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The crystal structure of lintisite, $Na_3LiTi_2[Si_2O_6]_2O_2 \cdot 2\ H_2O$, a new titanosilicate from Lovozero (USSR)

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Abstract. Lintisite is a new titanosilicate with ideal chemical composition $Na_3LiTi_2Si_4O_{14} \cdot 2\ H_2O$, found at Lovozero, Kola peninsula, USSR. The mineral is monoclinic, space group $C2/c$, with $a = 28.583(4)$, $b = 8.600(1)$, $c = 5.219(1)$ Å, $\beta = 91.03(2)°$. The crystal structure of lintisite has been refined to $R = 0.033$, $R_w = 0.028$ for 1095 reflections collected with Mo$K\alpha$ radiation. The structure is formed by pyroxene-like chains of $[SiO_4]$ tetrahedra, chains of edge-sharing $[TiO_6]$ and $[Na(O,H_2O)_6]$ octahedra, columns of edge-sharing $[LiO_4]$ tetrahedra, and distorted $[NaO_8]$ cubes. The modular relationships among lintisite, vinogradovite and ramsayite are discussed. Finally the thermal behaviour of lintisite is explained in the light of the structural results.

Introduction

Lintisite is a new titanosilicate which was found in the hyperalkaline pegmatites of Mount Alluaiv, in the north-western part of the Lovozero massif, Kola peninsula, USSR.[1]

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[1] Both the mineral and its name were approved by the IMA Commission on New Minerals and Mineral Names before publication.

Table 1. Electron microprobe analysis (average of four analyses) and number of cations per 14 oxygens for lintisite.

Oxide	wt. %	Atoms on the basis of 14 O	
SiO_2	44.03	Si	4.03
TiO_2	27.68	Ti	1.91
Nb_2O_5	1.10	Nb	0.05
FeO	0.28	Fe	0.02
MnO	0.05	Mn	–
Na_2O	16.72	Na	2.97
K_2O	0.03	K	–
Li_2O	2.68[a]	Li	0.99
H_2O	6.55[b]	H_2O	2.00
Σ	99.12		

[a] Li_2O by flame spectrophotometry.
[b] H_2O by loss on ignition.

This paper deals mainly with the crystal structure analysis of lintisite, although some essential data on the mineral are presented. A more detailed account on all the pertinent mineralogical data, as well as on the geological environment in which lintisite was found, is given elsewhere (Khomyakov, Polezhaeva, Merlino, Pasero, 1990).

Selected mineral data

Lintisite occurs as aggregates of needle-like crystals, elongated on [001], up to 5 mm long and 0.5 mm across, sometimes as pseudomorphs after ramsayite and associated with nepheline, sodalite, potassium-feldspar, arfvedsonite, ussingite, gmelinite, and a number of high-alkaline silicates, phosphates, titano-, niobo- and zirconosilicates.

The mineral is transparent, colorless to pale yellow. It presents perfect cleavage (100) and (010), and twinning with [100] as twin axis. The density 2.77(5) $g\,cm^{-3}$ was measured by heavy liquids, the calculated value is 2.825 $g\,cm^{-3}$. Optically lintisite is biaxial (−), $2\,V = 85(1)°$, dispersion $r < v$ strong. The measured refractive indices are $n_\alpha = 1.672(2)$ and $n_\beta = 1.739(2)$; the third index n_γ ($= 1.802$) was calculated from the values of n_α, n_β and $2\,V$. The optical orientation is $Y = b$, $Z{:}c = 2°$.

A chemical analysis of lintisite was performed on a *Cameca* MS-46 electron microprobe and is given in Table 1. The standards used were ramsayite (for Si, Ti and Na), wadeite (for K), Fe_2O_3 (for Fe), and metallic Nb and Mn. Lithium was determined by flame spectrophotometry on 1.3 mg of material. The water content has been determined by loss on ignition after heating to 1000° C. The chemical data point to the chemical formula $Na_{2.97}Li_{0.99}(Ti_{1.91}Nb_{0.05}Fe_{0.02})Si_{4.03}O_{14} \cdot 2.00\ H_2O$, which can be ideally written as $Na_3LiTi_2Si_4O_{14} \cdot 2\ H_2O$.

Experimental

A crystal (dimensions ca. $2 \times 0.1 \times 0.02$ mm) was chosen for the intensity data collection, which was carried out on an *Ital Structures* four-circle automatic diffractometer, using graphite monochromatized Mo$K\alpha$ radiation ($\lambda = 0.71069$ Å). The following unit cell parameters were derived through least square fit of 2ϑ values of 24 medium ϑ reflections: $a = 28.583(4)$, $b = 8.600(1)$, $c = 5.219(1)$ Å, $\beta = 91.03(2)°$. The collection was performed in ω-2ϑ scan mode up to $2\vartheta = 60°$, scan width 1.2° in ϑ, scan speed $0.033°\ s^{-1}$. 2170 reflections were measured with h -40 to 40, k 0 to 12, l 0 to 7. 1216 reflections out of those measured were considered observed having $I > 3\sigma(I)$, and were used in the least square calculations after reduction for Lorentz and polarization factors. Equivalent reflections were merged, thus obtaining a set of 1095 unique reflections.

The systematic absences and the statistical distribution of the normalized structure factors E indicated $C2/c$ as the space group for lintisite. The structure of lintisite was solved with direct methods and refined through alternating Fourier syntheses and least square refinement cycles. An empirical correction for the absorption effects was carried out through DIFABS (Walker, Stuart, 1983). The corrective factors were in the range 0.91 – 1.21. In the final stages of the refinement a maximum in the difference Fourier synthesis was found which unequivocally corresponded, on the basis of the electron density value and the coordination presented, to a Li^+ cation. This was subsequently confirmed by the calculations of the bond distances and the valence bond balance. It is worth noting that the presence of lithium in lintisite was suggested by the structural analysis, without any previous chemical indication. Subsequently the presence of lithium was confirmed by flame spectrophotometry. Moreover two further maxima in the difference Fourier synthesis indicated the presence of two hydrogen atoms linked to O8 which thus corresponds to a water molecule. The refinement was completed, using anisotropic thermal parameters for all the atoms apart from the hydrogens, up to $R = 0.033$ and $R_w = 0.028$ (weighting scheme $w = 1/\sigma^2[F_o]$) for 1095 unique reflections. The SHELX set of programs (Sheldrick, 1976) was used. The final atomic coordinates and U_{eq} thermal parameters are reported in Table 2.[2]

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[2] A list of observed and calculated structure factors and the anisotropic thermal parameters can be ordered from the Fachinformationszentrum Energie-Physik-Mathematik GmbH, D-7514 Eggenstein-Leopoldshafen 2, FRG. Please quote reference no. CSD 54304, the names of the authors and the title of the paper.

Table 2. Fractional coordinates and isotropic, U_{iso}, or equivalent isotropic, U_{eq}, thermal parameters given in Å^2 for lintisite. $U_{\mathrm{eq}} = 1/3\ \Sigma\Sigma\ U_{ij}a_i^* a_j^*(\mathbf{a}_i \cdot \mathbf{a}_j)$.

Atom	x	y	z	U_{eq} or U^*_{iso}
Ti	0.16503(3)	0.4050(1)	0.6243(2)	0.0051(2)
Na1	0.16517(7)	0.1872(2)	0.1161(4)	0.0155(5)
Na2	0.0	0.3483(3)	0.75	0.0244(8)
Li	0.0	0.0111(14)	0.25	0.0162(32)
Si1	0.26370(4)	0.4076(1)	0.2903(2)	0.0059(3)
Si2	0.09250(4)	0.0986(1)	0.5396(2)	0.0070(3)
O1	0.21562(10)	0.0124(3)	0.4464(6)	0.0079(7)
O2	0.21392(10)	0.2613(3)	0.7423(6)	0.0088(9)
O3	0.12500(10)	0.2511(3)	0.4917(6)	0.0091(9)
O4	0.03770(9)	0.1261(3)	0.5189(6)	0.0105(10)
O5	0.13637(9)	0.4304(3)	0.9273(6)	0.0075(8)
O6	0.11023(9)	0.0265(3)	0.8184(6)	0.0092(9)
O7	0.20683(9)	0.4164(3)	0.2883(5)	0.0069(8)
O8	0.04486(14)	0.3969(6)	0.1178(8)	0.0268(13)
H1	0.0449(20)	0.334(7)	0.201(12)	0.045(26)*
H2	0.0736(19)	0.415(7)	0.101(13)	0.066(24)*

Discussion

The crystal structure of lintisite as seen along [001] is presented in Figure 1. The bond distances in the various coordination polyhedra are reported in Table 3, together with O···O distances and O – T – O bond angles in [LiO_4] and [SiO_4] tetrahedra. All the geometrical calculations were computed using the PARST program (Nardelli, 1983).

The structure is characterized by pyroxene-like [SiO_4] tetrahedral chains, by columns of edge-sharing [LiO_4] tetrahedra, and by two types of edge-sharing octahedral chains, one of [TiO_6] and the other of [$Na(O, H_2O)_6$] octahedra, all running parallel to [001]. All these modules are interconnected in an elegant way. In the cavities of the structure additional sodium cations, in eight-fold coordination, are located: therefore sodium is present in the structure of lintisite in two different coordinations, as both six- and eight-fold coordinated (Na2 and Na1 sites, respectively).

Modular features

The modular nature of the crystal structure of lintisite and its structural relationships with other minerals may be appreciated by a description in terms of structural "slabs", periodic in two dimensions, and with finite thickness, which are stacked along [100]. In lintisite four different slabs are present.

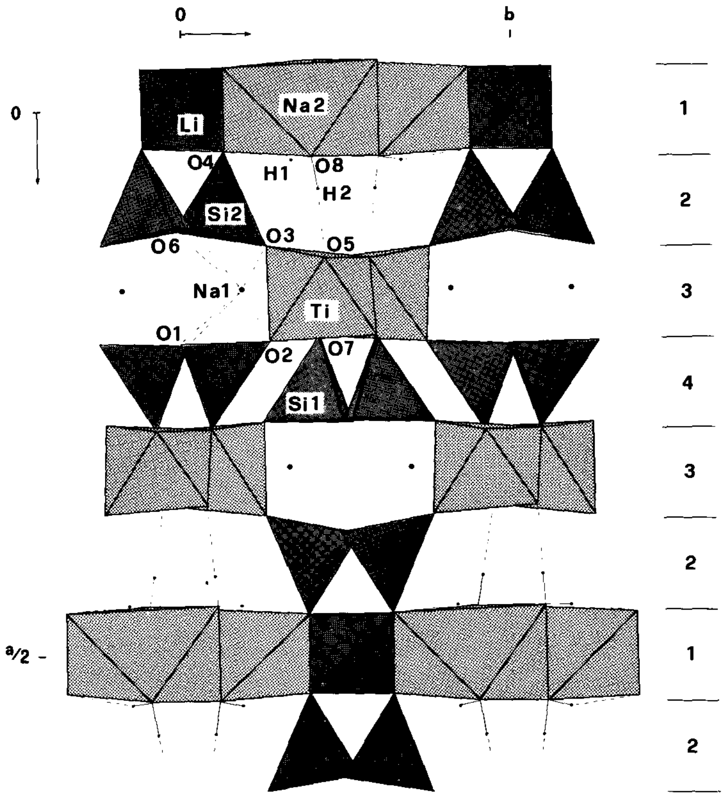

Fig. 1. The crystal structure of lintisite, as seen along [001]. The sequence of the slabs, as defined in the text, is indicated.

Slab 1. It is formed by columns of edge-sharing [LiO_4] tetrahedra and zig-zag chains of edge-sharing [$Na(O,H_2O)_6$] octahedra (Na2 atoms). Such a module is represented in Figure 2 as seen along [100].

Slab 2. Pyroxene-like chains of [SiO_4] tetrahedra (Si2 atoms) and water molecules. More precisely the water molecules are shared with the preceding slab. We decided to attribute them to the slab 2 to stress the difference with the slab 4 (see below) which is formed by tetrahedral chains only.

Slab 3. Chains of edge-sharing [TiO_6] octahedra and Na^+ cations in eight-fold coordination (Na1 atoms).

Slab 4. Pyroxene-like chains of [SiO_4] tetrahedra (Si1 atoms). At difference from slab 2, slab 4 is closely similar to the corresponding slabs in pyroxenes, with two tetrahedral chains per unit *b* translation.

Some of these modules are present also in two minerals structurally related to lintisite, namely vinogradovite (Rastsvetaeva, Andrianov, 1984)

Table 3. Selected interatomic distances (Å) and angles (°) in lintisite (distances and angles marked with an asterisk occur twice).

Na1–O1	2.687(3)	Na2–O4	2.513(3)*	Ti–O2	1.956(3)
–O1*a*	2.419(3)	–O8*c*	2.328(4)*	–O3	1.874(3)
–O2*b*	2.500(4)	–O8*d*	2.638(4)*	–O5	1.807(3)
–O3	2.355(4)	Average	2.493	–O5*e*	1.923(3)
–O5*b*	2.448(3)	All others	⩾3.58	–O7	2.141(3)
–O6*b*	2.589(3)			–O7*e*	2.116(3)
–O6*a*	2.649(3)			Average	1.970
–O7	2.464(3)			All others	⩾3.51
Average	2.514				
All others	⩾3.47				

			O...O	O–T–O
Li–O4	2.014(6)*	O4 –O4*g*	3.061(4)*	99.0(1)*
–O4*a*	2.013(7)*	O4 –O4*a*	3.393(4)*	114.8(1)*
Average	2.014	O4 –O4*f*	3.508(4)	121.1(1)
All others	⩾3.18	O4*a* –O4*g*	3.263(4)	108.3(1)
Si1–O1*h*	1.638(3)	O1*h* –O1*i*	2.618(4)	105.7(1)
–O1*i*	1.648(3)	O1*h* –O2*h*	2.640(4)	109.4(2)
–O2*h*	1.597(3)	O1*h* –O7	2.665(4)	109.4(2)
–O7	1.628(3)	O1*i* –O2*h*	2.584(4)	105.5(2)
Average	1.628	O1*i* –O7	2.683(4)	110.0(2)
		O2*h* –O7	2.741(4)	116.4(2)
Si2–O3	1.629(3)	O3 –O4	2.723(4)	115.8(2)
–O4	1.586(3)	O3 –O6	2.616(4)	105.7(2)
–O6	1.653(3)	O3 –O6*a*	2.585(4)	103.5(2)
–O6*a*	1.663(3)	O4 –O6	2.712(4)	113.7(2)
Average	1.633	O4 –O6*a*	2.681(4)	111.2(2)
		O6 –O6*a*	2.649(4)	106.0(1)

O8–H1	0.69(6)	O8...O4	3.141(6)	O8–H1–O4	174(6)
O8–H2	0.84(5)	O8...O5*b*	2.829(4)	O8–H2–O5*b*	159(6)
H1–O8–H2	103(6)	Li–O4–Si2	119.3(2)	Li–O4*a*–Si2*a*	114.2(2)
Si1–O1*h*–Si1*d*	136.9(2)	Si2–O6*a*–Si2*a*	139.6(2)		

Symmetry code:

a. $x, -y, z-1/2$	*d*. $x, -y+1, z+1/2$	*g*. $-x, -y, -z+1$
b. $x, y, z-1$	*e*. $x, -y+1, z-1/2$	*h*. $-x+1/2, -y+1/2, -z+1$
c. $x, y, z+1$	*f*. $-x, y, -z+1/2$	*i*. $-x+1/2, y+1/2, -z+1/2$

and ramsayite (Sundberg, Lehtinen, Kivekäs, 1987). In vinogradovite the slabs nos. 2, 3 and 4 occur, in ramsayite the slabs nos. 3 and 4 occur. It is possible to describe the structure of these minerals by giving the sequences of modules in the stacking direction [100]:

ramsayite	3 3 4 3 3 4 ...
vinogradovite	2 3 4 3 2 2 3 4 3 2 ...
lintisite	1 2 3 4 3 2 1 2 3 4 3 2 ...

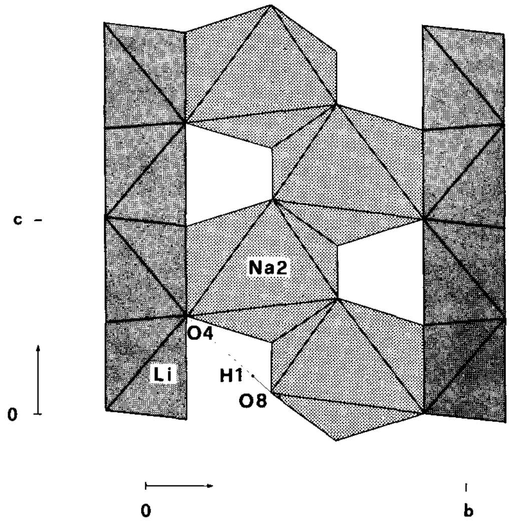

Fig. 2. The structural slab 1, formed by columns of edge-sharing [LiO_4] tetrahedra and zig-zag chains of edge-sharing [$Na(O,H_2O)_6$] octahedra, as seen along [100].

Table 4. Comparison of unit cell constants of ramsayite, vinogradovite and lintisite. The transformation matrices from the original cell choices (ref. cit.) to the cell orientation of lintisite are given.

	1	2	3	4
a (Å)	14.487	24.066	24.242	28.583
b	8.713	8.720	8.691	8.600
c	5.233	5.128	5.219	5.219
β		92.6°	92.4°	91.0°
s.g.	*Pnca*	*I*	*I*2/*c*	*C*2/*c*
matrix	[001/100/010]	[$101/0\bar{1}0/00\bar{1}$]	[101/010/100]	

1. Ramsayite, $Na_4Ti_4[Si_2O_6]_2O_6$ (Sundberg et al., 1987).
2. Mineral X, $Na_3K_{0.1}Ti_{2.2}Nb_{0.2}Fe_{0.1}Al_{0.8}Si_4O_{15.6} \cdot H_2O$ (Karup-Møller, 1986).
3. Vinogradovite, $(Na,Ca)_4(Ti,Nb)_4[Si_2O_6]_2[(Si,Al)_4O_{10}]O_4 \cdot 3\,H_2O$ (Rastsvetaeva, Andrianov. 1984).
4. Lintisite, $Na_3LiTi_2[Si_2O_6]_2O_2 \cdot 2\,H_2O$ (present work).

From the sequences of the building modules, it appears evident that close structural relationships exist between lintisite and vinogradovite. In fact the structure of lintisite may be derived from that of vinogradovite simply by disjoining the double [Si_4O_{10}] chains and inserting between them the structural slab formed by [LiO_4] tetrahedra and [$Na(O,H_2O)_6$] octahedra (slab 1).

Table 5. Valence bond balance for lintisite, computed according to Brown and Altermatt (1985). The contributions for the hydrogen bonds were computed following Ferraris and Ivaldi (1988). $\Sigma_a v$ = valence of bonds emanating from cation summed over the bonded anions. $\Sigma_c v$ = valences of bonds reaching anions.

	Ti	Na1	Na2	Li	Si1	Si2	H-bonds	$\Sigma_c v$
O1		0.09 0.19			0.96 0.94			2.18
O2	0.68	0.15			1.08			1.91
O3	0.85	0.22				0.99		2.06
O4			0.15	0.23 0.23		1.11	0.11	1.83
O5	1.02 0.75	0.17					0.17	2.11
O6		0.12 0.10				0.92 0.90		2.04
O7	0.44 0.41	0.17			0.99			2.01
O8			0.24 0.10				−0.11 −0.17	0.06
$\Sigma_a v$	4.15	1.21	0.98	0.92	3.97	3.92		

The elementary slabs 1 to 4 were introduced to make easier the description and the understanding of the structural features of lintisite and its relationship with vinogradovite and ramsayite. However it should be remarked that all three structures present the sequence of slabs … 3 4 3 …, which thus appears as a basic module in any rigorous polysomatic approach to this family.

In Table 4 the unit cell constants of lintisite, ramsayite, vinogradovite and "mineral X" are compared. This last mineral is formed by alteration of murmanite and is described by Karup-Møller (1986) as a possible new mineral species. Indeed its chemical composition and unit cell constants, when conveniently transformed, strongly indicate that "mineral X" is vinogradovite.

The analogies among the cell constants of ramsayite, vinogradovite and lintisite – *b* and *c* are almost identical, *a* depends on the particular stacking sequence of the constituent slabs – confirm the modular nature of such minerals.

Structural details

Valence sums and [TiO_6] *octahedra*

The valence balance summations were computed following Brown and Altermatt (1985) and are presented in Table 5. The sums of the bond

Table 6. Comparison of the Ti–O distances (Å) in the $[TiO_6]$ octahedra for lintisite, vinogradovite and ramsayite. In the papers on vinogradovite and ramsayite (ref. cit.) the oxygen atoms are labelled in a different way, with respect to the labelling here used.

	1	2	3
Ti–O2	1.956	1.953	1.968
–O3	1.874	1.868	1.884
–O5	1.807	1.815	1.820
–O5*e*	1.923	1.938	1.939
–O7	2.141	2.139	2.181
–O7*d*	2.116	2.128	2.143
Average	1.970	1.974	1.989

1. Lintisite (present work).
2. Vinogradovite (Rastsvetaeva, Andrianov, 1984).
3. Ramsayite (Sundberg et al. 1987).

strengths reaching the oxygen anions display minor deviations from the expected values, 2 for atoms O1 to O7, 0 for O8. It should be observed that satisfactory bond valence sums for the various oxygen atoms are obtained through considerable distortions of the various polyhedra, mainly $[TiO_6]$ octahedra. For instance, severe undersaturation for O5 and oversaturation for O7 would result from regular $[TiO_6]$ octahedra with Ti–O bond lengths corresponding to the average value of 1.970 Å: under- and oversaturation are removed in the actual structure in which the Ti–O bonds range between 1.807 and 2.141 Å, with the lowest value corresponding to a Ti–O5 bond and the highest value corresponding to a Ti–O7 bond. Significant differences also exist among the O–O distances of the $[TiO_6]$ polyhedron, ranging from 2.523 Å for O5–O7 (the shared edge) to 2.979 Å. These distortions result in the shifting of the Ti^{4+} cation by about 0.16 Å from the central position towards the least-square plane passing through O3 and O5 atoms, and away from the least-square plane passing through O2 and O7 atoms.

Similar polyhedral distortions occur in the crystal structure of two minerals which, as already shown, are related to lintisite, namely vinogradovite (Rastsvetaeva, Andrianov, 1984) and ramsayite (Sundberg et al., 1987). A comparison of the six corresponding Ti–O distances in lintisite, vinogradovite and ramsayite is given in Table 6.

$[SiO_4]$ *and* $[LiO_4]$ *tetrahedra*

As regards the two independent $^1_\infty[T_2O_6]$ pyroxene-like chains, close analogies exist among the chains occurring in lintisite and those occurring in vinogradovite (Rastsvetaeva, Andrianov, 1984) and ramsayite (Sundberg et al., 1987). The Si1-centered tetrahedral chains form the above-defined slab 4 and are present in lintisite as well as in vinogradovite and ramsayite. As already observed by Sundberg et al. (1987) in their refinement of ramsayite, and similarly to vinogradovite (Rastsvetaeva, Andrianov, 1984), the Si1 – O (non-bridging) bonds are shorter than the Si1 – O (bridging) bonds, and the O2 – Si1 – O7 angle – the one including the two non-bridging oxygen atoms – is significantly larger (116.4°) than the other O – T – O angles. This represents a typical structural feature of the pyroxene-type chains, and is discussed in detail by Cameron and Papike (1980). The Si2-centered tetrahedral chains – which belong to the slab 2 – are similar to the corresponding tetrahedral chains in vinogradovite (Rastsvetaeva, Andrianov, 1984). However, in vinogradovite the tetrahedral sites host both silicon and aluminium with statistical occupancy ($Si_{0.69}Al_{0.31}$), and the average T – O distance is 1.66 Å. Moreover in lintisite the apical O4 atoms are shared with the edge-sharing [LiO_4] tetrahedral chains, whereas in vinogradovite the apical O1 atoms are shared with a similar, symmetry related, tetrahedral chain.

The Si2-centered tetrahedra in lintisite – and in vinogradovite, too – are more wide apart than the Si1-centered tetrahedra. This can be appreciated in two different ways, besides by giving a glance to Figure 1:

a) The distance between the apical oxygen of two neighbour tetrahedra is 2.979 Å for Si1 chains, and 3.393 Å for Si2 chains.

b) The dihedral angle between the planes defined by the basal oxygens of two neighbour tetrahedra is 177.5° for Si1 chains, and 158.5° for Si2 chains.

Within the edge-sharing [LiO_4] tetrahedra, the four Li – O bonds are nearly equal, and the average Li – O distance, 2.014 Å, is slightly greater than the predicted value, 1.97 Å, based on the effective ionic radii given by Shannon (1976). The shortest O – O distance corresponds to the shared edge, as expected.

An interesting structural feature of lintisite is represented by the occurrence of three-membered rings of tetrahedra: in fact [T_5O_{14}] groups are present, formed by pairs of three-membered rings sharing the central [LiO_4] tetrahedron (cf. Fig. 1). These groups build up, through edge and corner sharing, the complex module represented in Figure 3. Such a configuration appears as highly unstable if [SiO_4] tetrahedra only are involved, because of the great internal strains. In fact it has been found to date only in the structure of the beryllosilicate lovdarite (Merlino, 1990), in which [T_5O_{14}] groups exist which contain two [BeO_4] tetrahedra, one in each three-membered ring. Moreover [$Be_2SiO_8(OH)$] 3-rings were found in the crystal structure of the new tin beryllosilicate sverigeite (Rouse, Peacor, Metz, 1989).

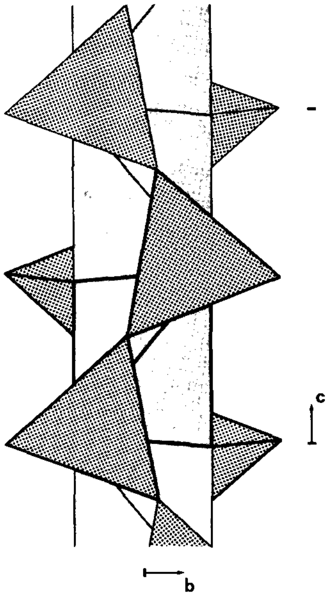

Fig. 3. A pair of condensed [T_5O_{14}] groups of tetrahedra, as seen along [100]. Each group is formed by two three-membered rings of tetrahedra sharing a central [LiO_4] tetrahedron. A [T_5O_{14}] group is denoted by heavy lines.

Na-centered polyhedra

Two different Na-centered polyhedra were found in the structure of lintisite, with Na1 cations in distorted cubes and Na2 cations in octahedral coordination. Na1 cations are placed in the channels limited by chains of [TiO_6] octahedra and chains of either Si1- and Si2-centered tetrahedra. The oxygen atoms which build up the distorted cube coordination around Na1 are located at distances ranging from 2.355 to 2.687 Å, with an average distance of 2.514 Å. The Na1-centered polyhedra form – through sharing of the O1–O6 edge – zig-zag chains running along **c**. Na2 cations are octahedrally coordinated by two oxygen atoms and four water molecules and build up, by edge sharing, zig-zag chains running along **c**. The chains are connected by columns of edge-sharing [LiO_4] tetrahedra giving rise together with them to the structural slab 1, depicted in Figure 2.

Thermal behaviour

Heating experiments were carried out on lintisite (Khomyakov et al., 1990) and gave the following results: half of the water content of lintisite is released gradually when the mineral is heated from 150 to 550° C, the other half is lost quickly when heating just over 550° C. This thermal behaviour is amenable to a simple explanation in the light of the structural results. In fact the loss of half the water molecules (O8 atoms in Fig. 2) still allows a tetrahedral coordination for all the Na2 atoms, with minor shiftings of the remaining water molecules. This is no more possible for a further loss of water molecules on heating. Therefore the water molecules are lost slowly and continuously with increasing temperature up to a total loss of four water molecules per unit cell; contrarily the last four molecules are lost quickly, because at this stage any reasonable coordination for Na2 cations without considerable structural rearrangement is prevented.

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