

Sverigeite, a structure containing planar NaO₄ groups and chains of 3- and 4-membered beryllsilicate rings*

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ABSTRACT

Sverigeite, Na(Mn²⁺,Mg)₂Sn⁴⁺[Be₂Si₃O₁₂(OH)], is orthorhombic, *Imma*, with $a = 10.815(8)$, $b = 13.273(8)$, $c = 6.818(6)$ Å, and $Z = 4$. Its crystal structure has been determined by direct methods and refined to an unweighted residual of 0.054 for all 571 reflections. Sverigeite is a single-chain beryllsilicate, which may be described in terms of three structural elements: (1) octahedral single-chains of alternating, edge-sharing SnO₆ distorted octahedra and planar NaO₄ groups running parallel to [001]; (2) tetrahedral single-chains of alternating, vertex-sharing Be₂SiO₈(OH) 3-rings and Be₂Si₂O₁₁(OH) 4-rings running parallel to [100]; and (3) discrete M₂O₁₀ groups of edge-sharing distorted MO₆ octahedra ($M = \text{Mn}_{0.63}\text{Mg}_{0.37}$), which link adjacent octahedral chains and also adjacent tetrahedral chains. Na displays a most unusual 4-fold, rectangular-planar coordination [$\text{Na-O} = 2.433(5)$ Å], which may be regarded as a distorted octahedron with two vacant axial ligand sites. The next-nearest oxygen atoms are a distant 3.065(4) Å.

INTRODUCTION

The new tin beryllium silicate mineral sverigeite was described from the Långban Mine, Värmland, Sweden, by Dunn et al. (1984). They found it to be orthorhombic, *Ibmm* or *Ibm2*, with cell parameters $a = 6.818(6)$, $b = 13.273(8)$, $c = 10.815(8)$ Å and calculated unit-cell contents of Na_{4.18}Mg_{4.26}Mn_{3.53}Fe_{0.09}²⁺Zn_{0.31}Be_{8.23}Sn_{4.01}Si_{11.83}O_{48.77}H_{2.83}. The formula was provisionally idealized as NaMgMnBe₂SnSi₃O₁₂(OH) with $Z = 4$. A determination of the crystal structure, which is reported here, confirms the essential correctness of this formulation and, in addition, reveals the existence of two unusual structural entities: (1) 3-membered beryllsilicate rings of composition Be₂SiO₈(OH) alternating with 4-membered Be₂Si₂O₁₁(OH) rings in infinite chains and (2) Na in 4-fold, rectangular-planar coordination by oxygen.

STRUCTURE SOLUTION AND REFINEMENT

Intensity measurements were made on an irregularly shaped crystal fragment of dimensions 0.43 × 0.29 × 0.15 mm; the unit cell as defined by Dunn et al. (1984) was used. The intensities of 571 reflections constituting one asymmetric unit ($\sin \theta \leq 0.46$) were collected with a computer-controlled Supper-Pace diffractometer system employing Weissenberg equi-inclination geometry, monochromatized MoK α radiation, scanning rates of 2°/min and 4°/min, and high- and low-side background counting times of 25 s. The intensities were converted to structure-factor amplitudes by correction for Lorentz, polarization, and absorption effects ($\mu_1 = 46 \text{ cm}^{-1}$). Twelve

of the 571 reflections had $|F|_{\text{obs}} < 3\sigma|F|_{\text{obs}}$, where σ is the standard deviation derived from the counting statistics, and these twelve were considered to be unobserved.

The structure was determined by direct methods using the MITHRIL package of Gilmore (1983). Statistical tests performed by MITHRIL indicated that sverigeite was noncentrosymmetric (a result that later proved to be erroneous) and the solution and refinement of the structure were initiated in space group *Ima2* after transforming indices from the nonstandard *Ibm2* setting. The first *E* map revealed the locations of Sn, Mn and Mg (both at the M site), Si, Be, and most of the oxygens; the remaining atoms were located by electron-density and difference-electron-density syntheses. Refinement of the structure was carried out with the SHELX-76 package of Sheldrick (1976), neutral-atom scattering factors (Doyle and Turner, 1968), and anomalous dispersion corrections for all atoms (Cromer and Liberman, 1970). Unit weights were initially employed and later replaced by a weighting scheme of the form $w = 1/[\sigma^2(F) + |g|(F^2)]$, where g is a refinable parameter, which ultimately converged to a value of 0.010.

With isotropic temperature factors, the structure refinement converged to a respectable value of 0.065 for the unweighted residual, but strong parameter interactions between pairs of nonequivalent atoms and the unrealistically low refined values for many temperature factors suggested a fundamental error in the model. Inspection of the atomic coordinates showed that the atoms in the model could be fitted to the equipoints of *Imma*, the centrosymmetric supergroup of *Ima2* with a reorientation of the cell axes. (The *Imam* setting is nonstandard.) The erroneous indication of noncentrosym-

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TABLE 1. Positional ($\times 10^4$) and thermal ($\text{\AA}^2 \times 10^4$) parameters in sverigeite

		x	y	z	U_{11} (or U_{60})	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	U_{eq}
Sn	4a	0	0	0	40(8)	69(7)	23(6)	4(2)	0	0	44
M	8g	1/4	6291(1)	1/4	85(11)	71(10)	63(9)	0	8(4)	0	73
Na	4b	0	0	1/2	398(78)	1453(160)	139(51)	-124(28)	0	0	663
Si(1)	4e	0	1/4	8606(3)	3(12)	91(13)	27(12)	0	0	0	40
Si(2)	8g	1/4	0832(2)	1/4	34(12)	77(11)	26(10)	0	9(5)	0	46
Be	8i	6353(9)	1/4	0262(13)	51(17)						
O(1)	16j	7855(3)	1479(2)	4421(5)	95(8)						
O(2)	16j	8664(4)	0021(2)	2130(6)	82(12)						
O(3)	8i	1213(3)	1/4	7211(5)	47(10)						
O(4)	8h	0	3501(7)	9932(6)	129(15)						
O(5)	4e	0	1/4	3834(10)	180(17)						

Note: Anisotropic temperature factors are of the form $\exp[-2\pi^2(h^2a^2U_{11} + k^2b^2U_{22} + \dots + 2hka^*b^*U_{12})]$. Esd's are in parentheses. Atom O(5) is the hydroxyl oxygen, and atom M represents (Mn_5Mg_3).

metry given by the intensity statistics is ascribed to the presence of a heavy atom, in this case Sn, in a special position (Giacovazzo, 1980).

With the change in space group and appropriate re-indexing of reflections, the residual remained at its previous value, but the parameter-interaction and temperature-factor problems disappeared. Refinement of the occupancy fraction of Mn in the M site produced a value of 0.315(7), which corresponds to a site content of ($\text{Mn}_{5.04}\text{Mg}_{2.96}$) or essentially (Mn_5Mg_3). The M site in the crystal used for intensity measurement is therefore substantially enriched in Mn compared to the site contents ($\text{Mn}_{3.5}\text{Mg}_{4.3}$) indicated by the chemical analysis of Dunn et al. (1984). Introduction of anisotropic temperature factors further reduced the residual to 0.046, but the temperature factors of the light atoms Be, O(2), O(3), and O(4) became nonpositive definite, and in the final cycles all Be and oxygen atoms were refined isotropically. The largest peak in the final difference synthesis occurred at (0,0.294,0.384) and had a density of $2.5 \text{ e}^-/\text{\AA}^3$. This peak is 0.6 \text{\AA} from the hydroxyl oxygen, O(5), and might represent four H atoms (there are four OH per cell) disordered over equipoint 8h. However, attempts to refine this position as H were unsuccessful, and the peak and its equivalent at (0,0.206,0.384) may represent an anisotropic thermal anomaly about the O(5) site or positional disorder of this atom. The anisotropic refinement of O(5) yielded an unusually large value of 0.060(6) \text{\AA} for U_{22} . (The values of U_{11} and U_{33} were 0.010(3) and 0.001(2) \text{\AA}^2, respectively.) A difference synthesis calculated from the results of the full anisotropic refinement also failed to reveal the H positions.

The final values of the residuals are 0.053 (unweighted) and 0.067 (weighted) for the 559 observed reflections and 0.054 (unweighted) and 0.070 (weighted) for all 571 reflections, including those that were unobserved. Table 1 contains the refined positional and thermal parameters; Table 2,¹ the observed and calculated structure factors;

Table 3, some selected interatomic distances and angles; and Table 4, empirical bond-valence sums calculated with the constants of Brown and Altermatt (1985).

In addition to the X-ray diffraction studies described above, sverigeite was investigated by transmission electron microscopy (TEM). The latter was used to investigate the possible existence of domain structures, such as twinning, that might not be detectable using X-ray diffraction and light microscopy. Crushed fragments spread on a holey C film were observed using a Philips CM-12 TEM. Diffraction patterns and bright-field images were observed for many grains over wide ranges of orientation and at magnifications up to 300 000 times. Diffraction patterns were sharp with no diffuseness or superlattice relations, and no special or unusual features were observed in bright-field images.

STRUCTURE DESCRIPTION

The structure of sverigeite may be described in terms of three architectural elements: (1) straight octahedral chains of edge-sharing SnO_6 octahedra and planar NaO_4 groups (incomplete octahedra) running parallel to [001]; (2) sinuous tetrahedral chains consisting of vertex-sharing beryllosilicate 3-rings and 4-rings running parallel to [100]; and (3) discrete M_2O_{10} groups of edge-sharing MO_6 octahedra, which serve to link adjacent octahedral chains in the [100] and [010] directions and adjacent tetrahedral chains in the [100] and [001] directions. Additional linkage between octahedral chains along [010] is provided by $\text{Si}(1)\text{O}_4$ groups from the tetrahedral chains. The silicate tetrahedra in sverigeite do not share vertices with one another, and the mineral is therefore an island silicate in the Bragg classification. However, each silicate tetrahedron does share two vertices with adjacent beryllosilicate (BeO_4) tetrahedra to form the tetrahedral chains, and sverigeite may therefore appropriately be termed a single-chain beryllosilicate in accordance with the Zoltai classification.

Octahedral chains

Figures 1 and 2 show two views of the aforementioned octahedral chains, which are located along the lines (0,0,z), (1/2,0,z), (0,1/2,z), and (1/2,1/2,z). The chains are all identical,

¹ A copy of Table 2 may be ordered as Document AM-89-422 from the Business Office, Mineralogical Society of America, 1625 I Street, N.W., Suite 414, Washington, D.C. 20006, U.S.A. Please remit \$5.00 in advance for the microfiche.

TABLE 3. Selected interatomic distances (Å) and angles (°) in sverigeite

		SnO₆ and MO₆ octahedra			
Sn-O(4)	1.991(10) × 2			M-O(3)	2.133(3) × 2
O(2)	2.049(5) × 4			O(1)	2.149(4) × 2
Mean	2.030			O(2)	2.164(4) × 2
				Mean	2.149
NaO₄(O₄) polyhedron					
Na-O(2)	2.433(5) × 4			O(2)-Na-O(2)	72.9(2) × 2
O(1)	3.065(4) × 4			O(2)-Na-O(2)	107.1(2) × 2
SiO₄ and BeO₄ tetrahedra					
Si(1)-O(4)	1.607(8) × 2			O(3)-Si(1)-O(3)	108.1(3)
O(3)	1.620(4) × 2			O(3)-Si(1)-O(4)	109.3(1) × 4
Mean	1.614			O(4)-Si(1)-O(4)	111.5(5)
		O(3)-O(3)	2.623(8)	Mean	109.5
		O(3)-O(4)	2.632(7) × 4		
		O(4)-O(4)	2.656(19)		
		Mean	2.634		
Si(2)-O(1)	1.612(4) × 2			O(2)-Si(2)-O(2)	100.0(3)
O(2)	1.675(4) × 2			O(1)-Si(2)-O(2)	106.6(2) × 2
Mean	1.644			O(1)-Si(2)-O(2)	113.5(2) × 2
				O(1)-Si(2)-O(1)	115.6(3)
				Mean	109.3
		O(2)-O(2)	2.567(10)		
		O(1)-O(2)	2.636(5) × 2		
		O(1)-O(1)	2.730(8)		
		O(1)-O(2)	2.750(5) × 2		
		Mean	2.678		
Be-O(5)	1.587(10)			O(1)-Be-O(3)	100.4(4) × 2
O(1)	1.618(6) × 2			O(3)-Be-O(5)	107.7(6)
O(3)	1.693(10)			O(1)-Be-O(1)	113.7(6)
Mean	1.629			O(1)-Be-O(5)	115.9(4) × 2
				Mean	109.0
		O(1)-O(3)	2.544(5) × 2		
		O(3)-O(5)	2.650(7)		
		O(1)-O(1)	2.709(7)		
		O(1)-O(5)	2.716(4) × 2		
		Mean	2.646		
Be₂SiO₆(OH) 3-ring					
Si(1)-Be	3.016(9) × 2			Be-Si(1)-Be	58.0(4)
Be-Be	2.926(19)			Si(1)-Be-Be	61.0(2) × 2
Si(1)-O(3)	1.620(4) × 2			Si(1)-O(3)-Be	131.1(4)
Be-O(3)	1.693(10) × 2			Be-O(5)-Be	134.3(8)
Be-O(5)	1.587(10) × 2				
Be₂Si₂O₁₁(OH) 4-ring					
Si(2)-Be	2.961(6) × 4			Be-Si(2)-Be	83.3(3) × 2
Be-Be	3.934(18)			Si(2)-Be-Si(2)	96.7(3) × 2
Si(2)-Si(2)	4.427(5)				
Be-O(1)	1.618(6) × 4			Si(2)-O(1)-Be	132.9(4) × 4
Si(2)-O(1)	1.612(4) × 4				

are of infinite extent along [001], and are composed of edge-sharing SnO₆ octahedra and NaO₄ groups, which alternate along the chain length. The SnO₆ octahedra show a slight bipyramidal distortion, but the small degree of this distortion and the empirical bond-valence sum of 4.3 v.u. (Table 4) confirm that the Sn is tetravalent rather than divalent. Sn in the latter valence state possesses an electron lone pair, which is usually sterically active and produces a strongly distorted, "one-sided" coordination around the Sn²⁺ ions.

The Na atom exhibits a most unusual rectangular-planar coordination by four O(2) atoms at 2.433(5) Å, with O(2)-Na-O(2) angles of 72.9(2)° (× 2) and 107.1(2)° (× 2). This NaO₄ group is strictly planar, as required by symmetry, and the next-nearest anions are four O(1) at

3.065(4) Å, which would ordinarily be considered too long to constitute a bonding distance. [Baur (1970) gave 2.26–2.86 Å and 2.44 Å as the range and mean, respectively, for Na-O distances.] Including O(1) among the anions coordinated to Na helps to mitigate the apparent underbonding of this atom (Table 2), but a Na-O(1) bond is doubtful at best. The only other possible candidates for Na ligands are two O(5) atoms at 3.412(2) Å. The latter would complete a distorted orthorhombic dipyrmaid around Na, but 3.412 Å is much too long to represent a bond and the charge neutralization requirements of O(5) [= OH] are already satisfied by two Be plus one H (Table 2). Also noteworthy in this regard is the very large thermal-vibration amplitude of Na along [010] (Table 1), which is the direction normal to the plane of the four

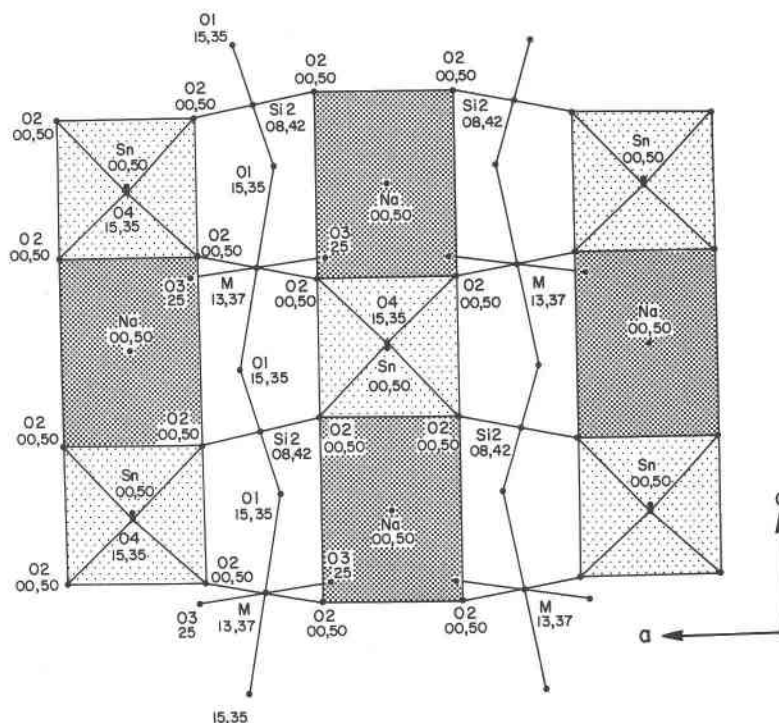


Fig. 1. A projection on (010) of slightly more than one unit cell from $y = 0$ to $1/2$, showing a side view of the octahedral chains of edge-sharing SnO_6 and NaO_4 groups running in the $[001]$ direction. The chains are linked by MO_6 and $\text{Si}(2)\text{O}_4$ groups, which are represented with line bonds rather than as polyhedra. The BeO_4 and $\text{Si}(1)\text{O}_4$ tetrahedra belong only to the tetrahedral chains and are omitted here for clarity. Numbers beneath atom labels are y coordinates $\times 100$.

O(2) ligands and the ideal locus for the two "missing" ligands. Indeed, all of the thermal-vibration parameters of Na are anomalously large, consistent with partial occupancy of this site. However, a site-occupancy refinement for Na, done simultaneously with the M-site refinement, yielded an occupancy factor of 0.24(2). Because this differs by less than one esd from the ideal (full-occupancy) value of 0.25, the Na site is considered to be fully occupied, as it must be to ensure a charge-balanced chemical formula.

Tetrahedral chains

Figures 3 and 4 show two views of the tetrahedral beryllosilicate chains that traverse the structure along $[100]$. Like the octahedral chains, they are all identical and of infinite extent, but unlike the former they are sinuous in form and are composed of vertex-sharing $\text{BeO}_3(\text{OH})$ and SiO_4 tetrahedra grouped into $\text{Be}_2\text{Si}(1)\text{O}_8(\text{OH})$ 3-rings and $\text{Be}_2\text{Si}(2)_2\text{O}_{11}(\text{OH})$ 4-rings. These two ring types alternate along the chain length and are oriented perpendicular to

TABLE 4. Empirical bond valences (v.u.) in sverigeite

	Sn	M	Si(1)	Si(2)	Na	Be	O(1)	O(2)	O(3)	O(4)	O(5)
Sn								0.68		0.79	
M							0.35	0.33	0.36 ($\times 2$)		
Si(1)									1.01	1.05	
Si(2)							1.03	0.87			
Na							0.03	0.18			
Be							0.53		0.43		0.57 ($\times 2$)
O(1)		0.35 ($\times 2$)		1.03 ($\times 2$)	0.03 ($\times 4$)	0.53 ($\times 2$)					
O(2)	0.68 ($\times 4$)	0.33 ($\times 2$)		0.87 ($\times 2$)	0.18 ($\times 4$)						
O(3)		0.36 ($\times 2$)	1.01 ($\times 2$)			0.43					
O(4)	0.79 ($\times 2$)		1.05 ($\times 2$)								
O(5)						0.57					
Σv	4.30	2.08	4.12	3.80	0.84	2.06	1.94	2.06	2.16	1.84	1.14

Note: Bond valences for the M site are a weighted average of (0.63 Mn^{2+} + 0.37 Mg). Atom O(5) is the hydroxyl oxygen.

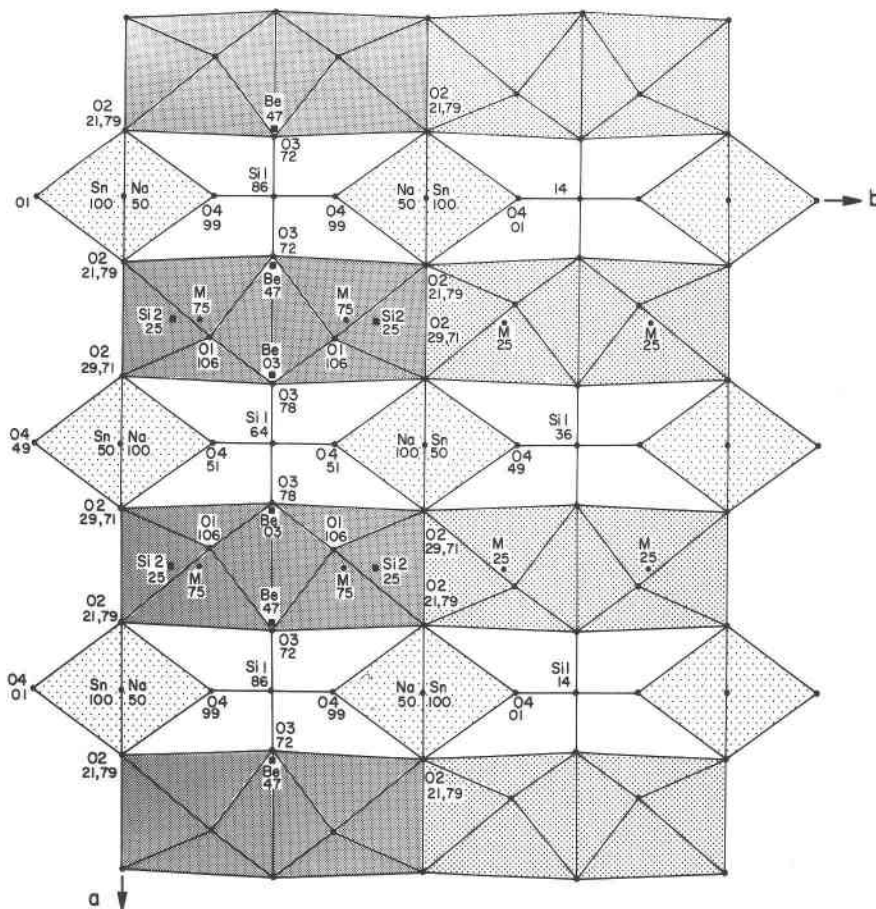


Fig. 2. A projection on (001) of slightly more than one unit cell, showing a top (end-on) view of the octahedral chains and their linkage in the [100] and [010] directions by M_2O_{10} groups and in the [010] direction by $Si(1)O_4$ groups. The latter are represented by line bonds and the $BeO_3(OH)$ and $Si(2)O_4$ tetrahedra are omitted for clarity. However, Be and Si(2) positions in one tetrahedral chain are plotted as squares. Numbers beneath atom labels are z coordinates $\times 100$. The apparent sharing of edges between M_2O_{10} groups at $z = 0.75$ and 0.25 in the [010] direction is an artifact of projection, and all M_2O_{10} groups are discrete.

one another; i.e., the 3-rings are parallel to (010) and the 4-rings are parallel to (001), with [100] being the chain direction. The $Si(1)O_4$ vertices of the 3-rings point alternately up and down parallel to [001].

The sinusoidal form of the tetrahedral chains is evident in Figure 3. If the chains are thought of as sine waves, their wavelength would be equal to the a cell translation (10.815 Å) and their amplitude, taken as the difference between the z coordinates of Si(1) and Si(2), would be $(0.8606 - 0.2500) \times 6.818 = 4.163$ Å, or very nearly $\frac{1}{2}bc$. Moreover, it will be seen from Figure 4 that if the cell is divided into two halves along [010], the chains in the two halves are 180° out of phase with one another because of the action of the n glide plane at $(x, \frac{1}{2}, z)$.

The $Be_2SiO_8(OH)$ 3-rings are all identical, and their cations, Si(1) and Be, lie on mirror planes at $(x, \frac{1}{4}, z)$ and $(x, \frac{3}{4}, z)$. The rings, as defined by their tetrahedral nodes, are therefore planar. They are also very nearly equilateral triangles, as their internal angles are $58.0(4)^\circ$ and $61.0(2)^\circ$ ($\times 2$) and their side lengths, $Si(1)-Be = 3.016(9)$ Å ($\times 2$)

and $Be-Be = 2.926(19)$ Å, differ by less than 0.1 Å (Table 3). The two $BeO_3(OH)$ groups in each ring share the hydroxyl oxygen, O(5), to form a $Be_2O_6(OH)$ dimer. In addition to being the only hydroxyl oxygen in the structure, O(5) is notable in two respects: It forms the shortest cation-oxygen bond in the structure [$Be-O(5) = 1.587(10)$ Å], and it has the highest temperature factor of any of the anions in Table 1. The short bond length can be rationalized when it is noted that the only cations to which the hydroxyl ion is bonded are the two Be^{2+} cations (Table 4), but the reason for the anomalous temperature factor is less obvious. The full anisotropic refinement showed that by far the largest component of this atom's thermal motion is along [010], normal to the $Be-O(5)-Be$ plane of the dimer. The relevant thermal parameters are 0.010(3), 0.060(6), and 0.001(2) Å², for U_{11} , U_{22} , and U_{33} , respectively. This phenomenon—that the bridging oxygens of T_2O_7 groups ($T =$ tetrahedral cation) have large temperature factors and the maximum vibrational amplitude is in the plane normal to the T-T vector (or nearly so)—is

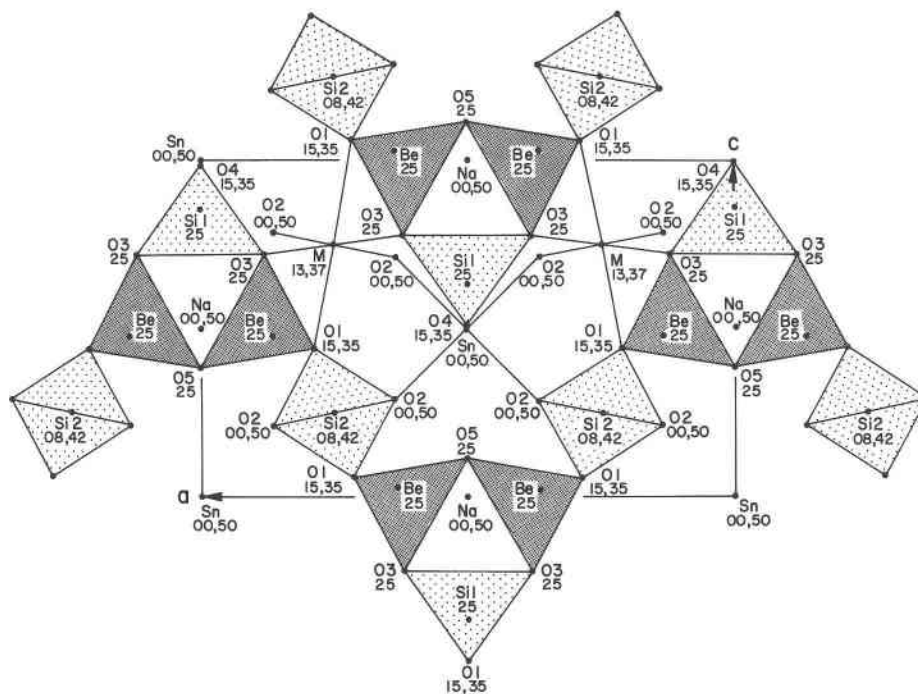


Fig. 3. A projection on (010) of one unit cell, showing a side view of one tetrahedral chain (and part of another) and their linkage by MO_6 and SnO_6 octahedra. The octahedra are represented by line bonds. Numbers beneath atom labels are y coordinates $\times 100$.

a common one (Liebau, 1985) and is not confined to silicates (e.g., Calvo, 1965a, 1965b).

The $\text{Be}_2\text{Si}_2\text{O}_{11}(\text{OH})$ 4-rings are likewise identical and planar. Each ring, as defined by its tetrahedral cations, is very nearly a square, with four equal sides [$\text{Si}(2)\text{-Be} = 2.961(6) \text{ \AA}$] and internal angles of $83.3(3)^\circ (\times 2)$ and $96.7(3)^\circ (\times 2)$. The ring symmetry is $2/m$. However, its $\text{Si}(2)\text{O}_4$ tetrahedra are strongly distorted, much more so than the $\text{Si}(1)\text{O}_4$ groups of the 3-rings (Table 3). In particular, there is a large disparity between the bond distances $\text{Si}(2)\text{-O}(1) = 1.612(4) \text{ \AA} (\times 2)$ and $\text{Si}(2)\text{-O}(2) = 1.675(4) \text{ \AA} (\times 2)$, and the bond angles range from $100.0(3)^\circ$ to $115.6(3)^\circ$. The origin of the unusually long $\text{Si}(2)\text{-O}(2)$ distance may lie in the fact that, aside from a possible weak $\text{Na}\text{-O}(1)$ interaction, $\text{O}(2)$ is the only anion bonded to Na (Table 4). Consequently, the Na^+ ion is underbonded, a condition that is partially relieved by positioning $\text{O}(2)$ closer to Na , and therefore farther from $\text{Si}(2)$.

M_2O_{10} GROUPS

The M_2O_{10} dimers are shown in Figure 2. Their constituent MO_6 polyhedra are moderately distorted octahedra [$\text{M}\text{-O}$ distances range from $2.133(3)$ to $2.164(4) \text{ \AA}$], each octahedron being related to the other member of the pair by a mirror plane through their shared edge, $\text{O}(3)\text{-O}(3)$. The contents of the M site derived from the occupancy factor refinement are $(\text{Mn}_{0.04}\text{Mg}_{2.96})$, from which an $\text{M}\text{-O}$ distance of 2.19 \AA is predicted using a weighted average of the ionic radii of 6-coordinated Mn^{2+} and Mg^{2+}

(Shannon, 1976). This value exceeds the observed mean $\text{M}\text{-O}$ distance by 0.04 \AA , with the discrepancy probably being due to minor amounts of the smaller cations Fe^{2+} and Zn^{2+} in the M site, as suggested by the chemical analysis of Dunn et al. (1984).

Inspection of Figure 2 shows what appears to be chains of MO_6 octahedra running in the $[010]$ direction, but this is misleading, as what appears to be a shared edge, $\text{O}(2)\text{-O}(2)$, between octahedra centered at $z = 0.25$ and 0.75 is actually two different edges superimposed in projection. The M_2O_8 dimers are thus discrete entities, which occur in the $(x, y, 1/4)$ and $(x, y, 3/4)$ planes and share no polyhedral elements with one another. They do, however, share vertices with the SnO_6 and NaO_4 groups of the octahedral chains, cross-linking adjacent chains in the $[100]$ and $[010]$ directions (Fig. 2). The MO_6 groups (Fig. 3) also share vertices with BeO_4 , $\text{Si}(1)\text{O}_4$, and $\text{Si}(2)\text{O}_4$ groups of the tetrahedral chains, linking the latter together in the $[100]$ and $[001]$ directions. The M_2O_{10} dimers thus function as the principal linkages in a structure dominated by chains, none of which are directly connected to one another. The $\text{Si}(1)\text{O}_4$ groups also play a subordinate role in cross-linking the octahedral chains.

DISCUSSION

Na with coordination number 4 is uncommon and is limited almost entirely to tetrahedral or distorted tetrahedral coordination (Cocco et al., 1972; Poonia and Bajaj, 1979). An example of this occurs in synthetic

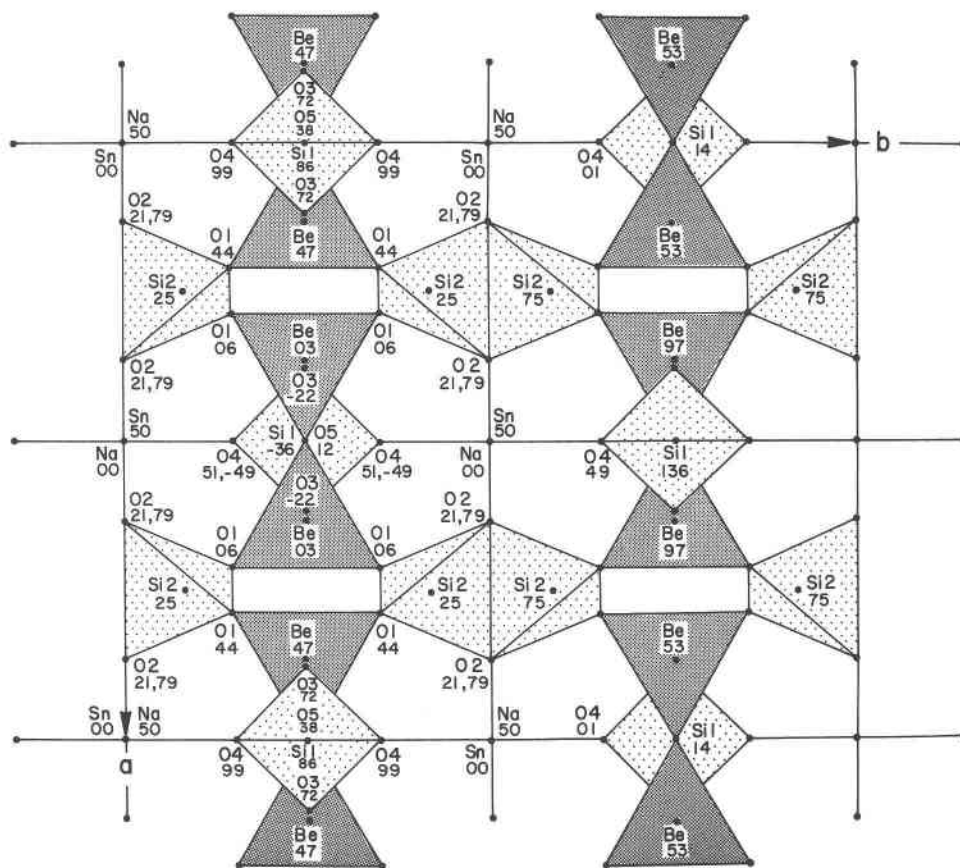


Fig. 4. Projection on (001) of one unit cell, showing a top view of two tetrahedral chains running in the [100] direction and their linkage in the [010] direction by SnO_6 octahedra represented by line bonds. The MO_6 octahedra are omitted for clarity. Numbers beneath atom labels are z coordinates $\times 100$.

$\text{Na}_2\text{Zn}_3(\text{SiO}_4)_2$ (Plakhov et al., 1975), which contains six nonequivalent Na sites, three of them tetrahedrally coordinated and the remainder octahedrally coordinated. The ranges and means of the Na-O distances are 2.21–2.53 Å and 2.34 Å for the tetrahedral sites and 2.25–2.90 Å and 2.48 Å for the octahedral sites. Synthetic $\text{Na}_4\text{P}_3\text{O}_{10}$ (phase I) also contains 4-coordinated Na but in an irregular, “one-sided,” nontetrahedral coordination having 2.22–2.59 Å and 2.37 Å as the range and mean, respectively, of Na-O (Corbridge, 1960). The Na-O distance in sverigeite [2.433(5) Å ($\times 4$)] is essentially equal to the mean value for octahedral Na (2.44 Å) given by Baur (1970); this is consistent with the fact that the radius ratios for ideal octahedral and square-planar coordinations are identical. We are aware of only one other occurrence of 4-coordinated Na in a mineral, that being in sodalite, where Na is surrounded by a distorted tetrahedron of three oxygens plus one Cl (Löns and Schulz, 1967). The review papers of Cocco et al. (1972) and Poonia and Bajaj (1979) list no examples of Na in square- (or rectangular-) planar coordination, and it may be that the 4-coordinated Na in sverigeite is unique in this respect.

As noted previously, neither of the final difference

syntheses revealed the H atom associated with O(5), and hence no direct evidence for hydrogen bonding in sverigeite is available from the structure refinement. However, a consideration of interatomic distances and bond-valence sums involving O(5) suggests that such bonding does occur. The shortest distances between O(5) and its oxygen neighbors are 2.650(7) Å ($\times 2$) to O(3) and 2.716(4) Å ($\times 2$) to O(1), all of which represent tetrahedron edges. The next-shortest distance is 2.974(9) Å ($\times 2$) to O(4) at (0,0.150,−0.007) and O(4)' at (0,0.350,−0.007). [Atom O(5) is located at (0,1/4,0.383), with site symmetry $mm2$.] Table 4 shows that O(4) is the only anion that has a conspicuously low valence sum (1.84 v.u.) and is therefore in need of a valence contribution from H by way of a hydrogen bond O(5)-H \cdots O(4). The length of the O(5)-O(4) separation is consistent with a weak hydrogen bond (Brown, 1976), and the fact that there are two potential acceptors, O(4) and O(4)', equidistant from the donor oxygen suggests that the bond is bifurcated. In this case, the obvious location for the four H atoms would be in equipoint $4e$, ca. 1 Å from O(5), at (0,1/4,~0.24). Alternatively, the four H atoms might be statistically distributed over $8h$ in positions (0, y , z), such that O(5)-H \cdots O(4)

bonds occur in some unit cells and O(5)-H···O(4)' bonds in others. A bifurcated bond would seem to be more probable, as it would help satisfy the valence requirements of both O(4) and O(4)' simultaneously.

Dunn et al. (1984) noted that sverigeite possesses one perfect cleavage, easily produced, on {010}. This observation may now be rationalized in terms of the known features of the structure. Inspection of Figures 2 and 4 shows that in the $(x, 0, z)$ and $(x, \frac{1}{2}, z)$ planes, the structure is held together only by Sn-O(4) bonds normal to {010} and Sn-O(2) and Na-O(2) bonds parallel to {010}. In addition, the tetrahedral chains run parallel to {010} in the [100] direction. Cleavage on {010} will therefore occur parallel to the tetrahedral chains and through the relatively weak Na-O and Sn-O ionic linkages. Cleavage in any other direction will necessarily occur through the chains and require breakage of their partially covalent and therefore relatively strong Si-O and Be-O bonds. Although cleavage should occur preferentially parallel to {010}, it may also occur through the tetrahedral chains, as shown by the existence of two lesser cleavages of unknown index mentioned by Dunn et al. (1984).

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