

GEOCHEMISTRY

Crystal Structure of Fukalite Dimorph $\text{Ca}_4[\text{Si}_2\text{O}_6](\text{CO}_3)(\text{OH})_2$ from the Gumeshevsk Deposit, the Urals

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Presented by Academician L.N. Kogarko July 27, 2005

Received June 2, 2005

Calcium carbonate–silicate $\text{Ca}_4[\text{Si}_2\text{O}_6](\text{CO}_3)(\text{OH},\text{F})_2$ with $\text{Ca} : \text{Si} = 2 : 1$ and both hydroxyl and carbonate groups was found in spurrite and gehlenite–spurrite apocalcareous metasomatites in Japan and named fukalite after the type locality Fuka [1]. According to [1], this mineral is related to the hydrothermal decomposition of spurrite and is associated with a wide range of calcium silicates. The authors of [1] did not determine the structure of fukalite. They reported only on parameters of the orthorhombic unit cell (based on the Weissenberg photographs) and precession data (based on powder XRD data) as $a = 5.48(1)$, $b = 3.78(1)$, and $c = 23.42(3)$ Å. They also indicated $Bm2_1b$, $B2mb$, and $Bmmb$ as the possible space groups.

A fukalite-type mineral was later found in the Urals as colorless long-prismatic and acicular crystals (up to 0.3 mm long) with perfect cleavage parallel to $\{100\}$ [2]. The Uralian mineral is similar to fukalite in terms of SAED data, Debyeograms, and chemical composition (the microprobe analysis detected Ca and Si, but F was not found). The presence of hydroxyl and carbonate groups was found by IR spectroscopy. We performed the X-ray study of prismatic monocrystal of the fukalite-type mineral taken from hydroxyllestadite metasomatite at the Gumeshevsk skarn–copper porphyry deposit in the Urals.*

Parameters of the orthorhombic unit cell were determined and refined from 25 reflections on a single crystal diffractometer. Unlike data in [1], period b seemed to be doubled. The inferred doubling of period a was

not confirmed experimentally. Characteristics of the crystal and experimental data are presented in Table 1.

The structure was determined by direct methods using an AREN program [3] in the framework of space group $P2_12_12_1$. The five-atom fragment found was used in the “phase correction” procedure realized with an AREN program. This procedure made it possible to model the entire structure (including C atoms) from a series of modified Fourier syntheses. Occupancy and thermal parameters of the atoms were refined to an R-factor of 8%. The thermal parameters in sites of Si and two linked oxygen atoms (9, 10) yielded overestimated values. In addition, these oxygen atoms multiplied by a short translation along a were twice incorporated in the

Table 1. Characteristics of crystal and experiment

Chemical formula of the mineral	$\text{Ca}_4[\text{Si}_2\text{O}_6](\text{CO}_3)(\text{OH})_2$
a , Å	3.786(1)
b , Å	10.916(2)
c , Å	23.379(6)
V , Å ³	966.2
Space group; Z	$P2_12_12_1$; 4
Radiation; λ , Å	$\text{MoK}\alpha$; 0.71073
Calculated density, g/cm ³	2.78
Crystal size, mm	$0.1 \times 0.15 \times 0.25$
Diffractometer	ENRAF-NONIUS
h, k, l limits	$-6 < h < 6$ $-17 < k < 17$ $0 < l < 37$
$\sin \theta / \lambda$	< 0.81
Total number of reflections	$3749 F > 3\sigma(F)$
Number of independent reflections	$1272 F > 3\sigma(F)$
R-factor of averaging of the equivalent reflections	0.044
R-factor of anisotropic refinement	0.063
Refinement program	AREN [3]
Program for absorption correction	DIFABS [4]

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* The sample was found by A.I. Grabezhev and kindly given to us for study.

Table 2. Coordinates of atoms, equivalent (B_{equiv}) parameters of atomic displacements, and occupancies (q) of sites

Atom	x/a	y/b	z/c	q	$B_{\text{equiv}}, \text{\AA}^2$
Ca(1)	0.2519(10)	0.3742(1)	0.4562(1)	1	0.55(3)
Ca(2)	0.2566(12)	0.0553(1)	0.6907(1)	1	0.74(4)
Ca(3)	0.2493(12)	0.3082(1)	0.1932(1)	1	0.79(4)
Ca(4)	0.2471(10)	0.1241(1)	0.9545(1)	1	0.58(3)
Si(1)	0.3275(10)	0.3734(5)	0.7216(1)	0.49(1)	0.51(6)*
Si(2)	0.1787(8)	0.3782(3)	0.5875(1)	0.52(2)	0.12(6)*
Si(3)	0.1533(12)	0.3756(6)	0.7137(1)	0.49(1)	0.54(5)
Si(4)	0.3384(16)	0.3712(7)	0.5839(2)	0.48(2)	1.3(1)
C	0.281(3)	0.1231(7)	0.0813(2)	1	0.29(8)
O(1)	0.262(4)	0.2550(4)	0.5515(2)	1	0.6(1)
O(2)	0.252(4)	0.5084(5)	0.0462(2)	1	0.6(1)
O(3)	0.248(5)	0.2284(5)	0.0523(2)	1	0.8(1)
O(4)	0.235(4)	0.0242(5)	0.0506(2)	1	0.9(1)
O(5)	0.211(3)	0.1281(7)	0.1351(2)	1	0.8(1)
O(6)	0.188(3)	0.4993(6)	0.2427(3)	1	1.5(2)
O(7)	0.237(9)	0.2461(6)	0.7413(2)	1	3.2(2)
O(8)	0.359(2)	0.3768(8)	0.6483(2)	1	1.1(1)
O(9)	0.238(7)	0.125(1)	0.2582(4)	0.53(2)	0.9(2)
O(10)	0.263(7)	0.123(1)	0.3980(4)	0.46(2)	0.9(3)
OH(1)	0.259(4)	0.1256(6)	0.8565(2)	1	0.9(1)
OH(2)	0.242(4)	0.3782(6)	0.3571(2)	1	0.8(1)
H(1)	0.255	0.058	0.849	1	3.0*
H(2)	0.243	0.314	0.342	1	3.0*

* Isotropic thermal parameters.

Si surrounding at a distance of 1.6 and 2.3 Å. Thus, the Si coordination number was increased to 5. The difference electron density map revealed additional peaks at a distance of 0.6–0.7 Å from both Si atoms (1, 2). The refinement of four independent Si sites of equal occupancy ~0.5 and O(9, 10) sites with the same occupancy

decreased the R factor to 6.3% and normalized thermal parameters for these atoms. We suppose that the locations of peaks determined by the difference synthesis may be identified as H atoms of hydroxyl groups OH(1) and OH(2). Coordinates and fixed thermal parameters of these atoms were not refined.

Coordinates of the atoms and characteristics of coordination polyhedrons are listed in Tables 2 and 3. The respective parameters of hydrogen bonds are given in Table 4.

The recorded splitting of Si sites eliminated the excess (remote) oxygen atoms and shifted them over a reasonable distance to the additional Si(3, 4) tetrahedrons. This made it possible to consider the statistical model of Si tetrahedral chains of two orientations shifted by $a/2$ relative to each other. Figure 1 shows one of the statistically possible distributions of chains of two orientations over the unit cell.

Silica–oxygen chains are strongly corrugated and can be ascribed to the batisite type with four-tetrahedral chain. However, the identity period of batisite along the chain is ~8 Å, whereas the period of fukalite-type mineral is two times less owing to the statistical distribution

Table 3. Characteristics of coordination polyhedrons

Site	CN	Cation–anion distance, Å		
		min	max	aver
Ca(1)	7	2.316(4)	2.580(5)	2.441
Ca(2)	7	2.27(1)	2.72(1)	2.43
Ca(3)	7	2.30(1)	2.54(2)	2.42
Ca(4)	7	2.292(5)	2.552(5)	2.437
Si(1)	4	1.48(1)	1.72(1)	1.58
Si(2)	4	1.58(1)	1.62(1)	1.60
Si(3)	4	1.58(1)	1.71(1)	1.65
Si(4)	4	1.51(1)	1.66(2)	1.57
C	3	1.28(1)	1.34(1)	1.31

of chains of different orientations over the crystal. The batisite chains are also typical of the haradaite structure. However, although chains of all three minerals (batisite, haradaite, and fukalite) consist of diorthogroups, they differ in terms of the turn of apical vertexes of their tetrahedrons and the reciprocal turns of tetrahedrons of diorthogroups. Vibrations of the batisite-type chain Si_4O_{12} are seen in the IR spectrum of the studied mineral as series of well-resolved bands within Si–O stretching vibrations ($880\text{--}1140\text{ cm}^{-1}$), Si–O–Si bending vibrations ($412\text{--}538\text{ cm}^{-1}$), as well as a band of mixed vibrations at 705 cm^{-1} . The IR characteristics of the same vibrations in batisite are as follows: $880\text{--}1160$, $407\text{--}525$, and 708 cm^{-1} .

The CO_3 group found in the structure is distorted, with unequal C–O distances varying within $1.29\text{--}1.34\text{ \AA}$. This is recorded in the IR spectrum as a strong splitting of the degenerated band of C–O stretching vibrations into components at 1523 (with a shoulder at 1540) and 1404 cm^{-1} . The absence of a local third-order axis for the CO_3 group eliminates the prohibition for absorption caused by completely symmetrical stretching vibrations of the carbonate anion (narrow band at 1037 cm^{-1}).

The OH groups were distinguished among anions on the basis of valence balance. Their presence is also supported by the localization of H atoms. The hydrogen bonds are bifurcated, and bridging oxygens in Si–O–Si are acceptors. The IR spectrum of the mineral contains

Table 4. Geometric characteristics of hydrogen bonds

$D\cdots H\cdots A$	$D\cdots H$, Å	$H\cdots A$, Å	$D\cdots A$, Å	$D\cdots H\cdots A$, degrees
$\text{OH}(1)\text{--H}(1)\cdots\text{O}(10)$	0.76	2.28	2.88	137
$\cdots\text{O}(8)$		2.46	3.07	140
$\text{OH}(2)\text{--H}(2)\cdots\text{O}(10')$	0.79	2.46	2.94	121
$\cdots\text{O}(8')$		2.55	3.14	133

Note: (D) Donor; (A) acceptor of hydrogen bonds.

doublet (3587 , 3572 cm^{-1}) that is ascribed to the stretching vibrations of two strongly differing OH groups with similar power spectrums, which are linked to Ca rather than to Si. Judging from the positions and small widths of the indicated bands, OH groups do not form strong hydrogen bonds, presumably, due to the bifurcation and significant deviation of the D–H–A angle from 180° (Table 4). This fact, in particular, facilitates the substitution of hydroxyl groups by F with respect to energy, as in pure fukalite from Japan.

Four crystallographically independent Ca atoms form seven-vertex hedrons, which include O atoms from Si tetrahedrons and CO_3 groups and OH groups unbound with these polyhedrons. Ca(1) and Ca(4) are surrounded by one OH group and two oxygen atoms ascribed to the CO_3 group. Together with four oxygen atoms, they make up trigonal prisms with an additional

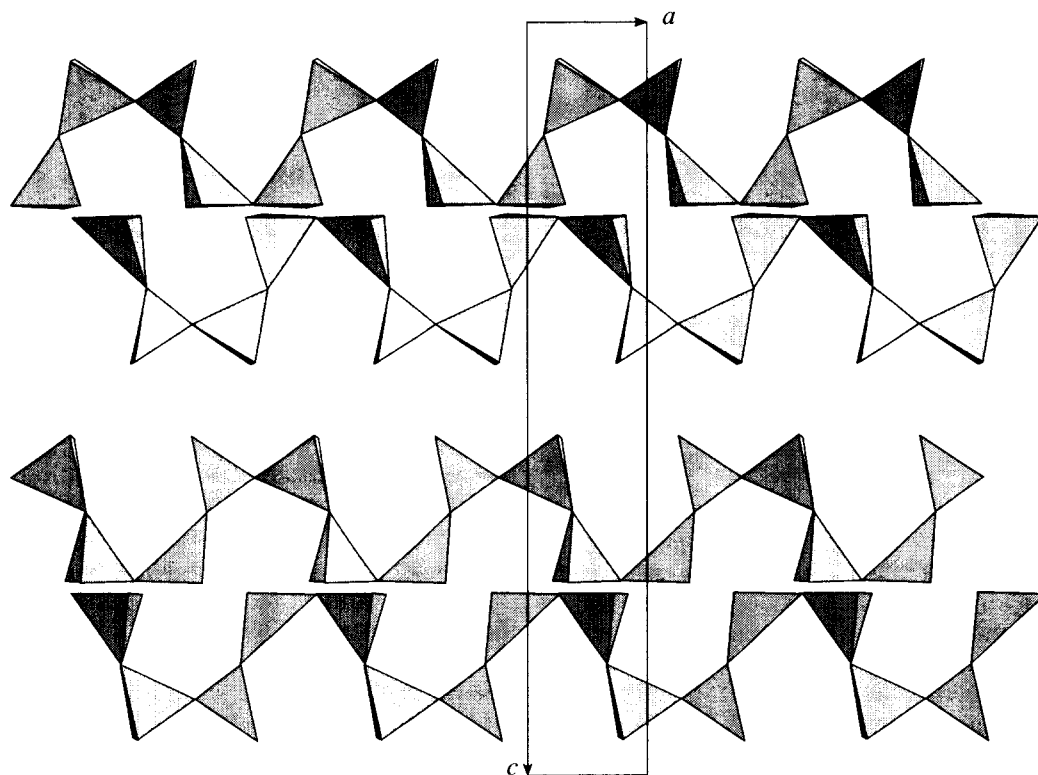


Fig. 1. Silica–oxygen chains of two orientations extended along short translation a .

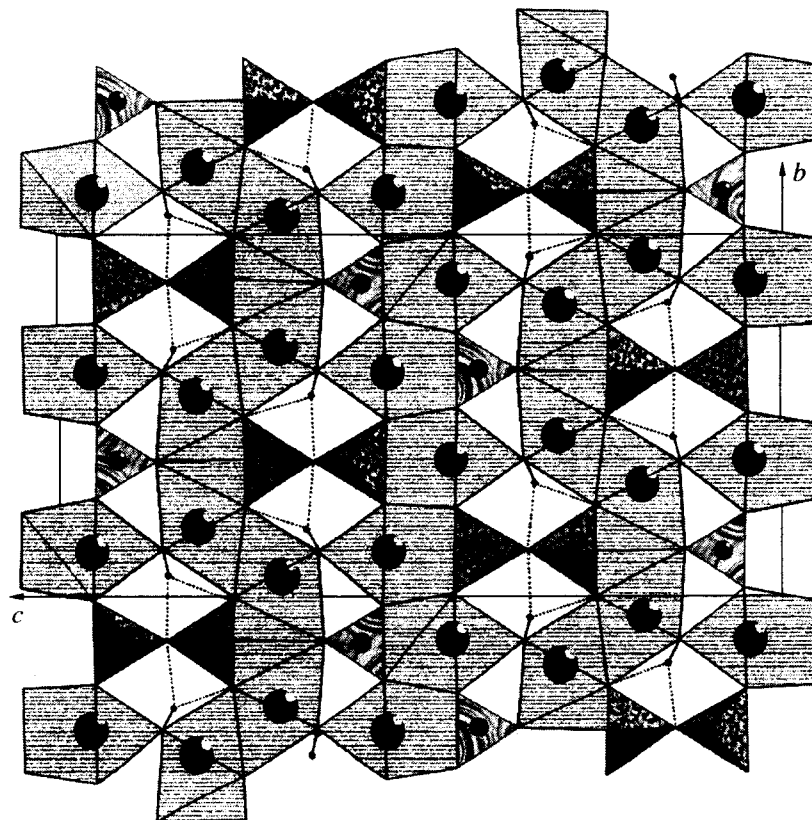


Fig. 2. Projection of the structure on the (100) plane. Shading shows layers (faces normal to the long period c are seen) of Ca seven-hedrons. Si-O chains (faces as diorthogroups) are distinguished by black. Ca cations are shown by large spheres; C, by medium spheres; and H, by small spheres. Dashed line shows bifurcated bonds of H atoms.

pyramid on one of the quadrangular sides. Seven-hedrons around Ca(2) and Ca(3) include two OH groups and one O atom from the CO_3 group. Thus, they represent distorted octahedrons with a centered triangular face. All Ca polyhedrons make up edge-bounded columns along the short period. Columns of Ca(1) and Ca(4) polyhedrons are linked by common edges into a weakly corrugated layer. Columns of Ca(2) and Ca(3) are also linked by edges, forming a strongly corrugated tilleyite-type layer (wall). Since the O(9) atom is statistically incorporated in Ca(2) and Ca(3) seven-hedrons, both polyhedrons in half of the unit cells are transformed into octahedrons, which are linked by vertexes, forming tilleyite walls also linked with Si tetrahedrons by vertexes.

The base of the crystal structure of the studied mineral consists of Ca,O walls of two types, which are linked by OH vertexes of Ca polyhedrons into a three-dimensional framework with channels along the short direction. Wide hexagonal channels contain Si chains (faces distinguished by black are seen in Fig. 2), while trapeziform narrow channels host CO_3 groups. Edges of the large Ca polyhedrons, common with C-triangles, are shortened within 2.23–2.28 Å. Three-dimensional octahedral frameworks are, in particular, typical of

some diorthosilicate structures (tilleyite, cuspidine, and seidozerite).

The studied calcium silicate is ascribed to C-S-H compounds [5], which are the major components of Portland cement. They differ in the composition (Ca/Si ratio and presence of H_2O , OH and/or CO_3 groups) and shape of Si radicals. Their structures are based on the layers (walls) of Ca polyhedrons. However, Ca polyhedrons forming these walls differ in shape (octahedrons, trigonal prisms, or seven-hedrons), while walls are corrugated to a variable extent. In particular, strongly corrugated tilleyite-type walls were found in structures of tobermorite [6], jennite [7], and jaffeite [8]. The layers are linked by different Si radicals, diorthogroups, or chains, which often show disordering, for example, as in wollastonite chains of tobermorite and jennite.

Thus, the structure of the first studied mineral contains four different modules, two different Ca,O layers, Si,O chains, and CO_3 groups. The chains extend along the short direction, while the layers are extended along the middle period. The structure described above cannot be realized in the framework of the model with a period of $b/2$, since pseudotranslation is observed only in one layer of the first type, whereas corrugated layers, chains, and CO_3 groups are distributed in accordance

with the true b translation. Although the fukalite structure is unknown, the structural similarity of these minerals is hardly possible within the framework of a unit cell with a period of $b/2$. Thus, we believe that the studied mineral is a fukalite dimorph.

In addition, unlike other calcium silicates, the fukalite-type mineral is characterized by the first established orientational disordering of the batisite-type Si-O chains, which are statistically distributed over unit cells with the preservation of the minimum period.

ACKNOWLEDGMENTS

We are grateful to I.A. Verin for the performance of diffraction study, as well as to A.I. Grabezhev, V.T. Dubinchik, and N.N. Pertsev for the help in primary study of the mineral.

This study was supported by the Russian Foundation for Basic Research (project no. 04-05-64192) and the Foundation of the President of the Russian Federa-

tion for the Support of Leading Scientific Schools (project no. NSh-1087.2003.5).

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