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Abstract

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R. M. GANIEV, Yu. A. KHARITONOV, V. V. ILYUKHIN,
Academician N. V. BELOV

CRYSTAL STRUCTURE OF CALCIUM CHONDRODITE

$Ca_5[SiO_4]_2(OH)_2 = Ca(OH)_2 \cdot 2Ca_2SiO_4$

Calcium chondrodite $Ca_5[SiO_4]_2(OH)_2 = 2Ca_2SiO_4 \cdot Ca(OH)_2$ was first obtained among the hydration products of basic cement (tricalcium) silicate C_3S (at $T = 600$–700° and $P = 2000$–3000 atm.) (^{1}).

For the X-ray investigation, single-crystal specimens synthesized under hydrothermal conditions from a charge with a ratio

Table 1

Atom	Coordinates	Model corresponding to the densest packing	Experimental data	Δ
Ca_I	x	0	0	0
Ca_I	y	0	0	0
Ca_I	z	0	0	0
Ca_{II}	x	$^3/_{10} = 0,300$	0,331	0,031
Ca_{II}	y	0	0,001	0,001
Ca_{II}	z	$^1/_5 = 0,200$	0,188	0,012
Ca_{III}	x	$^1/_{10} = 0,100$	0,119	0,019
Ca_{III}	y	0	0,006	0,006
Ca_{III}	z	$^2/_5 = 0,400$	0,418	0,018
Si	x	$^2/_{15} = 0,13(3)$	0,146	0,013
Si	y	$^3/_8 = 0,375$	0,429	0,054
Si	z	$^1/_5 = 0,200$	0,201	0,001
O_1	x	$-^1/_{30} = -0,03(3)$	0,018	0,051
O_1	y	$^1/_4 = 0,250$	0,302	0,052
O_1	z	$^1/_5 = 0,200$	0,206	0,006
O_2	x	$^1/_6 = 0,16(6)$	0,170	0,003
O_2	y	$^1/_4 = 0,250$	0,303	0,053

Atom	Coordinates	Model corresponding to the densest packing	Experimental data	Δ
O_2	z	0	0,048	0,048
O_3	x	$^{4}/_{15} = 0,26(6)$	0,253	0,014
O_3	y	$^{1}/_{4} = 0,250$	0,306	0,056
O_3	z	$^{2}/_{5} = 0,400$	0,349	0,051
O_4	x	$^{2}/_{15} = 0,13(3)$	0,147	0,014
O_4	y	$^{3}/_{4} = 0,750$	0,739	0,011
O_4	z	$^{1}/_{5} = 0,200$	0,202	0,002
O_5 (OH)	x	$^{13}/_{30} = 0,44(3)$	0,441	0,002
O_5 (OH)	y	$^{3}/_{4} = 0,750$	0,731	0,019
O_5 (OH)	z	$^{2}/_{5} = 0,400$	0,395	0,005

$CaO/SiO_2 = 2:1$ and $3:1$ were used, in the temperature range from 400 to 700° and pressures of 2000-3000 atm., and at NaOH concentrations of ~ 10 and 50% (^{2}). The monoclinic cell: $a = 11.42$; $b = 5.05$; $c = 8.94$ Å; $\beta = 109°18'$ contains two units of $2Ca_2SiO_4 \cdot Ca(OH)_2$. The holohedral Fedorov group is determined unambiguously from extinctions: $C_{2h}^5 = P2_1/a$.

The solution of the structure of calcium chondrodite was of interest also because, up to now, there has been no direct structural solution of the classical

Mg-chondrodite, one of the members of the series of olivine derivatives—from norbergite to clinohumite—$Ca(OH)_2 \cdot nCa_2SiO_4$ (^{3}).

The experimental material—500 nonzero reflections $h0l - h4l$ and $0kl$ (Mo K_α radiation, $\max \sin\vartheta/\lambda = 0.9$ Å^{-1}, KFOR camera)—made it possible to construct the three-dimensional Patterson function $P(uvw)$. Analysis of interaction peaks according to S. V. Borisov (^{4}) and of bond peaks according to Harker (^{5}) revealed the heavy Ca and medium Si atoms. The lighter O and $(OH)^{1-}$ were fixed at the stage of electron-density synthesis $\rho(xyz)$ at $R_{hkl} = 0.15$. Refinement by the least-squares method with a common isotropic thermal correction

$$B = 0.16 \text{ Å}^{-1}$$

reduced R_{hkl} to 0.12. The fixed coordinates of the basis atoms are given in Table 1; the interatomic distances calculated from them are shown in Fig. 1 and summarized in Table 2. The coordination polyhedra about all three independent Ca atoms proved to be octahedra: atom Ca_I is at a center of symmetry, while Ca_{II} and Ca_{III} occupy general positions. The distances Ca_I—O are almost identical: $2.34_5(2)$, $2.39_4(2)$, and $2.41_0(2)$ Å. Of the twelve edges of the elongated Ca_I octahedron, two, common with the Si tetrahedron, are shortened to 2.57 Å;

Fig. 1. Ca-chondrodite. Basic structural unit—a complex of five Ca octahedra. The edge lengths of the octahedra are indicated in Å

Figure 1: Fig. 1. Ca-chondrodite. Basic structural unit—a complex of five Ca octahedra. The edge lengths of the octahedra are indicated in Å

four edges are appreciably longer: 3.54(2) and 3.51(2) Å; and six intermediate ones are close to one another: 3.21(4) and 3.24(2) Å. For the two other crystallographically independent Ca atoms, the Ca—O distances remain within narrow limits: Ca_{II}—O = 2.31_1-2.51_8 Å and Ca_{III}—O = 2.29_8-2.46_8. Their octahedra are looser, with a considerable scatter in edge lengths:

Fig. 1. Ca-chondrodite. Basic structural unit—a complex of five Ca octahedra. The edge lengths of the octahedra are indicated in Å

O—O = 2.54_7-3.79_0 Å and 2.55_7-3.76_0 Å, respectively, for the Ca_{II} and Ca_{III} polyhedra. In these octahedra as well there is one shortened edge each, common with the Si tetrahedron: 2.54_7 and 2.55_7 Å. The Si tetrahedron is sufficiently regular, with distances Si—O = 1.56_6-1.61_1 Å and O—O = 2.54_7-2.66_0 Å.

In the structure of Ca-chondrodite the large Ca cation is represented in a sixfold coordination that is comparatively rare for it (cf. Ca(OH)_2, CaO, CaCO_3, etc.), which leads to the characteristic geometrical compromise already noted above between the short edges (shared with the Si tetrahedron) and the long edges of the octahedron. The octahedral environment of Ca makes it possible to describe the structure of the chondrodite-like cement compound within the framework of closest anion packing (analogously to Mg-chondrodite and to the two series headed by olivine and γ-C_2S).

The dimensions of the real cell deviate only slightly from the ideal ones (closest packing of O anions with $d = 1$): $a_0 = 2\sqrt{3}$, $b_0 = 2\sqrt{2}/\sqrt{3}$, $c_0 = \sqrt{7}$; $\beta = 109°05'$, $a_0 : b_0 : c_0 = 2.12 : 1 : 1.62$; $a = 11.42$, $b = 5.05$, $c = 8.94$; $\beta = 109°18'$, $a : b : c = 2.23 : 1 : 1.77$, and the deviations of the coordinates of all atoms from the ideal ones are likewise small (Table 1).

But the formal introduction into the structure of ideal Ca-olivine ($\equiv \gamma$-C_2S)

an additional chain (a Ca atom plus two OH) from the portlandite "interlayer" (cf. (3)) leads to a specification of the principal structural increment—it becomes (Fig. 1) a complex of five octahedra, a "butterfly" according to V. V. Bakakin (6). In contrast to its Ca—Mg progenitor (the structure of bultfonteinite (6)), in Ca-chondrodite the "butterfly" is composed of homogeneous cations Ca: the "body" —the core of the butterfly—is formed by a distorted (but centrosymmetric) Ca_{I}-octahedron, and the wings by large Ca_{II}- and Ca_{III}-octahedra in general positions. The common edges of the Ca-octahedra of one butterfly delimit tetrahedral voids, which are closed by the bases of two Si-tetrahedra. Only in the central (in the complex) Ca-octahedron are the vertices represented by O atoms (from Si-tetrahedra). In the remaining vertices of the four Ca-octahedra there

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are OH groups, and it is precisely through them that the butterflies (translationally identical along the *c* axis) are joined into a single zigzag chain and with the butterflies of the analogous chain lying above (below), which arises from the original one by the glide plane *a* (Fig. 2).

Fig. 2. Ca-chondrodite. Projection of the structure onto the plane (010). Zigzag chains extending along the *c* axis are emphasized. Shading marks a chain lying $1/2\,b$ lower (higher) than the original one.

Table 2

Interatomic distances (in Å) in the structure $Ca_5[SiO_4]_2(OH)_2$

	O_1	O_2	O_3	O_4	O_5
Ca_I	2.345	2.394		2.410	
Ca_{II}	2.319	2.4012.325	2.473	2.518	2.311
Ca_{III}	2.391		2.3682.337	2.468	2.3142.298
Si	1.609	1.611	1.599	1.566	

In Ca-chondrodite the portlandite layer is a wall, parallel to the plane (001), of OH particles and Ca semioctahedra (cf. (3)), passing through the junctions of the butterflies at both levels of the cell. The absence of an "integral" portlandite layer OH–Ca–OH somewhat lowers the cementing properties of calcium chondrodite in comparison with the hydrosilicates of the tobermorite-gillebrandite series.

Moscow State University
named after M. V. Lomonosov

Institute of Crystallography
Academy of Sciences of the USSR
Moscow

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