ilimaussaq, Greenland; Khibiny, Kola Peninsula, Russia and Mont Saint-Hilaire, Canada, have been refined as two components related by the TWIN matrix $(-1\ 0\ 0, 0\ -1\ 0, 1\ 0\ 1)$ (Mo- $K\alpha$ radiation). The crystals, $a = 7.4132-7.4414$, $b = 5.6595-5.6816$, $c = 18.8181-18.9431$ Å, $\beta = 101.353-101.424(2)^\circ$, $V = 776.1-786.7$ Å³, space group $P2_1/c$, $Z = 2$, $D_{\text{calc}} = 3.376-3.502$ g cm⁻³, were analysed using an electron microprobe subsequent to collection of the X-ray intensity data. Transmission electron microscopy confirmed the presence of pseudomorph twinning in rinkite crystals. The crystal structure of rinkite is a framework of TS (titanium silicate) blocks. The TS block consists of HOH sheets (H-heteropolyhedral, O-octahedral). The TS block in rinkite exhibits linkage and stereochemistry typical for Group I (Ti = 1 a.p.f.u.) of Ti disilicate minerals: two H sheets connect to the O sheet such that two (Si₂O₇) groups link to the *trans* edges of a Na polyhedron of the O sheet. The crystal chemistry of rinkite and nacareniobsite-(Ce) is discussed.

KEYWORDS: rinkite, crystal structure, EMP analysis, transmission electron microscopy, chemical formula, Ti disilicate minerals, Group I.

Introduction

RINKITE, ideally $\text{Na}_2\text{Ca}_4\text{REETi}(\text{Si}_2\text{O}_7)_2\text{OF}_3$, is listed as a questionable species in the official IMA list of minerals (<http://pubsites.uws.edu.au/ima-cnmmc/>). The latest structure refinement of rinkite was reported by Sokolova and Cámara

(2008a) under the name mosandrite as they studied a museum specimen labelled mosandrite from its type locality, Låven, Norway. The name rinkite was proposed by Lorenzen (1884) for a mineral found at Kangerdluarssuk, Greenland. The ideal formula for rinkite (see above) is in accord with Sokolova (2006). The name mosandrite was proposed by Erdman in 1841 (reported by Brøgger, 1890) for a mineral from Låven (Skådön), Langesundsfjorden, Larvik, Vestfold, Norway. Taking into account the temporal precedence of mosandrite (1841) over rinkite (1884), Slepnev (1957) recommended discreditation of the name rinkite. Rinkite was not discredited but acquired the status of a questionable species. Bellezza *et al.* (2009) studied the

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crystal structure and chemical composition of mosandrite from the type locality, Låven (Skådön), Langesundsfjorden, Larvik, Vestfold, Norway. They reported a rinkite-type structure and stated that mosandrite differed from rinkite by the presence of ~ 3 a.p.f.u. H_2O and a lower content of Na and Ca, and gave the simplified formula for mosandrite as follows: $Ti(\square, Ca, Na)_3(Ca, REE)_4(Si_2O_7)_2[H_2O, OH, F]_4 \sim 1H_2O$. There is a Nb-analogue of rinkite, nacareniobsite-(Ce), ideally $Na_3(Ca_3REE)Nb(Si_2O_7)_2OF_3$ (Petersen *et al.*, 1989; Sokolova and Hawthorne, 2008b). To summarize, rinkite has been considered a questionable mineral species because (1) mosandrite was described by Erdman in 1841 (reported by Brøgger, 1890) prior to the description of rinkite (Lorenzen, 1884), and (2) from 1890 to 2009 (Bellezza *et al.*, 2009), neither additional chemical nor structural data was reported for mosandrite. All previous structural work has been done on minerals labelled rinkite (see section 'Previous work' below).

Sokolova (2006) established the relation between structure topology and chemical composition for Ti disilicate minerals and divided them into four groups, characterized by different topology and stereochemistry of the titanium silicate (TS) block. Each group of structures has a different linkage of H (heteropolyhedral) and O (octahedral) sheets in the TS block and a different arrangement of Ti (= Ti + Nb) polyhedra. In Groups I, II, III and IV, Ti equals 1, 2, 3 and 4 a.p.f.u., respectively. Each group is defined by the topology, chemical composition and stereochemistry of the TS block. Sokolova (2006) considered rinkite as a mineral of Group I. In Group I, Ti = 1 a.p.f.u. and Ti (or Zr + Ti) occurs in the O sheet: $1 M^O = Ti$, $3 M^O = Na$, Ca and rarely Mn^{2+} ; $^{[6].[7]}M^H = Zr^{4+}$, Ca + REE, Ca, Mn^{2+} ; $A^P = Na$, Ca, Ca + REE. Sokolova (2006) wrote the general formula for minerals of Group I as $A^P_2M_2^H M_4^O(Si_2O_7)_2 X_4^O$ (see Table 1). There are eight minerals with known structures in Group I: götzenite, hainite, seidozerite, grenmarite, rinkite, nacareniobsite-(Ce), kochite and rosenbuschite (Table 1). Rinkite and nacareniobsite-(Ce) are isostructural.

Following Sokolova (2006), we have been investigating the Ti disilicate minerals, and in addition to the minerals mentioned above, we have discovered a new mineral of Group II, câmarait (Sokolova *et al.*, 2009a; Câmara *et al.*, 2009), determined the crystal structures of bornemanite, nechelyustovite, jinshajiangite,

nabalamprophyllite-2O (Câmara and Sokolova, 2007, 2009; Sokolova *et al.*, 2009b; Sokolova and Hawthorne, 2008a) and revised the chemical formula and crystal chemistry of delindeite, barytolamprophyllite and murmanite (Sokolova and Câmara, 2007, 2008b; Câmara *et al.*, 2008).

Although Bellezza *et al.* (2009) stated that the difference between rinkite and mosandrite involves the presence of H_2O and lower contents of Na and Ca in the latter, the former still remains a questionable species in the official IMA list of minerals. Here, we present new data on the chemical composition and crystal chemistry of rinkite, a TS-block mineral of Group I, that confirm it as a valid mineral species.

Previous work

The first structure determination of type rinkite from Kangerdluarssuk, Greenland, was done in triclinic symmetry, $a = 18.9$, $b = 7.47$, $c = 5.68$ Å, $\alpha \approx \gamma \approx 90$, $\beta = 101.3^\circ$, space group $P\bar{1}$, by Kheirov *et al.* (1963) who reported a reasonable basic structure and discussed its similarity to seidozerite (for ideal formula and references for the structures of Group I, see Table 1). Tê-yü *et al.* (1965) described the structure of type rinkite from Kangerdluarssuk, Greenland, as monoclinic based on the cell parameters of Kheirov *et al.* (1963) but with $\beta \sim 90^\circ$, space group $P2_1$, and emphasized the similarity of the topology of the rinkite structure to the structures of seidozerite and rosenbuschite (Table 1). Simonov and Belov (1968) used the atom coordinates of Tê-yü *et al.* (1965) to refine the crystal structure of rinkite with the monoclinic unit-cell parameters $a = 18.60$, $b = 7.421$, $c = 5.636$ Å, $\beta = 101.3^\circ$, $V = 762.9$ Å³, space group $P2_1$. They gave the formula of rinkite as $Na_2Ca(Ca, Ce)_4(Ti, Nb)(Si_2O_7)_2(O, F)_2F_2$, discussed the crystal chemistry of rinkite, compared it to seidozerite and defined a seidozerite–rinkite group. Galli and Alberti (1971) refined rinkite from Kangerdluarssuk, Greenland: $a = 7.437$, $b = 5.664$, $c = 18.843$ Å, $\beta = 101.38^\circ$, $V = 778.11$ Å³, space group $P2_1/c$, $Z = 2$, $D_{calc.} = 3.45$ g cm⁻³, with an approximate formula $(Ti, Nb, Al, Zr)(Na, Ca)_3(Ca, Ce)_4(Si_2O_7)_2(O, F)_4$. Rastsvetaeva *et al.* (1991) refined rinkite from the Khibiny massif, Kola Peninsula, Russia: $a = 5.679$, $b = 7.412$, $c = 18.835$ Å, $\alpha = 101.26^\circ$, $V = 777.6$ Å³, space group $P2_1$, $Z = 2$, $D_{calc.} = 3.36$ g cm⁻³, with the structural formula $\{TiF(O, F)[Si_2O_7]_2\}\{Na(Na, Ca)_2F(O, F)\}\{(Ca, TR)_4\}$. Galli and

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

| Mineral | Structural formula | <i>a</i> (Å) | <i>b</i> (Å) | <i>c</i> (Å) | $\alpha(^{\circ})$ | $\beta(^{\circ})$ | $\gamma(^{\circ})$ | Sp. gr. | Z | Ref. |
|---------------------|---|--------------|--------------|--------------|--------------------|-------------------|--------------------|-----------------------------------|---|------|
| Rinkite | $A^P_2 M^H_1$ (Ca ₃ REE) | 7.4184 | 5.6789 | 18.873 | | 101.410 | | <i>P2</i> ₁ / <i>c</i> | 2 | (1) |
| Nacareniobsite-(Ce) | M^O_4 Na(NaCa) | 7.468 | 5.689 | 18.891 | | 101.37 | | <i>P2</i> ₁ / <i>c</i> | 2 | (2) |
| Seidozerite | Na ₂ Zr ₂ | 5.5558 | 7.0752 | 18.406 | | 102.713 | | <i>P2</i> ₁ / <i>c</i> | 2 | (3) |
| Grenmarite | Na ₂ Zr ₂ | 5.608 | 7.139 | 18.575 | | 102.60 | | <i>P2</i> ₁ / <i>c</i> | 2 | (4) |
| Götzenite | Ca ₂ Ca ₂ | 9.6192 | 5.7249 | 7.3307 | 89.981 | 101.132 | 100.639 | <i>P</i> $\bar{1}$ | 1 | (5) |
| Haimite | [Ca ₃ (Y,REE)] | 9.6079 | 5.7135 | 7.3198 | 89.916 | 101.077 | 100.828 | <i>P</i> $\bar{1}$ | 1 | (6) |
| Kochite | Ca ₂ MnZr | 10.032 | 11.333 | 7.202 | 90.192 | 100.334 | 111.551 | <i>P</i> $\bar{1}$ | 2 | (7) |
| Rosenbuschite | Ca ₄ Ca ₂ Zr ₂ | 10.137 | 11.398 | 7.2717 | 90.216 | 100.308 | 111.868 | <i>P</i> $\bar{1}$ | 1 | (8) |
| Mosandrite** | Ti(□,Ca,Na) ₃ (Ca,REE) ₄ (Si ₂ O ₇) ₂ [H ₂ O,OH,F] ₄ ~1H ₂ O | 7.398 | 5.595 | 18.662 | | 101.37 | | <i>P2</i> ₁ / <i>c</i> | 2 | (9) |

The ideal structural formulae (except for mosandrite) are written in the form $A^P_2 M^H_1 M^O_4$ (Si₂O₇)₂ X₄ in accord with Sokolova (2006); M^H = cations of the H sheet; M^O = cations of the O sheet; X₄ = anions of the O sheet, A^P = cations at the peripheral (P) sites.

**For mosandrite, a simplified formula is given; it is not possible to write a structural formula for mosandrite as its simplified formula does not give the stoichiometry for the main cations and anions.
References (the latest reference on the structure is the first entry in the numbered list of references): (1) Sokolova and Cámara (2008a); Rastsvetaeva *et al.* (1991), Simonov and Belov (1968), Tê-yü *et al.* (1965), Kheirov *et al.* (1963); (2) Sokolova and Hawthorne (2008b); (3) Christiansen *et al.* (2003a), Pushcharovskii *et al.* (2002), Simonov and Belov (1966), Skszat and Simonov (1966); (4) Bellezza *et al.* (2004); (5) Christiansen *et al.* (2003a), Camillo *et al.* (1972); (6) Christiansen *et al.* (2003a), Rastsvetaeva *et al.* (1995); (7) Christiansen *et al.* (2003b); (8) Christiansen *et al.* (2003a), Shibaeva *et al.* (1964); (9) Bellezza *et al.* (2009).

Alberti (1971) stated that their results were in good agreement with the structure of Simonov and Belov (1968). Rastsvetaeva *et al.* (1991) stated that the lower symmetry of rinkite from Khibiny is due to the order of REEs and Ca and concluded that their model is in good agreement with all previous work. Christiansen *et al.* (1999) and Christiansen and Rønsbo (2000) analysed the structural relation between götzenite [$\text{Ca}_2\text{Ca}_2\text{NaCa}_2\text{Ti}(\text{Si}_2\text{O}_7)_2\text{OF}_3$, space group $P\bar{1}$; Table 1] and rinkite and stated that the models of Rastsvetaeva *et al.* (1991) and Galli and Alberti (1971) are the same except for the lower symmetry of the first due to minor ordering of some cations. As noted above, the latest structure refinement of rinkite was done by Sokolova and Cámara (2008a) and is in good agreement with the work of Galli and Alberti (1971).

Experimental details

Description of samples

We studied five samples of rinkite from alkaline rocks (Table 3): two samples, 1991c and 2909, came from Kangerdluarssuk, Greenland, Denmark, where rinkite was originally described by Lorenzen (1884); two samples, YuksFe and 3471, are from the Khibiny massif, Kola Peninsula, Russia, and sample H-08-02 is from Mont Saint-Hilaire, Quebec, Canada. Four samples were on loan from private collections and YuksFe was on loan from the Fersman Mineralogical Museum, Moscow, Russia. All samples were labelled *mosandrite*.

Crystal selection was difficult due to pseudo-hedral twinning. Rinkite crystals are yellow, milky on the surface and slightly more transparent inside, and have a flat-prismatic habit. Crystals from Mont Saint-Hilaire, Quebec, occur as sprays of laths within cavities. The single crystals of rinkite used in this work are of good optical quality.

Chemical analysis

Single crystals of rinkite previously used for structure analysis were analysed using a Cameca SX-100 electron microprobe operating in wavelength-dispersive 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 2 and 10 s, respectively. The following standards, spectral lines and analyzing crystals were used: F: fluororiebeckite (topaz for

1991c) (F- $K\alpha$; LTAP); Na: albite (Na- $K\alpha$, TAP); Al: andalusite (Al- $K\alpha$, LTAP); Si, Ca: diopside (Si- $K\alpha$, TAP; Ca- $K\alpha$, LPET); Nb: $\text{Ba}_2\text{NaNb}_5\text{O}_{15}$ (Nb- $L\alpha$, LPET); Fe: fayalite (Fe- $K\alpha$, LLIF); Pb: PbTe (Pb- $M\alpha$, LPET); Mn: spessartine (Mn- $K\alpha$, LLIF); Mg: forsterite (Mg- $K\alpha$, LTAP); Zr: zircon (Zr- $L\alpha$, LPET); Zn: gahnite (Zn- $K\alpha$, LLIF); Ce: CePO_4 (Ce- $L\alpha$, LLIF); La: LaPO_4 (La- $L\alpha$, LLIF); Nd: NdPO_4 (Nd- $L\beta$, LLIF); Pr: PrPO_4 (Pr- $M\beta$, LLIF); Sm: SmPO_4 (Sm- $M\beta$, LLIF); Gd: GdPO_4 (Gd- $M\beta$, LLIF); Dy: DyPO_4 (Dy- $M\beta$, LLIF); Ti: titanite (Ti- $K\alpha$, LPET); Ba: baryte (Ba- $L\alpha$, LPET); Sr: SrTiO_3 (Sr- $L\alpha$, LPET); Y: $\text{Y}_3\text{Al}_5\text{O}_{12}$ (YPO_4 for 1991c) (Y- $L\alpha$, LPET); Ta: $\text{MnNb}_2\text{Ta}_2\text{O}_9$ (Ta- $L\alpha$, LLIF); Th: ThO_2 (Th- $M\alpha$, LPET). Data were reduced using the $\varphi(\rho Z)$ procedure of Pouchou and Pichoir (1985). The chemical compositions of the five rinkite samples are the mean of 10 determinations for each sample and are given in Table 2. Table 2 also includes chemical analyses for rinkite taken from Lorenzen (1884) and Sokolova and Cámara (2008a, sample 14329), nacareniobsite-(Ce) (Petersen *et al.*, 1989; Sokolova and Hawthorne 2008b) and mosandrite (Brøgger, 1890; Bellezza *et al.*, 2009).

Transmission Electron Microscopy

We collected TEM data for additional crystals from sample 2909 with a Philips CM20 transmission electron microscope working at 200 kV with an EDAX EDS system for chemical analysis in STEM mode. The instrument has a CCD camera for acquisition of images. Samples were oriented in order to have [010] perpendicular to the polished surface, embedded in epoxy, thinned and doubly polished. The thin slices were glued to copper rings and thinned using a Gatan Dual ion miller until transparent to electrons.

X-ray data collection and structure refinement

Single crystals of rinkite were mounted on Bruker AXS SMART APEX (1991c, 2909, 3471) and Bruker P4 (H-08-02, YuksFe) diffractometers with CCD detectors and Mo- $K\alpha$ radiation. Details of data collection and structure refinement are given in Table 3. The intensities of reflections with $-10 \leq h \leq 10$, $-8 \leq k \leq 8$, $-26 \leq l \leq 26$ were collected for $2\theta \leq 60^\circ$ with a frame width of 0.2° and a frame time of 5 s, and an empirical absorption correction (SADABS, Sheldrick, 2008) was applied. The unit-cell parameters were refined from 2419–7110 reflections with

$I > 10\sigma I$. Refinement of each crystal structure was done in monoclinic symmetry using the atom coordinates of Sokolova and Cámara (2008a). The crystal structure of rinkite was refined with the Bruker *SHELXTL* Version 5.1 system of programs (Sheldrick, 2008) to $R_1 = 2.91-4.91\%$ (Table 3). We observed between several and several hundred violations of the c -glide extinction criterion and refined the structure as two components related by the TWIN matrix $(-1\ 0\ 0, 0\ -1\ 0, 1\ 0\ 1)$ (see discussion below) for all five samples. There were few observed reflections at high 2θ , and those that do occur show splitting due to pseudomorph twinning, and refinement of each structure was done for $2\theta \leq 55^\circ$, $-9 \leq h \leq 9$, $-7 \leq k \leq 7$, $-24 \leq l \leq 24$. The occupancies of five cation sites were refined with the following scattering curves: M^H and A^P sites: with two, Ca and Ce (the dominant REE^{3+}), scattering curves for each site; $M^O(1)$ site: Ti; $M^O(2)$ and $M^O(3)$ sites: Na and Ca, respectively. Refinement of the $M^O(2)$ site occupancy converged to an integer value (within 3 e.s.d.) and hence was fixed at full occupancy. The occupancies of the X_M^O and X_A^O anion sites were refined with the scattering curve of fluorine; refinement of the X_A^O site occupancy converged to an integer value (within 3 e.s.d.) and was fixed at full occupancy. Scattering curves for neutral atoms were taken from the *International Tables for Crystallography* (Wilson, 1992). Final atom coordinates and equivalent displacement parameters are given in Table 4, selected interatomic distances and angles in Table 5, refined site-scattering values and assigned populations for selected sites in Table 6, and bond-valence values for the X_M^O and X_A^O anion sites in Table 7. Lists of observed and calculated structure factors and anisotropic displacement parameters have been deposited with the Principal Editor of *Mineralogical Magazine* and are available from www.minersoc.org/pages/e_journals/dep_mat.html.

Site-population assignment

There are seven cation sites in the crystal structure of rinkite: three M^O sites in the O sheet and the M^H , A^P and two Si sites in the H sheet; site labelling is in accord with Sokolova (2006). Consider first the Ti-dominant $M^O(1)$ site. We assign cations to this site based on our previous work on Ti disilicate minerals: Ti (+ Nb) dominant sites are always fully occupied. In

rinkite, the $M^O(1)$ site is occupied by Ti and Nb and minor Ta and Zr: for the $M^O(1)$ site in five crystals, Table 2 gives a mean sum of 1.01 a.p.f.u. with mean calculated scattering of 27.9 e.p.f.u., and a mean aggregate refined scattering at these five sites is 26.1 e.p.f.u. (Table 6). The mean bond-lengths around the $M^O(1)$ site vary from 1.987 to 2.003 Å. Assigned site-populations for the $M^O(1)$ site in the five rinkite structures result in a mean scattering value of 27.2 e.p.f.u.

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 (Sokolova, 2006; Sokolova and Cámara, 2008a). The cations to be assigned to the M^H and A^P sites are Ca, REE^{3+} , Y, Th, Ba, Sr and Na (Table 1). Let us first decide if we should assign Na to these sites. First, we assign all REE^{3+} , Y and Th, the totals of which vary from 0.73 (H-08-02) to 1.10 a.p.f.u. (2909) (Table 2). Next, we assign the large cations, Sr and Ba, which substitute for Ca. The $\langle A^P-\phi \rangle$ distance of 2.480 Å is longer than the $\langle M^H-\phi \rangle$ distance of 2.452 Å (where ϕ = unspecified anion) (Table 5) and scattering at the A^P site is lower than that at the M^H site, and hence we assign the larger and lighter (compared to REE^{3+}) Sr (+ minor Ba) to the A^P site. We are now left with 2.91 (1991c), 2.89 (2909), 2.79 (YuksFe), 2.86 (3471) and 3.26 (H-08-02) a.p.f.u. to be assigned to the M^H and A^P sites. The total refined site scattering for these sites is: 122.1 (1991c, 2909, YuksFe), 118.1 (3471) and 111.5 e.p.f.u. (H-08-02). Site-scattering values calculated from EMPA for ($REE^{3+} + Y + Th + Ba + Sr$) are as follows: 61.94 (1991c), 63.90 (2909), 60.58 (YuksFe), 60.75 (3471) and 41.68 (H-08-02) e.p.f.u. Therefore we must assign: 2.91 a.p.f.u. with a scattering curve (s.c.) of $(122.1-61.94)/2.91 = 20.8$ el. (1991c); 2.89 a.p.f.u. with a s.c. of $(122.1-63.09)/2.89 = 20.4$ el. (2909); 2.79 a.p.f.u., with a s.c. of $(122.1-60.58)/2.79 = 22.0$ el. (YuksFe); 2.86 a.p.f.u. with a s.c. of 20.1 el. (3471) and 3.26 a.p.f.u., with a s.c. of 21.4 el. (H-08-02). For all five samples, 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, 5).

Consider next the $M^O(2)$ and $M^O(3)$ sites in the O sheet occupied by alkali cations. In accord with structure-refinement results, we assign Na to the $M^O(2)$ site. The refined site-scattering at the $M^O(3)$ site varies from 29.5 to 33.2 e.p.f.u. and we assign all Na and Ca (remaining after the

TABLE 2. Chemical composition and unit formula for rinkite, nacareniobsite-(Ce) and mosandrite.

| Sample Ref. | Rinkite | | | Nacareniobsite-(Ce) | | | Mosandrite | | | |
|--------------------------------|--------------------|-----------|----------|---------------------|----------|-------------|------------|-------|--------------------|-------------|
| | 14329 (2) | 1991c (3) | 2909 (3) | YuksFe (3) | 3471 (3) | H-08-02 (3) | (4) | (5) | (6) | (7) |
| Chemical composition wt. % | | | | | | | | | | |
| Oxide | | | | | | | | | | |
| Ta ₂ O ₅ | n.a. | n.d. | 0.18 | 0.00 | 0.00 | 0.20 | 0.34 | 0.33 | n.a. | n.a. |
| Nb ₂ O ₅ | n.a. | 5.20 | 5.48 | 1.89 | 2.42 | 4.78 | 11.61 | 12.01 | n.a. | 1.40 |
| ThO ₂ | n.a. | n.d. | 0.08 | 0.12 | 0.27 | 0.34 | n.d. | n.d. | 0.34 | 1.04 |
| ZrO ₂ | n.a. | 0.59 | 0.81 | 0.62 | 0.09 | 0.70 | n.d. | n.d. | 7.43 | 1.45 |
| TiO ₂ | 13.36 | 6.06 | 5.81 | 8.21 | 8.34 | 6.70 | 2.79 | 2.24 | 5.33 | 8.89 |
| SiO ₂ | 29.08 | 29.43 | 29.09 | 29.36 | 29.56 | 30.26 | 29.63 | 28.30 | 30.71 | 28.64 |
| Yb ₂ O ₃ | n.a. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.a. | 0.19 |
| Er ₂ O ₃ | n.a. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | 0.39 |
| Dy ₂ O ₃ | 0 ^a | 0.26 | 0.26 | 0.41 | 0.21 | 0.16 | 0.05 | n.d. | 0 | 0.32 |
| Gd ₂ O ₃ | n.a. | n.d. | 0.55 | 0.52 | 0.56 | 0.20 | n.d. | 0.47 | n.a. | 0.31 |
| Sm ₂ O ₃ | n.a. | 0.79 | 0.78 | 0.58 | 0.56 | 0.20 | 0.81 | 0.64 | n.a. | 0.28 |
| Nd ₂ O ₃ | n.a. | 4.85 | 4.91 | 3.58 | 3.76 | 1.89 | 4.19 | 4.34 | n.a. | 2.13 |
| Pr ₂ O ₃ | n.a. | 1.22 | 1.16 | 1.01 | 0.83 | 0.70 | 1.42 | 1.12 | n.a. | 1.19 |
| Ce ₂ O ₃ | 22.12 ^a | 9.25 | 9.23 | 9.00 | 7.63 | 6.98 | 10.32 | 10.55 | 16.50 ^b | 8.22 |
| La ₂ O ₃ | 0 ^a | 3.14 | 3.21 | 3.56 | 2.62 | 3.16 | 4.09 | 4.42 | 0 | 3.81 |
| Y ₂ O ₃ | 0.98 | 1.38 | 1.27 | 1.83 | 1.07 | 1.12 | 0.78 | 0.57 | 3.52 | 2.82 |
| Al ₂ O ₃ | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | 0.40 |
| BaO | n.a. | n.d. | 0.06 | 0.10 | 0.09 | 0.08 | n.d. | n.d. | n.d. | n.a. |
| SrO | n.a. | n.d. | 0.07 | 1.73 | 3.07 | 0.17 | 0.27 | 0.45 | n.d. | n.a. |
| FeO | 0.44 | n.d. | 0.11 | n.d. | n.d. | 0.17 | n.d. | n.d. | 0.50 ^b | 0.25 |
| MnO | n.a. | n.d. | 0.08 | 0.13 | 0.15 | 0.17 | n.d. | n.d. | 0.45 | 0.60 |
| CaO | 23.26 | 23.05 | 23.09 | 24.43 | 26.00 | 29.31 | 19.92 | 19.79 | 22.53 | 24.74 |
| MgO | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | 0.63 | n.d. |
| K ₂ O | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | 0.38 | 0.05 |
| Ni ₂ O | 8.98 | 8.36 | 8.54 | 8.37 | 7.75 | 8.05 | 10.01 | 10.07 | 2.44 | 1.06 |
| Cl | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | 2.06 | 0.04 |
| F | 5.82 | 5.86 | 6.96 | 6.47 | 6.92 | 7.04 | 6.87 | 6.15 | 2.06 | 2.08 |
| H ₂ O** | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | 7.70 | 7.50–8.00 |
| –O=Cl | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | 0.01 |
| –O=F | 2.45 | 2.47 | 2.93 | 2.72 | 2.91 | 2.96 | 2.89 | 2.59 | 0.87 | 0.88 |
| Total | 101.59 | 97.11 | 98.80 | 99.20 | 98.99 | 99.05 | 100.21 | 98.86 | 99.65 | 96.91–97.41 |

Unit formulae a.p.f.u.

| | | | | | | | | | | |
|----|------|------|------|------|------|------|------|------|------|------|
| Si | 3.90 | 4.03 | 4.02 | 4.03 | 4.02 | 4.02 | 4.08 | 4.01 | 4.00 | 4.00 |
|----|------|------|------|------|------|------|------|------|------|------|

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| | | | | | | | | | | | |
|---|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| Ti ⁴⁺ | 1.35 | 0.86 | 0.64 | 0.60 | 0.85 | 0.85 | 0.67 | 0.29 | 0.24 | 0.52 | 0.93 |
| Nb | 0 | 0.08 | 0.33 | 0.34 | 0.12 | 0.15 | 0.29 | 0.72 | 0.77 | 0 | 0.08 |
| Ta | 0 | 0 | 0 | 0.01 | 0 | 0 | 0.01 | 0.01 | 0.01 | 0 | 0 |
| Zr | 0 | 0.05 | 0.04 | 0.06 | 0.04 | 0.01 | 0.05 | 0 | 0 | 0.47 | 0 |
| ΣM ^O (1) | 1.35 | 0.99 | 1.01 | 1.01 | 1.01 | 1.01 | 1.02 | 1.02 | 1.02 | 0.99 | 1.01 |
| Na | 2.33 | 1.99 | 2.28 | 2.29 | 2.23 | 2.04 | 2.07 | 2.67 | 2.77 | 0.62 | 0.29 |
| Ca | 0.50 | 0.85 | 0.56 | 0.53 | 0.80 | 0.92 | 0.91 | 0.07 | 0.20 | 0.17 | 0.79 |
| Fe ²⁺ | 0.05 | 0 | 0 | 0.01 | 0 | 0 | 0 | 0 | 0 | 0.05 | 0.03 |
| Mn | 0 | 0 | 0 | 0.01 | 0.02 | 0.02 | 0.02 | 0 | 0 | 0.05 | 0.07 |
| K | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0.06 | 0.01 |
| ΣM ^O (2)+2M ^O (3) | 2.88 | 2.84 | 2.84 | 2.84 | 3.05 | 2.98 | 3.00 | 2.74 | 2.97 | 0.89 | 1.18 |
| Ca | 2.84 | 3.08 | 2.91 | 2.89 | 2.79 | 2.86 | 3.26 | 2.87 | 2.81 | 2.97 | 2.91 |
| Ba | 0 | 0 | 0 | 0 | 0.01 | 0.01 | 0 | 0 | 0 | 0 | 0 |
| Sr | 0 | 0.02 | 0 | 0.01 | 0.14 | 0.24 | 0.01 | 0.02 | 0.04 | 0 | 0 |
| ΣM ²⁺ *** | 2.84 | 3.10 | 2.91 | 2.90 | 3.24 | 3.11 | 3.27 | 2.87 | 2.85 | 2.97 | 2.91 |
| Yb ³⁺ | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0.01 |
| Er ³⁺ | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0.02 |
| Dy ³⁺ | 0 | 0.01 | 0.01 | 0.01 | 0.02 | 0.01 | 0.01 | 0 | 0 | 0 | 0.01 |
| Gd ³⁺ | 0 | 0 | 0 | 0.03 | 0.02 | 0.03 | 0 | 0 | 0.02 | 0 | 0.01 |
| Sm ³⁺ | 0 | 0.02 | 0.04 | 0.04 | 0.03 | 0.03 | 0.01 | 0.04 | 0.03 | 0 | 0.01 |
| Nd ³⁺ | 0 | 0.13 | 0.24 | 0.24 | 0.18 | 0.18 | 0.09 | 0.21 | 0.22 | 0 | 0.11 |
| Pr ³⁺ | 0 | 0.04 | 0.06 | 0.06 | 0.05 | 0.04 | 0.03 | 0.07 | 0.06 | 0 | 0.06 |
| Ce ³⁺ | 1.09 | 0.41 | 0.48 | 0.47 | 0.45 | 0.38 | 0.34 | 0.52 | 0.55 | 0.79 | 0.42 |
| La ³⁺ | 0 | 0.16 | 0.16 | 0.16 | 0.18 | 0.13 | 0.16 | 0.21 | 0.23 | 0 | 0.20 |
| Y ³⁺ | 0.07 | 0.13 | 0.10 | 0.09 | 0.13 | 0.08 | 0.08 | 0.06 | 0.04 | 0.24 | 0.21 |
| Th ⁴⁺ | 0 | 0 | 0 | 0 | 0 | 0.01 | 0.01 | 0 | 0 | 0 | 0.03 |
| Σ~REE*** | 1.16 | 0.90 | 1.09 | 1.10 | 1.06 | 0.89 | 0.73 | 1.11 | 1.15 | 1.03 | 1.09 |
| Σ2M ^H +2A ^P | 4.00 | 4.00 | 4.00 | 4.00 | 4.00 | 4.00 | 4.00 | 4.00 | 4.00 | 4.00 | 4.00 |
| Σcations | 12.12 | 11.87 | 11.98 | 11.87 | 12.09 | 12.01 | 12.04 | 11.84 | 12.00 | 10.09 | 10.38 |
| F | 2.47 | 3.20 | 2.60 | 3.04 | 2.81 | 2.97 | 2.96 | 2.99 | 2.76 | 0.85 | 0.92 |
| O | 15.53 | 14.80 | 15.40 | 14.96 | 15.19 | 15.03 | 15.05 | 15.01 | 15.24 | 18.19 | 19.06 |
| H ⁺ | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 6.70 | 7.02 |

References: wet chemistry: (1) Lorenzen (1884) and (6) Brøgger (1890); electron-microprobe analysis: (2) Sokolova and Cámara (2008a), (3) this work; (4) Petersen *et al.* (1989); (5) Sokolova and Hawthorne (2008b); (7) Bellezza *et al.* (2009).

* For rinkite and macarenobsite-(Ce), unit formulae were calculated on the basis of 18 (O + F) a.p.f.u.; for mosandrite, Si 4 a.p.f.u. For the calculation of the unit formula for mosandrite of Bellezza *et al.* (2009), we used H₂O = 7.59 wt.% (cf. 7.50–8.00 wt.%).

** added as difference to 100% (Brøgger, 1890) and measured with TG-DSC (Bellezza *et al.*, 2009).

*** M²⁺ = Ca,Ba,Sr; REE = REE³⁺,Y³⁺,Th⁴⁺;

^a recalculated Ce₂O₃ from CeO [= (Ce,La,Dy)O] = 21.01 wt.% in Lorenzen (1884);

^b recalculated: (a) Ce₂O₃ from [CeO₂ = 6.34 wt.% + Ce₂O₃ [= (Ce,La,Dy)₂O₃] = 10.45 wt.%] and (b) FeO from Fe₂O₃ = 0.56 wt.% in Brøgger (1890).

TABLE 3. Miscellaneous refinement* data for rinkite, space group $P2_1/c$, $Z = 2$.

| Sample | 14329 (Sokolova and Câmara, 2008a) | 1991C This work | 2909 This work | YuksFe This work | 3471 This work | H-08-02 This work |
|--|--|--|--------------------------------|--|--|--------------------------------|
| Provenance | Låven, Larvik, Vestfold, Norway | Kangerdluarsuk, Ilmaussaq, Greenland | Ilmaussaq, Greenland | Yuskpor Mt., Khibiny, Kola, Russia | Takhtarvumchoor Mt., Khibiny, Kola, Russia | Mont Saint-Hilaire, Canada |
| a (Å) | 7.4184(8) | 7.4328(3) | 7.4414(3) | 7.4263(3) | 7.424(1) | 7.4132(3) |
| b | 5.6789(6) | 5.6595(2) | 5.6628(2) | 5.6774(2) | 5.7083(8) | 5.6816(2) |
| c | 18.873(2) | 18.818(8) | 18.8315(7) | 18.8261(7) | 18.941(3) | 18.8455(7) |
| β | 101.410(2) | 101.353(1) | 101.383(1) | 101.390(1) | 101.424(4) | 101.370(1) |
| V (Å ³) | 779.35(5) | 776.1(5) | 777.93(5) | 778.11(5) | 786.7(5) | 778.2(5) |
| Refl. $I_0 > 10\sigma I$ | 2419 | 6133 | 6303 | 7110 | 3729 | 6868 |
| Abs. coeff. (mm ⁻¹) | 5.14 | 5.60 | 5.76 | 6.04 | 5.92 | 4.84 |
| $F(000)$ | 758.1 | 776.4 | 781.4 | 780.8 | 775.0 | 761.6 |
| $D_{calc.}$ (g/cm ³) | 3.363 | 3.482 | 3.502 | 3.490 | 3.420 | 3.376 |
| Second component** | 0 | 0.85 | 0.58 | 0.46 | 0.01 | 0.37 |
| Reflections violating c glide plane ($I > 3\sigma$) | 3 | 277 | 292 | 176 | 21 | 298 |
| n glide plane ($I > 3\sigma$) | 195 | 205 | 272 | 174 | 268 | 321 |
| Crystal size (mm) | $0.33 \times 0.21 \times 0.18$ | $0.25 \times 0.20 \times 0.07$ | $0.33 \times 0.31 \times 0.27$ | $0.28 \times 0.10 \times 0.10$ | $0.24 \times 0.20 \times 0.14$ | $0.20 \times 0.18 \times 0.08$ |
| 2θ -max [†] (°) | 50.0 | 55.0 | 55.0 | 55.0 | 55.0 | 55.0 |
| R (int) (%) | 3.60 | 2.03 | 2.08 | 1.73 | 2.70 | 2.03 |
| Reflections collected [‡] | 7604 | 11751 | 11751 | 7687 | 19454 | 11995 |
| Unique reflections | 1371 | 1875 | 1879 | 1888 | 1903 | 1870 |
| $F_0 > 4\sigma F$ | 1113 | 1810 | 1842 | 1851 | 1489 | 1810 |
| Final R indices (%) | | | | | | |
| R_1 [$F_0 > 4\sigma F$] | 6.33 | 2.94 | 2.9 | 3.66 | 4.91 | 2.9 |
| R_2 | 7.55 | 3.05 | 2.97 | 3.73 | 5.99 | 3.05 |
| wR_2 | 16.56 | 8.23 | 8.22 | 9.73 | 13.84 | 8.23 |
| Goodness of fit on F^2 | 1.190 | 1.123 | 1.133 | 1.103 | 1.065 | 1.123 |

* Radiation/filter: Mo- $K\alpha$ /graphite; Refinement method: full-matrix least squares on F^2 , fixed weights proportional to $1/\sigma F_0^2$; No. of refined parameters: 145 (this work);** 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 $(-1\ 0\ 0\ 0\ -1\ 0\ 1\ 0\ 1)$;

† for structure refinement;

‡ in accord with 2θ -range for structure refinement.

$M^O(2)$ and ($M^H + A^P$) site assignments) and minor Fe^{2+} and Mn^{2+} to this site (Table 6). For the $M^O(3)$ site in five samples, the difference in mean refined, 31.0 e.p.f.u., and calculated site-scattering, 28.1 e.p.f.u., is 10%.

There are nine anion sites in the crystal structure of rinkite. We assign O atoms to the O(1–7) sites that constitute tetrahedral coordination of $Si(1)$ and $Si(2)$ sites. Anions at two sites, X_M^O and X_A^O , receive bond valence from four cations, $M^O(1)$, $2M^O(3)$, and M^H , and $M^O(2)$, $2M^O(3)$, and A^P , respectively (Table 7). We expect the X_M^O atom to receive a higher bond valence as it is bonded to Ti at the $M^O(1)$ site, and the X_A^O atom, a lower bond valence as it is bonded to Na at the $M^O(2)$ site. Moreover, the contribution to the X_M^O anion from the M^H cation is slightly higher than that to the X_A^O anion from the A^P cation as the content of *REE* is higher at the M^H site (Tables 6, 7). Calculation of bond-valence sums at the X_M^O and X_A^O anions (using cation-oxygen parameters) gave a lower sum for the X_A^O anion. Therefore we assigned 2F a.p.f.u. to the X_M^O site and the remaining F and O atoms to the X_A^O site. This assignment is identical to the anion assignment for other minerals of Group I, götzenite, hainite, seidozerite, rosenbuschite and kochite (Christiansen *et al.*, 2003a,b). Hence we calculated bond valence for the X_M^O and X_A^O anions with cation-oxygen and cation-fluorine parameters, respectively (Table 7). Chemical analysis gives 2.6–3.04 F a.p.f.u. for the rinkite samples, hence we subtract 2 a.p.f.u. from the total F (Table 2) and assign the remaining F to the X_M^O site [1991c: (O_{1.40}F_{0.60}); 2909: (F_{1.04}O_{0.96}); YuksFe: (O_{1.19}F_{0.81}); 3471: (O_{1.03}F_{0.97}); H-08-02: (O_{1.04}F_{0.96}) p.f.u.].

The crystal structure

General topology

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 (Sokolova and Cámara, 2008a) that consist of HOH sheets. 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 Na and Ca (Fig. 1a). 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. 1b). In rinkite, the TS block exhibits

linkage and stereochemistry typical of Group I (Ti = 1 a.p.f.u.) Ti disilicate minerals: two H sheets connect to the O sheet such that two (Si_2O_7) groups link to the *trans* edges of a Na polyhedron of the O sheet (Fig. 1c). The TS blocks link via common vertices of (Si_2O_7) groups and common vertices and edges of [7]-coordinated M^H and A^P polyhedra (Fig. 1d). In the crystal structure of rinkite, two adjacent TS blocks are related by the c_y glide plane.

Cation sites

There are seven cation sites in the crystal structure of rinkite. In the O sheet, there are two octahedrally coordinated sites, $M^O(1)$ and $M^O(3)$, and one [8]-coordinated $M^O(2)$ site.

The $M^O(1)$ site is occupied primarily by Ti with subordinate Nb and minor Zr, and it is coordinated by four O atoms and two (O,F) anions (= X_M^O). At the $M^O(1)$ site, the content of Ti varies from 0.60–0.64 (2909, 1991c) to 0.85 a.p.f.u. (YuksFe, 3471) and correspondingly, the content of Nb varies from 0.12–0.14 (YuksFe, 3471) to 0.33–0.34 a.p.f.u. (1991c, 2909) (Table 6). The amount of Zr is minor, ~0.04 a.p.f.u. The ideal composition of the $M^O(1)$ site is Ti^{4+} a.p.f.u. The longest bond is from the $M^O(1)$ cation to the X_M^O anion, where $M^O(1)-X_M^O$ varies from 2.018 to 2.034 Å (Table 5). The shortest $M^O(1)-X_M^O$ distance of 2.018 Å occurs in the structure of H-08-02, the most Ca-rich and *REE*-poor rinkite sample. The $M^O(2)$ site is coordinated by six O atoms and two F atoms (= X_A^O) and is occupied by Na (Table 5). The shortest bond length, $M^O(2)-X_A^O$ varies from 2.261 to 2.272 Å (Table 5). The shortest $M^O(2)-X_M^O$ bond length of 2.261 Å occurs in the structure of 3471, which has the smallest amount of both *REE* and Ca and the largest content of Sr at the A^P site, $Ca_{1.48}REE_{0.27}Sr_{0.24}Ba_{0.01}$ (Table 6). The $M^O(3)$ site is coordinated by two O and two F atoms (X_A^O) and two X_M^O anions where $X_M^O = (O,F)$. The $M^O(3)$ site is occupied mainly by Na and Ca (Table 6). In three crystals, YuksFe, 3471 and H-08-02, the Na:Ca ratio is ~1:1 (Table 6), and we can write the ideal composition of the $M^O(3)$ site as (NaCa) a.p.f.u. In two crystals, 1991c and 2909, the Na:Ca ratio is ~2:1 (Ca 0.56–0.55 a.p.f.u., including 0.01 $Fe^{2+} + 0.01$ Mn in 2909). There is ~8% vacancy at the $M^O(3)$ site (1991c, 2909, Table 6). Note that in the 1991c and 2909 structures, the $M^O(1)$ site has the highest content of Nb, 0.33–0.34 a.p.f.u. For the three crystals, YuksFe, 3471 and H-08-02, the

alkali sites in the O sheet, $M^O(2)$ and $M^O(3)$, sum to Na_2Ca ideally with a total charge of +4 and the O sheet cations give $\text{Na}(\text{NaCa})\text{Ti}$ (4 a.p.f.u.).

In the H sheet, there are two tetrahedrally coordinated sites occupied by Si and two [7]-coordinated sites, M^H and A^P , occupied by Ca and REE^{3+} in the ratio ~3:1 (Table 6). The M^H site is coordinated by six O atoms and an X_M^O anion, and the A^P site is coordinated by six O atoms and one F atom at the X_A^O site (Table 5; Fig. 1*d*). The shortest A^P -anion bond length, $A^P-X_A^O$ varies from 2.333 to 2.401 Å (Table 5), and the longest $A^P-X_A^O$ distance of 2.401 Å occurs in the structure of 3471, which has the largest content of Sr at the A^P site, 0.24 a.p.f.u. (Table 6). The mean total of the M^H and A^P cations is ~3.03 Ca + 0.97 REE^{3+} (Table 6). The 2H-sheets cations give $(\text{Ca}_3\text{REE})\text{Si}_4$ (8 a.p.f.u.). The total number of cations is ideally 12 a.p.f.u.: $\text{Na}(\text{NaCa})\text{Ti}$ (O sheet) + $(\text{Ca}_3\text{REE})\text{Si}_4$ (2H sheets).

Anion sites

In the structure of rinkite, there are nine anion sites. Seven sites are occupied by O atoms [O(1–7)], giving O_{14} a.p.f.u. The X_A^O site is

occupied by F, and the X_M^O site is statistically occupied by O and F in the ratio ~1:1. The two sites, X_M^O and X_A^O , sum to OF_3 ideally. The total number of anions is 18 a.p.f.u.: $\text{O}_{14} + \text{OF}_3$.

Pseudomorphed twinning in rinkite

In their work on the structure of rinkite (labelled mosandrite), Sokolova and Cámara (2008*a*) suggested that the 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 a second orientation. We suggest that this is the origin of the $h0l$ reflections with $h + l = 2n + 1$ that seem to violate the c_y glide of the structure. We may deal with this situation by incorporating a second component of the crystal into the refinement, a component that is related to the first by the transformation matrix $(-1 \ 0 \ 0, 0 \ -1 \ 0, 1 \ 0 \ 1)$ (Fig. 2). Sokolova and Cámara

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

| Atom | | 1991c | 2909 | YuksFe | 3471 | H-08-02 |
|----------|-----------------|---------------|---------------|---------------|---------------|---------------|
| M^H | x | 0.09387(5) | 0.09372(10) | 0.09489(13) | 0.09346(7) | 0.09353(13) |
| | y | 0.65970(6) | 0.66011(6) | 0.65997(8) | 0.66259(9) | 0.66103(10) |
| | z | 0.19180(2) | 0.19176(2) | 0.19196(2) | 0.19128(3) | 0.19198(3) |
| | U_{eq} | 0.01475(15) | 0.01496(15) | 0.01210(18) | 0.0205(2) | 0.0153(2) |
| A^P | x | 0.59679(6) | 0.59661(11) | 0.59781(15) | 0.59697(8) | 0.59661(15) |
| | y | 0.66290(6) | 0.66340(6) | 0.66229(10) | 0.66591(11) | 0.66459(12) |
| | z | 0.19029(2) | 0.19035(2) | 0.19035(3) | 0.19049(3) | 0.19059(3) |
| | U_{eq} | 0.01572(17) | 0.01603(17) | 0.0140(2) | 0.0223(3) | 0.0176(2) |
| $M^O(1)$ | x | 0 | 0 | 0 | 0 | 0 |
| | y | 0 | 0 | 0 | 0 | 0 |
| | z | 0 | 0 | 0 | 0 | 0 |
| | U_{eq} | 0.0241(2) | 0.0237(2) | 0.0247(4) | 0.0269(4) | 0.0244(4) |
| $M^O(2)$ | x | $\frac{1}{2}$ | $\frac{1}{2}$ | $\frac{1}{2}$ | $\frac{1}{2}$ | $\frac{1}{2}$ |
| | y | 0 | 0 | 0 | 0 | 0 |
| | z | 0 | 0 | 0 | 0 | 0 |
| | U_{eq} | 0.0207(4) | 0.0193(4) | 0.0172(5) | 0.0229(6) | 0.0197(6) |
| $M^O(3)$ | x | 0.75082(13) | 0.75091(13) | 0.75299(16) | 0.75492(16) | 0.75336(18) |
| | y | 0.50105(18) | 0.50102(19) | 0.5008(3) | 0.5009(2) | 0.5010(3) |
| | z | 0.00059(5) | 0.00053(5) | 0.00011(7) | 0.00095(7) | 0.00060(8) |
| | U_{eq} | 0.0330(4) | 0.0337(4) | 0.0258(5) | 0.0388(6) | 0.0309(5) |

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TABLE 4. (contd.)

| Atom | | 1991c | 2909 | YuksFe | 3471 | H-08-02 |
|---------------------------|-----------------|-------------|-------------|-------------|-------------|-------------|
| Si(1) | <i>x</i> | 0.35095(11) | 0.35046(13) | 0.34990(17) | 0.35087(17) | 0.35070(17) |
| | <i>y</i> | 0.15441(14) | 0.15495(17) | 0.1532(3) | 0.1560(2) | 0.1548(3) |
| | <i>z</i> | 0.14023(4) | 0.14028(4) | 0.13975(6) | 0.13998(7) | 0.14025(7) |
| | U_{eq} | 0.0134(2) | 0.0146(3) | 0.0116(3) | 0.0175(3) | 0.0138(3) |
| Si(2) | <i>x</i> | 0.78379(11) | 0.78401(12) | 0.78452(16) | 0.78416(17) | 0.78337(16) |
| | <i>y</i> | 0.15361(14) | 0.15402(16) | 0.1527(3) | 0.1554(2) | 0.1535(3) |
| | <i>z</i> | 0.13782(4) | 0.13788(4) | 0.13747(6) | 0.13773(7) | 0.13756(7) |
| | U_{eq} | 0.0133(2) | 0.0137(3) | 0.0104(3) | 0.0174(3) | 0.0125(3) |
| O(1) | <i>x</i> | 0.2162(3) | 0.2174(4) | 0.2169(5) | 0.2180(5) | 0.2163(5) |
| | <i>y</i> | 0.1506(4) | 0.1507(5) | 0.1496(8) | 0.1496(6) | 0.1496(8) |
| | <i>z</i> | 0.06154(12) | 0.06154(13) | 0.06121(17) | 0.06081(18) | 0.06125(18) |
| | U_{eq} | 0.0241(5) | 0.0247(6) | 0.0205(8) | 0.0311(8) | 0.0217(8) |
| O(2) | <i>x</i> | 0.8323(3) | 0.8317(4) | 0.8330(5) | 0.8313(5) | 0.8322(5) |
| | <i>y</i> | 0.1414(4) | 0.1408(6) | 0.1394(8) | 0.1402(6) | 0.1384(8) |
| | <i>z</i> | 0.05804(12) | 0.05798(12) | 0.05802(17) | 0.05808(17) | 0.05759(18) |
| | U_{eq} | 0.0236(5) | 0.0261(6) | 0.0201(8) | 0.0291(8) | 0.0222(8) |
| O(3) | <i>x</i> | 0.3384(3) | 0.3390(6) | 0.3366(7) | 0.3376(5) | 0.3391(8) |
| | <i>y</i> | 0.3954(5) | 0.3959(5) | 0.3950(6) | 0.3977(7) | 0.3966(6) |
| | <i>z</i> | 0.18501(12) | 0.18498(12) | 0.18369(17) | 0.1827(2) | 0.18365(18) |
| | U_{eq} | 0.0217(5) | 0.0227(5) | 0.0190(7) | 0.0317(9) | 0.0233(8) |
| O(4) | <i>x</i> | 0.8437(4) | 0.8442(6) | 0.8431(8) | 0.8431(5) | 0.8435(8) |
| | <i>y</i> | 0.3966(5) | 0.3974(5) | 0.3951(6) | 0.3995(7) | 0.3987(7) |
| | <i>z</i> | 0.18042(13) | 0.18036(13) | 0.17974(18) | 0.1779(2) | 0.1783(2) |
| | U_{eq} | 0.0246(5) | 0.0255(6) | 0.0218(7) | 0.0378(10) | 0.0266(8) |
| O(5) | <i>x</i> | 0.3352(3) | 0.3351(6) | 0.3331(7) | 0.3336(5) | 0.3338(8) |
| | <i>y</i> | 0.9299(4) | 0.9308(5) | 0.9305(6) | 0.9349(7) | 0.9326(6) |
| | <i>z</i> | 0.19112(11) | 0.19097(11) | 0.19113(16) | 0.19092(18) | 0.19124(17) |
| | U_{eq} | 0.0195(5) | 0.0206(5) | 0.0157(7) | 0.0292(9) | 0.0201(8) |
| O(6) | <i>x</i> | 0.8538(3) | 0.8538(6) | 0.8508(8) | 0.8559(5) | 0.8534(8) |
| | <i>y</i> | 0.9319(4) | 0.9319(4) | 0.9322(6) | 0.9384(7) | 0.9344(6) |
| | <i>z</i> | 0.18976(11) | 0.18989(11) | 0.18995(15) | 0.19034(17) | 0.19039(17) |
| | U_{eq} | 0.0193(5) | 0.0206(5) | 0.0169(7) | 0.0290(9) | 0.0208(8) |
| O(7) | <i>x</i> | 0.5575(3) | 0.5578(4) | 0.5575(5) | 0.5579(5) | 0.5568(5) |
| | <i>y</i> | 0.1412(5) | 0.1414(5) | 0.1399(7) | 0.1403(7) | 0.1381(8) |
| | <i>z</i> | 0.12067(13) | 0.12068(13) | 0.12029(18) | 0.1209(2) | 0.12004(19) |
| | U_{eq} | 0.0305(6) | 0.0320(6) | 0.0264(8) | 0.0378(9) | 0.0290(8) |
| X_{M}^{O} | <i>x</i> | 0.0314(4) | 0.0303(7) | 0.0247(8) | 0.0313(5) | 0.0322(8) |
| | <i>y</i> | 0.7029(4) | 0.7027(4) | 0.7026(5) | 0.7041(6) | 0.7049(5) |
| | <i>z</i> | 0.06158(11) | 0.06163(11) | 0.06143(15) | 0.06004(18) | 0.06072(15) |
| | U_{eq} | 0.0270(7) | 0.0284(7) | 0.0222(9) | 0.0354(11) | 0.0234(10) |
| X_{A}^{O} | <i>x</i> | 0.5312(4) | 0.5293(8) | 0.5241(9) | 0.5296(6) | 0.5312(9) |
| | <i>y</i> | 0.6572(4) | 0.6577(4) | 0.6566(5) | 0.6575(6) | 0.6556(6) |
| | <i>z</i> | 0.06383(12) | 0.06364(11) | 0.06327(15) | 0.0612(2) | 0.06253(17) |
| | U_{eq} | 0.0325(5) | 0.0332(5) | 0.0285(7) | 0.0469(9) | 0.0339(7) |

TABLE 5. Interatomic distances (Å) and angles (°) for rinkite.

| | 1991c | 2909 | YuksFe | 3471 | H-08-02 |
|--|-----------------|-----------------|-----------------|-----------------|-----------------|
| Si(1)—O(5) a | 1.609(2) | 1.606(3) | 1.612(4) | 1.609(4) | 1.606(4) |
| Si(1)—O(1) | 1.616(2) | 1.613(2) | 1.608(3) | 1.624(3) | 1.620(3) |
| Si(1)—O(3) | 1.615(3) | 1.614(3) | 1.616(4) | 1.613(4) | 1.610(4) |
| Si(1)—O(7) | <u>1.649(3)</u> | <u>1.657(3)</u> | <u>1.655(4)</u> | <u>1.650(4)</u> | <u>1.649(4)</u> |
| <Si(1)—O> | 1.622 | 1.623 | 1.623 | 1.624 | 1.621 |
| Si(2)—O(4) | 1.610(3) | 1.612(3) | 1.606(4) | 1.606(4) | 1.611(4) |
| Si(2)—O(2) | 1.613(2) | 1.615(2) | 1.608(3) | 1.617(3) | 1.620(4) |
| Si(2)—O(6) a | 1.613(2) | 1.616(3) | 1.611(4) | 1.613(4) | 1.614(4) |
| Si(2)—O(7) | <u>1.651(3)</u> | <u>1.652(3)</u> | <u>1.655(4)</u> | <u>1.649(4)</u> | <u>1.649(4)</u> |
| <Si(2)—O> | 1.622 | 1.624 | 1.620 | 1.621 | 1.624 |
| Si(1)—O(7)—Si(2) | 155.8(2) | 155.8(2) | 155.9(2) | 155.9(3) | 154.8(2) |
| Si(1)—O(7)—Si(2)* | 204.2(2) | 204.2(2) | 204.1(2) | 204.1(3) | 205.2(2) |
| M ^H —O(6) b | 2.352(2) | 2.352(4) | 2.377(5) | 2.361(4) | 2.358(5) |
| M ^H —O(5) | 2.359(2) | 2.363(4) | 2.345(4) | 2.366(4) | 2.359(5) |
| M ^H —O(4) b | 2.359(3) | 2.356(4) | 2.375(5) | 2.364(4) | 2.353(5) |
| M ^H —O(3) | 2.377(3) | 2.383(4) | 2.371(5) | 2.390(4) | 2.390(5) |
| M ^H —X _M ^O | 2.415(2) | 2.415(2) | 2.421(3) | 2.448(4) | 2.438(3) |
| M ^H —O(6) c | 2.538(2) | 2.539(2) | 2.534(3) | 2.544(4) | 2.526(3) |
| M ^H —O(4) d | <u>2.712(3)</u> | <u>2.717(3)</u> | <u>2.718(4)</u> | <u>2.780(5)</u> | <u>2.751(4)</u> |
| <M ^H —φ**> | 2.445 | 2.446 | 2.449 | 2.465 | 2.454 |
| A ^P —X _A ^O | 2.333(2) | 2.340(2) | 2.347(3) | 2.401(4) | 2.367(3) |
| A ^P —O(4) | 2.410(3) | 2.416(4) | 2.409(5) | 2.425(4) | 2.420(5) |
| A ^P —O(3) | 2.433(3) | 2.430(4) | 2.447(5) | 2.442(4) | 2.425(5) |
| A ^P —O(6) | 2.444(3) | 2.446(4) | 2.426(5) | 2.473(4) | 2.445(5) |
| A ^P —O(5) | 2.465(3) | 2.468(4) | 2.489(5) | 2.487(4) | 2.474(5) |
| A ^P —O(5) c | 2.556(2) | 2.557(2) | 2.554(3) | 2.567(4) | 2.552(4) |
| A ^P —O(3) d | <u>2.651(2)</u> | <u>2.652(3)</u> | <u>2.674(3)</u> | <u>2.700(4)</u> | <u>2.671(4)</u> |
| <A ^P —φ> | 2.470 | 2.473 | 2.478 | 2.499 | 2.479 |
| M ^O (1)—O(1) × 2 | 1.980(2) | 1.987(3) | 1.977(3) | 1.984(3) | 1.974(4) |
| M ^O (1)—O(2) b × 2 | 1.981(2) | 1.984(3) | 1.973(3) | 1.991(3) | 1.969(4) |
| M ^O (1)—X _M ^O × 2 | <u>2.029(2)</u> | <u>2.032(2)</u> | <u>2.034(3)</u> | <u>2.024(3)</u> | <u>2.018(3)</u> |
| <M ^O (1)—φ> | 1.997 | 2.001 | 1.995 | 2.000 | 1.987 |
| M ^O (2)—X _A ^O × 2 | 2.270(2) | 2.267(2) | 2.274(3) | 2.261(3) | 2.272(3) |
| M ^O (2)—O(7) × 2 | 2.365(2) | 2.368(2) | 2.358(3) | 2.383(4) | 2.353(4) |
| M ^O (2)—O(2) × 2 | 2.622(3) | 2.619(3) | 2.620(4) | 2.613(4) | 2.609(4) |
| M ^O (2)—O(1) × 2 | <u>2.735(3)</u> | <u>2.731(3)</u> | <u>2.725(4)</u> | <u>2.719(4)</u> | <u>2.727(4)</u> |
| <M ^O (2)—φ> | 2.498 | 2.496 | 2.494 | 2.494 | 2.490 |
| M ^O (3)—O(1) e | 2.329(3) | 2.328(3) | 2.329(4) | 2.342(4) | 2.335(5) |
| M ^O (3)—O(2) | 2.329(3) | 2.331(3) | 2.344(5) | 2.343(4) | 2.344(5) |
| M ^O (3)—X _A ^O | 2.372(3) | 2.386(5) | 2.426(6) | 2.378(4) | 2.367(6) |
| M ^O (3)—X _A ^O e | 2.380(3) | 2.371(5) | 2.342(5) | 2.383(4) | 2.381(6) |
| M ^O (3)—X _M ^O f | 2.455(3) | 2.451(4) | 2.408(5) | 2.429(4) | 2.444(5) |
| M ^O (3)—X _M ^O e | <u>2.463(3)</u> | <u>2.471(4)</u> | <u>2.481(5)</u> | <u>2.439(4)</u> | <u>2.440(5)</u> |
| <M ^O (3)—φ> | 2.388 | 2.390 | 2.388 | 2.386 | 2.385 |

* a reflex angle toward the O sheet;

** φ - unspecified anion;

a: x, y-1, z; b: x-1, y, z; c: -x+1, y-1/2, -z+1/2; d: -x+1, y+1/2, -z+1/2; e: -x+1, -y+1, -z; f: x+1, y, z.

TABLE 6. Refined site-scattering values and assigned site-populations for rinkite.

| Sample | Refined site-scattering (e.p.f.u.) | Assigned site-population (a.p.f.u.) | Calculated site-scattering (e.p.f.u.) | $\langle X-\rho \rangle^*_{\text{calc}}$ (Å) | $\langle X-\rho \rangle^*_{\text{obs}}$ (Å) |
|---------|---|--|---------------------------------------|--|---|
| | | ¹⁶¹M^O(1) | | | |
| 1991c | 27.7(1) | 0.64 Ti + 0.33 Nb + 0.03 Zr | 28.8 | 1.990 | 1.997 |
| 2909 | 27.8(1) | 0.60 Ti + 0.34 Nb + 0.06 Zr | 29.5 | 1.994 | 2.001 |
| YuksFe | 24.2(1) | 0.85 Ti + 0.12 Nb + 0.03 Zr | 24.8 | 1.983 | 1.995 |
| 3471 | 24.2(1) | 0.85 Ti + 0.14 Nb + 0.01 Zr | 24.8 | 1.981 | 2.000 |
| H-08-02 | 26.4(1) | 0.67 Ti + 0.29 Nb + 0.04 Zr | 28.2 | 1.990 | 1.987 |
| | | ¹⁶¹M^O(3) | | | |
| 1991c | 29.5(2) | 1.28 Na + 0.56 Ca + 0.16 □ | 25.3 | 2.361 | 2.463 |
| 2909 | 29.5(2) | 1.29 Na + 0.53 Ca + 0.01 Fe ²⁺ + 0.01 Mn + 0.16 □ | 25.3 | 2.359 | 2.471 |
| YuksFe | 30.7(2) | 1.20 Na + 0.80 Ca | 29.2 | 2.359 | 2.481 |
| 3471 | 33.2(3) | 1.04 Na + 0.92 Ca + 0.02 Mn + 0.02 □ | 30.3 | 2.360 | 2.440 |
| H-08-02 | 31.9(2) | 1.07 Na + 0.91 Ca + 0.02 Mn | 30.5 | 2.360 | 2.439 |
| | | ¹⁷¹M^H | | | |
| 1991c | 63.4(3) | 1.39 Ca + 0.61 REE | 62.5 | 2.439 | 2.445 |
| 2909 | 63.5(3) | 1.37 Ca + 0.63 REE | 63.4 | 2.439 | 2.446 |
| YuksFe | 64.5(3) | 1.32 Ca + 0.68 REE | 64.7 | 2.439 | 2.449 |
| 3471 | 63.2(3) | 1.38 Ca + 0.62 REE | 63.2 | 2.439 | 2.465 |
| H-08-02 | 58.6(3) | 1.56 Ca + 0.44 REE | 56.1 | 2.438 | 2.454 |
| | | ¹⁷¹A^P | | | |
| 1991c | 58.7(3) | 1.52 Ca + 0.48 REE | 57.7 | 2.432 | 2.470 |
| 2909 | 58.6(3) | 1.52 Ca + 0.47 REE + 0.01 Sr | 57.6 | 2.439 | 2.473 |
| YuksFe | 57.6(3) | 1.47 Ca + 0.38 REE + 0.14 Sr + 0.01 Ba | 56.7 | 2.444 | 2.478 |
| 3471 | 54.9(3) | 1.48 Ca + 0.27 REE + 0.24 Sr + 0.01 Ba | 54.8 | 2.451 | 2.499 |
| H-08-02 | 52.9(3) | 1.70 Ca + 0.29 REE + 0.01 Sr | 50.8 | 2.432 | 2.479 |
| | | ~3.03 Ca + 0.97 REE (4 a.p.f.u.) | | | |
| | | REE | | a.p.f.u. | s.c. (el.)** |
| 1991c | 0.01Dy + 0.04Sm + 0.24Nd + 0.06Pr + 0.48Ce + 0.16La + 0.10Y | | | 1.09 | 56.82 |
| 2909 | 0.01Dy + 0.03Gd + 0.04Sm + 0.24Nd + 0.06Pr + 0.47Ce + 0.16La + 0.09Y | | | 1.10 | 57.17 |
| YuksFe | 0.02Dy + 0.02Gd + 0.03Sm + 0.18Nd + 0.05Pr + 0.45Ce + 0.18La + 0.13Y | | | 1.06 | 53.26 |
| 3471 | 0.01Dy + 0.03Gd + 0.03Sm + 0.18Nd + 0.04Pr + 0.38Ce + 0.13La + 0.08Y + 0.01Th | | | 0.89 | 57.38 |
| H-08-02 | 0.01Dy + 0.01Sm + 0.09Nd + 0.03Pr + 0.34Ce + 0.16La + 0.08Y + 0.01Th | | | 0.73 | 56.82 |
| | | $\langle \Sigma M^H + A^P \rangle$ | | | |

* ionic radii from Shannon (1976); ρ = unspecified anion; ** s.c. = scattering curve for REE³⁺

TABLE 7. Bond-valence* table for rinkite.

| Anion | M ^H | A ^P | M ^O (1) | M ^O (2) | M ^O (3) | Σ |
|-----------------------------|----------------|----------------|--------------------|--------------------|--------------------|------|
| 1991c | | | | | | |
| X _M ^O | 0.34 | | 0.61 | | 0.19 | 1.33 |
| | | | | | 0.19 | |
| X _A ^O | | 0.32 | | 0.19 | 0.17 | 0.85 |
| | | | | | 0.17 | |
| 2909 | | | | | | |
| X _M ^O | 0.35 | | 0.62 | | 0.19 | 1.35 |
| | | | | | 0.19 | |
| X _A ^O | | 0.31 | | 0.19 | 0.17 | 0.83 |
| | | | | | 0.16 | |
| YuksFe | | | | | | |
| X _M ^O | 0.34 | | 0.57 | | 0.24 | 1.35 |
| | | | | | 0.20 | |
| X _A ^O | | 0.30 | | 0.19 | 0.21 | 0.87 |
| | | | | | 0.17 | |
| 3471 | | | | | | |
| X _M ^O | 0.32 | | 0.57 | | 0.23 | 1.35 |
| | | | | | 0.23 | |
| X _A ^O | | 0.27 | | 0.19 | 0.20 | 0.86 |
| | | | | | 0.20 | |
| H-08-02 | | | | | | |
| X _M ^O | 0.31 | | 0.62 | | 0.23 | 1.38 |
| | | | | | 0.22 | |
| X _A ^O | | 0.28 | | 0.19 | 0.20 | 0.87 |
| | | | | | 0.20 | |

* bond-valence parameters (v.u.) from Brown (1981); bond-valence contributions from cations were calculated for X_M^O and X_A^O as bonds to oxygen and fluorine, respectively; the following chemical composition was used to calculate bond-valence: M^H, A^P: Ca + Ce; M^O(1) Ti + Nb; M^O(2): Na; M^O(3): Ca + Na + □.

(2008a) were not able to refine the structure of rinkite (14329) as two components, probably due to the very small size of the second domain. However, Sokolova and Hawthorne (2008b) refined the crystal structure of nacareniobsite-(Ce) as two components in the ratio ~1:1.

There are two settings for the space group no. 14, which correspond to space groups $P2_1/c$ and $P2_1/n$. Sokolova and Cámara (2008a) pointed out that Simonov and Belov (1968) and Rastsvetaeva *et al.* (1991) refined the structure of rinkite in space group $P2_1$ and in the setting that corresponds to the second choice of cell for space group no. 14, i.e. $P2_1/n$ (fig. 1b in Sokolova and Cámara, 2008a). Conversely, Galli and Alberti (1971) and Sokolova and Cámara

(2008a) refined the structure of rinkite in space group $P2_1/c$, which corresponds to the first choice of the cell, β_1 (Fig. 2). Sokolova and Cámara (2008a) stated that they did not find any additional order of cations as in the $P2_1$ -structure of rinkite of Rastsvetaeva *et al.* (1991) if compared to the structure of rinkite (Galli and Alberti, 1971; Sokolova and Cámara, 2008a). Therefore the lower symmetry described by space group $P2_1$ is not justified. It is apparent that the epitactic intergrowth suggested by Sokolova and Cámara (2008a) is a pseudomerohedral twinning of rinkite crystals. The pseudomerohedral twins correspond to two different cell choices for space group no. 14. Pseudomerohedral twinning results in the apparent loss of the glide plane and

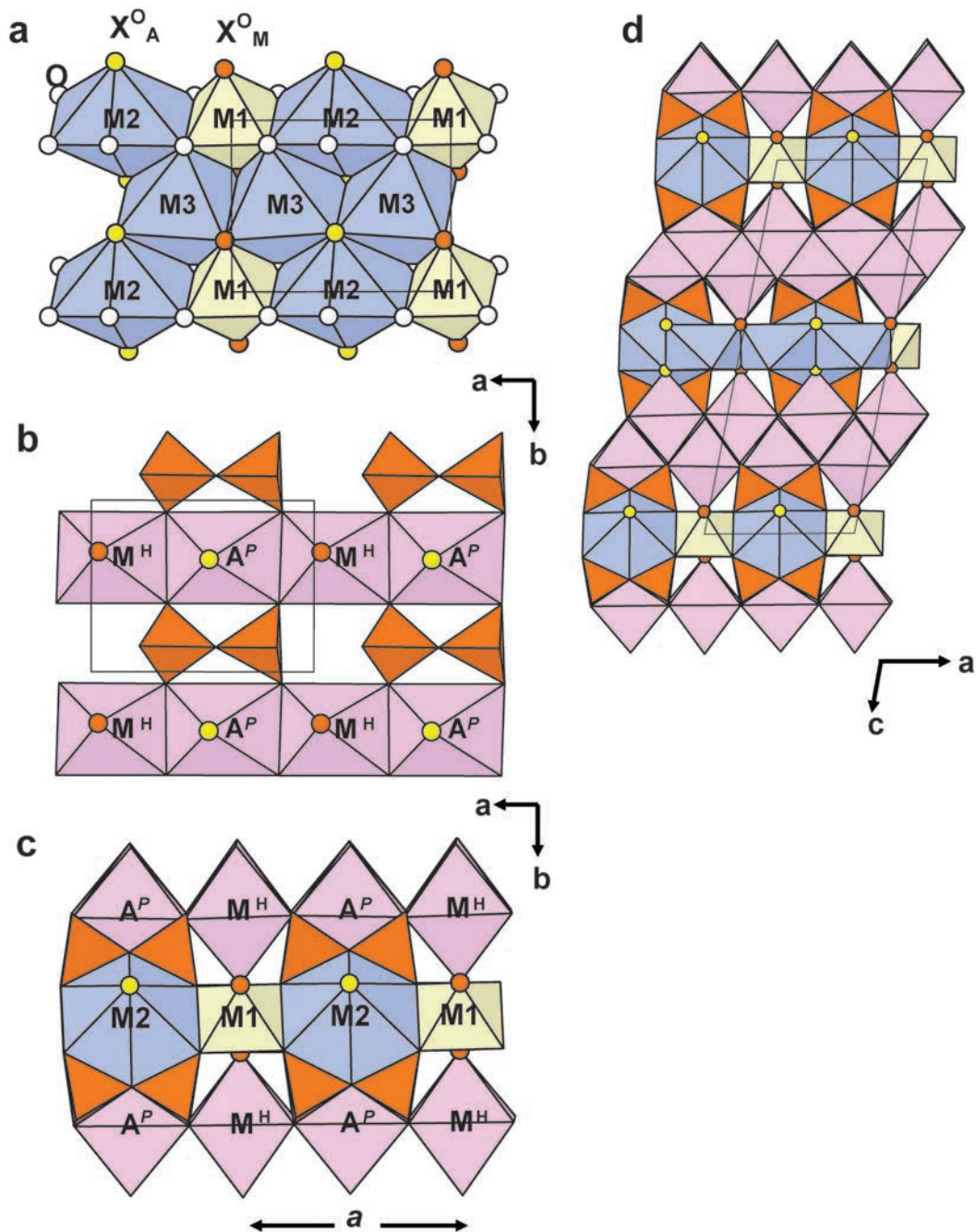


FIG. 1. The crystal structure of rinkite: (a) the O sheet; (b) the H sheet; (c) the TS block; (d) general view of the structure viewed down $[010]$; (SiO_4) tetrahedra are orange, Ti^{4+} -dominant $M^O(1)$ octahedra are yellow, Na-dominant $[8]$ -coordinated $M^O(2)$ polyhedra and $(NaCa)$ $M^O(3)$ octahedra are navy blue, Ca-dominant $[7]$ -coordinated M^H and A^P polyhedra are pink, X_M^O (O,F) and X_A^O (= F) anions are shown as orange and yellow spheres, respectively; in (a) O atoms are shown as white spheres.

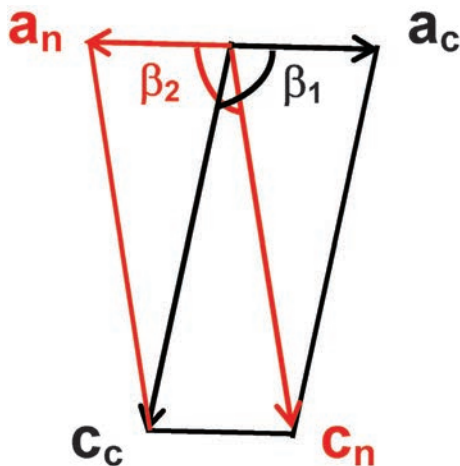


FIG. 2. The relationship between two components in the rinkite crystal: unit cells are shown in black (first component) and red (second component).

apparent reduction of symmetry to space group $P2_1$. As mentioned above, we observed a number of c -glide violations in each of five samples. Our structure refinement shows that the volume of the second component varies from 1 to 85% per crystal (Table 3). Hence pseudomorph twinning is common in rinkite. Polysynthetic twinning on (001) was reported to be common by Lorenzen (1884), although later work did not find these twin lamellae. Bøggild (1953) found that twin lamellae were very common.

The TEM observations of sample 2909 showed it to be pervasively twinned on (001) (Fig. 3a). This is in accord with the twin ratio of 0.58 obtained from structure refinement of this sample (Table 3). The size of every lamella is <200 nm, which is too small to resolve by optical microscopy and explains the milky and inconsistent optical character of the crystals. The size of lamellae is variable and can be as little as one c -length (Fig. 3b). The perfect match of the two overlapping cells at low resolution is clearly shown in the inset in Fig. 3b where no splitting of spots can be detected. The enhancement of reflections with $l = 2n+1$ was reported by Gottardi (1966).

Discussion: the crystal chemistry of rinkite

Ideal mineral formula for rinkite

Sokolova and Cámara (2008a) wrote the ideal formula of rinkite of the form

$A^P_2M_2^HM_4^O(Si_2O_7)_2X_4^O$ as the sum of cation and anion sites, 2H sheets: $(Ca_3REE)Si_4 + O$ sheet: $Na(NaCa)Ti + O_{14} + OF_3 = (Ca_3REE)Na(NaCa)Ti(Si_2O_7)_2OF_3$ in accord with Sokolova (2006), and in the short form $Na_2Ca_4REETi(Si_2O_7)_2OF_3$, $Z = 2$. The ideal formula of rinkite is in close accord with the empirical formula for rinkite of Lorenzen (1884), 14329 (Sokolova and Cámara, 2008a) and the rinkite samples studied in this work (Table 2). The ideal composition of the O sheet, $Na(NaCa)Ti$, reasonably approximates the composition of the $M^O(1-3)$ sites for YuksFe, 3471 and H-08-02 where Na:Ca = 1:1 at the $M^O(3)$ site (Table 6). Although at the $M^O(3)$ site for 1991c and 2909, Na:Ca is ~2:1, Ca >0.5 a.p.f.u. formally allows us to write the same ideal formula for these two samples. The ideal formula for nacareniobsite-(Ce) is $Na_3Ca_3REENb(Si_2O_7)_2OF_3$ (Petersen *et al.*, 1989; Sokolova and Hawthorne, 2008b). Therefore, the samples 1991c and 2909 are intermediate compositions between rinkite and nacareniobsite-(Ce).

Cation and anion substitution in the rinkite structure

Petersen *et al.* (1989) considered the $Nb^{5+} + Na^+ \leftrightarrow Ti^{4+} + Ca^{2+}$ substitution relating ideal nacareniobsite-(Ce), $Na_3Ca_3REENb(Si_2O_7)_2OF_3$, and the Nb-free endmember, the dominant component in rinkite, $Na_2Ca_4REETi(Si_2O_7)_2OF_3$. Sokolova and Hawthorne (2008b) reported the dominance of Nb^{5+} at the $M^O(1)$ site in the nacareniobsite-(Ce) structure and stated that it results in partial substitution of Na for Ca at the $M^O(3)$ site in the O sheet. Petersen *et al.* (1989) and Sokolova and Hawthorne (2008b) discussed a double cation substitution relating rinkite and nacareniobsite-(Ce). They made this assumption considering $(REE + Y)^{3+} \cong \text{constant}$. However, Petersen *et al.* (1989) made an observation that Nb^{5+} and REE^{3+} are distinctly higher in nacareniobsite-(Ce) than in rinkite, whereas Ca and Ti are lower. Table 2 gives $(REE + Y)^{3+}$ of 1.11–1.15, <1.13> for nacareniobsite-(Ce) and 0.73–1.09, <0.96> a.p.f.u. for rinkite [here we do not consider the data of Lorenzen (1884)]. Chemical data for rinkite samples 1991c and 2909 support this trend (Table 2): a high content of Nb^{5+} , 0.33 and 0.34 a.p.f.u., is accompanied by a high content of $(REE+Y)^{3+}$, 1.09 and 1.10 a.p.f.u., which results in low Ca, 0.56 and 0.53 a.p.f.u. plus vacancies of 0.16 □ p.f.u. in the O sheet (Table 6). However, the latter pattern

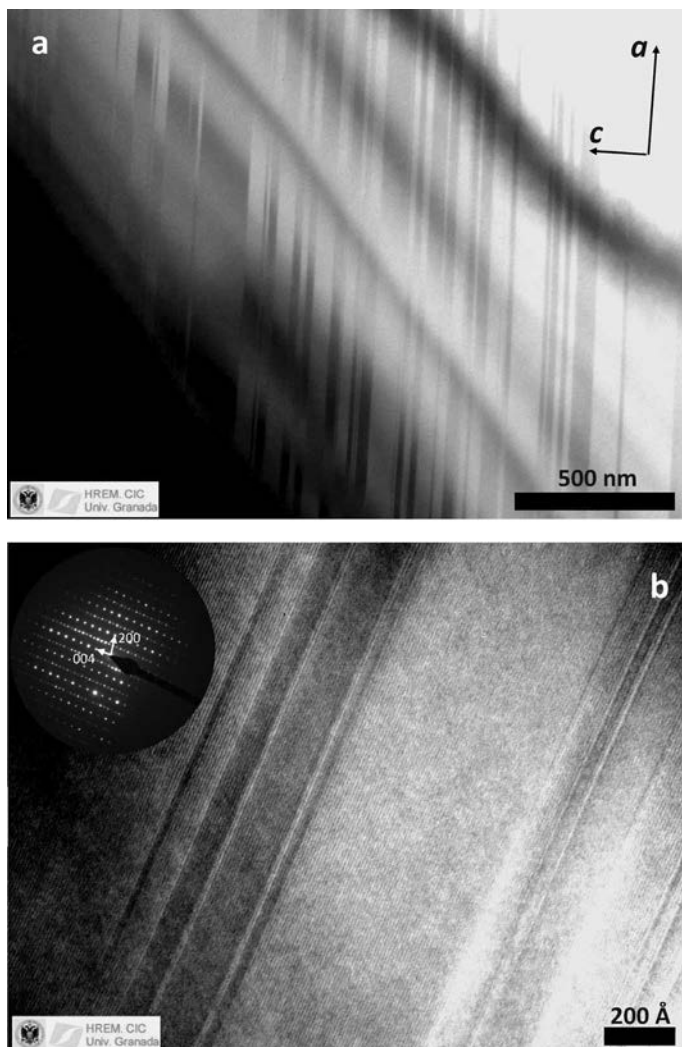


FIG. 3. Transmission electron microscopy images of rinkite 2909 viewed down [010]: (a) low magnification showing the pervasive character of twinning on (001); (b) high resolution detail of some twin lamellae from a few tens of nm wide to hundreds of nm wide. The interface between lamellae is coherent. Upper left inset in (b) shows selected area diffraction of the [010] zone axis; enhancement of reflections with $l = 2n + 1$ in levels with $h = 2n + 1$ is evident.

does not work for H-08-02 (Table 2): a high content of $\text{Nb}^{5+} = 0.29$ a.p.f.u. is accompanied by a low content of $(\text{REE}^{3+} + \text{Y}^{3+} + \text{Th}^{4+})$, 0.73 a.p.f.u., whereas Ca is 0.91 a.p.f.u., a common value for Ca in the O sheet in rinkite (Table 6). Our data clearly indicate that there are three principal cation substitutions in rinkite: (1) $\text{REE}^{3+} \leftrightarrow \text{Ca}^{2+}$ at the M^{H} and A^{P} sites in the H sheet; (2) $\text{Nb}^{5+} \leftrightarrow \text{Ti}^{4+}$ at the $M^{\text{O}}(1)$ site in the

O sheet; (3) $\text{Na}^{+} \leftrightarrow \text{Ca}^{2+}$ at the $M^{\text{O}}(3)$ site in the O sheet; Fig. 4 shows the relation between three cation components in the rinkite structure: **(REE + Y + Th)**, **(Nb + Ta)** and Na a.p.f.u., dominant cations of the components are shown in bold. All data lie close to the plane described by the equation $z = 1.34 + 0.81x + 0.67y$, where $x = \text{Nb}$, $y = \text{REE}$ and $z = \text{Na}$ a.p.f.u. ($R^2 = 0.96$). We conclude that a triple cation substitution is

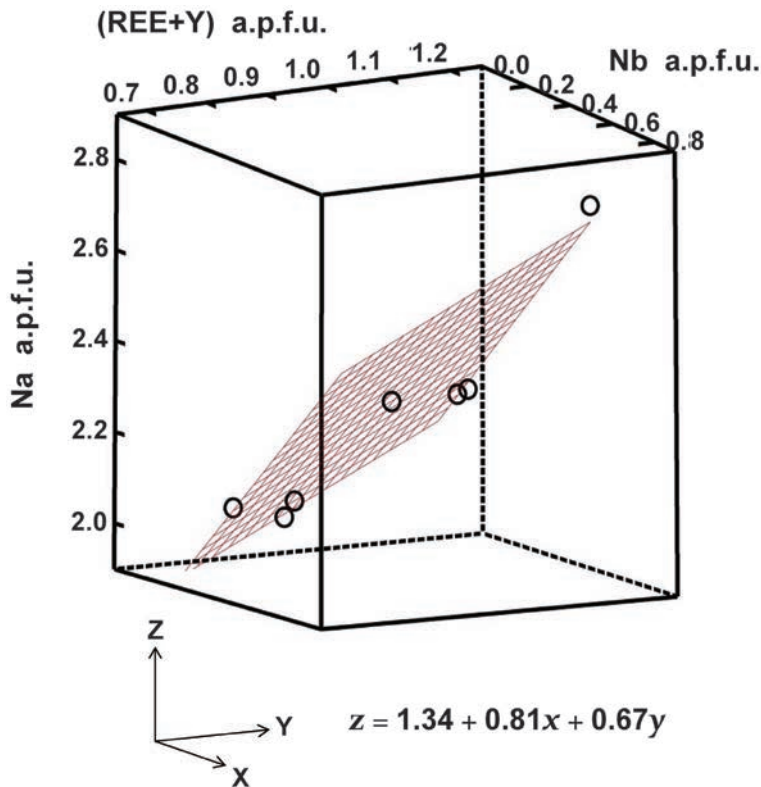


FIG. 4. Three-dimensional plot showing relation between three variable components in rinkite and nacareniobsite-(Ce): $(REE + Y)$ ($= REE + Y + Th$), Nb ($= Nb + Ta$) and Na a.p.f.u. The plot is fitted by a plane with the equation given in the figure. Chemical data are for the five samples used in this work, 14329 (Sokolova and Cámara, 2008a) and nacareniobsite-(Ce) (Sokolova and Hawthorne, 2008a).

characteristic for the rinkite structure. There is one anion substitution in rinkite, $O^{2-} \leftrightarrow F^-$ at the X_M^O site.

On mosandrite

Table 2 shows that chemical analyses of mosandrite are different from those of rinkite and nacareniobsite-(Ce) (Table 2). Mosandrite differs from rinkite in the lower contents of Na and Ca and the presence of H_2O (Bellezza *et al.*, 2009). For mosandrite, Bellezza *et al.* (2009) gave two variants of a simplified formula: $Ti(\square, Ca, Na)_3(Ca, REE)_4(Si_2O_7)_2(OH, F)_4 \cdot \sim 2H_2O$ and $Ti(\square, Ca, Na)_3(Ca, REE)_4(Si_2O_7)_2[H_2O, OH, F]_4 \cdot \sim 1H_2O$. The latter formula is written in accord with the structure-refinement results. The H sheets in rinkite, nacareniobsite-(Ce) and mosandrite are identical and contain the M^H and A^P sites fully occupied by Ca and REE^{3+} ,

$(Ca, REE)_4$. Bellezza *et al.* (2009) suggested that one H_2O group substitutes for OH and F at the X_M^O and X_A^O anion sites, $[H_2O, OH, F]_4$ and another H_2O group substitutes for Na and Ca at the $M^O(2)$ site in the O sheet: $Ti(\square, Ca, Na) + \sim 1H_2O = Ti(\square, H_2O, Ca, Na)$. Thus in the mosandrite of Bellezza *et al.* (2009), the O sheet has the composition $(Ti_{0.93}Nb_{0.08})(\square_{1.82}Ca_{0.79}Mn_{0.07}Fe_{0.03}Na_{0.29})$ and Ca is a dominant cation in the O sheet. We used this structure model for mosandrite (Bellezza *et al.*, 2009) and assigned groups of cations from the chemical analysis of Brøgger (1890). This results in an O sheet of composition $(Ti_{0.52}Zr_{0.47})(\square_{2.11}Na_{0.62}Ca_{0.17}Mn_{0.05}Fe_{0.05})$ (Table 2) where Na is a dominant cation at the alkali $M^O(2)$ and $M^O(3)$ sites. We hesitate to write the ideal formulae for mosandrites of Bellezza *et al.* (2009) and Brøgger (1890) as these two minerals have different dominant alkali cations in the O

sheet. It seems to us that these two mosandrites are different minerals. Mosandrite as a mineral species needs to be properly defined.

Conclusions

There are two major conclusions from this study. (1) Rinkite, ideally $\text{Na}_2\text{Ca}_4\text{REETi}(\text{Si}_2\text{O}_7)_2\text{OF}_3$, is a valid mineral species and a TS-block mineral of Group I. (2) Mosandrite needs to be formally redefined as a mineral species.

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