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Structural chemistry of borosilicates, part II: Searlesite, $NaBSi_2O_5(OH)$: Absolute configuration, hydrogen locations, and refinement of the structure

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Abstract

Searlesite, $NaBSi_2O_5(OH)_2$ is monoclinic, space group $P2_1$, with cell dimensions: a = 7.9814(12), b = 6.0657(8), c = 4.9054(4)Å, and β = 93.95(1)°. The absolute configuration and hydrogen positions have been determined from a refinement of the structure using 811 reflections measured by Cu$K\alpha$ radiation, and the atomic coordinates determined by Kravchenko (1964). The structure has been refined using anisotropic temperature factors for all atoms except hydrogen to an R factor of 0.035 for 1694 reflections measured by Mo$K\alpha$ radiation. The crystal structure of searlesite consists of highly kinked pyroxene-type silicate chains parallel to the c axis, connected through corner-sharing $BO_2(OH)_2$ tetrahedra to form borosilicate sheets parallel to the (100) plane; these sheets are held together by spiral columns of edge-sharing Na–O octahedra running parallel to the b axis (as found by Kravchenko, 1964) and by one of the two types of hydrogen bonds. Within the tetrahedral $BO_2(OH)_2$ group, the O–H distances are 0.87 and 0.88Å and the B–O–H angles are 114° and 113°. Both hydrogen atoms are involved in hydrogen bonds, the H···O distances being 2.32 and 2.04Å, and the O–H···O angles 147° and 170°. The bridging B–O distances (av. 1.490Å) are much longer than the non-bridging B–O distances (av. 1.455Å). Within each of the two crystallographically distinct SiO_4 tetrahedra, the Si–O bond involving oxygen belonging to the Si–O–B bridge is significantly shorter (av. 1.591Å) than those involving oxygens belonging to the Si–O–Si bridges (Av. Si–O 1.617Å). The average B–O, Si(1)–O and Si(2)–O distances are 1.472, 1.614, and 1.608Å respectively. The $NaO_2(OH)_4$ octahedron is highly distorted; the average Na–O distance is 2.485Å.

Introduction

In part I of this series of papers on the structural chemistry of borosilicates, we have described the structure of garrelsite, $NaBa_3Si_2B_7O_{16}(OH)_4$ (Ghose, Ulbrich, and Wan, 1975). Garrelsite contains a new type of borosilicate chain, consisting of two types of four-membered rings with alternating B-and Si-tetrahedra; in addition, there is a $[B_5O_{12}]$ polyanion, consisting of three borate tetrahedra and two borate triangles.

In this paper we present the details of the structure of searlesite, $NaBSi_2O_5(OH)_2$. This mineral is widespread in the Searles Lake area in California and in the Green River formation in Utah and Wyoming. The unit cell dimensions and space group of searlesite were determined by Fahey and Axelrod (1950). The crystal structure was determined by Kravchenko (1964) using an acicular crystal from Cave Springs, Nevada. Kravchenko (1964) collected intensity data on 1524 (1258 non zero) reflections by visual estimation from Weissenberg films. The structure was refined by the least-squares method using isotropic temperature factors to an R factor of 19.5 percent for all reflections and 13.9 percent for non-zero reflections. The hydrogen positions were not determined. We have undertaken a further refinement of the searlesite structure, first, to obtain more precise bond distances and angles (Si–O–B angles in particular) and compare them with other borosilicates; second, to determine the absolute configuration; and third, to determine the hydrogen positions directly and discuss the nature of the hydrogen bonding.

Crystal data

The cell dimensions of an acicular crystal from Cave Springs, Nevada, were determined by the least-squares refinement of 15 reflections with 2θ values between 35° and 45° measured with Mo$K\alpha$ radiation on a single crystal X-ray diffractometer (Table 1). Fahey and Axelrod (1950) found searlesite to be piezoelectric with space group $P2_1$. This space group has been confirmed by the structure determination of Kravchenko (1964) and the structure refinement reported in this paper. Differential thermal analysis indicates a minor sharp peak at 395°C and a major one at 425°C, which suggests the presence of two (OH) radicals rather than a water molecule. A broad peak at 600°C probably indicates the breakdown of the searlesite structure.

Collection of intensity data

A needle-shaped crystal of searlesite (0.2 × 0.2 × 0.4 mm) from Cave Springs, Nevada, was used for the first set of intensity data collection. The intensity data were collected by the 2θ-θ scan method on a computer controlled automatic X-ray diffractometer with scintillation counter (Syntex $P\bar{1}$) and Mo$K\alpha$ radiation, monochromatized by reflection from a graphite "single" crystal. The needle-axis was made parallel to the phi-axis of the diffractometer. A variable scan rate was used, the minimum scan rate being 0.5°/min. All reflections with 2θ less than 65° were measured, a total of 1694 reflections, of which 24 were below $3\sigma(I)$, $\sigma(I)$ being the standard deviation of I, as measured by the counting statistics. For the reflections for which I is less than $0.7\sigma(I)$, I was set equal to $0.7\sigma(I)$, regardless of whether I was positive or negative. The intensity data were corrected for Lorentz and polarization factors. An absorption correction was neglected, since the linear absorption coefficient of searlesite for Mo$K\alpha$ radiation is small, 7.04 cm^{-1}.

A second set of data comprising 811 reflections of the type hkl, $\bar{h}kl$, $h\bar{k}l$ and $\bar{h}\bar{k}l$ were measured with Cu$K\alpha$ radiation on a Picker diffractometer, because the anomalous scattering of the searlesite atoms with Cu radiation is larger than that with Mo radiation. Thus the absolute configuration and hydrogen positions can be determined from these data. These intensities were corrected for Lorentz and polarization factors but not for absorption (μ, Cu$K\alpha$ = 65.25 cm^{-1}).

TABLE 1. Searlesite: Crystal Data

Searlesite, $NaBSi_2O_5(OH)_2$: Cave Springs, Nevada, NMNH #96080
Monoclinic, colorless transparent prismatic, piezoelectric
(Fahey and Axelrod, 1950)

a:	7.9814(12) Å	Cell content:	$2[NaBSi_2O_5(OH)_2]$
b:	7.0657(8) Å	D_m:	2.46 g cm^{-3}
c:	4.9054(4) Å	D_c:	2.46 g cm^{-3}
β:	93.95(1)°	μ(MoKα):	7.04 cm^{-1}
Cell volume:	276.98 Å^3	μ(CuKα):	65.25 cm^{-1}
Space group:	$P2_1$		

Determination of the hydrogen positions and absolute configuration

Since searlesite crystallizes in the space group $P2_1$, two configurations are possible; the first is represented by the set of atomic positional coordinates x, y, z as given by Kravchenko (1964) and the second by the set $x, \bar{y}, z$. We first attempted to determine the absolute configuration from reflections of the type hkl and $h\bar{k}l$, measured with Mo$K\alpha$ radiation, through refining the structure by the least-squares method in both configurations, neglecting the contributions of the hydrogen atoms. For the two configurations x, y, z and $x, \bar{y}, z$, the R factors were 0.038 and 0.037 respectively, which left the question of the absolute configuration undecided. At this stage, an attempt to determine the hydrogen positions from a Difference Fourier map corresponding to the x, y, z configuration yielded the position of only one of the two hydrogen atoms. Therefore, using the atomic coordinates (x, y, z set) of the non-hydrogen atoms obtained from the previous refinement, structure factors were calculated for the Cu data. The Difference Fourier map subsequently calculated yielded the positions of both hydrogen atoms clearly.

Refinement of the structure using the Cu data was carried out for both configurations using anisotropic temperature factors for all atoms except hydrogen, for which isotropic temperature factors were used. After convergence, the R factors for the x, y, z and $x, \bar{y}, z$ configurations were 0.050 and 0.044 respectively, the lower R factor definitely favoring the $x, \bar{y}, z$ configuration.

Final refinement of the structure

For all refinements, the full matrix least-squares program RFINE (Finger, 1969) was used. The atomic scattering factors of Na, B, Si, O, and H were taken from Cromer and Mann (1968). Anomalous dispersion factors were taken from Cromer and Liberman (1970). The structure factors (F_o) were weighted using the formula $F_o/\sigma^2(F_o)$, where $\sigma(F_o)$ is the standard error of measurement of F_o derived from the counting statistics.

A final refinement of the structure in the $x, \bar{y}, z$ configuration was carried out using the Mo data and anisotropic temperature factors for all atoms except hydrogen, for which isotropic temperature factors were used. Convergence was reached after three cycles of refinement, at which stage the average shift versus error was 0.02, the maximum being 0.50, which involved the *y* coordinate of the H(1) atom. The final *R* factor for 1694 reflections is 0.035. Final atomic positional and thermal parameters are listed in Table 2 and a list of observed and calculated structure factors in Table 3.[1]

The bond lengths and angles as well as thermal ellipsoids and their standard deviations were calculated using the program ERROR (Finger, private communication, 1972) and are listed in Tables 4 and 5 respectively. The standard deviation in Na–O, Si–O, and B–O bond lengths is ±0.002 Å; and in O–Si–O, O–Na–O, and O–B–O angles ±0.06, ±0.08, and ±0.15°, respectively. Because the origin of the structure was defined by fixing the *y* coordinate of the Na atom, the standard deviation in O–Na–O angle turns out to be smaller than that for O–Si–O angles.

Description of the structure

The structure of searlesite consists of borosilicate sheets running parallel to the (100) plane, held together by spiral columns of edge-sharing $NaO_2(OH)_4$ octahedra. The borosilicate sheet is composed of a $BO_2(OH)_2$ tetrahedron and two crystallographically distinct SiO_4 tetrahedra.

The configuration of the $BO_2(OH)_2$ tetrahedron and hydrogen bonding

The configuration of the $BO_2(OH)_2$ tetrahedron is shown in Figure 1. It is distorted, with bridging B–O distances 1.492 and 1.487Å, while the non-bridging B–O distances are 1.456 and 1.454Å. Kravchenko (1964) found a much larger distortion with bridging B–O distances 1.47 and 1.52Å, while the non-bridging B–O distances were reported to be 1.41 and 1.49Å. Our results indicate that the lengths of each of the two bridging B–O bonds are the same within the limits of error, as are each of the two non-bridging B–O bonds. The bridging B–O bonds are significantly longer by 0.035Å compared to the non-bridging ones. The O–B–O angles range from 106.1 to 113.6°. The deviation from the ideal tetrahedral angle is not simply related to the deviations in B–O bond distances from the average value of 1.472Å.

The non-bridging B–O bonds involve oxygen atoms, which are part of (OH) groups. The O(6)–H(1) and O(7)–H(2) distances are 0.87 and 0.88Å, while the B–O(6)–H(1) and B–O(7)–H(2) angles are 114° and 113° respectively. The B–O–H angles are close to the ideal tetrahedral angle, which

TABLE 2. Searlesite, $NaBSi_2O_5(OH)_2$: Atomic Positional and Thermal Parameters*
(Standard deviations in parentheses)

Atom	*x*	*y*	*z*	B eq.*	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Na	0.4390(1)	0.0000	0.9812(2)	1.662(12)	71(1)	68(2)	197(3)	-6(1)	32(2)	37(2)
B	0.3514(2)	0.7984(3)	0.3984(3)	0.608(20)	19(2)	28(2)	83(4)	-2(2)	-1(2)	-3(3)
Si(1)	0.13465(6)	0.41571(18)	0.21207(9)	0.501(7)	15(1)	24(1)	67(1)	-4(1)	-6(1)	5(1)
Si(2)	0.08340(6)	0.98671(18)	0.31053(8)	0.441(6)	13(1)	20(1)	63(1)	1(1)	1(1)	2(1)
O(1)	0.1651(2)	0.1903(3)	0.2492(4)	1.31(2)	50(2)	25(2)	223(6)	-16(2)	-13(3)	27(3)
O(2)	0.0851(2)	0.4610(3)	0.8931(2)	0.87(2)	22(2)	71(2)	64(3)	3(2)	-3(2)	13(2)
O(3)	0.2202(2)	0.8314(3)	0.2566(3)	1.09(2)	41(2)	47(2)	137(4)	30(18)	7(2)	3(2)
O(4)	0.3114(2)	0.5110(2)	0.3087(3)	0.76(2)	18(2)	23(2)	141(4)	-3(1)	-12(2)	-10(2)
O(5)	0.0222(2)	0.9842(3)	0.6177(3)	1.13(2)	29(2)	102(3)	71(3)	-3(2)	13(2)	-3(3)
O(6)	0.3604(2)	0.7261(3)	0.6953(3)	1.09(2)	39(2)	74(2)	84(3)	-15(2)	4(2)	-11(2)
O(7)	0.4858(2)	0.2563(3)	0.7005(3)	0.93(2)	25(17)	55(2)	111(4)	16(2)	6(2)	13(2)
H(1)	0.267(4)	0.699(6)	0.769(7)	-0.9(5)						
H(2)	0.578(5)	0.424(6)	0.416(8)	-0.5(6)						

*Equivalent isotropic B, calculated from anisotropic temperature factors except for H(1) and H(2) where B was refined directly.

Form of anisotropic temperature factors (x10 ^{4}): $\exp\{-\sum_{i=1}^{3}\sum_{j=1}^{3} h_i h_j \beta_{ij}\}$

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[1] For a copy of Table 3, order Document AM-76-016 from the Business Office, Mineralogical Society of America, 1909 K Street, N.W., Washington, D. C. 20006. Please remit $1.00 in advance for the microfiche.

means that the bonding of oxygen atoms O(6) and O(7) involve the hybridized sp^3 state. H(1) is hydrogen bonded to O(2), a corner of the adjacent Si(1)O_4 tetrahedron (Fig. 1). The H(1)-O(2) distance is 2.32Å, and the angle O(6)-H(1)-O(2) is 147°. Hence, the hydrogen bond is a bent bond, the hydrogen position deviating considerably from the O(6)-O(2) direction. H(2) is hydrogen bonded to O(4), which forms another corner of the Si(1)O_4 tetrahedron (Fig. 1). H(2)-O(4) distance is 2.04Å and the O(7)-H(2)-O(4) angle is 170°, indicating a small deviation of the hydrogen position from the straight O-H···O bond. The hydrogen atom H(1) bridges corners from a borate to a silicate tetrahedron within the same borosilicate sheet, whereas H(2) bridge corners of borate and silicate tetrahedra from different but adjacent borosilicate sheets (Fig. 1).

TABLE 4. Searlesite, $NaBSi_2O_5(OH)_2$: Interatomic Distances (Å) and Angles (°)
(Standard deviations in parentheses)

	Na - Octahedron		
Na - O(3')	2.566(2)	O(6) - Na - O(4)	81.60(5)
Na - O(4)	2.521(2)	O(6) - Na - O(7)	85.96(6)
Na - O(6)	2.442(2)	O(6) - Na - O(3)	111.21(6)
Na - O(6')	2.694(2)	O(6) - Na - O(7')	76.93(6)
Na - O(7)	2.316(2)	O(4) - Na - O(7)	102.65(6)
Na - O(7')	2.369(2)	O(7) - Na - O(3)	57.90(5)
Mean	2.485	O(3')- Na - O(7')	144.65(7)
O(6) - O(4)	2.436(2)	O(7')- Na - O(4)	58.46(5)
O(6) - O(7)	3.460(2)	O(6')- Na - O(4)	83.28(6)
O(6) - O(3')	2.467(2)	O(6')- Na - O(7)	81.18(6)
O(6) - O(7')	3.130(2)	O(6')- Na - O(3)	77.17(6)
O(4) - O(7)	2.911(2)	O(6')- Na - O(7')	108.82(7)
O(7) - O(3')	2.395(2)	Mean	89.15
O(3')- O(7')	4.702(3)		
O(7')- O(4')	2.368(2)		
O(6')- O(7)	3.130(2)		
O(6')- O(3)	3.125(2)		
O(6')- O(7')	3.460(2)		
O(6')- O(4)	3.298(2)		
Mean	3.074		
	B - Tetrahedron		
B - O(3)	1.492(2)	O(3) - B - O(4)	106.13(14)
B - O(4)	1.487(2)	O(3) - B - O(6)	113.58(15)
B - O(6)	1.456(2)	O(3) - B - O(7)	108.74(15)
B - O(7)	1.454(2)	O(4) - B - O(6)	111.74(15)
Mean	1.472	O(4) - B - O(7)	107.26(14)
O(3) - O(4)	2.382(2)	O(6) - B - O(7)	109.15(15)
O(3) - O(6)	2.467(2)	Mean	109.43
O(3) - O(7)	2.395(2)		
O(4) - O(6)	2.436(2)		
O(3) - O(7)	2.369(2)		
O(6) - O(7)	2.371(2)		
Mean	2.403		
	Si(1) - Tetrahedron		
Si(1)- O(1)	1.616(2)	O(1) - Si(1) - O(2)	109.15(9)
Si(1)- O(2)	1.616(1)	O(1) - Si(1) - O(4)	104.91(8)
Si(1)- O(4)	1.602(1)	O(1) - Si(1) - O(5)	110.50(10)
Si(1)- O(5)	1.621(2)	O(2) - Si(1) - O(4)	110.76(8)
Mean	1.614	O(2) - Si(1) - O(5)	106.95(7)
O(1) - O(2)	2.634(2)	O(4) - Si(1) - O(5)	114.52(8)
O(1) - O(4)	2.552(2)	Mean	109.47
O(1) - O(5)	2.660(3)		
O(2) - O(4)	2.648(2)		
O(2) - O(5)	2.602(2)		
O(4) - O(5)	2.711(2)		
Mean	2.635		
	Si(2) - Tetrahedron		
Si(2)- O(1)	1.613(2)	O(1) - Si(2) - O(2')	108.14(8)
Si(2)- O(2')	1.626(1)	O(1) - Si(2) - O(3)	107.12(9)
Si(2)- O(3)	1.579(2)	O(1) - Si(2) - O(5)	109.55(10)
Si(2)- O(5)	1.612(1)	O(2')- Si(2) - O(3)	111.72(8)
Mean	1.608	O(2')- Si(2) - O(5)	106.36(7)
O(1) - O(2')	2.623(2)	O(3) - Si(2) - O(5)	113.83(9)
O(1) - O(3)	2.569(2)	Mean	109.45
O(1) - O(5')	2.634(2)		
O(2')- O(3)	2.653(2)		
O(2')- O(5')	2.602(2)		
O(3) - O(5')	2.674(2)		
Mean	2.626		
	Hydrogen Bonds		
H(1) - O(6)	0.87(3)	O(6) - H(1) - O(2)	146.6(3.7)
H(1) - O(2)	2.32(4)	B - O(6) - H(1)	114.2(2.3)
[H(1) - B	1.98(3)]	Na - O(6) - H(1)	97.6(2.6)
H(2) - O(7)	0.88(4)	Na - O(6) - H(1)	96.4(2.5)
H(2) - O(4)	2.04(4)	O(7) - H(2) - O(4)	170.02(3.8)
H(2) - B	1.98(4)	B - O(7) - H(2)	113.27(2.5)
		Na - O(7) - H(2)	98.1(2.8)
		Na' - O(7) - H(2)	134.7(2.6)
Cation-Cation Distances (<3.5Å)		*Si-O-Si and B-O-Si Angles*	
Na-B	2.970(2)	Si(1) - O(1) - Si(2)	146.82(13)
Na-B'	3.014(2)	Si(1) - O(2) - Si(2)	138.72(9)
Na-Si(2)	3.353(1)	Si(1) - O(5) - Si(2)	140.80(11)
Si(1)-B	2.803(1)	B - O(3) - Si(2)	142.59(13)
Si(2)-B	2.090(2)	B - O(4) - Si(1)	130.24(12)
Si(1) - Si(2)	3.0946(7)		
Si(1) - Si(2')	3.0343(6)		
Si(1) - Si(2")	3.0460(7)		

TABLE 5. Searlesite, $NaBSi_2O_5(OH)_2$: Thermal Ellipsoids
(Standard deviations in parentheses)

Atom	Axis	rms amplitude (Å)	Angle (°) with respect to +*a*	+*b*	+*c*
Na	*r*1	0.107	68(3)	137(2)	57(2)
	*r*2	0.150	38(5)	57(5)	76(4)
	*r*3	0.171	118(4)	68(2)	34(3)
B	*r*1	0.075	153(20)	64(19)	81(7)
	*r*2	0.086	117(23)	152(23)	95(10)
	*r*3	0.101	81(7)	98(8)	15(9)
Si(1)	*r*1	0.062	153(5)	65(5)	78(3)
	*r*2	0.076	105(5)	148(3)	61(3)
	*r*3	0.097	66(2)	69(3)	36(2)
Si(2)	*r*1	0.063	162(7)	108(8)	89(2)
	*r*2	0.072	72(8)	160(8)	83(3)
	*r*3	0.087	87(2)	83(3)	10(3)
O(1)	*r*1	0.064	108(3)	21(2)	99(1)
	*r*2	0.125	24(3)	76(3)	113(3)
	*r*3	0.174	69(2)	76(2)	29(2)
O(2)	*r*1	0.077	140(16)	101(4)	48(15)
	*r*2	0.092	131(13)	84(3)	135(13)
	*r*3	0.136	93(2)	12(2)	78(2)
O(3)	*r*1	0.063	48(3)	43(3)	89(2)
	*r*2	0.128	96(5)	86(4)	170(3)
	*r*3	0.145	137(6)	47(6)	86(6)
O(4)	*r*1	0.063	138(12)	50(10)	76(5)
	*r*2	0.081	129(2)	141(12)	88(4)
	*r*3	0.135	75(2)	97(2)	20(2)
O(5)	*r*1	0.082	50(8)	91(2)	44(8)
	*r*2	0.103	39(11)	94(2)	133(11)
	*r*3	0.160	87(2)	4(2)	92(2)
O(6)	*r*1	0.097	118(19)	68(12)	34(14)
	*r*2	0.105	138(32)	75(18)	124(34)
	*r*3	0.145	65(3)	26(3)	97(2)
O(7)	*r*1	0.074	150(4)	120(4)	87(3)
	*r*2	0.112	108(6)	70(5)	150(6)
	*r*3	0.132	114(5)	35(5)	64(5)

TABLE 6. Si-O-B Angles in Borosilicates

Borosilicate	Si-O-B angles (°)	Reference
Searlesite $NaBSi_2O_5(OH)_2$	130.2(1), 142.6(1)	This paper
Garrelsite $NaBa_3Si_2B_7O_{16}(OH)_4$	126.9(2), 125.4(2) 128.4(2), 123.1(2) Mean 126.0	Ghose, Ulbrich & Wan (1975)
Datolite $CaBSiO_4(OH)$	123.0(1), 122.4(1), 127.5(1) Mean 124.3	Foit, Phillips & Gibbs (1973)
Danburite $CaB_2Si_2O_8$	132.4(1), 126.3(1), 128.1(1) Mean 128.9	Phillips, Gibbs & Ribbe (1974)
Reedmergnerite $NaBSi_3O_8$	135.4(3), 124.9(3)	Appleman & Clark (1965)
Howlite $Ca_2SiB_5O_9(OH)_5$	135(2), 127(2)	Finney, Kumbasar, Konnert & Clark (1970)

The SiO_4 tetrahedra

Topochemically both $Si(1)O_4$ and $Si(2)O_4$ tetrahedra are similar. Each SiO_4 tetrahedron shares three corners with three different SiO_4 tetrahedra of the other kind and a fourth corner with $BO_2(OH)_2$ tetrahedron. The Si-O distances involving oxygens bonded to a boron are much shorter [(Si(1)-O(4) 1.602Å; Si(2)-O(3) 1.579Å] than those involving oxygens bonded to another silicon. The latter set of Si-O distances are very similar to each other and average 1.618Å for Si(1) and 1.617Å for Si(2) tetrahedra. The short Si(1)-O(4) and Si(2)-O(3) bonds apparently have significantly more covalent character than the other Si-O bonds. This feature can be explained from the point of view of charge balance, since oxygens O(3) and O(4) receive a smaller charge contribution from B^{3+} as opposed to other oxygens, each of which are bonded to two silicons. In terms of O-Si-O angles, the Si(1) tetrahedron is slightly more distorted than the Si(2) tetrahedron.

The $NaO_2(OH)_4$ octahedron

The highly distorted octahedral coordination around Na is achieved by two oxygen atoms and four (OH) radicals (Fig. 1). The Na-O distances range from 2.442 to 2.694Å. The Na-O(1) distance, 2.944Å,

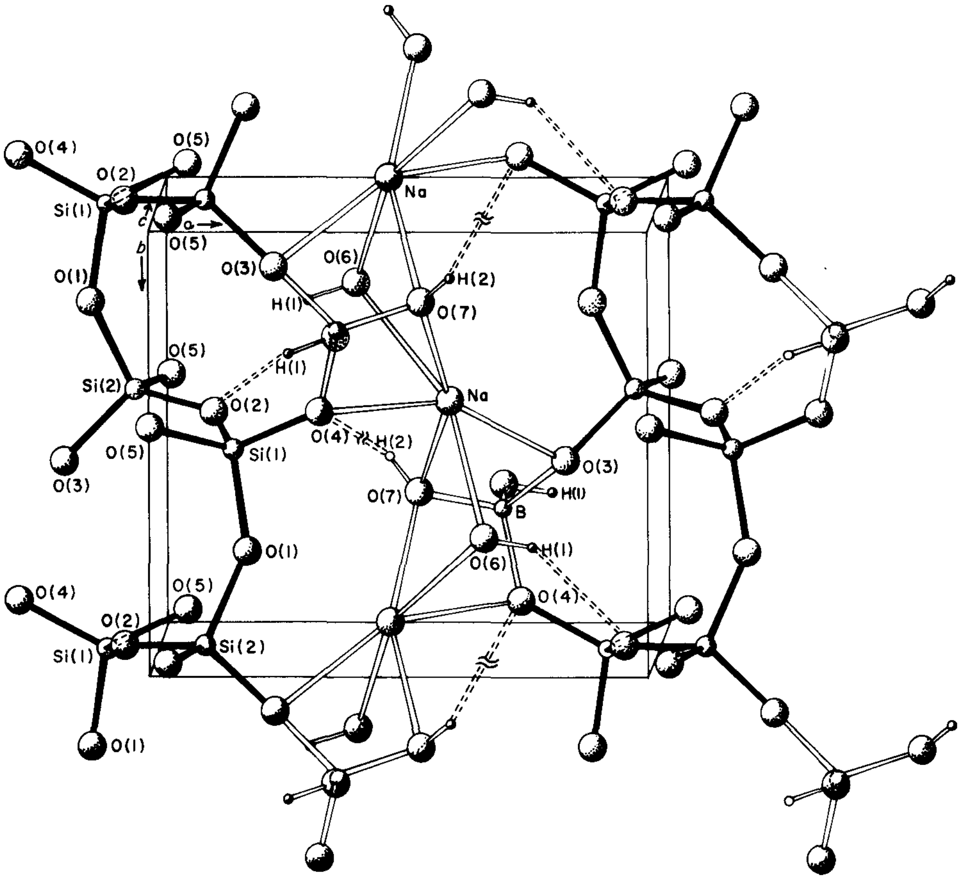

FIG. 1. A view of the searlesite, $NaBSi_2O_5(OH)_2$ structure, showing the spiral silicate chains and columns of Na octahedra running parallel to the b axis, connected by $BO_2(OH)_2$ tetrahedra.

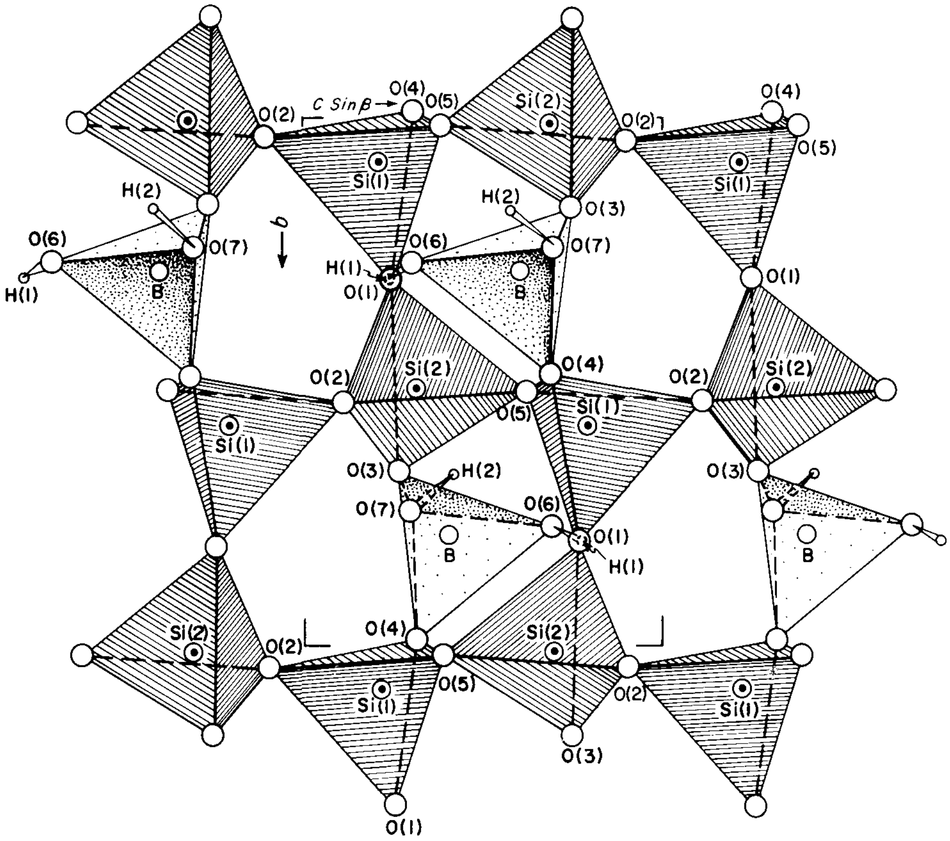

FIG. 2. The borosilicate sheet in searlesite, $NaBSi_2O_5(OH)_2$, parallel to the (100) plane; the $BO_2(OH)_2$ tetrahedron is stippled. Note the pyroxene type silicate chain parallel to the c axis. The sodium atoms have been omitted.

is larger than the Si(1)–B distance, 2.803Å, and is not considered a bonding distance. The distortion in the $NaO_2(OH)_4$ octahedron is mainly caused by an unusually long octahedral edge, O(3′)–O(7′) 4.702Å, which subtends an angle of 114.7° at Na (Fig. 1). The other octahedral edges are much smaller and average 2.93Å. Two of the shortest Na–O distances, Na–O(7) 2.316Å and Na–O(6) 2.442Å, involve oxygen atoms which are part of (OH) radicals. In garrelsite, $NaBa_3Si_2B_7O_{16}(OH)_4$ (Ghose *et al.*, 1975), where the sodium atom has a distorted octahedral $NaO_4(OH)_2$ coordination, the shortest Na–O bonds (2.321Å) also involve oxygens which are part of (OH) radicals.

The sheet structure

Spiral silicate chains consisting of alternating Si(1)- and Si(2)-tetrahedra sharing corners run parallel to the two-fold screw axis (*i.e.*, b axis) (Fig. 1). The $BO_2(OH)_2$ tetrahedron shares one oxygen corner each with Si(1)- and Si(2)-tetrahedra to form infinite chains of composition $BSi_2O_7(OH)_2$ also running parallel to the b axis (Fig. 1). Each silicate tetrahedron within this chain shares the fourth corner with an additional SiO_4 tetrahedron along the c direction, thereby forming a sheet parallel to the (100) plane. Alternately, these sheets may be regarded to consist of pyroxene-type silicate chains (*Zweiereinfachketten*), running parallel to the c axis, which are connected by borate tetrahedra (Fig. 2). The pyroxene-type chains are highly kinked, the O(5)–O(2)–O(5′) and O(2)–O(5)–O(2″) angles both being 140.96°. Such a high degree of kinking results in a chain repeat distance of 4.9Å rather than 5.2Å as in pyroxenes (Kravchenko, 1964).

The $NaO_2(OH)_4$ octahedron shares two edges, O(6)–O(7) and O(6′)–O(7′) with two adjacent Na octahedra, thereby forming a spiral column running parallel to the b axis (Fig. 1). The Na octahedron in addition shares two edges, O(4)–O(7) and O(7′)–O(3) with two $BO_2(OH)_2$ tetrahedra, and two corners, O(4) and O(3), with two SiO_4 tetrahedra; each of the two B and Si tetrahedra in each case belong to two adjacent borosilicate sheets. The Na–O bonds and the hydrogen bond O(7)–H(2)···O(4) help bind the borosilicate sheets together. The very good micaceous (100) cleavage in searlesite apparently breaks through these bonds, leaving the borosilicate sheets intact.

The five-membered borosilicate rings

One of the most interesting features of the searlesite structure is the presence of five-membered borosilicate rings, which condense to form the sheet structure parallel to the (100) plane (Fig. 2). Two types of rings can be recognized; in an anti-clockwise fashion, the first type has the sequence B-Si(2)-Si(1)-Si(2)-Si(1) and the second type B-Si(1)-Si(2)-Si(1)-Si(2). Within the first type of ring, the Si(2)–O(5)–Si(1) angle is 140.8°; and within the second type, the Si(1)–O(2)–Si(2) angle is 138.7°. The Si(1)–O(1)–Si(2) angle, common to both types of rings, is 146.8°. On the other hand, the B–O(3)–Si(2) angle is 142.6° and the B–O(4)–Si(1) angle is 130.2°.

The average B–O–Si angle in other well refined borosilicates (see Table 6) that contain four-membered borosilicate rings is 127.6°. The B–O(3)–Si(2) angle, which is much larger than this average value, can be attributed to the stereochemical requirements of the formation of a five-membered ring system, rather than unusual bonding effects.

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