Refinement of the crystal structure of the Ca, Mg-carbonatoborate borcarite $Ca_4Mg/B_4O_6(OH)_6/(CO_3)_2$

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Borcarite, a Ca, Mg carbonatoborate, was discovered in the Solongo contact metasomatite deposit in the Buryat ASSR and transmitted to us for study by S. V. Malinko.

The crystal structure of the mineral borcarite with the gross composition $4CaO \cdot MgO \cdot 2B_2O_3 \cdot 2CO_2 \cdot 3H_2O$ (ref. 1) has been solved ($R_{hkl} = 11.5\%$) by L. P. Solov'eva and V. V. Bakakin.[2] The first chemical analyses of borcarite samples from Solongo showed an excellent ratio CaO : MgO = 2 :1, which raised the question of refining its structure.

The powder pattern diagram and the unit cell parameters: $a = 4.445 \pm 0.001$, $b = 17.843 \pm 0.003$, $c = 8.378 \pm 0.004$ Å, $\gamma = 101°.94 \pm 0°.02$, which were refined on a "Sinteks" $P\bar{1}$ autodiffractometer, agree satisfactorily with those given in ref. 2.

The experimental material for structural interpretation of borcarite – 1620 independent nonzero reflections – was recorded by the $(2\theta : \theta)$ method with a variable scanning speed of 6–24 deg/min on the same $P\bar{1}$ autodiffractometer (Mo radiation, plane graphite monochromator, $-8 \le h \le 8$, $0 \le k \le 34$, $0 \le l \le 15$, $\max(\sin\theta/\lambda) = 1.00$ Å^{-1}). The conversion of intensities into $|F_{hkl}|$ and all the subsequent calculations were performed in the specialized XTL "Sinteks" calculation system.

The systematic extinctions indicated three possible Fedorov groups A2/m, A2, Am. The selection in favor of

TABLE 1. Borcarite $Ca_4Mg[B_4O_6(OH)_6](CO_3)_2$. Basal Atom Coordinates and the Isotropic and Anisotropic Temperature Factors

Atom	x/a	y/b	z/c	B_j
Ca	0.1548 (1)	0.15531 (3)	0.23368 (5)	0.67 (1)
	0.1554 (1) *	0.1552 (3)	0.2333 (3)	0.77
Mg	0	0	0	0.51 (3)
				0.77
B_1	0.500	0	0.2408 (4)	0.55 (5)
			0.2405 (16)	0.59
B_2	0.6181 (8)	0.0949 (2)	0	0.59 (5)
	0.6179 (21)	0.0956 (5)		0.63
C	0.7509 (7)	0.1954 (2)	0.500	0.72 (5)
	0.7522 (18)	0.1954 (4)		0.94
O_1	0.3074 (5)	0.0992 (1)	0	0.65 (4)
	0.3067 (13)	0.0986 (4)		0.71
O_2	0.7203 (3)	0.0549 (1)	0.1426 (2)	0.61 (3)
	0.7218 (11)	0.0553 (3)	0.1424 (9)	0.68
$O_3(OH)$	0.3095 (4)	0.0415 (1)	0.3391 (2)	0.76 (3)
	0.3092 (12)	0.0416 (3)	0.3388 (8)	0.83
O_4	0.6465 (4)	0.2153 (1)	0.3659 (2)	1.42 (4)
	0.6486 (15)	0.2154 (4)	0.3658 (12)	1.61
$O_5(OH)$	0.8230 (5)	0.1742 (1)	0	0.74 (4)
	0.8231 (17)	0.1740 (4)		0.87
O_6	0.9617 (6)	0.1566 (2)	0.500	1.24 (5)
	0.9574 (23)	0.1557 (6)		1.58

$$T = \exp[-1/4(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)$$

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Ca	0.85 (1)	0.58 (1)	0.59 (1)	0.08 (1)	−0.08 (1)	−0.04 (1)
Mg	0.46 (5)	0.36 (5)	0.73 (6)	0.04 (4)	0	0
B_1	0.64 (9)	0.52 (8)	0.59 (10)	0.02 (7)	0	0
B_2	0.51 (10)	0.59 (10)	0.66 (10)	0.04 (8)	0	0
C	0.68 (9)	0.61 (9)	0.86 (10)	−0.16 (7)	0	0
O_1	0.55 (7)	0.64 (7)	0.77 (8)	0.09 (5)	0	0
O_2	0.64 (5)	0.58 (4)	0.58 (5)	−0.01 (4)	−0.01 (4)	0.08 (4)
O_3	0.78 (5)	0.82 (5)	0.71 (5)	0.28 (4)	0.11 (4)	−0.15 (4)
O_4	1.68 (7)	1.02 (6)	1.59 (7)	−0.28 (5)	−0.88 (6)	0.48 (5)
O_5	0.72 (8)	0.49 (7)	1.04 (8)	−0.01 (6)	0	0
O_6	1.18 (9)	1.44 (9)	1.28 (9)	0.57 (7)	0	0

Note: 1) Standard deviations are given in parentheses. 2) The asterisk indicates the basal atom coordinates according to ref. 1.

TABLE 2. Interatomic Distances in the Structure of Borcarite $Ca_4Mg[B_4O_6(OH)_6](CO_3)_2$

Ca polyhedron			CO_3 triangle
Ca–O_1 2.361 (1)	O_1–O_2 2.830 (3) *	O_3–O_4 3.162 (2)	C–O_4 (II) 1.290 (3)
2.36_0 **	2.82_5	3.15_8	1.28_8
O_2 2.468 (2)	O_3 3.023 (2)	O_6 3.120 (3)	O_6 1.274 (4)
2.46_2	3.00_8	3.12_0	1.26_7
O_3 2.440 (2)	O_4 3.832 (2)	O_4–O_4' 2.779 (3)	
2.43_7	3.83_2	2.77_5	Average 1.285
O_4 2.493 (2)	O_4' 3.462 (3)	O_6 3.217 (3)	1.28_1
2.49_7	3.46_4	3.24_5	O_4–O_4'' 2.284 (3)
O_4' 2.441 (2)	O_5 2.759 (3)	O_4'–O_6 3.998 (3)	2.24_4
2.43_1	2.76_8	4.00_4	O_6 (II) 2.213 (3) *
O_4'' 2.904 (2)	O_2–O_3 3.144 (2)	O_4'' 3.669 (3)	2.20_8
O_5 2.515 (2)	3.11_1	O_5 2.959 (3)	Average 2.224
2.51_4	O_4'' 3.488 (2)	2.96_0	2.22_0
O_6 2.392 (1)	O_5 2.400 (2)	O_4''–O_5 3.282 (2)	
2.39_8	2.38_5	O_6 2.213 (3) *	
Average 2.502	O_6 3.550 (2)	Average 3.160	
2.44_3	3.53_7	3.22_9	

Mg octahedron	B tetrahedra	
Mg–O_1 (II) 2.000 (1)	B_1–O_2 (II) 1.482 (2)	B_2–O_1 1.399 (4)
1.98_9	1.48 (9)	1.39_9
O_2 (IV) 2.106 (2)	O_3 (II) 1.484 (3)	O_2 (II) 1.509 (3)
2.10_6	1.48_7	1.51_1
		O_5 1.50_1
Average 2.071	Average 1.483	Average 1.483
2.06_7	1.48_8	1.48_0
O_1–O_2 (IV) 2.830 (3) *	O_2–O_2' 2.467 (2)	O_1–O_2 (II) 2.454 (3)
2.82_5	2.48_5	2.45_6
O_2' (IV) 2.978 (2)	O_3 (II) 2.433 (2)	O_5 2.402 (3)
2.96_5	2.44_0	2.41_2
O_2–O_2' (II) 3.469 (2)	O_3' (II) 2.365 (2)	O_2–O_5 (II) 2.400 (2) *
3.74_4	2.36_2	2.38_5
O_2'' (II) 2.390 (2) *	O_3–O_3' 2.470	O_2–O_2'' 2.390 (2) *
2.38_1	2.44_2	2.38_5
Average 2.913	Average 2.422	Average 2.417
2.95_1	2.42_2	2.41_2

Note: 1) The Arabic numerals in parentheses indicate standard deviations and the Roman numerals the number of distances. 2) One asterisk indicates common edges of the Ca, Mg, and B polyhedra and two asterisks the interatomic distances according to ref. 1.

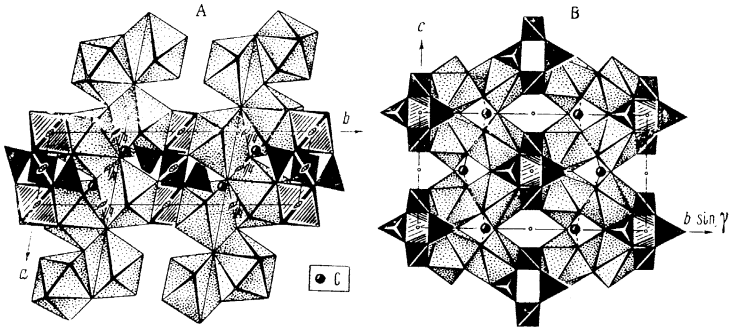

Fig. 1. Borcarite $Ca_4Mg[B_4O_6(OH)_6](CO_3)_2$. A) xy projection; B) yz projection, the lines showing the (C–O) bonds.

the centrosymmetric group was made on the basis of the results of the three-dimensional intensity statistics.

Analysis of the three-dimensional Patterson function confirmed the positions of the eight Ca and two Mg atoms found in ref. 2.

On the three-dimensional electron-density distribution constructed with allowance for the identified Mg and the preliminarily refined Ca atoms, we localized six O, one C, and two B atoms, whose coordinates are close to those found in ref. 2.

The refinement by the least-squares method of the positional and thermal parameters of the basal atoms in the isotropic and anisotropic full-matrix approximation has been improved to $R_{hkl} = 5.9\%$ and $R_{hkl} = 4.1\%$, respectively. The final coordinates of the basal atoms with isotropic and anisotropic temperature corrections and their corresponding interatomic distances (Tables 1 and 2) agree satisfactorily with those obtained earlier.[2]

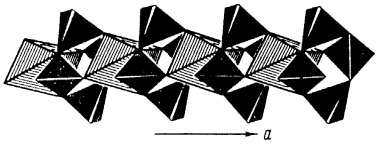

Fig. 2. Borcarite $Ca_4Mg[B_4O_6(OH)_6](CO_3)_2$. Fragment of the structure. Column of Mg octahedra cemented by $[B_4O_6(OH)_6]$ rings.

The crystal structure analysis of the model obtained of the structure showed that the ratio CaO:MgO = 2:1 noted earlier can hold good only if the Mg atoms are present in the second system of centers with coordinates $(0\,0\,{}^1/_2)$. Upon specifying an additional Mg in the position indicated, the divergence factor was increased by 16%, and consequently for the borcarite from Solongo, the CaO : MgO ratio should be 4 : 1. Accordingly, the structural formula of borcarite $Ca_4Mg[B_4O_6(OH)_6](CO_3)_2$ is similar to that established in ref. 2, and a unit cell contains Z = 2 units of the above composition.

Around the Ca cations the seven closest O atoms are at a distance of 2.904 Å, and for O(OH)−O(OH) = 2.213-3.998 Å. If the eighth ligand is included in the coordination, the Ca polyhedron is a distorted Thomson cube.

The Mg cations are situated in octahedra with distances Mg−O = 2.000-2.106 Å for O−O = 2.390-3.469 Å.

Two kinds of B atoms in the structure of borcarite from the $[B_4O_6(OH)_6]$ ring with 2/m symmetry, and angle $B_1-O_2-B_2 = 121°.98$ (17). In the B_1 tetrahedron with symmetry 2 $B_1-O(OH)$ = 1.482-1.484 Å for O(OH)−O(OH) = 2.365-2.470 Å and in the B_2 tetrahedron (with symmetry m) $B_2-O(OH)$ = 1.399-1.509 Å for O(OH)−O(OH) = 2.390-2.454 Å.

In the triangles around the C atoms the C−O distances are 1.274-1.290 Å for O−O = 2.213-2.284 Å.

The base of the structure of borcarite is constituted by Ca layers − walls parallel to the xz plane at levels y = ${}^1/_4$ and ${}^3/_4$ (Fig. 1a); the walls are formed by the zigzag chains, extending along axis *a*, of eight-vertex Ca polygons connected along the edges. The discrete chains are multiplied by mirror planes and combine through the vertices and edges of the Ca polyhedra to form a single two-layer stack − a wall which receives additional rigidity from the CO_3 triangles (Fig. 1b). The centrosymmetric Mg octahedra translationally identical along the *a* axis are connected by the $[B_4O_6(OH)_6]$ rings into characteristic columns with constrictions (Fig. 2) and combine the Ca walls into a single three-dimensional frame.

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