

FROM STRUCTURE TOPOLOGY TO CHEMICAL COMPOSITION. II. TITANIUM SILICATES: REVISION OF THE CRYSTAL STRUCTURE AND CHEMICAL FORMULA OF DELINDEITE

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ABSTRACT

The crystal structure of delindeite, ideally $\text{Ba}_2\text{Na}_2\text{Ti}_3(\text{Si}_2\text{O}_7)_2\text{O}_2(\text{OH})_2(\text{H}_2\text{O})_2$, a 10.6452(9), b 13.713(1), c 21.600(2) Å, β 93.804(3)°, V 3146.15(5) Å³, space group $C2/c$, $Z = 8$, D_{calc} 3.74 g.cm⁻³ from Mt. Yukspor, Khibina alkaline massif, Kola Peninsula, Russia, has been solved by direct methods and refined to an R_1 value of 6.4% on the basis of 3559 unique reflections ($F_o \geq 4\sigma F$) collected on a Bruker AXS SMART APEX diffractometer with a CCD detector and MoK α radiation. Electron-microprobe analyses gave (wt.%): SiO₂ 27.08, Al₂O₃ 0.29, Nb₂O₅ 1.98, TiO₂ 24.33, Fe₂O₃ 1.07, FeO 0.40, MnO 0.19, BaO 33.20, Na₂O 4.63, K₂O 1.37, F 1.41, H₂O 5.29 (calculated from structure refinement), O=F -0.59, total 100.65. The empirical formula is $(\text{Ba}_{1.92}\text{K}_{0.08})_{\Sigma 2.00}(\text{Na}_{1.33}\text{K}_{0.18}\text{Fe}^{2+}_{0.05}\text{Mn}^{2+}_{0.02}\square_{1.42})_{\Sigma 3.00}(\text{Ti}_{2.70}\text{Fe}^{3+}_{0.12}\text{Nb}_{0.13}\text{Al}_{0.05})_{\Sigma 3.00}(\text{Si}_2\text{O}_7)_2[\text{O}_{1.53}(\text{OH})_{0.47}]_{\Sigma 2.00}[(\text{OH})_{1.34}\text{F}_{0.66}]_{\Sigma 2.00}(\text{H}_2\text{O})_{1.70}$, $Z = 8$, calculated on the basis of 4 Si (*apfu*). The crystal structure of delindeite can be described as combination of two blocks. The first block consists of HCH sheets (H: heteropolyhedral, C: central), and it is related to the TS (titanium silicate) block in Ti disilicate minerals. In the TS block, there are seven fully occupied cation sites, four [4]-coordinated *Si* sites with <Si-O> 1.622 Å and three [6]-coordinated Ti-dominant sites. Two sites, *M*(1) and *M*(2), are coordinated by five O atoms and one OH group, <M(1,2)-O,OH> 1.974 Å; they give $\text{Ti}_{1.88}\text{Nb}_{0.07}\text{Al}_{0.05}$; the *M*(3) site, of composition $\text{Ti}_{0.82}\text{Fe}^{3+}_{0.12}\text{Nb}_{0.06}$, is coordinated by four O atoms and two OH groups, <M(3)-O,OH> 1.964 Å. There are four partially occupied sites: the *Na*(1) and *Na*(2) sites are occupied by Na with minor Fe²⁺ and Mn²⁺ at 70%, <Na(1,2)-O,OH,H₂O> 2.31 Å; the [8]-coordinated *Na*(3) site of composition $(\text{Na}_{0.70}\square_{0.30}, \text{Na(3)-O, H}_2\text{O}) > 2.52$ Å), and the [7]-coordinated *K* site of composition $(\text{K}_{0.18}\square_{0.82}, \text{K-O}) > 2.90$ Å), are at a short distance, 1.25 Å. The *M*(1,2) octahedra and (Si₂O₇) groups constitute the H sheet that is completely ordered. In the C sheet, *M*(3) octahedra and H₂O groups [O(19)] are long-range ordered, whereas Na(1-3) and K atoms and three H₂O groups [O(20-22)] with 46, 44 and 50% occupancy are long-range disordered. Three SRO (short-range order) arrangements have been considered for the C sheet: (1) Na(1), Na(2), 2 Na(3), H₂O [O(22)]; (2) K; (3) 2 H₂O [O(20) and O(21)]. Two H₂O sites [O(20) and O(21)] correspond to two cation sites in the close-packed O sheet of octahedra (O sheet). The substitution $\text{H}_2\text{O} + 2\square \leftrightarrow \text{Na}^+ + 2\text{O}^{2-}$ describes the relation between the composition of the C and O sheets. Linkage of H and C sheets occurs via common vertices of *M*(1,2) octahedra and (Si₂O₇) groups with *M*(3) octahedra. The second or intermediate *I* block includes the [10]-coordinated *Ba*(1) and *Ba*(2) sites of composition $\text{Ba}_{0.92}\text{K}_{0.08}$ and $\text{Ba}_{1.00}$, <Ba(1)-O> 2.961 and <Ba(2)-O> 2.873 Å. The HCH and *I* block, which is a layer of Ba atoms, alternate along *c*. The ideal formula of delindeite is $\text{Ba}_2\text{Na}_2\text{Ti}_3(\text{Si}_2\text{O}_7)_2\text{O}_2(\text{OH})_2(\text{H}_2\text{O})_2$, $Z = 8$. The crystal structure reported here explains why the TS block in delindeite exhibits topology different from that of the titanium disilicate minerals, where the central sheet is trioctahedral.

Keywords: delindeite, Ti disilicate minerals, structure refinement, electron-microprobe data, structure topology, chemical formula, TS block.

SOMMAIRE

Nous avons résolu la structure cristalline de la delindéite, dont la formule idéale serait $\text{Ba}_2\text{Na}_2\text{Ti}_3(\text{Si}_2\text{O}_7)_2\text{O}_2(\text{OH})_2(\text{H}_2\text{O})_2$, a 10.6452(9), b 13.713(1), c 21.600(2) Å, β 93.804(3)°, V 3146.15(5) Å³, groupe spatial $C2/c$, $Z = 8$, D_{calc} 3.74 g.cm⁻³, provenant du mont Yukspor, complexe alcalin de Khibina, péninsule de Kola, en Russie, jusqu'à une valeur de R_1 de 6.4%; nous nous sommes servis de 3559 réflexions uniques ($F_o \geq 4\sigma F$) mesurées avec un diffractomètre Bruker AXS SMART APEX muni d'un détecteur CCD (rayonnement MoK α). Les analyses effectuées avec une microsonde électronique ont donné: SiO₂ 27.08, Al₂O₃ 0.29, Nb₂O₅ 1.98, TiO₂ 24.33, Fe₂O₃ 1.07, FeO 0.40, MnO 0.19, BaO 33.20, Na₂O 4.63, K₂O 1.37, F 1.41, H₂O 5.29 (calculé à partir des données structurales), O=F -0.59, pour un total de 100.65% (poids). La formule empirique, fondée sur une base de quatre atomes de Si par formule unitaire, est $(\text{Ba}_{1.92}\text{K}_{0.08})_{\Sigma 2.00}(\text{Na}_{1.33}\text{K}_{0.18}\text{Fe}^{2+}_{0.05}\text{Mn}^{2+}_{0.02}\square_{1.42})_{\Sigma 3.00}(\text{Ti}_{2.70}\text{Fe}^{3+}_{0.12}\text{Nb}_{0.13}\text{Al}_{0.05})_{\Sigma 3.00}(\text{Si}_2\text{O}_7)_2[\text{O}_{1.53}(\text{OH})_{0.47}]_{\Sigma 2.00}[(\text{OH})_{1.34}\text{F}_{0.66}]_{\Sigma 2.00}(\text{H}_2\text{O})_{1.70}$, $Z = 8$. On peut décrire la structure de la delindéite en termes d'une

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combinaison de deux blocs. Le premier consiste de feuillets HCH (H: heteropolyédrique, C: central); il ressemble au bloc TS (silicate de titane) dans les minéraux disilicatés de Ti. Dans le bloc TS, il y a sept sites de cations remplis, quatre sites *Si* à coordination [4] avec $\langle \text{Si-O} \rangle$ égal à 1.622 Å, et trois sites où le Ti est prédominant, à coordination [6]. Deux sites, *M*(1) et *M*(2), sont coordonnés à cinq atomes d'oxygène et un groupe OH, $\langle \text{M}(1,2)\text{-O,OH} \rangle$ 1.974 Å, et ont une population $\text{Ti}_{1.88}\text{Nb}_{0.07}\text{Al}_{0.05}$; le site *M*(3), de composition $\text{Ti}_{0.82}\text{Fe}^{3+}_{0.12}\text{Nb}_{0.06}$, est coordonné par quatre atomes d'oxygène et deux groupes OH, $\langle \text{M}(3)\text{-O,OH} \rangle$ 1.964 Å. Il y a quatre sites à occupation partielle: le site *Na*(1) et les sites *Na*(2) sont occupés par Na avec une proportion mineure de Fe^{2+} et Mn^{2+} à un taux de 70%, $\langle \text{Na}(1,2)\text{-O,OH,H}_2\text{O} \rangle$ 2.31 Å; le site *Na*(3), à coordination [8], de composition $(\text{Na}_{0.70}\square)_{0.30}$, $\langle \text{Na}(3)\text{-O,H}_2\text{O} \rangle$ 2.52 Å, et le site *K*, à coordination [7], de composition $(\text{K}_{0.18}\square)_{0.82}$, $\langle \text{K-O} \rangle$ 2.90 Å, sont situés à une courte distance, 1.25 Å, l'un de l'autre. Les octaèdres *M*(1,2) et les groupes (Si_2O_7) forment le feuillet H, qui est complètement ordonné. Dans le feuillet C, les octaèdres *M*(3) et les groupes H_2O [O(19)] sont ordonnés à longue échelle, tandis que les atomes *Na*(1–3) et *K* et les trois groupes H_2O [O(20–22)], avec un taux d'occupation de 46, 44 et 50%] sont désordonnés à longue échelle. Trois agencements ordonnés à courte échelle ont été considérés pour le feuillet C: (1) *Na*(1), *Na*(2), 2 *Na*(3), H_2O [O(22)]; (2) *K*; (3) 2 H_2O [O(20) et O(21)]. Deux sites H_2O [O(20) et O(21)] correspondent à deux sites de cations dans le feuillet O, qui est un empilement compact d'octaèdres. La substitution $\text{H}_2\text{O} + 2\square \leftrightarrow \text{Na}^+ + 2\text{O}^{2-}$ décrit la relation entre la composition des feuillets C et O. Les liaisons entre les feuillets H et C sont assurées via les vertex des octaèdres *M*(1,2) et des groupes (Si_2O_7) avec les octaèdres *M*(3). Le second bloc (ou le bloc intermédiaire) **I** inclut les sites à coordination [10], *Ba*(1) et *Ba*(2) de composition $\text{Ba}_{0.92}\text{K}_{0.08}$ et $\text{Ba}_{1.00}$, $\langle \text{Ba}(1)\text{-O} \rangle$ 2.961 et $\langle \text{Ba}(2)\text{-O} \rangle$ 2.873 Å. Les agencements HCH et le bloc **I**, qui est une couche d'atomes *Ba*, alternent le long de *c*. La formule idéale de la delindeite est $\text{Ba}_2\text{Na}_2\text{Ti}_3(\text{Si}_2\text{O}_7)_2\text{O}_2(\text{OH})_2(\text{H}_2\text{O})_2$, *Z* = 8. D'après la structure cristalline décrite ici, on peut voir pourquoi le bloc TS de la delindeite possède une topologie différente de celle des minéraux disilicatés de titane, dans lesquels le feuillet central est trioctaédrique.

(Traduit par la Rédaction)

Mots-clés: delindeite, minéraux disilicatés de Ti, affinement de la structure, données de microsonde électronique, topologie de la structure, formule chimique, bloc TS.

INTRODUCTION

Delindeite was originally described from nepheline syenites of the Magnet Cove alkaline complex, Arkansas, U.S.A. (Appleman *et al.* 1987), with the formula $(\text{Na,K})_{2.7}(\text{Ba,Ca})_4(\text{Ti,Fe,Al})_6\text{Si}_8\text{O}_{26}(\text{OH})_{14}$, *Z* = 1, and the following properties, including unit-cell parameters refined from X-ray powder data: *a* 21.617(13), *b* 6.816(5), *c* 5.383(3) Å, β 94.03(5)°, *V* 791.18 Å³, space group *C2/m*, *Z* = 2, *D*_{calc} = 3.7 g cm⁻³, *D*_{obs} = 3.3 g cm⁻³. Khomyakov (1995) reported the second occurrence of delindeite at Mt. Yukspor, Khibina alkaline massif, Kola Peninsula, Russia, and gave the ideal formula for the Khibina delindeite as $\text{Na}_2\text{Ba}_2\text{Ti}_3\text{Si}_4\text{O}_{16}(\text{OH,F})_2$, *Z* = 2. The third occurrence of delindeite was reported by A.S. Podlesnyi at the Kirovskii apatite mine in the Khibina alkaline complex (Ferraris *et al.* 2001). The crystal structure of delindeite was reported by Ferraris *et al.* (2001): *a* 5.327(2), *b* 6.856(2), *c* 21.51(3) Å, β 93.80(4)°, *V* 783.96 Å³, space group *A2/m*, *Z* = 2, *D*_{calc} = 3.815 g cm⁻³, *R* = 5.4%. They gave the empirical formula as $(\text{Na}_{1.40}\text{K}_{0.20}\text{Sr}_{0.02}\text{Ca}_{0.01}\square_{1.37})_{\Sigma 3.00}\text{Ba}_{2.02}(\text{Ti}_{2.60}\text{Fe}^{3+}_{0.33}\text{Mn}^{2+}_{0.05}\text{Nb}_{0.03}\text{Zn}_{0.01})_{\Sigma 3.02}(\text{Si}_{3.91}\text{Al}_{0.09})_{\Sigma 4.00}\text{O}_{15.26}(\text{OH})_{2.74}(\text{H}_2\text{O})_{1.62}$, calculated on the basis of 4 (*Si* + *Al*) *apfu*, (atoms per formula unit). An ideal formula, $\text{Ba}_2\{(\text{Na,K},\square)_3(\text{Ti,Fe})[\text{Ti}_2(\text{O,OH})_4\text{Si}_4\text{O}_{14}](\text{H}_2\text{O,OH})_2\}$, was reported by Ferraris *et al.* (2001).

Sokolova (2006) considered the structural hierarchy and stereochemistry for twenty-four titanium disilicate minerals containing the TS block, a trioctahedral central sheet and two adjacent sheets containing different

polyhedra including (Si_2O_7) groups. Sokolova (2006) established the relation between structure topology and chemical composition for those minerals and divided them into four groups, each characterized by a different topology and stereochemistry of the 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 *apfu*, respectively. Delindeite was not considered by Sokolova (2006), as the central sheet is not trioctahedral. However, the structure reported for delindeite is not in accord with the topological and stereochemical findings of Sokolova (2006). In delindeite, Ti is equal to 3 *apfu*, and therefore the TS block should have the stereochemistry of Group III. In Group III, Ti occurs in the O and H sheets, and the (Si_2O_7) groups link to the Ti octahedron of the O sheet. In contrast, in the crystal structure of delindeite reported by Ferraris *et al.* (2001), (Si_2O_7) groups link to the partly occupied Na octahedron of the O sheet, as in Group I. The reason for this was not apparent from the structure.

A sample of delindeite from Mt. Yukspor, Khibina alkaline massif, Kola Peninsula, Russia, was kindly provided by Adriana and Renato Pagano, Milan, Italy, from their mineral collection (Collezione Mineralogica, sample #6270). This sample of delindeite came from A.P. Khomyakov and was described in Khomyakov (1995). In this paper, we present a revision of the chemical formula and crystal structure of delindeite, and we explain why the topology of the TS block is different from its topology in titanium disilicate minerals.

ELECTRON-MICROPROBE ANALYSIS

One fragment of the crystal of delindeite previously used for the structure refinement was analyzed with a Cameca SX100 electron microprobe operating in wavelength-dispersion mode with an accelerating voltage of 15 kV, a specimen current of 20 nA, a beam size of 10 μm , and count times on peak and background of 20 and 30 s for major and minor elements (<1 wt.%), respectively. The following standards and crystals were used for *K* or *L* X-ray lines: F: riebeckite, Na: jadeite, Ba: barite, Si, Ca: diopside, Fe: fayalite, Mn: spessartine, K: orthoclase, Ti: titanite, Zn: zircon, Nb: BaNaNbO₆, Mg: forsterite, Sr: strontianite, and Al: andalusite. The data were reduced using the $\phi(\rho Z)$ procedure of Pouchou & Pichoir (1985). The crystal of delindeite was analyzed for Li by laser-ablation – inductively coupled plasma – mass spectrometry (LA-ICP-MS), and no Li was detected. The chemical composition of delindeite is given in Table 1 and is the mean of 10 determinations.

The empirical formula is $(\text{Ba}_{1.92} \text{K}_{0.08})_{\Sigma 2.00} (\text{Na}_{1.33} \text{K}_{0.18} \text{Fe}^{2+}_{0.05} \text{Mn}^{2+}_{0.02} \square_{1.42})_{\Sigma 3.00} (\text{Ti}_{2.70} \text{Fe}^{3+}_{0.12} \text{Nb}_{0.13} \text{Al}_{0.05})_{\Sigma 3.00} (\text{Si}_2\text{O}_7)_2 [\text{O}_{1.53} (\text{OH})_{0.47}]_{\Sigma 2.00} [(\text{OH})_{1.34} \text{F}_{0.66}]_{\Sigma 2.00} (\text{H}_2\text{O})_{1.70}$, $Z=8$, calculated on the basis of 4 Si (*apfu*). The ideal formula $\text{Ba}_2 \text{Na}_2 \text{Ti}_3 (\text{Si}_2\text{O}_7)_2 \text{O}_2 (\text{OH})_2 (\text{H}_2\text{O})_2$ is in very close agreement (excluding H_2O) with the ideal formula of Khomyakov (1995), $\text{Na}_2 \text{Ba}_2 \text{Ti}_3 \text{Si}_4 \text{O}_{16} (\text{OH}, \text{F})_2$.

DATA COLLECTION AND CRYSTAL-STRUCTURE REFINEMENT

A single crystal of delindeite was mounted on a Bruker AXS SMART APEX diffractometer equipped with graphite-filtered $\text{MoK}\alpha$ X-radiation and a CCD detector. The intensities of 35700 reflections with $-15 < h < 15$, $-19 < k < 19$, $-30 < l < 30$ were collected to 64.06° 2θ using 20 s per 0.2° frame, and an empirical

absorption-correction (SADABS, Sheldrick 1998) was applied. The refined unit-cell parameters (Table 2) were obtained from 8655 reflections with $I > 10\sigma I$. Analysis of the distribution of intensities showed that $R_{(\text{int})}$ is significantly higher where $57.00 < 2\theta < 64.06^\circ$. The refinement thus was done with $2\theta < 57.00^\circ$ and $-14 < h < 14$, $-18 < k < 18$, $-28 < l < 28$, respectively. On the basis of 4056 unique observed reflections ($F_o > 4\sigma F$), the crystal structure of delindeite was refined in space group *C2/m* with the Bruker SHELXTL Version 5.1 system of programs (Sheldrick 1997) to $R_1 = 6.4\%$ and a GoF of 1.27. Scattering curves for neutral atoms were taken from the International Tables for Crystallography (1992). The *R* indices are given in Table 2, and are expressed as percentages. Site occupancies for the *M*, *Na*, *K*, *Ba* and H_2O sites were refined with the scattering curves of Ti, Na, K, Ba and O, respectively. The structure refinement was also done in space group *C2/c*, and refinement parameters are given in brackets in Table 2. Although there are 66 reflections violating the *c* glide (3559 versus 3625 in Table 2) and refinement parameters are very similar in both space groups, *C2/c* and *C2/m*, the latter space-group corresponds to a structure model with (1) negative principal mean square atomic-displacement parameters for approximately one third of the cations and one third of the anions; (2) more pronounced disorder of anions and resulting inadequate coordination-numbers for Si [*e.g.*, 5, as in Ferraris *et al.* (2001)]. The *c*-glide violations are probably due to a *c* parameter modulation that produces an incommensurate structure. We noted evidence of this modulation in the diffraction pattern, but our attempts to refine the modulated structure were unsuccessful.

The unit-cell volume of delindeite reported here, 3146.15 \AA^3 , is four times larger than those reported by Appleman *et al.* (1987), 791.18 , and by Ferraris *et al.* (2001), 783.96 \AA^3 . The quadruple increase in the unit-cell volume results from doubling of two unit-cell parameters, *a* $10.6452(9)$, *b* $13.713(1) \text{ \AA}$ (Table 2), compared to *a* $5.327(2)$, *b* $6.856(2) \text{ \AA}$ (Ferraris *et al.* 2001) and *b* $6.816(5)$, *c* $5.383(3) \text{ \AA}$ (Appleman *et al.* 1987). Doubling of two unit-cell parameters is in accord with a conclusion of Appleman *et al.* (1987) that “continuous diffraction streaks parallel to \mathbf{a}^* double the *b* and *c* axes”.

At the last stages of refinement, four peaks were found in the difference-Fourier map, close to the *M*(1), *M*(2), *Ba*(11) and *Ba*(2) sites (0.56, 0.57, 0.66 and 0.69 \AA , respectively). These subsidiary sites were included in the refinement, and their site occupancies were refined with the scattering curves of Ti and Ba. The refined site-occupancies are approximately 10% of the occupancies of the associated *Ti* sites and 2% of the occupancies of the associated *Ba* sites. These four subsidiary sites are probably due to the modulated structure of delindeite, and they are listed at the bottom of Table 3.

Details of the data collection and structure refinement are given in Table 2, final atom-parameters are given

TABLE 1. CHEMICAL COMPOSITION* AND UNIT FORMULA** OF DELINDEITE

SiO_2 wt. %	27.08	Si <i>apfu</i>	4.00	Na <i>apfu</i>	1.33
Nb_2O_5	1.98	Σ	4.00	K	0.18
TiO_2	24.33			Fe^{2+}	0.05
MnO	0.19	Ti^{2+}	1.88	Mn^{2+}	0.02
Fe_2O_3	1.07	Nb	0.07	$\Sigma 3\text{M}^\circ$	1.58
Al_2O_3	0.29	Al	0.05		
Na_2O	4.63	$\Sigma 2\text{M}^\dagger$	2.00	Ba	1.92
FeO	0.40			K	0.08
K_2O	1.37	Ti^{3+}	0.82	$\Sigma 2\text{A}^\ddagger$	2.00
BaO	33.20	Fe^{3+}	0.12		
F	1.41	Nb	0.06	O^{2-}	1.53
H_2O^{***}	5.29	$\Sigma 1\text{M}^\circ$	1.00	$(\text{OH})^-$	0.47
O=F	-0.59			$\Sigma 2\text{X}^\ddagger_{14}$	2.00
Total	100.65			F^-	0.66
				(OH)	1.34
				$\Sigma 2\text{X}^\circ_{15}$	2.00
				H_2O	1.70

* MgO , SrO , CaO and Li_2O were not detected. ** Formula contents on a basis of 4 Si^{4+} . *** Calculated from structure refinement.

in Table 3, selected interatomic distances and angles in Table 4, refined site-scattering values and assigned populations for selected sites in Table 5, bond-valence values in Table 6, and proposed hydrogen bonding in Table 7. A structure-factor table may be obtained from the Depository of Unpublished Data on the MAC web site [document Delindeite cm45_xxx].

DESCRIPTION OF THE STRUCTURE

Cation sites

H sheet: In the crystal structure of delindeite, there are four tetrahedrally coordinated sites occupied by Si with a grand $\langle\text{Si-O}\rangle$ distance of 1.622 Å. There are two [6]-coordinated Ti-dominant sites, *M*(1) and *M*(2), coordinated by five O atoms and one OH-dominant group, with $\langle\text{M}(1)\text{-O,OH}\rangle$ equal to 1.969 and $\langle\text{M}(2)\text{-O,OH}\rangle$ equal to 1.978 Å (Table 4); these two sites are occupied by $\text{Ti}_{1.88}\text{Nb}_{0.07}\text{Al}_{0.05}$ (Table 5). We refer to the OH-dominant group as the OH group.

C sheet: The *M*(3) site, $\text{Ti}_{0.81}\text{Fe}^{3+}_{0.13}\text{Nb}_{0.06}$, is coordinated by four O atoms and two OH groups with $\langle\text{M-O,OH}\rangle$ equal to 1.964 Å. There are four sites partly occupied by alkali cations. The *Na*(1) and *Na*(2) sites are [6]-coordinated by two O atoms, two OH and two H₂O groups, and are each 70% occupied by Na with minor Fe^{2+} and Mn^{2+} (Table 5), with $\langle\text{Na}(1,2)\text{-O,OH,H}_2\text{O}\rangle$ equal to 2.31 Å. The [8]-coordinated *Na*(3) site, $\text{Na}_{0.70}\square_{0.30}$, is coordinated by six O atoms and two H₂O groups [central atoms O(19) and O(22), the latter is 50% occupied] with $\langle\text{Na}(3)\text{-O,H}_2\text{O}\rangle$ equal to 2.52 Å. The *K* site is coordinated by seven O atoms with $\langle\text{K-O}\rangle$ equal to 2.90 Å. There is a short *Na*(3)–*K* distance, 1.25 Å. The *Na*(3) and *K* sites add to $(\text{Na}_{0.70}\text{K}_{0.18}\square_{0.12})$.

I block: There are two [10]-coordinated *Ba*(1) and *Ba*(2) sites, which are occupied by $\text{Ba}_{1.92}\text{K}_{0.08}$, with $\langle\text{Ba}(1)\text{-O}\rangle$ equal to 2.961 and $\langle\text{Ba}(2)\text{-O}\rangle$ equal to

2.873 Å. The significant difference in observed and calculated mean *Ba*(1)–O distances results from Ba disorder around the *Ba*(1) site (Table 5). The aggregate *Ba*(1) content is the sum of the three sites, *Ba*(11), *Ba*(12), *Ba*(13). The *Ba*(11) site is 88% occupied, $\text{Ba}_{0.80}\text{K}_{0.08}$; the *Ba*(12) and *Ba*(13) sites are occupied by Ba at 5 and 7%. In Table 5, calculated and observed $\langle\text{X-}\phi\rangle$ values correspond to $\langle\text{Ba}(11)\text{-O}\rangle$, as there is no possibility to build reasonable polyhedra around *Ba*(12) and *Ba*(13) atoms.

Anion considerations

There are 14 anion sites, O(1)–O(14), occupied by O atoms which constitute the tetrahedral coordination of the Si atoms (Tables 3, 4). There are two sites, O(15) and O(16), that receive a bond-valence of 1.44 and 1.46 valence units (*vu*), respectively (Table 6). The assignment of anion species to these particular sites is ambiguous if one considers bond valences only; in addition, we need to consider $\text{Ti}^{\text{H}}\text{-X}_{\text{M}}^{\text{P}}$ bond lengths (Fig. 1). The bond lengths *M*(1)–O(15) and *M*(2)–O(16) [*M*(1) and *M*(2) = $\text{M}^{\text{H}} = \text{Ti}^{\text{H}}$, and O(15) and O(16) = $\text{X}_{\text{M}}^{\text{P}}$ in the terminology of Sokolova (2006)] are shorter than usual for $\text{Ti}^{\text{H}}\text{-OH}$ bonds and are in accord with $\text{Ti}^{\text{H}}\text{-O}$ bonds. Nevertheless, we assign aggregate $\text{O}_{1.53}\text{OH}_{0.47}$ to these two sites. This assignment is dictated by the electroneutrality of the formula unit, and we will discuss this issue later. There are two sites, O(17) and O(18), which receive bond-valences of 1.12 and 1.16 *vu*, from two Ti atoms [*M*(1) + *M*(3) and *M*(2) + *M*(3)] and two Na atoms [*Na*(2) and *Na*(1)], respectively (Table 6). Therefore, they must be occupied by monovalent anions. The chemical analysis gives F 0.66 *apfu* (Table 1), O(17) and O(18) sites constitute 2 *apfu*, and therefore we assign $\text{OH}_{0.66}\text{F}_{0.33}$ to both O(17) and O(18). This assignment is supported by the variation of $\text{Ti}^{\text{H}}\text{-X}_{\text{M}}^{\text{P}}$ bond lengths in Ti disilicate minerals with the TS block, shown in Figure 1. There are four H₂O sites, O(19), O(20), O(21) and O(22), occupied by H₂O groups at 100, 44, 46 and 50%, respectively (Tables 3, 5). The resultant total content of H₂O is 1.70 *apfu*.

Structure topology

In the Ti disilicate minerals (Sokolova 2006), the TS block consists of HOH sheets, where H stands for a heteropolyhedral sheet including (Si₂O₇) groups, and O stands for a trioctahedral close-packed sheet. In the crystal structure of delindeite, (SiO₄) tetrahedra link together to form (Si₂O₇) groups. The (Si₂O₇) groups and *M*(1,2) octahedra share common vertices to form the H sheet, as in Ti disilicate minerals (Fig. 2a). The trioctahedral sheet is of the form $\text{M}^{\text{O}}\text{X}^{\text{O}}_2$, where M^{O} are cations and X^{O} are anions. Structures with the TS block have characteristic two-dimensional minimal cell in the plane of the O sheet with $t_1 \approx 5.5$ and $t_2 \approx 7.1$ Å, $\mathbf{t}_1 \wedge \mathbf{t}_2 \approx 90^\circ$, and this minimal cell contains 4 [$\text{M}^{\text{O}}\text{X}^{\text{O}}_2$]. In

TABLE 2. MISCELLANEOUS DATA RELEVANT TO THE STRUCTURE REFINEMENT OF DELINDEITE

<i>a</i> (Å)	10.6968(3)	Space group	<i>C2/c</i> (<i>C2/m</i>)*
<i>b</i>	13.7535(4)	<i>Z</i>	8
<i>c</i>	21.5758(7)	Absorption coefficient (mm ⁻¹)	6.79
β (°)	93.975(1)	<i>F</i> (000)	3332.1
<i>V</i> (Å ³)	3166.2(2)	<i>D</i> _{calc} (g/cm ³)	3.74
		Crystal size (mm)	0.12 × 0.06 × 0.02
		Radiation/filter	MoK α /graphite
2 θ range for data collection (°)	57		
<i>R</i> (int) (%)	3.5 (3.6)		
Reflections collected	37500		
Independent reflections	4027 (4188)		
$F_o > 4\sigma F_o$	3559 (3625)		
Refinement method	Full-matrix least-squares on <i>F</i> ² , fixed weights proportional to $1/\sigma F_o^2$		
Goodness of fit on <i>F</i> ²	1.27 (1.28)		
Final <i>R</i> (obs) (%) [$F_o > 4\sigma F_o$]	6.37 (7.37)		
<i>R</i> indices (all data) (%)	<i>R</i> _w = 7.07 (9.15)		
	<i>WR</i> ₂ = 13.25 (16.82)		
	GoF = 1.27 (1.28)		

* refinement parameters in space group *C2/m* are given in brackets.

TABLE 3. FINAL POSITIONS AND DISPLACEMENT PARAMETERS OF ATOMS IN DELINDEITE

ATOM	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	U_{eq}	
M(1)	0.38757(16)	0.85893(14)	0.09448(11)	0.0020(7)	0.0042(8)	0.0654(14)	0.0012(8)	-0.0012(7)	0.0002(6)	0.0240(5)	
M(2)	0.88604(16)	0.89329(14)	0.09518(12)	0.0024(7)	0.0046(9)	0.0639(14)	0.0002(9)	-0.0000(7)	0.0002(6)	0.0238(6)	
M(3)	0.25190(13)	0.87424(11)	0.25012(6)	0.0200(7)	0.0081(6)	0.0106(6)	0.0008(4)	-0.0056(5)	0.0013(5)	0.0132(4)	
Si(1)	0.6349(2)	1.00912(15)	0.12935(9)	0.0135(9)	0.0107(9)	0.0085(9)	0.0056(7)	-0.0031(8)	-0.0066(8)	0.0111(4)	
Si(2)	0.13225(19)	0.73988(14)	0.12996(10)	0.0064(8)	0.0053(8)	0.0153(10)	0.0053(7)	-0.0016(7)	-0.0051(7)	0.0091(4)	
Si(3)	0.6546(2)	0.73819(14)	0.12726(10)	0.0142(10)	0.0026(8)	0.0147(10)	0.0027(7)	-0.0021(8)	0.0039(7)	0.0106(4)	
Si(4)	0.15760(18)	1.00927(15)	0.12797(9)	0.0043(8)	0.0113(9)	0.0076(9)	0.0038(7)	-0.0007(7)	0.0042(7)	0.0078(4)	
Na(1)	0	0.0035(4)	¼	0	0.0061(17)	0.020(2)	0.017(2)	0	0.0036(13)	0	0.0141(11)
Na(2)	0	0.2466(5)	¼	0	0.0061(17)	0.020(2)	0.017(2)	0	0.0036(13)	0	0.0141(11)
Na(3)	0.2733(6)	0.1240(4)	0.2459(2)	0.043(3)	0.013(2)	0.016(2)	-0.0043(19)	-0.010(2)	0.010(2)	0.0244(12)	
K	0.3797(12)	0.1275(9)	0.2255(6)	0.035(6)	0.027(6)	0.035(6)	0.002(5)	-0.009(5)	-0.005(5)	0.033(3)	
Ba(1)											
Ba(11)	0.37632(7)	0.12358(7)	0.02637(3)	0.00937(17)	0.0115(2)	0.01483(15)	0.00405(14)	-0.00034(13)	-0.0010(3)	0.01197(11)	
Ba(12)	0.3791(13)	0.1486(9)	0.0268(6)	0.0094(2)	0.01154(17)	0.0148(2)	0.00405(15)	-0.00034(14)	-0.00103(13)	0.01197(12)	
Ba(13)	0.3687(10)	0.1080(7)	0.0173(5)	0.0094(2)	0.01154(17)	0.0148(2)	0.00405(15)	-0.00034(14)	-0.0010(13)	0.01197(12)	
Ba(2)	0.87711(4)	0.12669(4)	0.01767(2)	0.0094(2)	0.01154(17)	0.0148(2)	0.00405(15)	-0.00034(14)	-0.00103(13)	0.01197(12)	
O(1)	0.5170(6)	0.9602(4)	0.0896(3)	0.016(3)	0.014(3)	0.015(3)	-0.005(2)	-0.001(2)	0.002(2)	0.0151(12)	
O(2)	0.7599(5)	0.9979(5)	0.0931(3)	0.006(2)	0.027(3)	0.024(3)	0.020(2)	-0.000(2)	0.001(2)	0.0192(13)	
O(3)	0.6512(6)	0.9714(4)	0.2002(2)	0.023(3)	0.020(3)	0.005(2)	0.003(2)	-0.006(2)	-0.001(2)	0.0163(12)	
O(4)	0.5944(6)	1.1267(4)	0.1341(3)	0.020(3)	0.008(2)	0.025(3)	-0.001(2)	-0.003(2)	-0.003(2)	0.0179(12)	
O(5)	0.2578(5)	0.7563(4)	0.0948(3)	0.012(3)	0.018(3)	0.028(3)	0.006(2)	0.008(2)	-0.007(2)	0.0190(13)	
O(6)	0.0136(5)	0.7907(5)	0.0929(3)	0.005(2)	0.033(3)	0.022(3)	-0.009(3)	-0.003(2)	0.009(2)	0.0198(13)	
O(7)	0.1540(6)	0.7789(4)	0.2009(3)	0.031(3)	0.012(3)	0.022(3)	-0.002(2)	0.001(3)	-0.010(3)	0.0218(14)	
O(8)	0.7505(6)	0.7946(5)	0.0844(3)	0.016(3)	0.022(3)	0.023(3)	-0.001(2)	0.003(2)	-0.002(2)	0.0199(13)	
O(9)	0.6737(6)	0.7705(4)	0.1998(3)	0.021(3)	0.010(2)	0.015(3)	-0.002(2)	0.004(2)	-0.005(2)	0.0153(12)	
O(10)	0.5130(4)	0.7549(4)	0.1008(3)	0.003(2)	0.009(2)	0.029(3)	0.002(2)	-0.001(2)	0.0016(19)	0.0138(12)	
O(11)	0.2997(5)	0.6251(4)	0.3746(3)	0.013(2)	0.010(2)	0.019(3)	0.001(2)	-0.000(2)	-0.003(2)	0.0139(11)	
O(12)	0.0152(6)	0.9986(5)	0.1012(3)	0.016(3)	0.039(4)	0.019(3)	0.013(3)	-0.009(2)	-0.006(3)	0.0252(15)	
O(13)	0.1751(6)	0.9801(5)	0.2007(3)	0.018(3)	0.025(3)	0.004(2)	0.002(2)	-0.003(2)	0.004(2)	0.0158(12)	
O(14)	0.2560(5)	0.9573(4)	0.0850(3)	0.012(2)	0.019(3)	0.009(2)	0.003(2)	-0.002(2)	0.008(2)	0.0132(11)	
O(15)	0.3838(5)	0.8486(5)	0.0079(3)	0.007(2)	0.047(4)	0.007(2)	-0.001(3)	-0.0014(19)	0.002(2)	0.0202(14)	
O(16)	0.8794(5)	0.9031(4)	0.0082(3)	0.009(2)	0.016(3)	0.013(2)	0.006(2)	-0.002(2)	-0.001(2)	0.0130(11)	
O(17)	0.3870(5)	0.8666(4)	0.1906(3)	0.017(3)	0.014(3)	0.017(3)	-0.000(2)	0.003(2)	-0.000(2)	0.0158(12)	
(OH)											
O(18)	0.1173(6)	0.8837(5)	0.3094(3)	0.016(3)	0.028(3)	0.014(3)	-0.001(2)	0.002(2)	0.002(3)	0.0190(13)	
(OH)											
O(19)	0.1023(8)	0.1258(7)	0.3056(4)	0.042(4)	0.054(5)	0.049(4)	-0.003(5)	0.010(3)	0.003(5)	0.045(2)	
H ₂ O											
O(20)	½	0.985(2)	¼	0.042(4)	0.054(5)	0.049(4)	-0.003(5)	0.010(3)	0.003(5)	0.045(2)	
H ₂ O											
O(21)	0	0.777(2)	¼	0.042(4)	0.054(5)	0.049(4)	-0.003(5)	0.010(3)	0.003(5)	0.048(2)	
H ₂ O											
O(22)	½	0.126(2)	¼	0.042(4)	0.054(5)	0.049(4)	-0.003(5)	0.010(3)	0.003(5)	0.048(2)	
H ₂ O											
FINAL SUBSIDIARY POSITIONS AND ISOTROPIC DISPLACEMENT PARAMETERS											
Ba(1A)	0.390(2)	0.1107(16)	-0.0022(13)	0.05							
Ba(2A)	0.860(2)	0.1391(19)	0.0469(14)	0.05							
M(1A)	0.402(2)	0.104(2)	0.5872(17)	0.05							
M(2A)	0.8806(18)	0.1466(16)	0.6029(13)	0.05							

delindeite, $a = 2t_1$ and $b = 2t_2$; there are four planar minimal cells in the cell **a**, **b** of delindeite; the C sheet must have the composition of 16 $[M^O X C_2]$.

In the structure of delindeite, the central sheet of the TS block [the planar cell **a**, **b** ($= 2t_1$, $2t_2$)] can have sixteen cations at the M^O sites corresponding to the trioctahedral sheet. However, only twelve M^O sites are fully or partly occupied: **four** $M(3)$ sites are fully occupied primarily by Ti; **two** $Na(1)$, **two** $Na(2)$ and **four** $Na(3)$ sites are 70% occupied primarily by Na

(Fig. 2b, Table 5). However, **four** potential M^O sites are partly occupied by H_2O groups, and they are, in fact, dominated by vacancies: **two** $[O(20) + O(21)]$ sites give 2 $[H_2O_{0.45} \square_{0.55}]$. Ideally, 16 M^O sites are 75% occupied by cations, and we can write the cation content of the central sheet as $Ti_4 Na_8 \square_4$. In the cell $(2t_1, 2t_2)$, there are six additional sites that do not belong to the trioctahedral sheet: **four** K sites are \square -dominant, and **two** $O(22)$ sites, 50% are occupied by H_2O . Moreover, out of 32 X^O anion sites corresponding to the trioc-

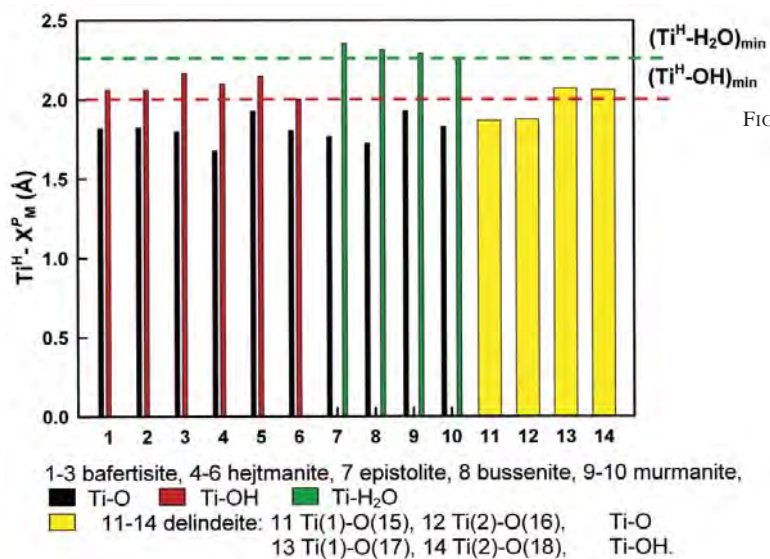


FIG. 1. Variation of $\text{Ti}^{\text{H}}\text{-X}_M^{\text{P}}$ bond lengths in minerals with the TS block, where Ti^{H} corresponds to ^{16}Ti in the H sheet and X_M^{P} corresponds to the apical anion of this Ti^{H} octahedron pointing into the intermediate space between two TS blocks. Black, red and green bars correspond to $\text{X}_M^{\text{P}} = \text{O}^{2-}$, OH^- and H_2O , respectively. Dashed green and red lines indicate minimal values of bond lengths for $\text{Ti}^{\text{H}}\text{-H}_2\text{O}$ and $\text{Ti}^{\text{H}}\text{-OH}$. Yellow bars indicate delindeite (this work). Data are reported for bafertisite (Guan *et al.* 1963), hejzmanite (Rastsvetaeva *et al.* 1991), epistolite (Sokolova & Hawthorne 2004), busenite (Zhou *et al.* 2002), and murmanite (Khalilov 1989).

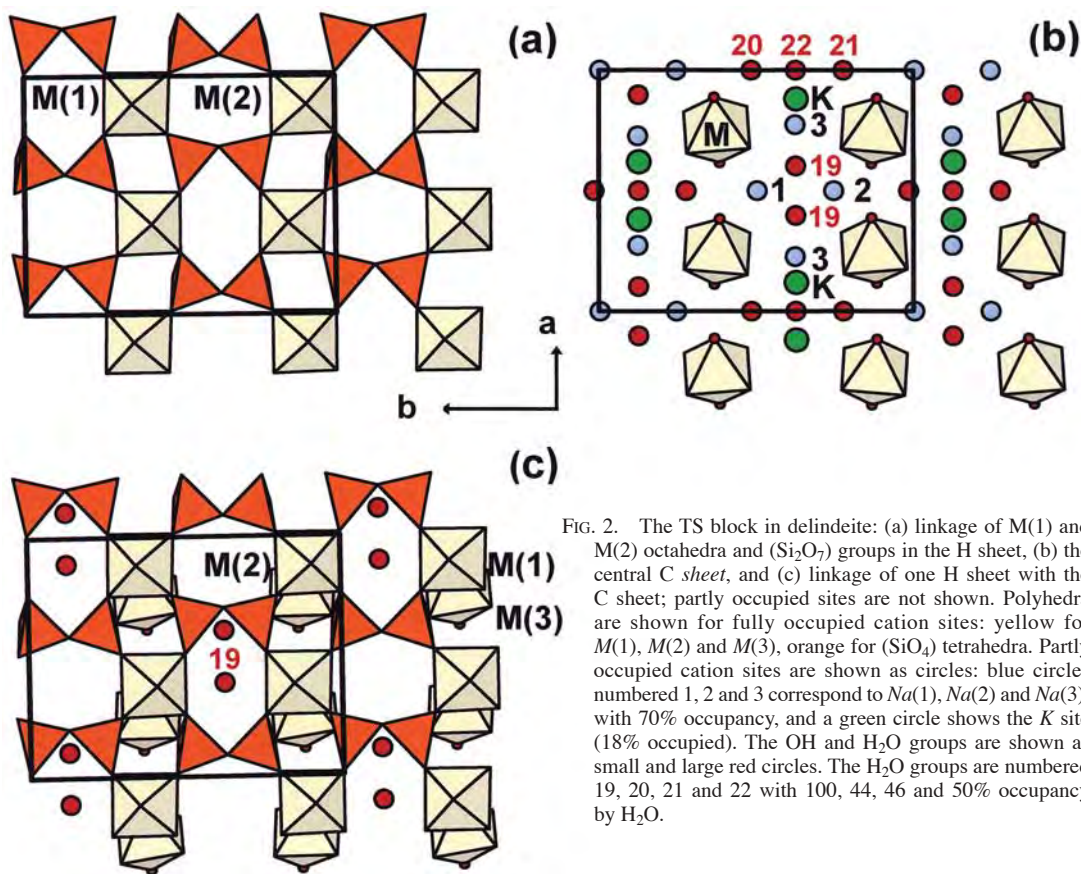


FIG. 2. The TS block in delindeite: (a) linkage of $M(1)$ and $M(2)$ octahedra and (Si_2O_7) groups in the H sheet, (b) the central C sheet, and (c) linkage of one H sheet with the C sheet; partly occupied sites are not shown. Polyhedra are shown for fully occupied cation sites: yellow for $M(1)$, $M(2)$ and $M(3)$, orange for (SiO_4) tetrahedra. Partly occupied cation sites are shown as circles: blue circles numbered 1, 2 and 3 correspond to $\text{Na}(1)$, $\text{Na}(2)$ and $\text{Na}(3)$, with 70% occupancy, and a green circle shows the K site (18% occupied). The OH and H_2O groups are shown as small and large red circles. The H_2O groups are numbered 19, 20, 21 and 22 with 100, 44, 46 and 50% occupancy by H_2O .

TABLE 4. SELECTED INTERATOMIC DISTANCES (Å) AND ANGLES (°) IN DELINDEITE

<i>M</i> (1)–O(15)	1.871(6)	<i>M</i> (2)–O(16)	1.877(6)	<i>M</i> (3)–O(9)b	1.928(6)
<i>M</i> (1)–O(14)	1.953(6)	<i>M</i> (2)–O(6)a	1.966(6)	<i>M</i> (3)–O(7)	1.946(6)
<i>M</i> (1)–O(10)	1.959(5)	<i>M</i> (2)–O(2)	1.970(6)	<i>M</i> (3)–O(13)	1.952(6)
<i>M</i> (1)–O(1)	1.972(6)	<i>M</i> (2)–O(8)	1.988(6)	<i>M</i> (3)–O(3)b	1.964(6)
<i>M</i> (1)–O(5)	1.980(6)	<i>M</i> (2)–O(12)a	1.999(7)	<i>M</i> (3)–O(18)(OH)	1.995(6)
<i>M</i> (1)–O(17)(OH)	2.078(6)	<i>M</i> (2)–O(18)(OH)b	2.065(6)	<i>M</i> (3)–O(17)(OH)	2.001(6)
< <i>M</i> (1)–O,OH>	1.969	< <i>M</i> (2)–O,OH>	1.978	< <i>M</i> (3)–O,OH>	1.964
<i>Si</i> (1)–O(2)	1.602(6)	<i>Si</i> (2)–O(5)	1.603(5)	<i>Si</i> (3)–O(10)	1.598(5)
<i>Si</i> (1)–O(3)	1.611(5)	<i>Si</i> (2)–O(6)	1.612(6)	<i>Si</i> (3)–O(8)	1.625(7)
<i>Si</i> (1)–O(1)	1.621(6)	<i>Si</i> (2)–O(4)c	1.613(6)	<i>Si</i> (3)–O(9)	1.627(6)
<i>Si</i> (1)–O(4)	1.679(6)	<i>Si</i> (2)–O(7)	1.624(7)	<i>Si</i> (3)–O(11)b	1.632(6)
< <i>Si</i> (1)–O>	1.628	< <i>Si</i> (2)–O>	1.614	< <i>Si</i> (3)–O>	1.621
<i>Si</i> (4)–O(12)	1.598(6)	<i>Na</i> (1)–O(13)d	2.241(6) × 2	<i>Na</i> (2)–O(9)c	2.238(6) × 2
<i>Si</i> (4)–O(13)	1.617(6)	<i>Na</i> (1)–O(19)H ₂ O	2.30(1) × 2	<i>Na</i> (2)–O(19)H ₂ O	2.28(1) × 2
<i>Si</i> (4)–O(14)	1.617(6)	<i>Na</i> (1)–O(18)(OH)d	2.389(7) × 2	<i>Na</i> (2)–O(17)(OH)c	2.368(7) × 2
<i>Si</i> (4)–O(11)e	1.659(6)	< <i>Na</i> (1)–O,OH,H ₂ O>	2.31	< <i>Na</i> (2)–O,OH,H ₂ O>	2.30
< <i>Si</i> (4)–O>	1.623	<i>Na</i> (3)–O(19)H ₂ O	2.31(1)	<i>K</i> –O(7)h	2.66(1)
<i>Si</i> (1)–O(4)– <i>Si</i> (2)f	149.3(4)	<i>Na</i> (3)–O(13)d	2.415(8)	<i>K</i> –O(3)g	2.71(1)
<i>Si</i> (3)b–O(11)		<i>Na</i> (3)–O(22)H ₂ O	2.421(6)	<i>K</i> –O(11)h	2.79(1)
– <i>Si</i> (4)h	146.2(4)	<i>Na</i> (3)–O(9)c	2.456(8)	<i>K</i> –O(9)c	2.98(1)
		<i>Na</i> (3)–O(3)g	2.506(8)	<i>K</i> –O(13)d	3.00(1)
<i>Na</i> (3)– <i>K</i>	1.25(1)	<i>Na</i> (3)–O(7)h	2.517(8)	<i>K</i> –O(4)g	3.02(1)
		<i>Na</i> (3)–O(11)h	2.664(7)	<i>K</i> –O(4)d	3.13(1)
<i>M</i> (1)– <i>M</i> (1A)	0.56(3)	<i>Na</i> (3)–O(4)g	2.863(8)	< <i>K</i> –O>	2.90
<i>M</i> (2)– <i>M</i> (2A)	0.57(2)	< <i>Na</i> (3)–O,H ₂ O>	2.52		
<i>Ba</i> (11)–O(15)i	2.746(6)	<i>Ba</i> (2)–O(16)k	2.733(5)	<i>Ba</i> (11)– <i>Ba</i> (12)	0.35(3)
<i>Ba</i> (11)–O(16)i	2.809(5)	<i>Ba</i> (2)–O(2)d	2.765(6)	<i>Ba</i> (11)– <i>Ba</i> (13)	0.30(3)
<i>Ba</i> (11)–O(8)j	2.893(6)	<i>Ba</i> (2)–O(14)i	2.798(6)	<i>Ba</i> (12)– <i>Ba</i> (13)	0.60(1)
<i>Ba</i> (11)–O(11)h	2.944(6)	<i>Ba</i> (2)–O(5)j	2.806(6)	<i>Ba</i> (11)– <i>Ba</i> (1A)	0.66(7)
<i>Ba</i> (11)–O(14d)	2.952(6)	<i>Ba</i> (2)–O(15)j	2.827(6)	<i>Ba</i> (2)– <i>Ba</i> (2A)	0.69(3)
<i>Ba</i> (11)–O(1)d	2.983(6)	<i>Ba</i> (2)–O(10)j	2.843(5)		
<i>Ba</i> (11)–O(8)c	3.025(6)	<i>Ba</i> (2)–O(12)l	2.858(6)		
<i>Ba</i> (11)–O(6)j	3.034(6)	<i>Ba</i> (2)–O(6)i	2.957(7)		
<i>Ba</i> (11)–O(1)i	3.047(6)	<i>Ba</i> (2)–O(15)j	3.030(7)		
<i>Ba</i> (11)–O(4)d	3.177(6)	<i>Ba</i> (2)–O(16)d	3.082(6)		
< <i>Ba</i> (11)–O>	2.961	< <i>Ba</i> (2)–O>	2.873		

a: $x + 1, y, z$; b: $-x + 1, y, -z + \frac{1}{2}$; c: $x - \frac{1}{2}, y - \frac{1}{2}, z$; d: $x, y - 1, z$; e: $-x + \frac{1}{2}, y + \frac{1}{2}, -z + \frac{1}{2}$; f: $x + \frac{1}{2}, y + \frac{1}{2}, z$; g: $-x + 1, y - 1, -z + \frac{1}{2}$; h: $-x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{1}{2}$; i: $-x + 1, -y + 1, -z$; j: $x + \frac{1}{2}, y - \frac{1}{2}, z$; k: $-x + 2, -y + 1, -z$; l: $x + 1, y - 1, z$.

TABLE 5. REFINED SITE-SCATTERING VALUES (*epfu*) AND ASSIGNED SITE-POPULATIONS FOR DELINDEITE

Site	Multiplicity	Site-scattering	Site population <i>apfu</i>	Calculated site-scattering	<X–φ> _{calc.} [*] Å	<X–φ> _{obs} Å
<i>M</i> (1)	1	22.0(1)	1.88 Ti + 0.07 Nb + 0.05 Al	44.9	1.979	1.969
<i>M</i> (2)	1	22.0(1)			1.979	1.978
<i>M</i> (3)	1	22.9(1)	0.82 Ti + 0.12 Fe ³⁺ + 0.06 Nb	23.6	1.967	1.964
<i>Na</i> (1)	0.5	4.47(9)	0.34 Na + 0.01 Mn ²⁺ + 0.03 Fe ²⁺ + 0.15 □	4.44	2.36	2.31
<i>Na</i> (2)	0.5	4.24(8)	0.32 Na + 0.01 Mn ²⁺ + 0.02 Fe ²⁺ + 0.15 □	4.29	2.34	2.3
⁶³ Na(3)	1	7.40(2)	0.70 Na + 0.30 □	7.7	2.56	2.52
⁷¹ K	1	3.6(2)	0.18 K + 0.82 □	3.4	2.84	2.9
¹¹⁶ Ba(1)	1	53.6(4)**	0.92 Ba + 0.08 K	53.07	2.906**	2.961**
¹³⁵ Ba(2)	1	55.0(1)**	1.0 Ba	56	2.900**	2.873**
O(20)	0.5	1.76(8)	0.22 H ₂ O + 0.28 □	1.76		
O(21)	0.5	1.84(8)	0.23 H ₂ O + 0.27 □	1.84		
O(22)	0.5	2.00(8)	0.25 H ₂ O + 0.25 □	2.00		

* ionic radii for ⁶³O²⁻, ¹⁶O²⁻, ¹⁹F⁻, ⁷¹F⁻, Ti, Nb, Al, Mn²⁺, Fe²⁺, Fe³⁺, Na, Ba, K are from Shannon (1976).

** site scattering for *Ba*(1) equals to sum of three sites, *Ba*(11), *Ba*(12), *Ba*(13); calculated and observed <X–φ> values correspond to <*Ba*(11)–O> and <*Ba*(2)–O>.

TABLE 6. BOND-VALENCE* TABLE FOR DELINDEITE

	Si(1)	Si(2)	Si(3)	Si(4)	M(1)	M(2)	M(3)	Na(1)	Na(2)	Na(3)	K	Ba(11)**	Ba(2)	Σ
O(1)	1.02				0.63							0.14		1.91
												0.12		
O(2)	1.08					0.64							0.27	1.99
O(3)	1.05						0.65			0.11	0.04			1.85
O(4)	0.88	1.05								0.06	0.01	0.09		2.10
												0.01		
O(5)	1.07				0.62								0.24	1.93
O(6)	1.05					0.65						0.12	0.17	1.99
O(7)	1.02						0.68			0.11	0.04			1.85
O(8)			1.01			0.61						0.12		1.91
												0.17		
O(9)			1.01				0.72		0.20* ²¹	0.13	0.02			2.08
O(10)			1.09		0.66							0.22		1.97
O(11)		0.99	0.93							0.09	0.03	0.15		2.19
O(12)			1.09		0.59								0.21	1.89
O(13)			1.03				0.67	0.21* ²¹		0.13	0.02			2.06
O(14)			1.03	0.67								0.15	0.25	2.10
O(15)				0.83								0.25	0.13	1.44
												0.23		
O(16)						0.82						0.21	0.13	1.46
													0.30	
O(17) (OH _{0.67} F _{0.33})					0.44		0.55		0.13* ²¹					1.12
O(18) (OH _{0.67} F _{0.33})						0.46	0.56	0.14* ²¹						1.16
O(19) H ₂ O								0.18* ²¹	0.18* ²¹	0.16				0.52
O(20) H ₂ O (44%)														
O(21) H ₂ O (46%)														
O(22) H ₂ O (50%)										0.13* ²¹				
Total	4.03	4.19	4.1	4.08	3.85	3.77	3.83	1.06	1.02	0.86	0.17	1.52	2.15	
Aggr. charge	4	4	4	4	4.01	4.01	3.93	0.8	0.76	0.67	0.18	1.7	2	

* Bond-valence parameters are from Brown (1981); ** Ba(11) = 0.81 Ba + 0.08 K + 0.11 □. The bond valences are expressed in valence units, *vu*.

hedral sheet, four sites are vacant, and we write the anion content of the central sheet O₁₆ (OH)₈ (H₂O)₄ □₄. Therefore, in delindeite, the central sheet of the TS block is not a trioctahedral sheet as (1) it contains [6]-, [7]- and [8]-coordinated cations; (2) 25% of cation and anion sites corresponding to the O sheet are either replaced by H₂O groups or vacant. We call it instead the C (central) sheet. Therefore, we consider M^C cations and X^C anions of the C sheet (*cf.* M^O cations and X^O anions of the O sheet). The H and C sheets link *via* common vertices of M(1,2), Si and M(3) polyhedra (Fig. 2c). The M(1,2) and M(3) octahedra share (OH,F) anions, and the Si and M(3) polyhedra share O atoms.

There are two TS blocks per unit cell in the structure of delindeite (Fig. 3). Along the *c* direction, the TS blocks alternate with layers of Ba(1, 2) atoms, which constitute the intermediate I block.

Hydrogen bonding

It was not possible to locate the H atoms of the (OH) and (H₂O) groups in delindeite directly. However, bond-valence calculations show that O(19), O(20), O(21) and O(22) are O atoms of (H₂O) groups, and O(17)

TABLE 7. PROPOSED HYDROGEN BONDING FOR DELINDEITE*

Species	D	A	D-A (Å)
OH	O(17)	O(3)	3.166(8)
OH	O(18)	O(7)a	3.234(9)
H ₂ O ¹	O(19)	O(2)b	3.10(1)
		O(10)c	3.02(1)
H ₂ O ²	O(19)	O(9)d	3.16(1)
		O(13)e	3.16(1)

a: -x, y, -z + ½; b: -x + 1, y - 1, -z + ½; c: -x + ½, y - ½, -z + ½; d: x - ½, y - ½, z; e: x, y - 1, z. * H₂O¹ and H₂O² correspond to SRO arrangements 1 and 3.

and O(18) are O atoms of (OH) groups (Table 6). Note that the O(17) and O(18) sites are each occupied by OH_{0.67}F_{0.33}. A proposed scheme of hydrogen bonding is given only for fully occupied anion sites (Table 7). There are two sets of D-A bonds [H₂O¹ and H₂O²] that can occur at O(19), depending on local arrangement of cations (see Table 7). There is hydrogen bonding involving (OH) groups within the C sheet (Table 7, Fig. 4a). For these particular bonds, the mean D (donor)-A (acceptor) distance is 3.20 Å, corresponding to weak hydrogen-bonding. Some of hydrogen bonds

proposed are quite long, but as shown by Brown (1976), significant interactions still occur at such distances. The arrangement of hydrogen bonds is shown in Figures 4a and 4c and is discussed later.

Short-range order

Long-range disorder of cations and H₂O groups forces us to consider short-range order (SRO) arrangements in the C sheet. The SRO approach (Hawthorne 1997) allows us to check whether certain local arrangements of cations (and anions) can occur in the crystal structure. In Table 8, we list ten anions that are coordinated to cations at the partly occupied sites, *Na*(1–3) and *K*. The bond-valence sums at these anions [excluding input of *Na*(1–3) and *K*] vary from 1.70 to 2.07 *vu* for O atoms (Σ_1 in Table 8), and the Σ_1 is low for O(3), O(7), O(9) and O(13). We will examine certain local arrangements to see if they can satisfy the bond-valence requirements at these anions. All cation and anion sites in the C sheet are shown in Figure 2b. In the long-range structure, the *Na*(1), *Na*(2) and *Na*(3) sites are 70% occupied. Where these three sites are 100% occupied, they can form a four-membered cation cluster, SRO–1, which is shown in Figure 4a. Four cation sites with 70% occupancy give 2.8 or approximately 3 *Na pfu* and with SRO–1, three Na atoms occur. The possible distributions of three atoms over four sites are shown in schemes I, II and III (Fig. 4a). Bond-valence sums at anions corresponding to schemes I–III, given in Table 8 (columns 7–10), support the occurrence of all four local arrangements (including a cluster of four Na atoms). The bond-valence sums at O(3) and O(7) are still low, but possible hydrogen bonds O(17)–O(3) and O(18)–O(7) (Table 7) add to the sum. Note that O(17) and O(18) are occupied by OH and F at 67 and 33%; hydrogen bonding at 67% thus is in agreement with 70% occupancy of atoms *Na*(1–3). There is hydrogen bonding between the H₂O group at O(19) and O(2) and O(10) (labeled H₂O¹ in Table 7). In the long-range structure, *Na*(3)–*K* is equal to 1.25 Å, and therefore either the *Na*(3) or the *K* site is occupied. Arrangement SRO–2 involves the *K* atom (Fig. 4b), and bond-valence sums

at anions are given in Table 8. Arrangement SRO–3 involves H₂O groups at O(20) and O(21) (Fig. 4c) that are involved in hydrogen bonding with O(3) and O(7). In the long-range structure, there are short distances, about 2.02–2.19 Å, from O(20) to O(3) and from O(21) to O(7), *i.e.*, to the O atoms coordinating the M(3) atom. In the local environment, H₂O groups are probably displaced toward the center of the cavity (the direction of displacement is shown by red arrows), and the donor–acceptor distances increase. There is hydrogen bonding between the H₂O group at O(19) and O(9) and O(13) (labeled H₂O² in Table 7).

STRUCTURAL FORMULA FOR DELINDEITE

Sokolova (2006) wrote the general formula for the TS block as a combination of O and H sheets, plus peripheral *P* sites, based on a planar cell with $t_1 \sim 5.5$ and $t_2 \sim 7$ Å. This formula is $A^P_2 B^P_2 M^{H_2} M^{O_4} (Si_2O_7)_2 X_{4+n}$, where M^{H_2} and M^{O_4} are cations of H and O sheets, A^P and B^P are cations at the peripheral (*P*) sites, $X_{4+n} = X^{O_4} + X^{P_{M2}} + X^{P_{A2}}$, X^O are anions of the O sheet, X^P are anions coordinating M^H and *P* cations, *n* is the number of X^P anions, and $n = 2$ where the M^H site is [6]-coordinated and the A^P polyhedron links to the next TS block. In the structure of delindeite, the B^P and X^P_A sites are vacant, and therefore the formula is $A^P_2 M^{H_2} M^{O_4} (Si_2O_7)_2 X^C_4 X^P_{M2}$. (Note that M^C and X^C represent cations and anions of the C sheet.) In delindeite, the **I** block occludes the peripheral sites A^P_2 , which correspond to *Ba*(11), *Ba*(12), *Ba*(13) and *Ba*(2) sites [$Ba_{1.92} K_{0.08}$]. In the two H sheets, M^{H_2} corresponds to the *M*(1) + *M*(2) sites, which give Ti_2 , and X^P_{M2} corresponds to the O(15) and O(16) sites [$O_{1.53} OH_{0.47}$]. In the C sheet, there are sites that formally correspond to the O sheet: 4 M^C include the cation sites *M*(3), *Na*(1), *Na*(2), *Na*(3) and the anion sites O(20) and O(21); X^C_4 corresponds to O(17), O(18) and O(19) sites. In the C sheet, there are two additional sites that do not correspond to the topology of the O sheet; they are *K* and O(22) sites. We now write the chemical formula of delindeite using the minimal cell (t_1 , t_2) in terms of the TS-block components ($Z = 8$) and the dominant cation at each site:

<i>C sheet</i>		<i>add.* sites</i>	<i>2H sheets</i>	<i>P sites</i>
M^C_4	X^C_4		$M^{H_2} (Si_2O_7)_2$	$X^P_{M2} A^P_2$
[Ti $Na_{1.40} \square_{0.60}$] _{3.0}	[(OH,F) ₂ H ₂ O] _{4.0}	$K_{0.18} \square_{0.82}$	$Ti_2 (Si_2O_7)_2$	(O,OH) ₂ Ba_2
[(H ₂ O) _{0.45}] _{1.0}		(H ₂ O) _{0.25} $\square_{0.25}$		

*additional sites

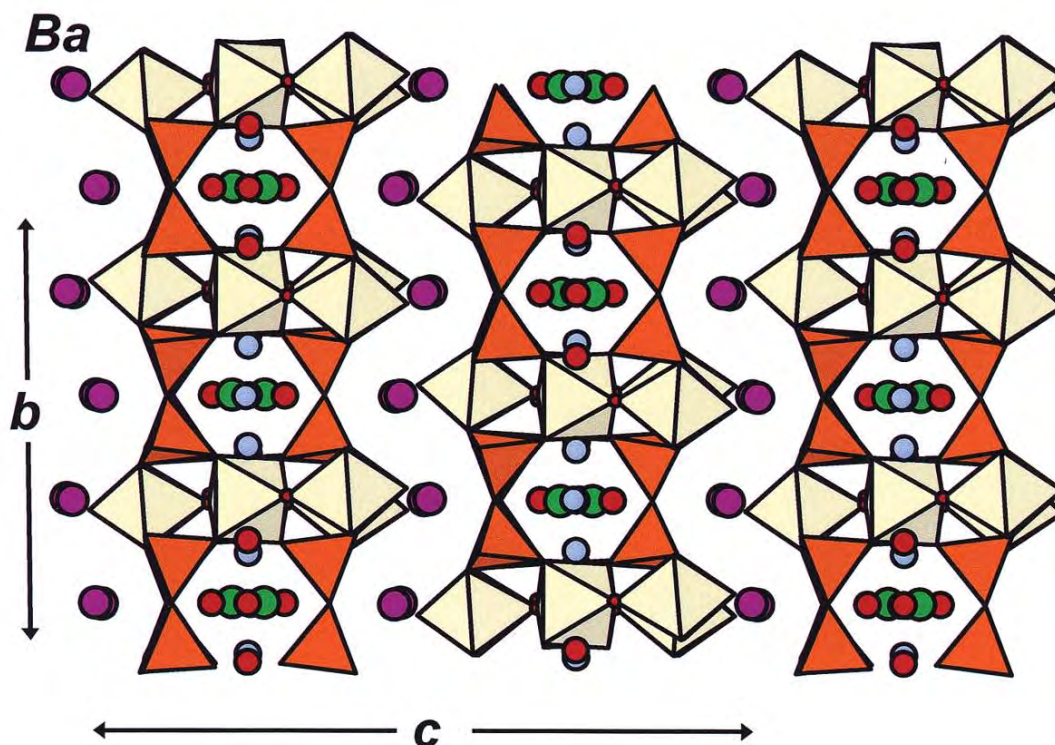


FIG. 3. The crystal structure of delindeite viewed down [100]. Legend as in Figure 2; Ba atoms are shown as fuchsia circles.

We combine the M^C_4 group with the additional sites to give a better representation of the composition of the C sheet: Ti (Na_{1.40} K_{0.18}) (OH,F)₂ (H₂O)_{1.70} or Ti Na₂ (OH)₂ (H₂O)₂, and then write the ideal formula of delindeite as Ba₂ Na₂ Ti₃ (Si₂O₇)₂ O₂ (OH)₂ (H₂O)₂. Note that in this formula, X^C_4 follows X^P_{M2} to list the anions in decreasing magnitude of valence state.

WHY IS THE TOPOLOGY OF THE TS BLOCK IN DELINDEITE DIFFERENT FROM ITS TOPOLOGY IN TITANIUM DISILICATE MINERALS?

In her work on the bond topology and stereochemistry of the TS block titanium-silicate minerals, Sokolova (2006) identified several common features of these structures. In particular, (1) there are three topologically distinct types of linkage between the O sheet and the (Si₂O₇) groups of the H sheet (see Fig. 5 in Sokolova 2006), and (2) there are four types of stereochemistry of linkage depending on the composition of the octahedra of the O sheet and the linkage of the (Si₂O₇) groups of the H sheet. This led Sokolova (2006) to divide these minerals into four groups based on these two factors. Moreover, the minerals of each of

these groups have different contents of Ti [1, 2, 3 and 4 *apfu* Ti (= Ti + Nb)], corresponding to the number of the group. Recall that Sokolova (2006) did not consider the delindeite structure as a TS block mineral, as the central (C) sheet of delindeite is not trioctahedral but contains significant vacancies *and* additional anion species relative to the O sheet in TS block minerals. However, in the previous structure of delindeite, the linkage between the C and H sheets is that of Group I (Ti: 1 *apfu*, Fig. 5a), whereas the stereochemistry and chemical composition of the TS block are those of Group III (Ti: 3 *apfu*, Fig. 5b). Even considering the fact that delindeite is formally not a TS block mineral, this anomaly requires an explanation.

Figure 5a shows the linkage of O and H sheets in Group I: (Si₂O₇) groups on either side of the O sheet link to the [8]-coordinated Na polyhedron of the O sheet; the M^H octahedron of the H sheet links to the X^O_M anion of the O sheet. In Figure 5a, one M^H octahedron is shown in green (M^H = Zr), and another octahedron is outlined with a red line to show the place of the X^O_M anion (shown as a green circle), which is a common vertex for three octahedra of the O sheet, *i.e.*, three M^O octahedra: two Na and one Ti (a scheme in the center

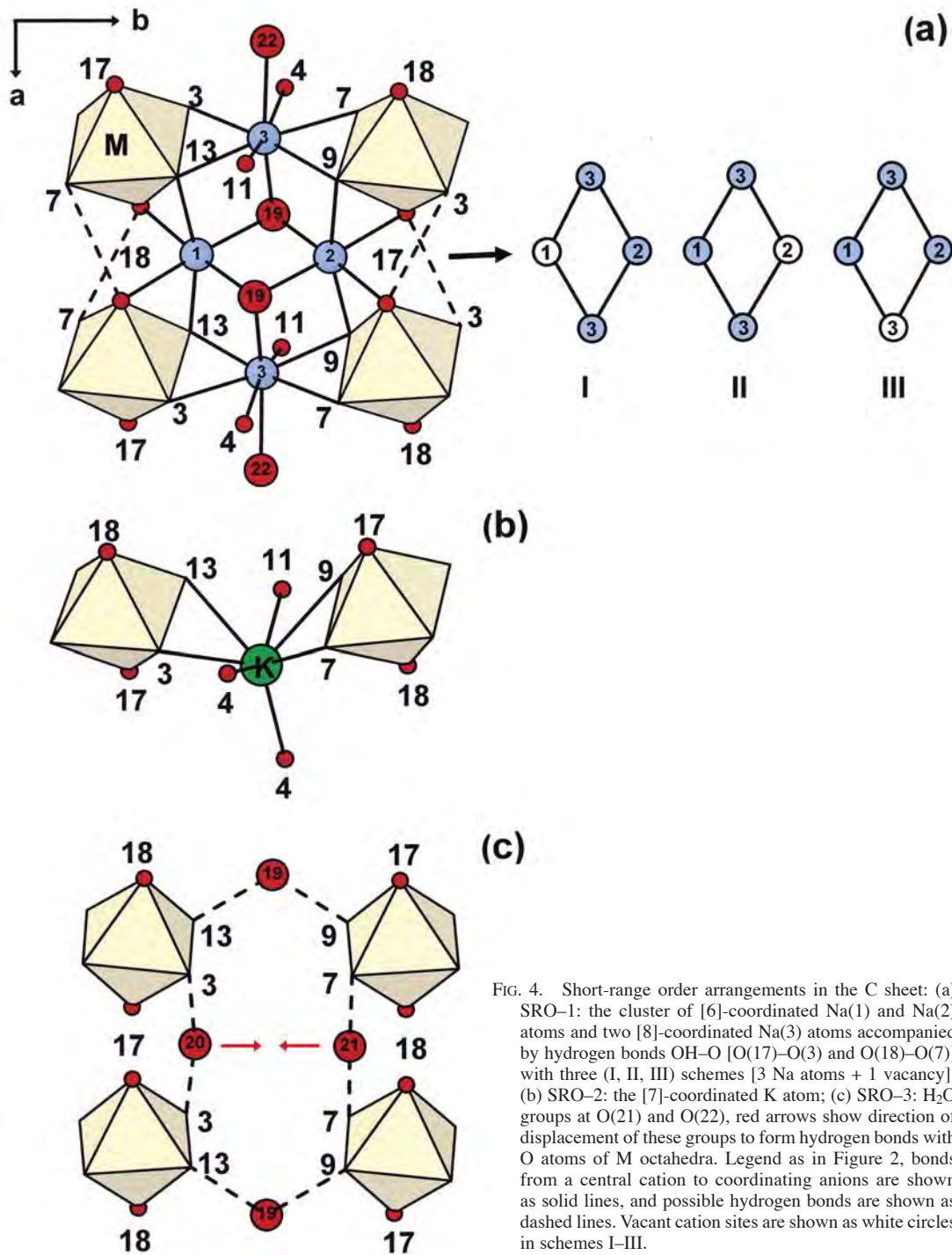


TABLE 8. BOND-VALENCE TABLE FOR LOCAL ARRANGEMENTS OF CATIONS IN DELINDEITE

Atom	Σ_i^*	Na (1)	Na (2)	Na (3)	K	ΣNa (1-3)**	ΣNa (2,3)**	ΣNa (1,3)**	ΣNa (1,2,3)** a b	ΣK	
O(3)	1.70			0.16	0.22	1.86	1.86	1.86	1.86	1.70	1.92
O(4)	2.02			0.09	0.11	2.12	2.11	2.11	2.12	2.02	2.13
O(7)	1.70			0.16	0.22	1.86	1.86	1.86	1.86	1.70	1.92
O(9)	1.73		0.29	0.09	0.11	2.11	2.11	1.82	2.11	2.02	1.84
O(11)	2.07			0.13	0.17	2.20	2.20	2.20	2.20	2.07	2.24
O(13)	1.70	0.28		0.19	0.11	2.17	1.89	2.17	2.17	1.98	1.81
O(17)OH	0.97		0.21			1.18	1.18	0.97	1.18	1.18	0.97
O(18)OH	1.00	0.22				1.22	1.00	1.22	1.22	1.22	1.00
O(19)H ₂ O	0	0.24	0.24	0.24		0.72	0.48	0.24	0.72	0.48	0
Total		1.48	1.48	1.16	0.94						
Aggr. charge		1.08	1.08	1.00	1.0						

Σ = sum of bond-valence (expressed in valence units, *vu*) received from

* Si(1-4), M(1-3), Ba(1,2);

** Total Σ = Σ_i^+ + bond-valence from

Na(1-3) cluster of 4 Na atoms, Figure 4a, main diagram;

Na(2,3) cluster of 2 Na(3) and Na(2), Figure 4a, scheme I;

Na(1,3) cluster of 2 Na(3) and Na(1), Figure 4a, scheme II;

Na(1,2,3) (a) cluster of Na(1), Na(2) and Na(3), Figure 4a, scheme III;

(b) cluster of Na(1), Na(2) and vacant Na(3) site, Figure 4a, scheme III;

K K atom, Figure 4b.

of Figure 5 shows the $M^H-X_M^O$ relation). Depending on the type of the M^H and M^O cations, the X_M^O anion can be either O^{2-} or F^- . Figure 5b shows the linkage of O and H sheets in Group III: (Si_2O_7) groups on either side of the O sheet link to the Ti octahedron of the O sheet; the Ti octahedron of the H sheet ($M^H = Ti$) links to the X_M^O anion of the O sheet. The X_M^O anion (shown as a green circle) is a common vertex for three Na octahedra of the O sheet. In Group III, the X_M^O anion is invariably O^{2-} . Note that in Groups I and III, apical O atoms of an (Si_2O_7) group are invariably shared with two Na polyhedra and one Ti octahedron of the O sheet. In delindeite, apical O atoms of an (Si_2O_7) group are shared with one Ti octahedron of the C sheet and either one or two Na polyhedra, which are 70% occupied by Na (Fig. 5c). The Ti octahedron of the H sheet links to the X_M^O anion, which is an OH group (encircled by a green line in Fig. 5c). Comparison of Figures 5a and 5c shows that the TS block in delindeite exhibits stereochemistry of Group I. However, the chemical composition of the TS block in delindeite corresponds to Group III. Note also that in all the known minerals of Group I (Ti: 1 *apfu*), TS blocks link directly (Sokolova 2006), whereas in delindeite (Ti: 3 *apfu*), the TS blocks do not link directly; they alternate with one intermediate layer of cations, as in several minerals of Group III (Ti: 3 *apfu*).

Let us consider linkage with stereochemistry of Group III for delindeite (Fig. 5d): (Si_2O_7) groups on either side of the C sheet link to the Ti octahedron of the C sheet, and the Ti octahedron of the H sheet ($M^H = Ti$) links to the X_M^O anion of the C sheet. In this case,

the X_M^O anion is either a vacancy or an H₂O group [= O(19)]. Note that an H₂O group [= O(22)], which is a common vertex for two [8]-coordinated Na(3) polyhedra, occurs at an additional site, different from anion sites of the sheet of octahedra. Therefore in the crystal structure of delindeite (with the stereochemistry of Group III), there are no anions in the central sheet to promote linkage of the M^H octahedron to the central sheet. Hence linkage of H and C sheets cannot occur, and the TS block cannot form. We can conclude that disorder of cations and anions in the C sheet of the TS block leads to the stereochemistry of the TS block as in Group I: (Si_2O_7) groups on either side of the C sheet link to the [8]-coordinated Na polyhedron of the C sheet.

The H sheet of the delindeite structure shows alternating deformation of rings composed by two Ti polyhedra and four Si tetrahedra, along both **a** and **b** axes (Figs. 2c, 5c). This arrangement is due to the order of H₂O and Na sites. Consequently, along the **b** axis, we found two different M(1)-M(2) distances (6.420 and 7.334 Å) that average to 6.877 Å, *i.e.*, the *b* repeat-distance described by Ferraris *et al.* (2001). In the same way, along the **a** axis, the bridging oxygen of the (Si_2O_7) groups, *i.e.*, O(4) and O(11), shows two different distances: 4.208 and 6.496 Å. These two anion positions are related to the split O(2) position in the average structure model of Ferraris *et al.* (2001).

A COMMENT ON LEACHING

Ferraris *et al.* (2001) ascribed the structure of delindeite to leaching of a pre-existing phase and

consequent disorder of the constituent cations and anions, although there is no evidence of leaching of the associated minerals listed: “*shcherbakovite, lamprophyllite, wadeite, umbite and kostylevite, among others*” (Ferraris *et al.* 2001). There are two other Ti-silicates in the sample from which we extracted the single crystal of delindeite: barytolamprophyllite, (BaK) $\text{Ti}_2\text{Na}_3\text{Ti}(\text{Si}_2\text{O}_7)_2\text{O}_2(\text{OH})_2$ (Rastsvetaeva *et al.* 1995), and monoclinic astrophyllite, $\text{K}_2\text{Na}[\text{Na}(\text{Fe},\text{Mn})_4\text{Mg}_2]\text{Ti}_2(\text{Si}_8\text{O}_{24})\text{O}_2(\text{OH})_4$ (Shi *et al.* 1998). We refined both structures (in prep.) and found that neither of these structures shows any disorder of cations or anions, and there are no vacancies in either structure. Thus barytolamprophyllite and monoclinic astrophyllite do not show any evidence of leaching of alkali cations (*i.e.*, Na) from the central sheet of octahedra.

Our model for the delindeite structure gives a better explanation for the cation and anion disorder (vacancies) observed, and shows that vacancies in delindeite cannot be a consequence of leaching. Delindeite is a barytolamprophyllite-like mineral; barytolamprophyllite belongs to Group III of Sokolova (2006). There are six minerals in this group: lamprophyllite (which has two polytypes, lamprophyllite-2O and lamprophyllite-2M (Krivovichev *et al.* 2003), barytolamprophyllite (Rastsvetaeva *et al.* 1995), nabalamprophyllite (Rastsvetaeva & Chukanov 1999), innelite (Chernov *et al.* 1971), epistolite (Sokolova & Hawthorne 2004) and vuonnemite (Ercit *et al.* 1998). In all structures of Group-III minerals, the composition of the O sheet of the TS block is $\text{Na}_3\text{TiO}_2(\text{OH})_2$, and two (Si_2O_7) groups link to the *trans* edges of a small Ti^{O} octahedron (Fig. 5b) [as compared to a large Na^{O} octahedron in Group I (Fig. 5a)]. In chemical composition, barytolamprophyllite, (BaK) $\text{Na}_3\text{Ti}_3(\text{Si}_2\text{O}_7)_2\text{O}_2(\text{OH})_2$ (Rastsvetaeva *et al.* 1995), is closely related to delindeite, $\text{Ba}_2\text{Na}_2\text{Ti}_3(\text{Si}_2\text{O}_7)_2\text{O}_2(\text{OH})_2(\text{H}_2\text{O})_2$ by the substitutions: (1) $\text{Na}^+ + 2\text{O}^{2-} \leftrightarrow \square + 2(\text{H}_2\text{O})$ in the central sheet, (2) $^{15}\text{Ti}_2 + 2\square \leftrightarrow ^{16}\text{Ti}_2 + 2\text{O}^{2-}$ in the H sheet and (3) $\text{K}^+ = \text{Ba}^{2+}$ in the I block. Because of Na vacancies and the presence of H_2O groups in the central sheet of the structure, linkage of H sheets to the central sheet changes (compared to Group III of Sokolova 2006). In delindeite, two (Si_2O_7) groups do not link to the *trans* edges of a small Ti^{C} octahedron, as in Group III (Fig. 5b). They link to the *trans* edges of a large Na^{C} polyhedron (Fig. 5c). The Ti of the H sheet links to the Ti octahedron in the C sheet (Fig. 5c). The excess in charge coming from Ti sites in the H sheets is compensated by an increase in coordination from [5] (as in barytolamprophyllite) to [6]. This explains why in delindeite the lengths of apical bonds in the Ti-polyhedra in the H sheet are inverted relative to Group-III minerals with [6]-coordinated Ti of the H sheet (epistolite and vuonnemite): the long Ti–OH bond is now pointing toward the center of the TS block, and

the short Ti–O bond points toward the I block, whereas in epistolite and vuonnemite, the very short Ti–O bond points toward the center of the TS block.

The reason for the alkali vacancies in delindeite must be related to depletion of Na or K (or both) in the natant fluid rather than leaching, which implies extraction of Na after crystallization. Delindeite crystallizes when the Na content in the coexisting fluid decreases. Delindeite probably follows the crystallization of barytolamprophyllite.

CONCLUSIONS

(1) The previous refinement of the structure of delindeite was done on a subcell: a 5.327(2), b 6.856(2), c 21.51(3) Å, β 93.80(4)°, V 783.96 Å³, space group $A2/m$. In this work, we report the crystal structure of delindeite: a 10.6452(9), b 13.713(1), c 21.600(2) Å, β 93.804(3)°, V 3146.15(5) Å³, space group $C2/c$.

(2) In delindeite, (a) the central sheet of the TS block contains [8]-, [7]- and [6]-coordinated cations, and (b) 25% of cation and anion sites [corresponding to the O sheet] are replaced by H_2O groups or are vacant. The central sheet in delindeite does not exhibit the topology of a trioctahedral close-packed sheet. We call it the central (C) sheet.

(3) In the C sheet, disorder of alkali cations decreases the number of anions that can be used for linkage of the H and C sheets. Note that in the H sheet, all cation and anion sites are fully occupied. In the C sheet, only O atoms and OH groups coordinating Ti atoms are fully occupied. That is why (Si_2O_7) groups of the H sheets share O atoms with the Ti octahedra of the C sheet.

(4) The HCH block in delindeite is different from the TS block (an HOH block) in Ti disilicate minerals. The substitution $\text{H}_2\text{O} + 2\square \leftrightarrow \text{Na}^+ + 2\text{O}^{2-}$ describes the relation between the composition of the C and O sheets.

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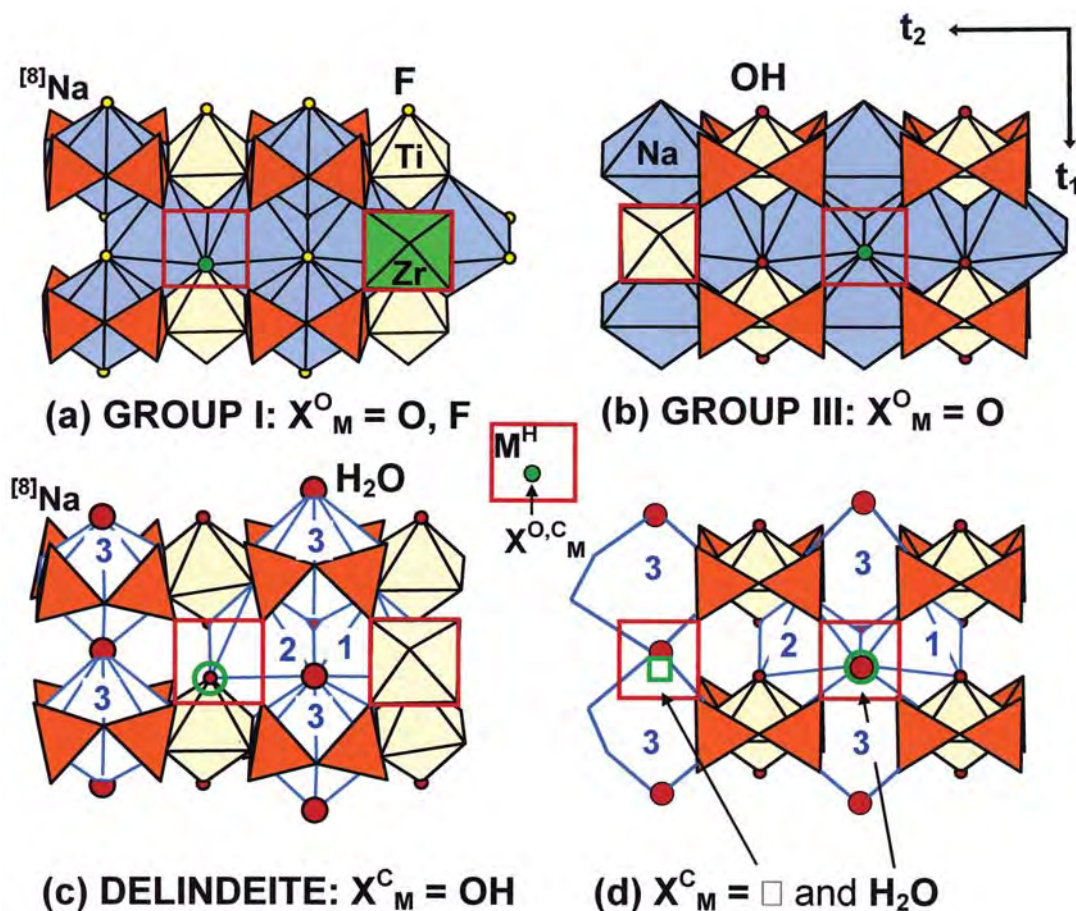


FIG. 5. Linkage of the M^H polyhedron to the central sheet of the TS block in (a) Group I and (b) Group III (taken from Sokolova 2006), (c) delindeite (this work), (d) hypothetical structure of delindeite with stereochemistry of Group III. The M^H polyhedron is encircled with a red line, the $X_M^{O,C}$ anion in the central sheet is shown in green in (a) and (b), and encircled with a green line in (c) and (d). The (SiO_4) groups are shown in orange; Ti, Na and Zr polyhedra are yellow, navy blue and green, respectively. The Na(1), Na(2) and Na(3) polyhedra with 70% occupancy are shown as white polyhedra with blue edges and labeled 1, 2 and 3, respectively. The F atoms are yellow circles, and OH and H_2O groups are small and large red circles, respectively.

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