THE CRYSTAL STRUCTURE OF SILINAITE, NaLiSi$_2$O$_6$•2H$_2$O: A MONOPHYLLOSILICATE

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ABSTRACT

The new species *silinaite*, NaLiSi$_2$O$_5$•2H$_2$O, is monoclinic A2/n, with a 5.061(1), b 8.334(2), c 14.383(3) Å, β 96.6(2)°, V 602.5 Å^3, and Z = 4. The crystal structure was solved by direct methods and refined on 792 observed reflections to residuals R = 3.0 and R_w = 2.6%. The monophyllosilicate layer parallel to (001) consists of a unique configuration of linked pyroxene-type chains. These slightly undulous layers are bonded together by interlayers of [LiO$_4$] tetrahedra and [Na(H$_2$O)$_4$O$_2$] octahedra. The structure is compared to that of searlesite and makatite. The results of the crystal-structure analysis were essential in determining the chemical composition of silinaite.

Keywords: silinaite, crystal structure, layer silicate.

SOMMAIRE

La nouvelle espèce minérale *silinaïte*, NaLiSi$_2$O$_5$•2H$_2$O, est monoclinique A2/n, avec a 5.061(1), b 8.334(2), c 14.383(3) Å, β 96.6(2)°, V 602.5 Å^3, et Z égal à 4. La structure cristalline a été affinée par méthodes directes en utilisant 792 réflexions observées, jusqu'à un résidu R de 3.0% (R_w = 2.6%). Le feuillet monophyllosilicaté parallèle à (001) contient un agencement unique de chaînes semblables à celles des pyroxènes. Ces feuillets légèrement ondulants sont liés par des tétraèdres [LiO$_4$] et des octaèdres [Na(H$_2$O)$_4$O$_2$] interfoliaires. La structure ressemble à celle de la searlesite et de la makatite. Les résultats de l'ébauche de la structure cristalline se sont avérés essentiels dans la détermination de la composition chimique de la silinaïte.

(Traduit par la Rédaction)

Mots-clés: silinaïte, structure cristalline, silicate en feuillets.

INTRODUCTION

Silinaite, a new mineral species from Mont Saint-Hilaire, Rouville County, Quebec, is described by Chao *et al.* (1991). When the crystal-structure determination of silinaite was commenced, the amounts of sodium and silicon were known, but the results of the electron-microprobe analysis totalled only 73 wt.%. The light elements lithium and hydrogen, as well as the number of formula units, Z = 4, were determined by crystal-structure analysis. The usefulness of this method as a technique to determine chemical composition was described in detail by Hawthorne & Grice (1990).

EXPERIMENTAL

A thin, platy, (001) cleavage fragment chosen from the type material of silinaite (CMN #56467) and measuring 0.27 × 0.20 × 0.075 mm was used for the data collection. Single-crystal precession photographs yielded two possible space-groups, A2/n and An. Intensity data were collected on a fully automated, Nicolet R3m four-circle diffractometer operating at 50 kV and 40 mA with graphite-monochromated MoKα radiation. A set of 25 intense reflections was used to orient the crystal and refine the cell dimensions: a 5.061(1), b 8.334(2), c 14.383(3) Å, β 96.6(2)° and V 602.5 Å^3. A unique set of intensity data up to 2θ = 60° was collected using a θ : 2θ canning mode. Two standard reflections were monitored every 46 measured reflections to check crystal orientation, crystal decrepitation and beam intensity. The crystal remained stable in the X-ray beam, and all fluctuations were found to be within ± 1%. Of the 883 unique intensities collected, 792 were considered observed [F > 2.5$\sigma(F)$].

Reduction of the intensity data and refinement of the structure were done with the SHELXTL package of programs. Data reduction included background, scaling, Lorentz and polarization and absorption corrections (μ = 6.3 cm^{-1} for MoKα radiation). For the absorption correction, 11 intense diffraction-maxima over the 2θ range 6 to 57° were chosen for Ψ-diffraction-vector scans after the method of North *et al.* (1968). The Ψ-scan set was used to refine an ellipsoidal empirical absorption-correction. Application of the absorption-correction reduced the merging R of the Ψ-scan data set from 1.7 to 1.2% which, when applied to the whole dataset, resulted in minimum and maximum transmissions of 0.680 and 0.722.

CRYSTAL-STRUCTURE ANALYSIS

Two E-maps were calculated from a set of normalized structure-factors. One of these was chosen for the initial model for least-squares refinement based on favorable bond-lengths between the atomic positions. The positional and thermal parameters of three atoms in this model refined to give a residual index R of 37%. Difference-Fourier maps showed additional atomic sites that were arbitrarily assigned the scattering factors for oxygen. Scattering curves

TABLE 1. POSITIONAL COORDINATES AND THERMAL PARAMETERS (X100) IN SILINAITE

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	Ueq
Na	1/4	0.6035(2)	1/4	2.01(7)	2.00(6)	2.47(7)	0	0.73(5)	0	2.12(4)
Li	1/4	0.2395(7)	1/4	1.19(22)	1.68(24)	1.68(23)	0	-.04(20)	0	1.53(14)
Si	0.0525(1)	0.1526(1)	0.4366(1)	0.71(2)	0.74(2)	0.78(2)	0.08(2)	0.05(2)	-.05(2)	0.74(1)
O1	0.0096(3)	0.1211(2)	0.3269(1)	1.19(6)	1.35(7)	0.88(6)	-.11(5)	0.08(5)	-.05(5)	1.14(4)
O2	0.3610(3)	0.2053(2)	0.4703(1)	0.73(6)	1.22(6)	1.15(6)	0.20(5)	0.00(5)	-.20(5)	1.04(4)
O3	0	0	1/2	1.88(11)	1.31(10)	1.65(10)	0.76(8)	0.25(8)	-.30(8)	1.61(6)
O4	0.0933(3)	0.8583(2)	0.1594(1)	2.21(8)	2.70(9)	1.47(7)	-.02(7)	0.24(6)	-.36(8)	2.13(5)
H1	0.041(7)	0.855(4)	0.109(2)	5.2(1.1)						
H2	0.219(6)	0.941(4)	0.164(2)	3.6(8)						

Note: Anisotropic temperature factor takes the form: $T=\exp[-(2\pi^2(U_{11}a^{*2}h^2....+2U_{12}a^*b^*hk +....))]$
Esd's are in parentheses

TABLE 2. SELECTED INTERATOMIC DISTANCES (Å) AND BOND ANGLES (°) IN SILINAITE

Na Octahedron

Na-O1	2.473(2)	x2
Na-O4	2.311(2)	x2
Na-O4	2.568(2)	x2
Mean	2.451	

O1-O4	4.037(4)	106.4(1) x2
O4-O4	3.392(3)	87.9(1) x2
O4-O1	3.780(3)	104.3(1) x2
O1-O1	3.232(3)	81.6(1)
O4-O1	3.319(3)	87.8(1) x2
O4-O4	2.889(3)	68.4(1)
O4-O4	3.108(3)	78.9(1) x2
Mean	3.449	90.5

H Bonds

H1-O4	0.74(3)
H1-O2	2.16(3)
H2-O4	0.94(2)
H2-O1	2.03(3)
H2-H1	1.34(4)
H2-O4-H1	105(3)

Li Tetrahedron

Li-O1	1.997(3)
Li-O1	1.990(3)
Mean	1.994

O1-O1	3.077(2)	101.0(1) x2
O1-O1	3.232(3)	108.6(3)
O1-O1	3.319(3)	112.7(1) x2
O1-O1	3.473(3)	120.8(3)
Mean	3.250	109.4

Si tetrahedron

Si-O1	1.590(1)
Si-O2	1.641(1)
Si-O2	1.639(2)
Si-O3	1.605(1)
Mean	1.619

O2-O1	2.657(2)	110.7(1)
O3-O1	2.693(1)	114.9(1)
O3-O2	2.575(1)	105.0(1)
O2-O1	2.697(2)	113.3(1)
O2-O2	2.638(1)	107.1(1)
O2-O3	2.577(1)	105.2(1)
Mean	2.640	109.4

Note: Esd's are in parentheses

for neutral atoms from Cromer & Mann (1968) and anomalous dispersion coefficients from Cromer & Liberman (1970) were used. At $R = 4.5\%$, the Na, Si and five crystallographically non-equivalent "O" sites had been located. The refined occupancy of one "O" site was found to be very low. This site has tetrahedral coordination with an average bond-length of 2.00 Å. The average interatomic distances (Ondik & Smith 1968) for light elements ($Z < 8$) in tetrahedral coordination are: Li–O 1.98, Be–O 1.65 and B–O 1.48 Å. Clearly Li is the only cation large enough to fill this tetrahedral site in the crystal structure of silinaite.

The final steps of the least-squares refinement involved a conversion to anisotropic temperature-factors for all cations and oxygen atoms. With a weighting scheme of $\sigma^{-2}(F)$, the refinement attained an R of 3.6% ($R_w = 3.4\%$). At this point in

the refinement, the ΔF synthesis gave clear evidence of the two hydrogen atoms associated with one oxygen (O4). Refinement of the positional parameters of the H atoms with isotropic temperature-factors increased the number of refinable parameters to 61 and gave final residuals of $R = 3.0\%$ and $R_w = 2.6\%$. It should be noted that when the occupancy of Na and Li sites was allowed to refine, Na was found to be 98(1) and Li, 100(2)%, *i.e.*, the positions are fully occupied. The excellent refinement of the Li occupancy is further proof of its existence in this site. The final positional and thermal parameters are given in Table 1, and the bond lengths and angles in Table 2. Table 3, the observed and calculated structure-factors, has been submitted to the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Canada K1A 0S2.

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

The most striking feature of the silinaite structure is the layer of [SiO4] tetrahedra parallel to (001). In Figure 1, the monophyllosilicate layer can be seen to consist of slightly kinked, pyroxene-type, unbranched *zweier* single chains, linked together and alternating, with one chain having apices up and the adjoining chain, apices down. The chains are parallel to the X axis. These two features of the structure (silicate sheets and chains reinforced by [LiO4] tetrahedra) are exemplified in the observed cleavages, (001) perfect and (010) distinct. The (001) plane is also the composition plane for the twin law of silinaite (Chao *et al.* 1991). In Figure 2, one can see that a rotation of 180° about the [001] axis through the Li atoms would readily produce the observed twin. On the composition plane, site vacancies would be necessitated in the Na positions, but the other anions and cations would require very little change in position.

This type of single-layer silicate is not illustrated in Liebau's (1985) classification of silicates. He stated (p. 216) that such a structure type is not known.
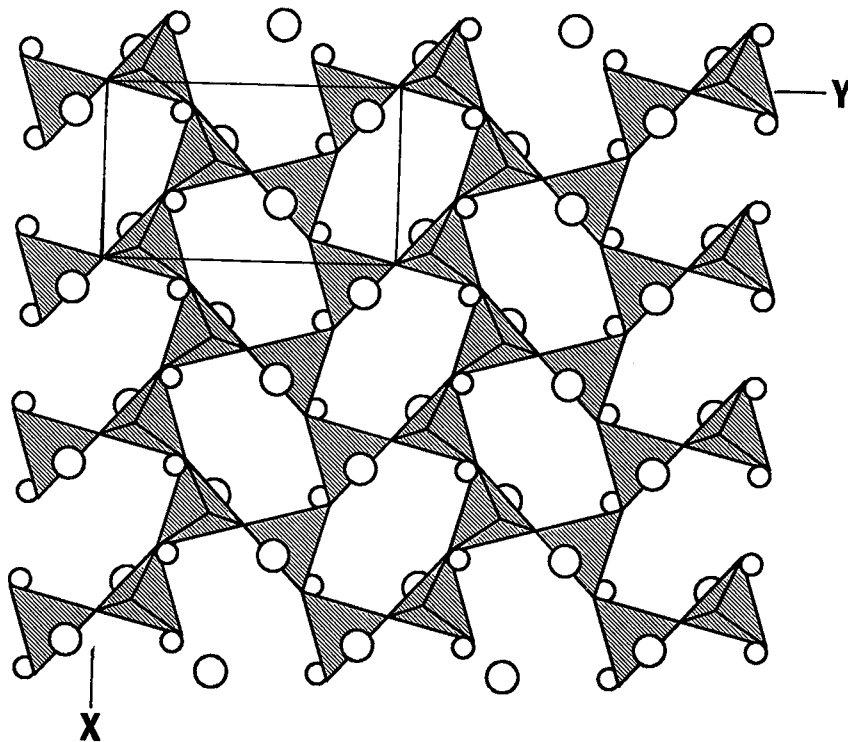
FIG. 1. The (001) layer of silicate tetrahedra of the silinaite structure, showing pyroxene-type chains parallel to the X axis. Na (large open circles) and Li (small open circles) atoms also are shown. The unit cell is outlined.

Silinaite is the first known example of a monophyllosilicate with this configuration of linked chains. Another unique feature of the silinaite silicate layer is the 180° bond angle of Si–O3–Si. The average bond-angle of a strain-free Si–O–Si bond is near 140° (Liebau 1985, p. 30), and the number of reliably determined crystal structures in which this angle is close to 180° is very limited. As O3 lies on a center of symmetry, the non-centrosymmetric space group An was tested to make sure of the center of symmetry that fixes the bond angle at 180°. The crystal structure in space group An refined to residual indices $R = 3.6$ and $R_w = 3.3\%$, which is significantly poorer than the refinement in space group $A2/n$. This confirms the linear Si–O3–Si bond. It is also of interest to note that the temperature factor, U_{eq}, of O3 is only slightly larger than U_{eq} for O1 and O2. This contrasts with the data presented in Liebau (1985, p. 29), which show a considerable increase in temperature factors for oxygen atoms in linear Si–O–Si bonds. An explanation of this may be that strain increases on this bond as it approaches 180°. In response to this strain, the central oxygen atom may assume a disordered position. If this disorder were not recognized in the structure refine-ment, it would be exemplified by large temperature-factors.

The silicate layers in the silinaite structure are bonded together by [LiO$_4$] tetrahedra (Fig. 2). The bond-valence sum based on the constants of Brown (1981) for the Li site is 0.93 v.u., which compares well with the ideal valence of 1 for Li. The agreement gives further evidence for the correct assignment of Li to this atomic site. These [LiO$_4$] tetrahedra are cross-linked by Na in octahedral coordination with two O atoms and four H$_2$O molecules. Each H$_2$O molecule, composed of O4, H1 and H2, is H-bonded to the silicate layer with an H1....O2 bond length of 2.16(3) Å and an H2....O1 bond length of 2.03(3) Å. Figure 2 illustrates the slight wave, or strain, in the silicate layer, with the [LiO$_4$] tetrahedra pulling layers together and the [Na(H$_2$O)$_4$O$_2$] octahedra bulging them apart.

Silinaite bears some resemblance, both chemically and structurally, to the minerals searlesite, NaBSi$_2$O$_5$(OH), and makatite, Na$_2$Si$_4$O$_8$(OH)$_2$·4H$_2$O, and the synthetic phases α-Na$_2$Si$_2$O$_5$, β-Na$_2$Si$_2$O$_5$, metastable Li$_2$Si$_2$O$_5$ and stable Li$_2$Si$_2$O$_5$. Ghose & Wan (1976) determined that searlesite is a single-layer
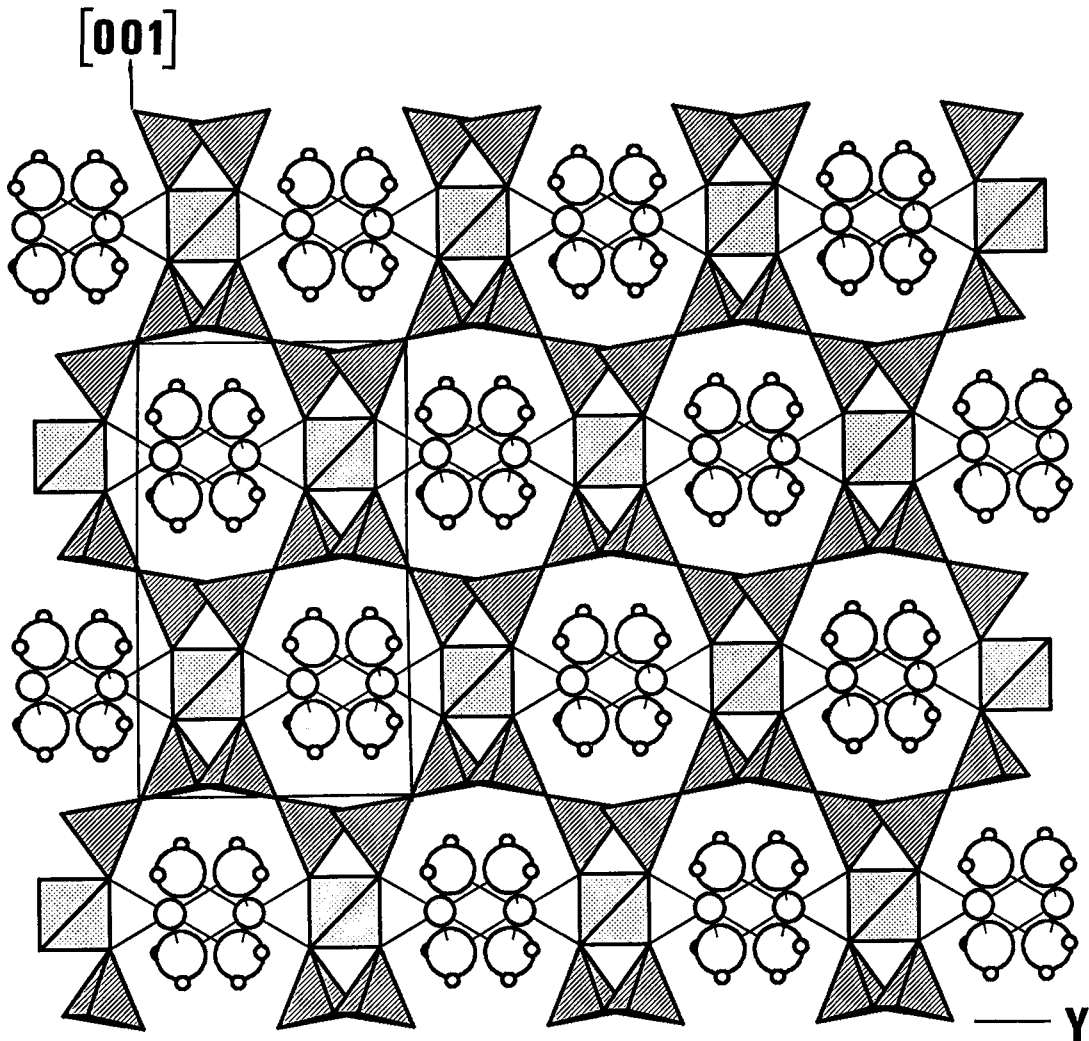
[001]

FIG. 2. An *X*-axis projection of the silinaite structure, showing the slightly wavy layer of silicate tetrahedra interleaved with [LiO₄] tetrahedra (shaded) and Na (small circles) in octahedral coordination, with four water molecules (large circles with two small circles for H) and two oxygen atoms shared with the [LiO₄] tetrahedron. The unit cell is outlined.

silicate formed by linking unbranched *zweier* single chains together. The phyllosilicate layers are held together by $[BO_2(OH)_2]$ tetrahedra and $[NaO_2(OH)_4]$ octahedra much like the linkage in silinaite; yet in searlesite, unlike in silinaite, the $[SiO_4]$ tetrahedra in the chain alternate up and down. The nearly planar phyllosilicate layer in silinaite and searlesite contrasts with that of makatite (Annehed *et al.* 1982), composed of *vierer* single chains, which are highly convoluted with the relatively large $[Na(H_2O)_6]$ polyhedra. Like makatite, synthetic β-$Na_2Si_2O_5$ (Pant 1968) has Na in both five- and six-fold coordination, but Na polyhedra in this dehydrated phase

are smaller and more uniform in size, and thus impose a more planar $[SiO_4]$ layer composed of *dreier* double chains almost identical to those of searlesite. The higher-temperature polymorph, α-$Na_2Si_2O_5$ (Pant & Cruickshank 1968), has each Na coordinated to five oxygen atoms, which corrugates the $[SiO_4]$ *dreier* single layer. Stable $Li_2Si_2O_5$ (Liebau 1961) has the same configuration of silicate sheet as α-$Na_2Si_2O_5$, but with tighter corrugations owing to the smaller $[LiO_4]$ tetrahedra. In metastable $Li_2Si_2O_5$ (Smith *et al.* 1990), the Li coordination and type of silicate layer are the same as for its polymorph, but adjacent silicate layers have tetrahedra

that "point" in opposite directions.

From the above discussion, it is evident that although the three minerals and four synthetic phases all have a single silicate layer composed of six-linked [SiO_4] tetrahedra, the crystal structure can accommodate a variety of cations with differing coordinations and polyhedral sizes. This variability is accommodated by varying numbers and types of chains composing the silicate layer as well as by corrugations of the layer itself.

REFERENCES

ANNEHED, H., FALTH, L. & LINCOLN, F.J. (1982): Crystal structure of synthetic makatite $Na_2Si_4O_8(OH)_2 \cdot 4H_2O$. Z. Kristallogr. **159**, 203-210.

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

CHAO, G.Y., GRICE, J.D. & GAULT, R.A. (1991): Silinaite, a new sodium lithium silicate hydrate mineral from Mont Saint-Hilaire. *Can. Mineral.* **29**, 359-362.

CROMER, D.T. & LIBERMAN, D. (1970): Relativistic calculation of anomalous scattering factors for X rays. *J. Chem. Phys.* **53**, 1891-1898.

_____ & MANN, J.B. (1968): X-ray scattering factors computed from numerical Hartree–Fock wave functions. *Acta Crystallogr.* **A24**, 321-324.

GHOSE, S. & WAN C. (1976): Structural chemistry of borosilicates. II. Searlesite, $NaBSi_2O_5(OH)$: Absolute configuration, hydrogen locations, and refinement of the structure. *Am. Mineral.* **61**, 123-129.

HAWTHORNE, F.C. & GRICE, J.D. (1990): Crystal-structure analysis as a chemical analytical method: application to first-row elements. *Can. Mineral.* **28**, 693-702.

LIEBAU, F. (1961): Untersuchungen an Schichtsilikaten des Formeltyps $A_m(Si_2O_5)_n$. I. Die Kristallstruktur der Zimmertemperaturform des $Li_2Si_2O_5$. *Acta Crystallogr.* **14**, 389-395.

_____ (1985): *Structural Chemistry of Silicates: Structure, Bonding and Classification.* Springer–Verlag, Berlin.

NORTH, A.C.T., PHILLIPS, D.C. & MATHEWS, F.S. (1968): A semi-empirical method of absorption correction. *Acta Crystallogr.* **A24**, 351-359.

ONDIK, H. & SMITH, D. (1968): Interatomic and interionic distances. *In* International Tables for X-ray Crystallography III (C.H. MacGillavry & G.D. Rieck, eds.). Kynoch Press, Birmingham, England.

PANT, A.K. (1968): A reconsideration of the crystal structure of β-$Na_2Si_2O_5$. *Acta Crystallogr.* **B24**, 1077-1083.

_____ & CRUICKSHANK, D.W.J. (1968): The crystal structure of α-$Na_2Si_2O_5$. *Acta Crystallogr.* **B24**, 13-19.

SMITH, R.I., HOWIE, R.A., WEST, A.R., ARAGÓN-PIÑA, A. & VILLAFUERTE-CASTREJÓN, M.E. (1990): The structure of metastable lithium disilicate, $Li_2Si_2O_5$. *Acta Crystallogr.* **C46**, 363-365.