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Structural Chemistry of Borosilicates.
I. Garrelsite, $NaBa_3Si_2B_7O_{16}(OH)_4$: a Silicoborate with the Pentaborate $[B_5O_{12}]^{9-}$ Polyanion

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The silicoborate mineral garrelsite $NaBa_3Si_2B_7O_{16}(OH)_4$ is monoclinic, space group $C2/c$ with $a=14{\cdot}639$ (3), $b=8{\cdot}466$ (2), $c=14{\cdot}438$ (3) Å, $\beta=114{\cdot}21$ (2)°, $Z=4$. The Ba atom positions were determined from a three-dimensional Patterson synthesis. The crystal structure was determined by the heavy-atom method and refined by the least-squares method with anisotropic temperature factors to an R value of 0·038 for 4017 reflections, measured on an automatic single-crystal diffractometer. The average standard errors in Na–O, Ba–O and Si–O bond lengths are ±0·002 Å, in B–O bond lengths ±0·004 Å and in O–Na–O, O–Ba–O, O–Si–O and O–B–O angles ±0·06, ±0·06, ±0·11 and ±0·22° respectively. The crystal structure of garrelsite is a three-dimensional framework composed of silicoborate sheets and Ba–O polyhedral layers both running parallel to (001). The silicoborate sheet in turn is composed of a new type of silicoborate chain, the pentaborate $[B_5O_{12}]^{9-}$ polyanion, and Na in octahedral coordination. The silicoborate chains consist of two types of alternating Si and B tetrahedral four-membered rings, the planes of which are normal to each other. The pentaborate polyanion consists of a central borate tetrahedron B(4), forming two trinuclear groups, each with two borate tetrahedra B(4) and B(2), and one borate triangle B(3). The polyanion has the point symmetry 2 and is in the *trans* configuration. The average B–O distances within the slightly distorted $B(1)O_3(OH)$, $B(2)O_4$ and $B(4)O_4$ tetrahedra are 1·477, 1·473 and 1·473 Å respectively. The $B(3)O_3$ borate triangle approximates the point symmetry m with an average B–O distance of 1·364 Å. The SiO_4 tetrahedron is slightly distorted (av. Si–O 1·629 Å). The average Si–O–B and B–O–B angles are 125·95 and 123·70° respectively. The $NaO_4(OH)_2$ octahedron is irregular (av. Na–O 2·442 Å). Both $Ba(1)O_6(OH)_4$ and $Ba(2)O_7(OH)_3$ are irregular polyhedra consisting of square pyramids and pentagonal pyramids with average Ba–O distances 2·911 and 2·868 Å respectively.

Introduction

As part of an investigation of the structural chemistry of borosilicates, particularly the nature of B–O coordination in the presence of tetrahedral Si, we have determined the crystal structure of garrelsite, $NaBa_3Si_2B_7O_{16}(OH)_4$. Among the known borosilicates, B occurs either in a triangular coordination as in tourmaline, $NaMg_3Al_6B_3Si_6O_{27}(OH,F)$ (Ito & Sadanaga, 1951; Donnay & Buerger, 1950) or in a tetrahedral coordination as in datolite, $CaBSiO_4OH$ (Ito & Mori, 1953), danburite, $CaB_2Si_2O_8$ (Johansson, 1959), *etc.* The only known exception to this rule is the silicoborate howlite, $Ca_2SiB_5O_9(OH)_5$ (Finney, Kumbasar, Konnert & Clark, 1970), where B occurs in both triangular and tetrahedral coordination. Howlite (with B:Si ratio 5:1) contains colemanite-type borate chains, composed of trinuclear groups formed by linking two borate tetrahedra and one triangle at corners. Garrelsite is another silicoborate (with B:Si ratio 7:2) where B occurs in two types of coordination. Furthermore, garrelsite contains the pentaborate $[B_5O_{12}]^{9-}$ polyanion consisting of three borate tetrahedra and two borate triangles. This polyanion is the anhydrous analog of the $[B_5O_6(OH)_6]^{3-}$ polyanion found in ulexite, $NaCaB_5O_6.5H_2O$ (Clark & Appleman, 1964).

Chemical composition of garrelsite

In the first report of this mineral, Milton, Axelrod & Grimaldi (1955) reported the chemical composition as $(Ba_{0.65}Ca_{0.29}Mg_{0.06})_4H_6Si_2B_6O_{20}$, based on wet chemical analysis of brown-colored authigenic crystals from dolomite marlstone of the Green River Formation, Utah. A few colorless crystals in ulexite were reported from the Kramer borate district of Kern County, California (Morgan & Erd, 1969). Christ (1959) reformulated garrelsite as $M_4B_4(SiO_4)_2(BO_3OH)_2(OH)_4$, where M = Ba, Ca, Mg, to emphasize its structural similarity to the datolite structure group.

The structure determination was initiated assuming the chemical composition reported by Milton *et al.* (1955). From the three-dimensional Patterson synthesis, the presence of three Ba atoms in the chemical formula was confirmed, but no suitable peaks for Ba–Ca vectors were found. The strong peaks, which showed up in the first Fourier synthesis in addition to those due to Ba and Si were assumed to be due to Ca. The site-occupancy refinement showed that if the atom concerned were Ca, the occupancy factor would be nearly 0·5. Such a defect structure was unlikely, because garrelsite formed in a low temperature-environment. We postulated the presence of one Na atom instead of 0·5 Ca and the chemical formula was believed to be $NaBa_3Si_2B_6O_{13}(OH)_7$ (Ghose & Ulbrich, 1972), based on the structure determination in the space group *Cc*. Partial microprobe analysis of the clear areas in the impure brown crystals indicated the presence of 3·5% Na_2O but no Ca, Mg or K (Ulbrich & Ghose, 1973). This result has been confirmed by chemical analysis of clear transparent garrelsite crystals by the atomic absorption method (Milton & Pabst, 1974). Later an extra B atom was found from the difference Fourier synthesis and the refinement of the structure was carried out in the centrosymmetric space group *C*2/*c*. The chemical formula of garrelsite is now established as $NaBa_3Si_2B_7O_{16}(OH)_4$ (Ghose & Ulbrich, 1973) through structure determination and partial microprobe and chemical analyses.

Table 1. *Garrelsite*: *crystal data*

$NaBa_3Si_2B_7O_{16}(OH_4)$
Monoclinic, colorless, transparent bipyramidal crystals, point group 2/*m*.

a	14·639 (3) Å
b	8·466 (2)
c	13·438 (3)
β	114·21 (2)°
Cell volume	1519·05 Å^3
Space group	*C*2/*c*
Cell content	$4[NaBa_3Si_2B_7O_{16}(OH)_4]$
D_m	3·68 g cm^{-3} (on impure crystals)
D_c	3·890
μ(Mo *Kα*)	78·34 cm^{-1}
λ(Mo *Kα*)	0·71069 Å

Crystal data

Milton *et al.* (1955) found garrelsite to be monoclinic, with $a=13·43$, $b=8·45$, $c=14·01$ Å, $\beta=114°19'$, space group *Aa* or *A*2/*a*. We have interchanged the *a* and *c* dimensions, so that the space-group orientation becomes *Cc* or *C*2/*c*. The structure determination confirmed the space group *C*2/*c*. The cell dimensions of a clear transparent crystal were determined by least-squares refinement, using 15 reflections with 2θ values between 40° and 50° measured on an automatic single crystal diffractometer (Table 1).

Experimental

A glass-clear single crystal of garrelsite from Utah [South Ouray No. 1, 2606 ft; see Milton & Pabst (1974)] was ground to a sphere of diameter 0·22 (±0·01) mm. The sphere was checked for crystal perfection by taking a transmission Laue photograph. Only sharp Bragg reflections were found along with a few diffuse reflections due to temperature diffuse scattering.

A first set of 1463 reflections was measured on a Syntex $P\bar{1}$ computer-controlled automatic single-crystal diffractometer, using Mo *Kα* radiation monochromatized by reflection from a graphite 'single' crystal, and a scintillation counter. These data were corrected for Lorentz, polarization and absorption factors and the resulting structure factors were used for the initial determination and refinement of the structure. A second set of intensity data (4017 reflections) within $2\theta=60°$ was measured on a Syntex $P\bar{1}$ diffractometer with variable scan rate, the minimum being 1° min^{-1}, and the 2θ–θ method. These data, after correction for Lorentz, polarization and absorption factors, were used for the final refinement. For intensity $I<0·7\sigma(I)$, where $\sigma(I)$ is the standard error of measurement, I was set equal to $0·7\sigma(I)$, regardless of whether I was positive or negative. A three-dimensional Patterson synthesis was calculated using the

Table 2. *Garrelesite*, $NaBa_3Si_2B_7O_{16}(OH)_4$: *positional and thermal parameters* (*with standard deviations in parentheses*)

Fractional coordinates and anisotropic temperature factors ×10^5. Form of the temperature factor $=\exp[-\{\sum_{i=1}^{3}\sum_{j=1}^{3}h_ih_j\beta_{ij}\}]$.

	x	y	z	B_{eq}(Å^2)	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ba(1)	0	59316 (3)	25000	0·682 (4)	80 (1)	225 (3)	121 (1)	0	25 (1)	0
Ba(2)	20878 (1)	6623 (2)	69714 (1)	0·603 (3)	98 (1)	191 (2)	100 (1)	−20 (1)	47 (1)	−6 (1)
Na	25000	−25000	50000	1·165 (28)	114 (9)	523 (25)	195 (11)	−52 (12)	60 (8)	−18 (13)
Si	36481 (6)	10344 (9)	49211 (6)	0·403 (9)						
B(1)	44136 (22)	−18705 (35)	46699 (24)	0·495 (35)	74 (12)	151 (29)	96 (14)	−5 (15)	43 (11)	−11 (16)
B(2)	15777 (22)	15868 (35)	38052 (23)	0·457 (34)	64 (12)	171 (29)	73 (14)	−3 (15)	30 (11)	19 (16)
B(3)	8095 (23)	−5896 (36)	44539 (25)	0·557 (35)	67 (12)	187 (30)	111 (14)	−2 (16)	37 (11)	−4 (17)
B(4)	0	1509 (50)	25000	0·474 (48)						
O(1)	4806 (15)	31989 (25)	53726 (17)	0·630 (26)	50 (8)	278 (23)	119 (11)	−24 (11)	29 (8)	27 (12)
O(2)	38512 (16)	−8553 (23)	51380 (17)	0·603 (26)	106 (9)	137 (21)	138 (11)	25 (11)	78 (8)	13 (12)
O(3)	9432 (16)	−14939 (24)	53367 (16)	0·607 (26)	120 (9)	140 (21)	75 (10)	−47 (11)	23 (8)	9 (12)
O(4)	1130 (15)	−9158 (24)	34249 (17)	0·610 (26)	91 (9)	177 (22)	94 (10)	−36 (11)	21 (8)	19 (12)
O(5)	35920 (15)	17100 (24)	60324 (16)	0·595 (26)	108 (9)	156 (21)	108 (10)	2 (11)	57 (8)	−22 (12)
O(6)	14845 (15)	6169 (24)	46626 (16)	0·629 (26)	104 (9)	228 (22)	81 (10)	−74 (12)	38 (8)	2 (12)
O(7)	23914 (15)	36016 (25)	61444 (16)	0·559 (25)	44 (8)	282 (23)	86 (10)	16 (11)	20 (8)	10 (12)
O(8)	9008 (15)	10786 (24)	27316 (16)	0·521 (25)	53 (8)	216 (21)	86 (10)	−44 (11)	19 (8)	−12 (12)
(OH) (1)	18539 (14)	−30397 (24)	31420 (16)	0·533 (25)	61 (8)	241 (22)	82 (10)	−7 (11)	32 (8)	28 (12)
(OH) (2)	41549 (16)	−13809 (25)	35321 (16)	0·651 (26)	120 (10)	214 (22)	84 (10)	12 (11)	46 (8)	22 (12)

Table 3. *Garrelsite*, $NaBa_3Si_2B_7O_{16}(OH)_4$: *interatomic distances* (Å) *and angles* (°) (*with standard deviations in parentheses*)

Ba(1) polyhedron			
Ba(1)——O(4)	2·920 (2) (×2)	O(4)——Ba(1)–OH(1)	71·80 (6) (×2)
Ba(1)——(OH) (1)	2·636 (2) (×2)	O(4)——Ba(1)–OH(2)	111·60 (6) (×2)
Ba(1)——(OH) (2)	2·449 (2) (×2)	O(4)——Ba(1)–O(2)′	69·66 (6) (×2)
Ba(1)——O(2)	2·920 (2) (×2)	O(4)——Ba(1)–O(4)′	47·86 (8)
Ba(1)——O(5)	3·131 (2) (×2)	(OH) (1) –Ba(1)–O(2)	66·10 (6) (×2)
Mean	2·911	(OH) (1) –Ba(1)–O(5)	72·92 (6) (×2)
O(4)——(OH) (1)	3·266 (3) (×2)	(OH) (2) –Ba(1)–O(2)	68·89 (6) (×2)
O(4)——(OH) (2)	4·110 (3) (×2)	(OH) (2) –Ba(1)–O(5)	61·60 (5) (×2)
O(4)——O(2)	3·332 (3) (×2)	(OH) (2) –Ba(1)–O(5)′	61·78 (5) (×2)
O(4)——O(4)′	2·369 (4)	O(2)——Ba(1)–O(5)	50·41 (5) (×2)
(OH) (1)–O(2)	3·040 (3) (×2)	O(5)——Ba(1)–O(5)′	88·85 (7) (×2)
(OH) (1)–O(5)	3·450 (3) (×2)	Mean	71·19
(OH) (2)–O(2)	3·320 (3) (×2)		
(OH) (2)–O(5)	3·117 (3) (×2)		
(OH) (2)–O(5)′	3·125 (3) (×2)		
O(2)——O(5)	2·584 (3) (×2)		
O(5)——O(5)′	4·384 (4)		
Ba(2) polyhedron			
Ba(2)——O(3)	2·819 (2)	O(3)——Ba(2)–OH(1)	66·54 (6)
Ba(2)——O(5)	3·083 (2)	O(3)——Ba(2)–O(4)	70·23 (6)
Ba(2)——O(6)	2·856 (2)	O(3)——Ba(2)–O(8)	71·39 (6)
Ba(2)——O(2)	2·834 (2)	O(5)——Ba(2)–(OH) (1)′	108·11 (6)
Ba(2)——O(4)	3·050 (2)	O(5)——Ba(2)–O(7)	48·22 (5)
Ba(2)——(OH) (1)	2·747 (2)	O(5)——Ba(2)–(OH) (2)	62·32 (5)
Ba(2)——O(8)	2·773 (2)	O(5)——Ba(2)–(OH) (1)	72·31 (5)
Ba(2)——(OH) (1)′	2·662 (2)	O(5)——Ba(2)–O(6)	60·92 (5)
Ba(2)——(OH) (2)	2·953 (2)	O(5)——Ba(2)–O(1)	89·10 (5)
Ba(2)——O(7)′	2·907 (2)	O(6)——Ba(2)–O(4)	88·70 (6)
Mean	2·868	O(6)——Ba(2)–O(7)	67·31 (6)
O(3)——(OH) (1)	3·054 (3)	O(6)——Ba(2)–O(8)	115·57 (6)
O(3)——O(4)	3·381 (3)	O(7)——Ba(2)–O(4)	101·19 (5)
O(3)——O(8)	3·263 (3)	O(7)——Ba(2)–(OH) (1)′	69·30 (6)
O(5)——(OH) (1)′	4·658 (3)	O(7)——Ba(2)–(OH) (2)	79·50 (6)
O(5)——O(7)	2·428 (3)	O(4)——Ba(2)–(OH) (1)′	70·57 (6)
O(5)——(OH) (2)	3·125 (3)	O(4)——Ba(2)–O(8)	47·56 (5)
O(5)——(OH) (1)	3·450 (3)	(OH) (1) –Ba(2)–OH(2)	76·64 (6)
O(5)——O(6)	3·017 (3)	(OH) (1) –Ba(2)–O(7)′	69·30 (6)
O(6)——O(4)	4·131 (3)	(OH) (1) –Ba(2)–O(8)	92·50 (6)
O(6)——O(7)	3·153 (3)	O(8)——Ba(2)–(OH) (1)′	86·12 (6)
O(6)——(OH) (1)	3·673 (3)	O(8)——Ba(2)–O(7)′	48·74 (6)
O(6)——O(8)	4·763 (3)	(OH) (1)′–Ba(2)–O(7)′	89·46 (6)
O(7)——O(4)	4·548 (4)	(OH) (2) –Ba(2)–O(7)′	71·26 (6)
O(7)——(OH) (1)′	3·128 (3)	Mean	69·83
O(7)——(OH) (2)	3·414 (3)		
O(4)——(OH) (1)′	3·314 (3)		
O(4)——O(8)	2·362 (3)		
(OH) (1)–OH(2)	3·485 (3)		
(OH) (1)–O(7)′	3·128 (3)		
(OH) (1)–O(8)	3·988 (3)		
O(8)——OH(1)′	3·712 (3)		
O(8)——O(7)′	2·347 (3)		
(OH) (1)–O(7)′	3·923 (3)		
(OH) (2)–O(7)′	3·414 (3)		
Na octahedron			
Na——O(2)	2·363 (2) (×2)	O(2)——Na——O(3)	56·63 (6) (×2)
Na——O(3)	2·640 (2) (×2)	O(2)——Na——(OH) (1)	75·64 (6) (×2)
Na——(OH) (1)	2·324 (2) (×2)	O(2)——Na——O(3)′	123·37 (6) (×2)
Mean	2·442	O(2)——Na——(OH) (1)′	99·15 (7) (×2)
O(2)——O(3)	2·386 (3) (×2)	O(3)——Na——(OH) (1)	75·64 (6) (×2)
O(2)——(OH) (1)	3·040 (3) (×2)	O(3)——Na——(OH) (1)′	104·36 (6) (×2)
O(2)——O(3)′	4·407 (3) (×2)	Mean	89·13
O(2)——(OH) (1)′	3·568 (3) (×2)		
O(3)——(OH) (1)	3·054 (3) (×2)		
O(3)——(OH) (1)′	3·296 (3)		

Table 3 (*cont.*)

Si tetrahedron			
Si——O(1)	1·618 (2)	O(1)——Si——O(5)	114·12 (9)
Si——O(5)	1·632 (2)	O(1)——Si——O(2)	109·44 (11)
Si——O(2)	1·632 (2)	O(1)——Si——O(7)	104·74 (11)
Si——O(7)	1·635 (2)	O(5)——Si——O(2)	104·72 (11)
Mean	1·629	O(5)——Si——O(7)	110·93 (11)
O(1)——O(5)	2·741 (3)	O(2)——Si——O(7)	112·16 (11)
O(1)——O(2)	2·652 (3)	Mean	109·35
O(1)——O(7)	2·576 (3)		
O(5)——O(2)	2·584 (3)		
O(5)——O(7)	2·691 (3)		
O(2)——C(7)	2·711 (3)		
B(1) tetrahedron			
B(1)——O(1)	1·458 (4)	O(1)——B(1)—(OH) (2)	114·28 (22)
B(1)——(OH) (2)	1·476 (4)	O(1)——B(1)—O(3)	108·88 (22)
B(1)——O(3)	1·479 (4)	O(1)——B(1)—O(2)	109·44 (22)
B(1)——O(2)	1·496 (4)	(OH) (2)- B(1)—O(3)	108·48 (22)
Mean	1·477	(OH) (2)- B(1)—O(2)	108·83 (22)
O(1)——(OH) (2)	2·464 (3)	O(3)——B(1)—O(2)	106·66 (21)
O(1)——O(3)	2·389 (3)	Mean	109·42
O(1)——O(2)	2·411 (3)		
(OH) (2)-O(3)	2·397 (3)		
(OH) (2)-O(2)	2·416 (3)		
O(3)——O(2)	2·386 (3)		
B(2) tetrahedron			
B(2)——O(8)	1·441 (4)	O(8)——B(2)—O(6)	111·85 (22)
B(2)——O(6)	1·466 (4)	O(8)——B(2)—O(7)	106·34 (21)
B(2)——O(7)	1·491 (4)	O(8)——B(2)—O(5)	110·31 (22)
B(2)——O(5)	1·494 (4)	O(6)——B(2)—O(7)	108·85 (22)
Mean	1·473	O(6)——B(2)—O(5)	110·55 (21)
O(8)——O(6)	2·408 (3)	O(7)——B(2)—O(5)	108·81 (21)
O(8)——O(7)	2·347 (3)	Mean	109·45
O(8)——O(5)	2·409 (3)		
O(6)——O(7)	2·405 (3)		
O(6)——O(5)	2·433 (3)		
O(7)——O(5)	2·428 (3)		
B(3) triangle			
B(3)——O(3)	1·357 (4)	O(3)——B(3)—O(6)	114·15 (25)
B(3)——O(6)	1·368 (4)	O(3)——B(3)—O(4)	123·39 (25)
B(3)——O(4)	1·368 (4)	O(6)——B(3)—O(4)	122·29 (25)
Mean	1·364	Mean	119·44
O(3)——O(6)	2·287 (3)		
O(3)——O(4)	2·399 (3)		
O(6)——O(4)	2·396 (3)		
B(4) tetrahedron			
B(4)——O(8)	1·455 (3) (×2)	O(8)——B(4)—O(8)′	114·64 (32)
B(4)——O(4)	1·490 (3) (×2)	O(8)——B(4)—O(4)	111·60 (11) (×2)
Mean	1·473	O(8)——B(4)—O(4)′	106·66 (11) (×2)
O(8)——O(8)′	2·449 (4)	O(4)——B(4)—O(4)′	105·36 (30)
O(8)——O(4)	2·435 (3)	Mean	109·42
O(8)——O(4)′	2·362 (3)		
O(4)——O(4)′	2·369 (4)		
Si-O-B angles		B-O-B angles	
Si-O(1)-B(1)	126·93 (18)	B(1)-O(3)-B(3)	126·81 (23)
Si-O(2)-B(1)	125·44 (17)	B(2)-O(8)-B(4)	124·50 (18)
Si-O(7)-B(2)	128·39 (17)	B(2)-O(6)-B(3)	123·33 (22)
Si-O(5)-B(2)	123·06 (17)	B(3)-O(4)-B(4)	120·18 (21)
Mean	125·95	Mean	123·70

first set of 1463 reflections with the Fourier program incorporated in the X-RAY 67 system.

Determination and refinement of the structure

From the three-dimensional Patterson synthesis, the Ba positions were easily determined from the strong peaks due to Ba–Ba vectors. Since no particular concentration of strong peaks was found in the plane $v=0$ of the Patterson synthesis, the space group was initially assumed to be *Cc*. The structure-factor calculation based on the Ba positions followed by two cycles of least-squares refinement yielded an R value of 0·27. Several cycles of structure-factor calculation followed by Fourier and difference Fourier syntheses yielded the Si, three B and ten O positions. With the space group *Cc* and the chemical composition as $NaBa_3Si_2B_6O_{13}(OH)_7$, the structure was refined by the method of least squares using anisotropic temperature factors to an *R* value of 0·056 for 1463 reflections. However, it was found that the individual tetrahedral Si–O and B–O distances were highly variable, from 1·50 to 1·77 Å and 1·23 to 1·63 Å respectively. Such variability in Si–O and B–O bond distances was unacceptable from crystal-chemical grounds in spite of the low *R* value and small standard deviations of positional parameters. A difference Fourier synthesis calculated at this stage indicated the presence of a seventh B atom. It was clear at this stage that the structure is indeed centrosymmetric. Final least-squares refinement using the second set of intensity data was carried out in the space group *C*2/*c* with the chemical composition $NaBa_3Si_2B_7O_{16}(OH)_4$. The full-matrix least-squares program *RFINE* (Finger, 1969) was used for the refinement. 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.

The atomic scattering factors for Na, Ba, Si, B and O were taken from Cromer (1965). Anomalous dispersion corrections were made according to Cromer & Waber (1965). After three cycles of refinement using isotropic temperature factors, *R* was 0·060 for 4017 reflections. The Si–O and B–O bond lengths showed much less variation and were within acceptable limits. It was found at this stage that there were large discrepancies between a number of very strong F_o's and the corresponding F_c's. The F_o's, which are always much less than the F_c's, are apparently affected either by secondary extinction or measurement errors. These reflections were omitted from the final three cycles of refinement using anisotropic temperature factors, resulting in considerable improvement in the accuracy of atomic parameters. The final *R* is 0·038 for all (4017) reflections and 0·031 for the set of 3945 reflections, omitting the 72 affected strong reflections. The average parameter shift/error at this stage was 0·02, the maximum being 0·12. The atomic positional and thermal parameters are listed in Table 2; the bond lengths and bond angles with standard deviations are tn Table 3.* The standard deviations in interatomic distances and angles were calculated by the program *ERROR* (Finger, 1972). The average standard errors in Na–O, Ba–O and Si–O bond lengths are ±0·002 Å, while the average error in B–O bond lengths is ±0·004 Å. The average error in O–Na–O and O–Ba–O angles is ±0·06° and in O–Si–O and O–B–O angles ±0·11 and ±0·22° respectively.

Description of the crystal structure

The crystal structure of garrelsite is a three-dimensional framework, composed of two principal components: (*a*) silicoborate sheets containing the pentaborate polyanions linked with silicate tetrahedra and (*b*) Ba–O polyhedral layers, both running parallel to the (001) plane (Fig. 1).

The pentaborate $[B_5O_{12}]^{9-}$ *polyanion*

The pentaborate polyanion consists of a central borate tetrahedron B(4), which shares the two O corners, O(4) on one side, with two triangularly coordinated B atoms, B(3), and the two other O corners, O(8), with two adjacent tetrahedrally coordinated B atoms, B(2). The borate triangle in addition shares an O corner, O(6), with the B(2) tetrahedron (Fig. 2). The pentaborate polyanion found in garrelsite is the anhydrous analog of the $[B_5O_6(OH)_6]^{3-}$ polyanion found in ulexite, $NaCaB_5O_6.5H_2O$ (Clark & Appleman, 1964). In ulexite the polyanion has the *cis* configuration (with point symmetry 1), where both the triangles are on the same side of the central borate tetrahedron. The polyanion in garrelsite, on the other hand, has the point symmetry 2 and has the *trans* configuration. The dimensions of this polyanion are shown in Fig. 2 and Table 3. Unfortunately the refinement of the ulexite structure is not complete and so a closer comparison of the stereochemistry of these two polyanions must be postponed to a later date.

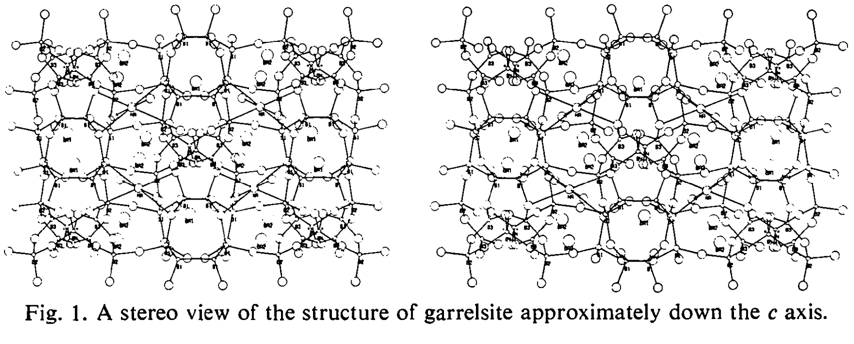

Fig. 1. A stereo view of the structure of garrelsite approximately down the *c* axis.

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31288 (78 pp., 2 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

The silicoborate sheet

The structure of garrelsite contains a new type of silicoborate chain running parallel to the [110] direction. These chains consist of two types of alternating tetrahedral four-membered rings, whose planes are at right angles to each other. The first type of ring is formed by alternating Si and B(1) tetrahedra and the second type by alternating Si and B(2) tetrahedra sharing corners. Each two rings have one Si tetrahedron in common (Fig. 3). In each four-membered ring, Si and B tetrahedra alternate as in datolite, $CaBSiO_4(OH)$ (Ito & Mori, 1953; Pant & Cruickshank, 1967; Foit, Phillips & Gibbs, 1973), danburite, $CaB_2Si_2O_8$ (Dunbar & Machatschki, 1930; Johansson, 1959; Phillips, Gibbs & Ribbe, 1974), reedmergnerite, $NaBSi_3O_8$ (Appleman & Clark, 1965), and howlite, $Ca_2SiB_5O_9(OH)_5$ (Finney, Kumbasar, Konnert & Clark, 1970).

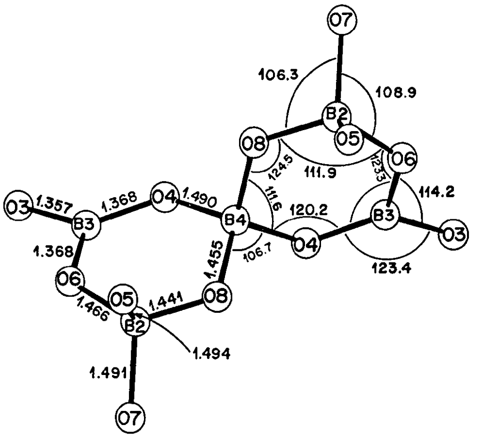

Fig. 2. A view of the pentaborate $[B_5O_{12}]^{9-}$ polyanion in garrelsite down the *b* axis. The polyanion is in the *trans* configuration and possesses the point symmetry 2. Some of the relevant bond distances (Å) and bond angles (°) are also shown.

Two adjacent silicoborate chains are connected along the *b* direction through the B(3) borate triangle sharing corner O(6) with the B(2) tetrahedron in the chain above and the corner O(3) belonging to the B(1) tetrahedron in the chain below. Silicoborate sheets thus formed run parallel to the (001) plane (Fig. 3).

The Na atom occurs within an eight-membered ring, consisting of four borate and two silicate tetrahedra and two borate triangles (Fig. 3). By sharing the edge O(2)–O(3) each with two B(1)-tetrahedra across the ring, the Na atom helps bind the silicoborate sheet together.

The B(4) tetrahedron, which is the central tetrahedron of the pentaborate polyanion, occurs within a hole in the Ba–O polyhedral layer. The silicoborate sheets occurring on either side of the Ba–O polyhedra

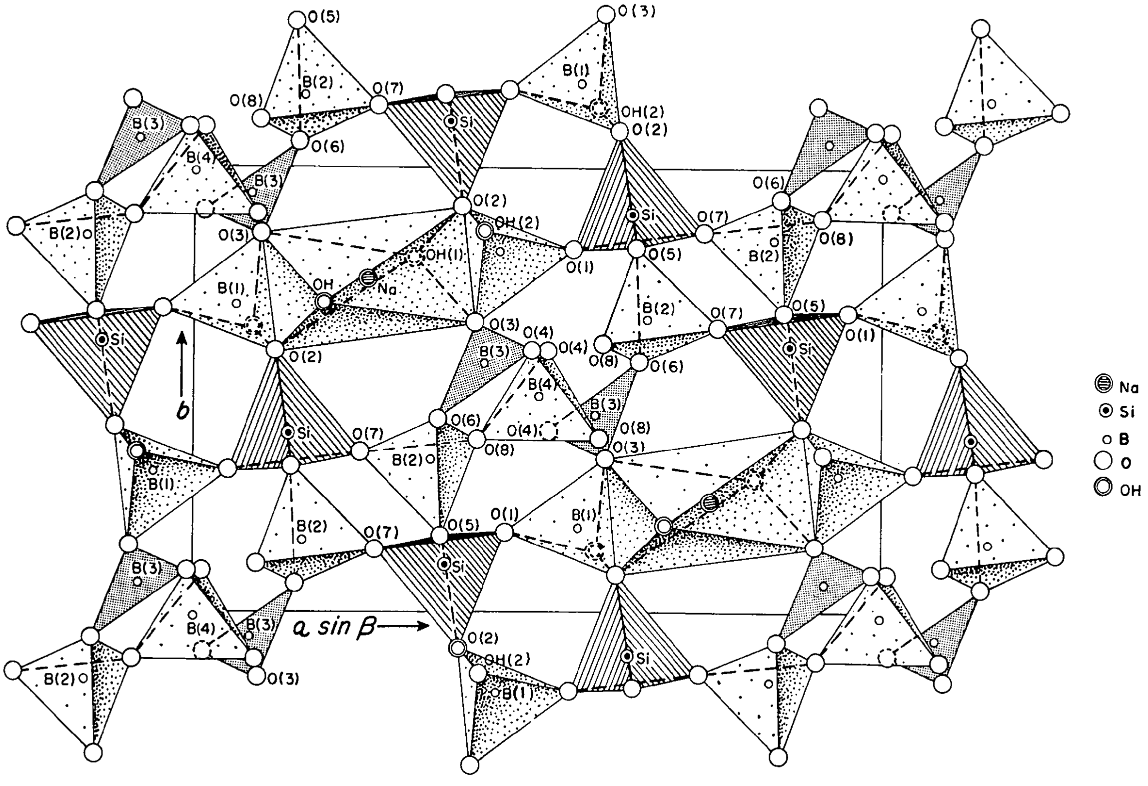

Fig. 3. Partial projection of the garrelsite structure on (001), showing the borosilicate sheet and the Na atom in octahedral coordination. The Ba atoms have been omitted.

layer are connected along the **c** direction into an open framework through this tetrahedron (Fig. 1). Thus, the B(4) tetrahedron shares corners O(8) with a B(2) tetrahedron belonging to the sheet above and O(8)′ with a B(2)′ tetrahedron belonging to the sheet below.

The borate tetrahedra

The B(4)O_4 tetrahedron, with point group symmetry 2, occupies a central position within the pentaborate polyanion. The two B(4)–O(4) distances (1·490 Å) are significantly longer than the other two B(4)–O(8) distances (1·455 Å). Likewise, the O(4)–B(4)–O(4) angle (105·4°) is much smaller than the O(8)–B(4)–O(8) angle (114·6°). O(4) is bridging the B(4) tetrahedron and B(3) triangle, while O(8) is bridging B(4) and B(2) tetrahedra. O(4) is further coordinated to Ba(1) and Ba(2), while O(8) is coordinated to Ba(2) and hydrogen bonded to (OH)(2). Since O(4) is strongly covalently bonded to triangular B(3), the long B(4)–O(4) bond appears reasonable.

Within the B(2)O_4 tetrahedron, which also belongs to the pentaborate polyanion, the B(2)–O(8) distance (1·441 Å) is significantly shorter than the three other B–O distances involving O(5), O(6) and O(7). O(5) and O(7) are further bonded to one Si and two Ba atoms each, while O(6) is further bonded to the triangular B(3) and one Ba(2) atom. Accordingly, B(2)–O(5) and B(2)–O(7) distances are very similar (1·494 and 1·491 Å respectively), while the B(2)–O(6) distance is 1·466 Å.

Within the B(1)O_3(OH) tetrahedron the B(1)–O(1) distance (1·458 Å) is much shorter and the B(1)–O(2) distance (1·496 Å) is much longer than the average B–O distance (1·477 Å). This is reasonable in view of the fact that O(1) is further bonded only to Si, while O(2) is further bonded to Si, Na and Ba(1). Consistent with this environment, O–B–O angles involving O(1) and O(2) show the largest variation [O(2)–B(1)–O(3) 106·7° and O(1)–B(1)–(OH)(2) 114·3°]. The average tetrahedral B–O distances are 1·477, 1·473 and 1·473 Å in the B(1), B(2) and B(4) tetrahedra respectively.

The B(3)O_3 *triangle*

The triangular B–O distances are the same within the limits of error, consistent with the fact that all three O atoms are shared by three different borate tetrahedra. The average triangular B–O distance is 1·364 ± 0·007 Å. Two of the O–B–O angles are very similar and larger (123·4° and 122·4°), while the third one is smaller (114·5°) than the average value 119·4 ± 5·2°. Hence, the triangular planar B(3)O_3 group has the point symmetry *m*, rather than the highest possible symmetry 3*m*.

The SiO_4 *tetrahedron*

Within the SiO_4 tetrahedron the Si–O(1) distance (1·618 Å) is significantly shorter than the other three Si–O distances involving O(2), O(5) and O(7), which are very similar and average 1·633 ± 0·002 Å. This fact is consistent with charge balance in the structure, since O(1) is further bonded only to a tetrahedral B, while the three other O atoms are further bonded to two Ba (or Ba and Na) atoms in addition to the tetrahedral boron. The average Si–O distance is 1·629 ± 0·011 Å. The O–Si–O angles range from 104·7° to 114·1° with an average of 109·4°.

The $NaO_4(OH)_2$ *octahedron*

The Na atom has a distorted octahedral coordination, the Na–O distances ranging from 2·324 to 2·640 Å. The Na–(OH) bond is significantly shorter than the Na–O bonds. The O–Na–O (or OH) angles range from 56·6° to 123·4°. The average Na–O distance is 2·442 ± 0·316 Å.

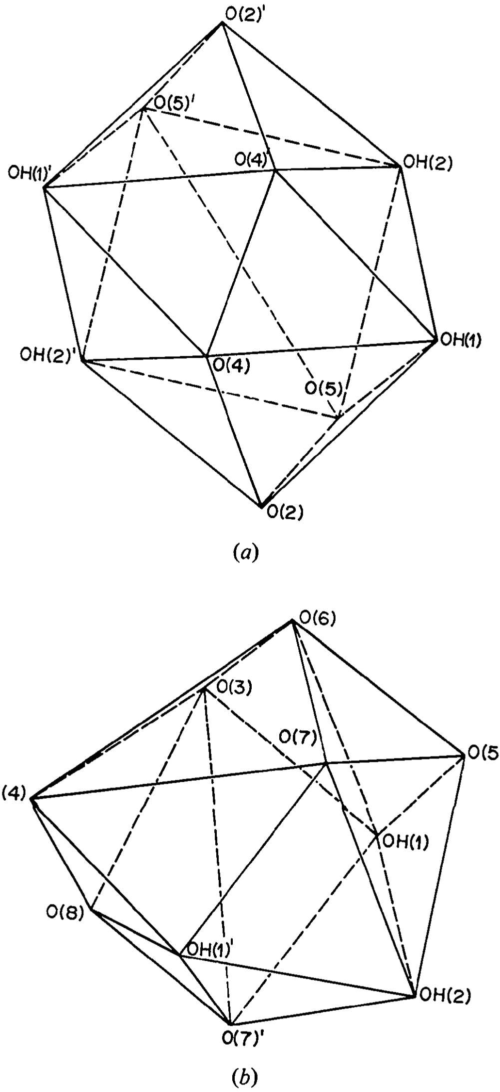

Fig. 4. (*a*) Ba(1)$O_6(OH)_4$ and (*b*) Ba(2)$O_7(OH)_3$ polyhedra in garrelsite viewed down the *b* axis.

The Ba–O *polyhedra*

Because the Ba–O distances show a large variation, we have arbitrarily chosen a cut-off limit of 3·2 Å. Within this limit, Ba(1) is coordinated to six O atoms and four (OH) ions. The Ba(1)$O_6(OH)_4$ polyhedron has the point group symmetry 2. The average Ba(1)–O distance is 2·911 Å, the shortest being Ba(1)–OH(1) (2·636 Å). The coordination polyhedron is irregular However, two types of basic units can be recognized: (*a*) two square pyramids, one of which consists of a square plane formed by O(5)′–OH(1)′–O(4)′–OH(2) with O(2)′ at the apex and its symmetry equivalent and (*b*) eight pentagonal pyramids, four of which are symmetry equivalent in pairs. One of the pentagonal pyramids, for example, consists of the pentagonal plane O(2)–OH(2)′–OH(1)′–O(4)′–OH(1) with O(4) at the apex [Fig. 4(*a*)].

The Ba(2) atom is also ten-coordinated with seven O atoms and three (OH) ions. The average Ba(2)–O distance is 2·868 Å. The Ba (2) polyhedron can also be considered to consist of two square pyramids and eight pentagonal pyramids. A square pyramid, for example, consists of the square plane O(6)–OH(1)′–OH(2)–O(7) with O(5) at the apex. A pentagonal pyramid, for example, is formed by the pentagonal plane O(4)–O(8)–O(7)′–OH(2)–O(7) with OH(1)′ at the apex [Fig. 4(*b*)].

Ba–O *polyhedral sheet*

The coordination polyhedra around Ba(1) and Ba(2) are connected to each other by sharing edges and faces to form an open polyhedral sheet parallel to (001). Thus, Ba(1) and Ba(2) polyhedra share the face OH(1)–OH(2)–O(5) and edges OH(1)–O(4). Two Ba(2) polyhedra share edges OH(1)–O(7) and OH(1)–O(5). Along the *b* axis, a Ba(2) polyhedron shares edges OH(1)–O(8) and OH(1)–O(7) with adjacent Ba(2) polyhedra. The Ba(2) polyhedron shares corner O(6) with another Ba(2) polyhedron. Furthermore, the Na octahedron shares octahedral edges OH(1)–O(2) with Ba(1), OH(1)–O(3) and OH(1)–O(6) with two adjacent Ba(2) polyhedra. In this fashion, Ba–O polyhedral sheets are bound into a three-dimensional framework.

The Ba–O polyhedral framework is connected to the silicoborate sheets by sharing a number of edges of the borate tetrahedra and triangle. However, they have no edges in common with the silicate tetrahedra. Thus, the Ba(1) polyhedron has a common edge O(2)–OH(2) with the B(1) tetrahedron. The Ba(2) polyhedron shares edges O(5)–O(7) and O(7)–O(8) with B(2) tetrahedron and the edge O(3)–O(6) with the B(3) triangle.

Hydrogen bonding

The OH(1) ion is bonded to one Na, one Ba(1) and two Ba(2) atoms in approximately tetrahedral coordination. Because of this fact, as well as lack of appropriate OH–O contact (~2·8 Å), the OH(1) ion is apparently not involved in hydrogen bonding.

The OH(2)–O(8) distance is 2·721 Å, which is appropriate for hydrogen bonding. OH (2), in addition, is bonded to B(1) (1·476 Å) and to Ba(1) (2·948 Å) and Ba(2) (2·953 Å). The coordination around OH(2) is approximately tetrahedral.

Anisotropic thermal vibration

The anisotropic thermal vibration of the sodium atom is pronounced. All other atoms are mildly anisotropic, while Si and B(4) are very nearly isotropic.

Conclusions

1. On the basis of the crystal structure determination and partial microprobe analysis, the chemical formula of garrelsite has been established as $NaBa_3Si_2B_7O_{16}(OH)_4$.

2. In garrelsite, B occurs in both tetrahedral and triangular coordination (in the ratio 5:2) in the presence of tetrahedral Si.

3. Garrelsite contains the pentaborate polyanion $[B_5O_{12}]^{9-}$, which consists of a central BO_4 tetrahedron forming two trinuclear groups of two BO_4 tetrahedra and one BO_3 triangle on either side by sharing corners. The polyanion has the point group symmetry 2 and occurs in the *trans* configuration.

4. The crystal structure of garrelsite is a three-dimensional framework consisting of (*a*) silicoborate sheets and (*b*) Ba–O polyhedral layers. The silicoborate sheets are formed by connected silicoborate chains, which in turn are formed from two types of four-membered tetrahedral rings, with B and Si alternating in each ring.

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The Crystal Structure of Bisguanidinium Hydrogen Phosphate Monohydrate

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The structure of $[C(NH_2)_3]_2HPO_4.H_2O$ has been determined from counter intensities. The space group is $P\bar{4}2_1c$ with $a=16{\cdot}843$ (3), $c=7{\cdot}251$ (1) Å, $Z=8$. The guanidinium ions are effectively planar with C–N ranging from 1·315 to 1·335 Å. The phosphate O–H···O hydrogen bond is short at 2·568 (7) Å. Thirteen of the fifteen H atoms are involved in hydrogen bonding.

Introduction

This compound is of interest since it is likely to contain multiple hydrogen bonds to O, the ratio of possible hydrogen-bonding H to O atoms being 3:1. It was also possible that a precise study might throw some light on the apparently significant lengthening of one of the C–N bonds in guanidinium carbonate (Adams & Small, 1974). The crystal data have been given by Adams & Pritchard (1975).

Experimental

Crystals were prepared by addition of guanidinium carbonate to orthophosphoric acid until effervescence ceased, followed by slow evaporation, whereupon hard colourless needles of square cross-section were formed. Photographs were used to obtain the space group, and cell dimensions (Table 1) in satisfactory agreement with those of Adams & Pritchard were obtained by a least-squares procedure based on θ values measured on the diffractometer (Small & Travers, 1961).

Table 1. *Crystal data*

Space group $P\bar{4}2_1c$; $a=16{\cdot}843(3)$, $c=7{\cdot}251(1)$Å
(Cu $K\alpha$, $\lambda=1{\cdot}5418$Å), $Z=8$; $d_m=1{\cdot}51$, $d_c=1{\cdot}52$g cm^{-3}

Determination of the structure

Initially the space group was mis-assigned as $P4_22_12$ since the conditions noted were: $h00$, $h=2n$; $00l$, $l=2n$. The intensities of the 1365 unique reflexions occurring at $\theta<82{\cdot}1°$ with Cu $K\alpha$ radiation ($\lambda=1{\cdot}5418$ Å) were collected on a diffractometer at room temperature. Intensities were corrected for Lorentz and polarization effects. A Wilson plot gave the relatively low overall temperature factor of 1·5 Å^2. E values were obtained for all reflexions.

MULTAN (Germain, Main & Woolfson, 1970) was used to solve the structure and since the version available at the time of the investigation was not applicable to symmetries higher than orthorhombic, it was necessary to treat the crystal as orthorhombic. The equivalent reflexions in one octant were generated and the 227 reflexions having $E>1{\cdot}6$ were used on the basis of space group $P2_12_12$. An E map computed with the phases from the set with the highest figure of merit revealed a chemically reasonable set of peaks.

Inspection of the coordinates of the two equivalent sets of atoms revealed that (110) was a glide plane, a fact inconsistent with $P4_22_12$. A shift of origin by $\mathbf{a}/2+\mathbf{c}/4$ resulted in symmetry consistent with $P\bar{4}2_1c$ which has conditions, $h00$, $h=2n$; hhl, $l=2n$; *i.e.* as for $P4_22_12$ but with inclusion of the more general second condition. The intensities of the hhl reflexions were in almost all cases <3 standard deviations of background intensity. These reflexions were removed and the posi-

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