

The Crystal Structure of Sorensenite, $\text{Na}_4\text{SnBe}_2(\text{Si}_3\text{O}_9)_2 \cdot 2\text{H}_2\text{O}$

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The mineral sorensenite crystallizes in space group $C2/c$ with $a=20.698$ (17), $b=7.442$ (5), $c=12.037$ (11) Å, $\beta=117.28$ (6)°; $Z=4$. X-ray data were collected on a semi-automatic diffractometer to give 1836 independent reflexions with $I > 2\sigma(I)$. The structure was solved by Patterson and Fourier methods and refined by least squares to $R=0.040$. The structure consists of $[\text{Si}_3\text{O}_9]_\infty$ chains along [010] and thus belongs to the wollastonite mineral group. Four chains are linked by pairs of BeO_4 tetrahedra sharing an edge. The Sn atoms are octahedrally coordinated by O atoms from four silicate chains.

Introduction

Sorensenite, $\text{Na}_4\text{SnBe}_2(\text{Si}_3\text{O}_9)_2 \cdot 2\text{H}_2\text{O}$, occurs in hydrothermal analcime veins in the Ilimaussaq alkaline intrusion in south-west Greenland. Sorensenite nucleated on the floor of miarolitic cavities in the analcime veins which cut coarse-grained lujavrites. It grew into split crystal fans of lengths up to 15 cm. The [010] directions of the crystal lamellae branch in a non-crystallographic way from the base and upwards to form sheaves. The splitting may develop at both ends of the b axis to form bow-tie growths. This growth habit is a salient feature of the wollastonite group. The developed forms are $\{201\}$, $\{100\}$ and $\{101\}$. The cleavage is parallel to $\{10\bar{1}\}$ and $\{100\}$. Regular intergrowths of unsplit sorensenite laths are rare, but small (~ 10 mm in diameter) pseudohexagonal piles with a^* as the pseudohexagonal axis do occur. Chemical analyses, optical properties and occurrence are given by Semenov, Gerassimovsky, Maksimova, Andersen & Petersen (1965).

Experimental

Because of the splitting it was difficult to find a single crystal for the X-ray investigation; eventually a fragment, $0.2 \times 0.1 \times 2.0$ mm, was selected under the polarizing microscope using the gypsum plate. Photographs taken with Cu $K\alpha$ radiation ($\lambda=1.5418$ Å) were used to determine the cell dimensions and space group, and a preliminary set of visually estimated $h0l$ data. An automatic diffractometer of Weissenberg type (Supper-Pace) was used to collect all reflexions in a hemisphere with $\sin \theta/\lambda < 0.7$, giving 2299 independent reflexions of which 1836 had $I > 2\sigma(I)$. Mo $K\alpha$ radiation from a graphite monochromator was used in conjunction with a pulse-height analyser. The diffractometer was controlled by an HP 2114A computer.

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Crystal data

Sorensenite, $\text{Na}_4\text{SnBe}_2(\text{Si}_3\text{O}_9)_2 \cdot 2\text{H}_2\text{O}$; molecular weight 721.26; monoclinic, b unique; $a=20.698$ (17), $b=7.442$ (5), $c=12.037$ (11) Å, $\beta=117.28$ (6)°; $a:b:c=2.789:1:1.622$; $Z=4$; $D_{\text{calc.}}=2.92$, $D_{\text{obs.}}=2.9$ g cm⁻³; $V=1647.9$ Å³. Systematic absences: hkl : $h+k \neq 2n$; $h0l$: $l \neq 2n$. No piezoelectric effect detected. Space group: $C2/c$ or Cc ($C2/c$ confirmed by structure analysis). $\mu_{\text{Mo}}=21.3$ cm⁻¹. Cell dimensions were refined from a Guinier powder diagram with NaCl ($a=5.6402$ Å) as standard from the 30 lines that could be indexed unambiguously. Table 1* contains d spacings, relative intensities, indexing, and calculated structure factors of the powder diagram. Final atomic coordinates and temperature factor parameters are given in Table 2.*

Structure determination

If the space group is $C2/c$ the Sn atom must be in a special position; the Patterson projection $P(u0w)$ confirmed this and some of the lighter atoms could also be found in projection but since there was considerable overlap, three-dimensional data were collected. Sn could be either on a centre of symmetry or on a two-fold axis and a few cycles of electron density calculations were made for each of the two possibilities before it was clear that the Sn atom had to be at the centre of symmetry. The chemical composition given by Semenov *et al.* (1965) was confirmed.

The structure was refined by the full-matrix least-squares program *LINUS*, and anisotropic temperature factor coefficients were introduced at $R = \sum |F_o| - |F_c| / \sum |F_o| = 0.10$. Anomalous scattering for Sn was in-

* Table 1 and a list of structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31759 (14 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

cluded, and an isotropic extinction factor was refined but the extinction effect was found to be negligible. The two independent H atoms could not be seen in a difference map calculated at $R=0.045$. They were expected to be joined to the only oxygen atom, O(7), in the structure that was not bonded to Si and to point towards other O atoms to form weak hydrogen bonds. The final value of R was 0.040 for the 1836 reflexions with $I > 2\sigma(I)$, 0.06 for all 2299 reflexions measured.

Description of the structure

Table 3 gives the bond lengths and some angles. Fig. 1 shows the structure seen along b . All three independent Si atoms are surrounded by O atoms in regular tetrahedra, the tetrahedra being linked by corner-sharing into infinite, 1–2 zigzag chains parallel to b so that sorensenite belongs to the wollastonite group although the arrangement of the chains is different.

The chains are linked in the c direction by pairs of Be atoms which are positioned on twofold axes.

Each Be coordinates O atoms from four different chains, and the two BeO_4 tetrahedra share an edge as is also found in epididymite (Fang, Robinson & Ohya, 1972). The $\text{O}\cdots\text{O}$ distance along the common edge is short, 2.38 Å in sorensenite, 2.42 Å in epididymite, indicating that the Be–O bonds have considerable covalent character even though the bridging Be–O distances are not much shorter than the sum of ionic radii (Pauling, 1960).

In the two-dimensional network of Si and Be tetrahedra there are holes where a Na^+ ion and a water molecule, O(7), can be accommodated.

In the a direction the structure is linked by Sn atoms octahedrally coordinated by O atoms from four different $(\text{Si}_3\text{O}_9)_\infty$ chains, and by one Na atom. Both Na atoms are seven coordinated, the coordination polyhedra being very irregular.

The average Si–O length is 1.624 Å, but in all three tetrahedra there is one short bond, average 1.598 Å, to an O atom which is shared only with Be and Na atoms, whereas bonds to O atoms that are shared with

Table 2. Final atomic coordinates ($\times 10^5$) and mean square vibration amplitudes, u_{ij} ($\times 10^4$)

Standard deviations in terms of the last digit are in parentheses.

	x	y	z	u_{11}	u_{22}	u_{33}	u_{12}	u_{13}	u_{23}
Sn	25000	25000	50000	72 (2)	103 (2)	115 (2)	–2 (1)	59 (1)	–3 (1)
O(1)	4384 (17)	47523 (34)	68797 (31)	130 (16)	138 (10)	142 (15)	4 (11)	46 (13)	27 (11)
O(2)	18295 (17)	4853 (34)	49599 (31)	104 (15)	127 (10)	222 (17)	–2 (10)	104 (13)	5 (11)
O(3)	30047 (16)	22843 (33)	69123 (27)	106 (13)	118 (13)	120 (13)	0 (10)	57 (11)	12 (10)
O(4)	4117 (17)	4062 (33)	86873 (31)	96 (15)	136 (10)	149 (15)	13 (11)	41 (12)	5 (11)
O(5)	8358 (17)	23994 (30)	52567 (29)	129 (14)	113 (10)	178 (14)	7 (11)	93 (11)	7 (11)
O(6)	31453 (17)	5318 (37)	48462 (32)	85 (15)	190 (11)	210 (17)	–1 (11)	90 (13)	–5 (12)
O(7)	18293 (21)	26439 (42)	85100 (36)	285 (20)	193 (12)	282 (19)	–25 (14)	155 (16)	–9 (15)
O(8)	44522 (16)	25862 (29)	76059 (28)	105 (13)	132 (10)	167 (13)	17 (11)	94 (11)	7 (12)
O(9)	39574 (18)	5964 (37)	88396 (31)	151 (16)	213 (12)	160 (16)	21 (12)	90 (13)	61 (12)
O(10)	38303 (18)	42096 (35)	88275 (31)	185 (16)	142 (10)	179 (16)	–3 (12)	96 (13)	–64 (11)
Si(1)	39711 (6)	5380 (13)	50164 (11)	68 (5)	100 (4)	109 (6)	4 (4)	57 (5)	–14 (4)
Si(2)	38279 (6)	24309 (12)	80364 (10)	67 (5)	85 (4)	101 (5)	2 (4)	58 (4)	2 (4)
Si(3)	10431 (7)	3979 (12)	49490 (11)	66 (5)	96 (4)	105 (6)	–1 (4)	49 (4)	9 (4)
Be(1)	50000	10140 (93)	75000	69 (34)	181 (25)	94 (36)	0	31 (29)	0
Be(2)	50000	41538 (75)	75000	112 (36)	43 (19)	147 (38)	0	60 (30)	0
Na(1)	24363 (12)	45290 (25)	76492 (22)	190 (10)	291 (8)	296 (12)	68 (8)	95 (9)	–65 (8)
Na(2)	5320 (11)	25979 (21)	69795 (20)	178 (9)	244 (8)	282 (10)	–1 (8)	146 (8)	0 (8)
H(1)	18779 (316)	16497 (775)	88850 (546)	163 (134)					
H(2)	18751 (424)	34251 (1064)	90966 (777)	515 (229)					

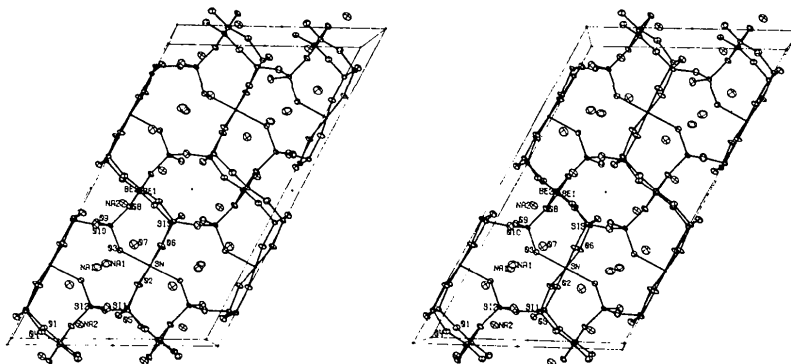


Fig. 1. A unit cell of sorensenite seen along b with c across the page.

Table 3. *Interatomic distances and angles*

Standard deviations in terms of the last digit are in parentheses.

Si(1)—O(1)	1.595 (4) Å	Na(1)—O(3)	2.400 (3) Å
Si(1)—O(5)	1.657 (3)	Na(1)—O(7)	2.411 (4)
Si(1)—O(6)	1.626 (4)	Na(1)—O(3)	2.432 (4)
Si(1)—O(9)	1.638 (4)	Na(1)—O(10)	2.578 (5)
Si(2)—O(8)	1.601 (3)	Na(1)—O(2)	2.664 (5)
Si(2)—O(3)	1.624 (4)	Na(1)—O(6)	2.677 (5)
Si(2)—O(9)	1.623 (3)	Na(1)—O(9)	2.726 (5)
Si(2)—O(10)	1.629 (3)	Na(2)—O(4)	2.384 (4)
Si(3)—O(4)	1.599 (4)	Na(2)—O(1)	2.403 (4)
Si(3)—O(2)	1.623 (4)	Na(2)—O(5)	2.431 (4)
Si(3)—O(5)	1.639 (3)	Na(2)—O(7)	2.465 (5)
Si(3)—O(10)	1.633 (3)	Na(2)—O(1)	2.676 (4)
Be(1)—O(1)	1.594 (5)	Na(2)—O(4)	2.723 (4)
Be(1)—O(8)	1.674 (6)	Na(2)—O(9)	2.832 (4)
Be(2)—O(4)	1.588 (5)	O(7)—H(1)	0.848 (59)
Be(2)—O(8)	1.672 (5)	O(7)—H(2)	0.886 (84)
Sn—O(2)	2.029 (3)	O(7)—O(2)	2.910 (5)
Sn—O(3)	2.053 (4)	O(7)—O(6)	2.905 (5)
Sn—O(6)	2.047 (3)		
O(1)—Si(1)—O(6)	114.3°	O(4)—Be(2)—O(8)	112.0 (2)°
O(1)—Si(1)—O(9)	111.4	O(4)—Be(2)—O(8)	116.4 (2)
O(1)—Si(1)—O(5)	112.9	O(4)—Be(2)—O(4)	108.1 (4)
O(6)—Si(1)—O(9)	106.8 (2)	O(8)—Be(2)—O(8)	91.5 (3)
O(6)—Si(1)—O(5)	108.2 (2)	O(8)—Be(1)—O(1)	118.2 (2)
O(9)—Si(1)—O(5)	102.5 (2)	O(8)—Be(1)—O(1)	110.5 (2)
O(8)—Si(2)—O(9)	108.4 (2)	O(8)—Be(1)—O(8)	91.3 (4)
O(8)—Si(2)—O(3)	115.4 (2)	O(1)—Be(1)—O(1)	107.8 (5)
O(8)—Si(2)—O(10)	110.1 (2)	O(2)—Sn—O(6)	86.4 (1)
O(9)—Si(2)—O(3)	105.3 (2)	O(3)—Sn—O(6)	91.6 (1)
O(9)—Si(2)—O(10)	112.3 (2)	O(3)—Sn—O(3)	87.7 (1)
O(3)—Si(2)—O(10)	105.2 (2)	Na(1)—O(7)—Na(2)	106.9 (2)
O(4)—Si(3)—O(2)	113.8 (2)	Na(1)—O(7)—H(1)	141.1 (41)
O(4)—Si(3)—O(10)	112.2 (2)	Na(1)—O(7)—H(2)	94.2 (52)
O(4)—Si(3)—O(5)	111.7 (2)	Na(2)—O(7)—H(1)	102.1 (39)
O(2)—Si(3)—O(10)	105.5 (2)	Na(2)—O(7)—H(2)	106.2 (51)
O(2)—Si(3)—O(5)	109.1 (2)	H(1)—O(7)—H(2)	101.8 (70)
O(10)—Si(3)—O(5)	103.8 (2)	O(7)—H(1)—O(2)	165.8 (57)
		O(7)—H(2)—O(6)	168.7 (73)

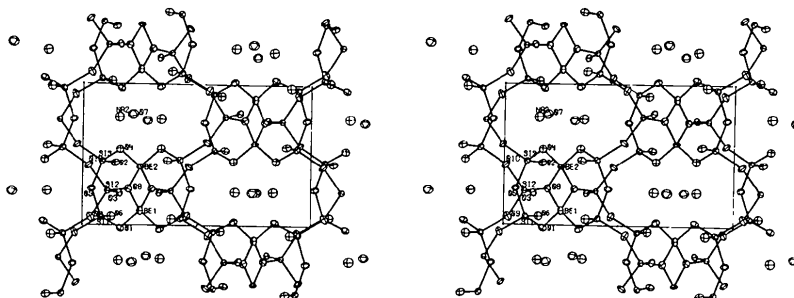
another Si atom are longer than the average. The angles in the tetrahedra are generally larger where a short Si—O bond is involved, in agreement with observations and M—O calculations by Louisnathan & Gibbs (1972). Judging from the Si—O bond length variations it may be concluded that Si—O bonds are stronger than Sn—O bonds and these again stronger than Be—O bonds. According to Semenov *et al.* (1965) the best cleavage is along {10 $\bar{1}$ }, and {100} is also a

prominent cleavage plane. We expect the {100} cleavage to take place in Be layers (Fig. 1), whereas the {10 $\bar{1}$ } cleavage must involve both Sn—O and Be—O bonds and it is difficult to see why this should be the more prominent cleavage direction.

The chemical formula was originally written with hydroxyl groups instead of with water of crystallization because of the high dehydration temperature (Semenov *et al.*, 1965). All O atoms in the structure except O(7) are, however, bonded to at least three atoms of which at least one is an Si atom. O(7) has as its nearest neighbours two Na atoms and two three-coordinated O atoms in such an arrangement that O(7) can achieve tetrahedral coordination and form hydrogen bonds to these two O atoms. We therefore conclude that O(7) is a water molecule. O(7) is in a hole in the structure and cannot escape without some strong bonds being broken. In fact a powdered sample heated to 800°C (water is given off at 600°C) for 48 h showed the powder lines of SnO₂ only, indicating that the structure had been destroyed. The infrared spectrum given by Semenov *et al.* (1965) cannot distinguish between water of crystallization and hydroxide groups.

Sorensenite may occasionally form pseudohexagonal complex twins with the normal to $\langle 011 \rangle$ in (100) as twin axis. The complex twinning is readily explained by the structure, which can be considered to be built up of layers parallel to {100} (Fig. 2), held together by Sn and Na(1) atoms. Fig. 3 shows a slice, 0.35 Å thick, of the structure parallel to {100}. The triangles are faces of Sn octahedra and the 'surface' of a sheet of Si and Be tetrahedra. It is seen that this layer is pseudohexagonal so that all Sn—O as well as Si—O and Be—O bonds fit if we rotate such a layer 180° about the twin axis. This rotation corresponds to a 120° rotation of the inverted layer about a normal to {100}, *i.e.* a^* . Even most of the Na...O contacts can be fitted if the water molecule (shown as circles drawn in thin lines in Fig. 3) keeps its position relative to the Sn—Na layer.

After this structure determination was completed, an abstract appeared of a paper by Maksimova, Ilyukin & Belov (1974). As far as we can tell, they obtain the same results except that they prefer the

Fig. 2. A layer of Si and Be tetrahedra, $0.30 \leq x \leq 0.70$, seen along a^* .

non-centrosymmetric space group Cc . Since our refinement proceeded smoothly to an R that agrees with what was expected, and since temperature parameters are reasonable, we see no reason to introduce more parameters by changing to the non-centrosymmetric space group.

Computational details

The scattering factors used were: Sn, average of the curves given in Cromer & Mann (1968) and Cromer & Waber (1974); Si, Na, Be, O, Cromer & Waber (1974); H, Stewart, Davidson & Simpson (1965); $\Delta f'$, $\Delta f''$ for Sn, Cromer & Liberman (1970).

Computer programs: diffractometer control program for HP2114A by J. Nyborg; data reduction: Algol program by T. la Cour and F. R. Poulsen; *JIMDAP*, modified version of Fourier program by A. Zalkin; *LINUS*, modification of *ORFLS* (Busing, Martin & Levy, 1962) by W. C. Hamilton, P. Coppens and J. Ibers; *ORFFE*, Busing, Martin & Levy (1964). *ORTEP2*, Johnson (1965), modified 1971.

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References

- BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). *ORFLS*. Oak Ridge National Laboratory Report ORNL-TM-305.
- BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1964). *ORFFE*. Oak Ridge National Laboratory Report ORNL-TM-306.
- CROMER, D. T. & LIBERMAN, D. (1970). *J. Chem. Phys.* **53**, 1891–1898.
- CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* **A24**, 321–324.

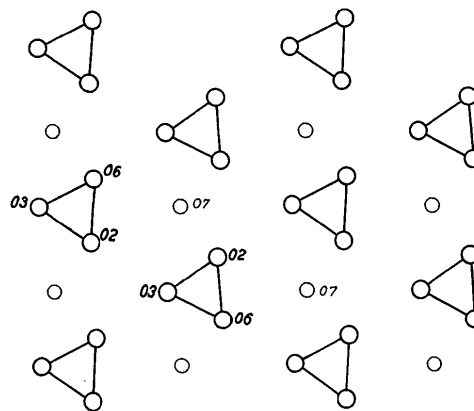


Fig. 3. Surface of the layer shown in Fig. 2 ($0.30 \leq x \leq 0.32$). The triangles are faces of the octahedra around tin, O(7) are water molecules.

- CROMER, D. T. & WABER, J. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV. Birmingham: Kynoch Press.
- FANG, J. H., ROBINSON, P. D. & OHYA, Y. (1972). *Amer. Min.* **57**, 1345–1354.
- JOHNSON, C. K. (1965). *ORTEP*. Oak Ridge National Laboratory Report ORNL-3794.
- LOUISNATHAN, S. J. & GIBBS, G. V. (1972). *Mater. Res. Bull.* **7**, 1281–1291.
- MAKSIMOVA, N. V., ILYUKIN, V. V. & BELOV, N. V. (1974). *Sov. Phys. Dokl.* **18**, 681–682 [*Dokl. Akad. Nauk. SSSR* (1973), **213**, 91–93].
- PAULING, L. (1960). *The Nature of the Chemical Bond*, 3rd ed. Ithaca: Cornell Univ. Press.
- SEMENOV, E. I., GERASSIMOVSKY, V. I., MAKSIMOVA, N. V., ANDERSEN, S. & PETERSEN, O. V. (1965). *Medd. Grønland*, **181**, 2–19.
- STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.