

GEOCHEMISTRY

Crystal Structure of Shibkovite

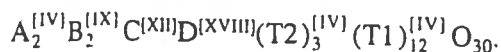
E. V. Sokolova*, V. B. Rybakov**, and L. A. Pautov*

Presented by Academician V.A. Zharikov January 19, 1998

Received January 26, 1998

(1) Shibkovite, $K_{2.26}Na_{0.34}(Ca,Mn,Na)_2Zn_3[Si_{12}O_{30}]$, is a new representative of the milarite group. It has been approved as a new mineral species by the Commission on New Minerals and Mineral Names of the International Mineralogical Association September 4, 1997.

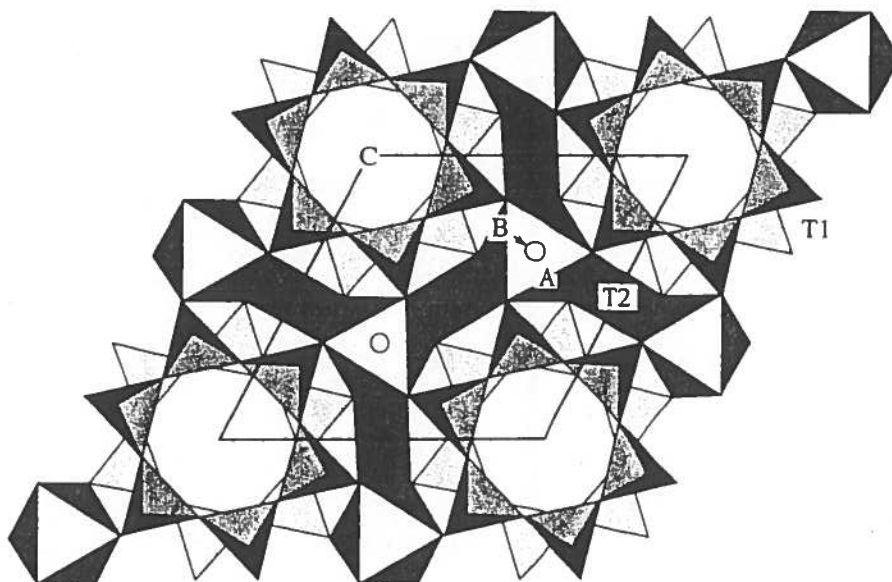
Shibkovite, a mineral that contains the isolated radical $[Si_{12}O_{30}]$ as double six-membered rings of the Si–O tetrahedra, is the sixth mineral of the milarite group. It was reported from the Dara-i-Pioz glacier moraine. The milarite structural type comprises 17 silicate minerals with the double six-membered rings $[Si_{12}O_{30}]$ and the following general formula [1]:



According to [2], a wide range of isomorphous substitutions is registered in sites A (Al, Fe^{3+} , Sn^{4+} , Mg, Zr, Fe^{2+} , Ca, Na, Y, REE), B (Na, H_2O , □), C (K, Na, Ba, □), D (□), T2 (Li, Be, B, Mg, Al, Si, Mn^{2+} , Zn), and T1

(Si, Al). These substitutions promote the discovery of new species and the increase of the number of the milarite group minerals. Recently, we studied crystal structures of two new minerals of this group from the Dara-i-Pioz Massif: dusmatovite and turkestanite [3, 4]. In spite of the fact that the turkestanite structure contains double four-membered rings in contrast to six-membered ones, some authors consider this mineral as a species related to the milarite structural type [2].

(2) *Sample description.* Shibkovite forms isometric grains 0.01–0.50 mm in size in quartz–microcline–reedmergerite rock with aegirine, eudialyte, pyrochlore, polyolithionite, sogdianite, albite, pectolite, turkestanite, and sphalerite. Shibkovite is optically uniaxial and positive; $n_0 = 1.561(2)$, $n_z = 1.563(2)$. A microprobe analysis of shibkovite fulfilled using a JCA-733 microprobe (experimental conditions: electron-beam diameter 10 μm ; accelerating voltage 20 kV;



Crystal structure of shibkovite.

* Geological Faculty, Moscow State University (MGU), Vorob'evy gory, Moscow, 119899 Russia

** Mineralogical Museum, Ilmeny State Nature Reserve, Miass, Chelyabinsk oblast, 456301 Russia

Table 1. Final atomic coordinates and equivalent temperature factors (\AA^2) of shibkovite

A	x	1/3	T2	x	0
	y	2/3		y	1/2
	z	1/4		z	1/4
	B_{eq}	0.81(5)		B_{eq}	0.79(4)
B	x	1/3	O1	x	0.1098(4)
	y	2/3		y	0.3676(4)
	z	0		z	0
	B_{eq}	1.39(8)		B_{eq}	1.2(1)
C	x	0	O2	x	0.2045(3)
	y	0		y	0.2707(2)
	z	1/4		z	0.1393(1)
	B_{eq}	1.17(7)		B_{eq}	1.06(7)
T1	x	0.0980(1)	O3	x	0.1403(2)
	y	0.3358(1)		y	0.4831(2)
	z	0.1121(0)		z	0.1674(1)
	B_{eq}	0.40(4)		B_{eq}	0.81(6)

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

beam current 2.7×10^{-8} A; standards: osumilite for Si, K, and Fe; scapolite for Na and Ca; augite for Mg and Al; ilmenite for Mn; and willemite for Zn) has yielded the following composition (wt %): SiO_2 61.00, Al_2O_3 0.05, FeO 0.13, CaO 5.99, Na_2O 0.98, K_2O 8.96, MnO 2.41, ZnO 20.96, $\Sigma = 100.48$; $\rho_{\text{exp}} = 2.89(2)$ g/cm³. A preliminary powder X-ray diffraction analysis of the mineral revealed the following unit cell parameters: $a = 10.505(1)$ and $c = 14.185(3)$ \AA . The X-ray investigation of the mineral, along with its optical study and data of the chemical analysis, have made it possible to assign shibkovite to the milarite structural type.

Determination of the crystal structure of shibkovite.

Unit cell parameters of shibkovite based on 20 reflections (within an area of $24.05^\circ < \theta < 30.00^\circ$) determined with a single-crystal diffractometer CAD-4, are as follows: $a = 10.502(1)$, $c = 14.184(2)$ \AA , and $V_0 = 1354.8(7)$ \AA^3 . The experimental set of intensities of 356 independent nonzero ($I \geq 1.96\sigma(I)$) reflections has been obtained from a single crystal $0.02 \times 0.03 \times 0.01$ mm. The experimental conditions were as follows: $\lambda\text{MoK}\alpha$ radiation; graphite monochromator; $\omega/2\theta$ investigation technique; $\max \sin\theta/\lambda \leq 0.58$ \AA^{-1} . A North-Phillips' empirical correction for absorption [5] was introduced into the intensity set. The intensity array was initially processed using the SDP software [6]; all other calculations were fulfilled using the AREN program [7]. The shibkovite structure was refined for the space group $P6/mcc$. In the course of this refinement, dusmatovite coordinates [3] were taken as starting ones. We refined the occupancies of sites by various atoms: site A (c. n. = 6) by Ca, Mn, and Na; site

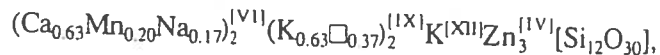
Table 2. Selected interatomic distances (\AA) and angles (degrees) in shibkovite

A-O3	$\times 6$	2.300(2)	T2-O3	$\times 4$	1.959(2)
O3-O3a	$\times 3$	2.973(3)	O3-O3a	$\times 2$	2.973(3)
O3-O3b	$\times 3$	3.164(3)	O3-O3e	$\times 2$	3.139(4)
O3-O3c	$\times 6$	3.428(3)	O3-O3f	$\times 2$	3.465(3)
(O-O)A		3.248	(O-O)T2		3.192
O3AO3a	$\times 3$	80.52°(8)	O3T2O3a	$\times 2$	98.70°(7)
O3AO3b	$\times 3$	86.93°(6)	O3T2O3e	$\times 2$	106.5°(2)
O3AO3c	$\times 6$	96.3°(1)	O3T2O3f	$\times 2$	124.36°(7)
(OAO)		90.0°	(OT2O)		109.9°
B-O1	$\times 3$	2.829(4)			
B-O3	$\times 6$	3.090(2)			
(B-O)		3.003			
C-O2	$\times 12$	3.009(2)			
T1-O1		1.616(6)	O1T1O2		108.8°(2)
T1-O2		1.622(3)	O1T1O2d		110.3°(2)
T1-O2d		1.626(1)	O1T1O3		109.2°(1)
T1-O3		1.586(2)	O2T1O2d		104.3°(1)
(T1-O)		1.613	O2T1O3		112.1°(2)
O1-O2		2.634(4)	O2dT1O3		111.7°(1)
O1-O2d		2.661(2)	(OT1O)		109.4°
O1-O3		2.611(3)			
O2-O2d		2.566(3)			
O2-O3		2.663(5)			
O2d-O3		2.660(3)			
(O-O)T1		2.633			

$$a = x, 1 - y + x, 1/2 - z; b = y - x, y, 1/2 - z; c = 1 - y, 1 - y + x, z; d = x - y, x, z; e = -x, 1 - y, z; f = -x, y - x, 1/2 - z.$$

B (c. n. = 9) by K and Na, simultaneously; and site C (c. n. = 12) by K.

(3) The single-crystal investigation of shibkovite has confirmed its milarite structural type. The crystal chemical formula of the mineral is as follows:



$z = 2$; sp. gr. $P6/mcc$, and $\rho_{\text{calc}} = 2.90$ g/cm³. The minimum R factor and the most adequate values of the temperature factors corresponded to the following occupancy of the mixed sites: A($\text{Ca}_{0.63}\text{Mn}_{0.20}\text{Na}_{0.17}$) and B($\text{K}_{0.63}\square_{0.37}$). The coordinates, equivalent temperature factors of the atoms, and selected interatomic distances correspond to the R factor = 2.49% (Tables 1, 2). A characteristic fragment of the shibkovite structure is the double six-membered rings $[\text{Si}_{12}\text{O}_{30}]$ (figure). The Si-O tetrahedron (T1) is characterized by the following angles and distances: $\angle\text{OT1O} = 108.8^\circ(2) - 112.1^\circ(2)$, $d(\text{T1-O})_{\text{cp}} = 1.613$ \AA . The Si-O3 distance, whose value is determined by the total sum of valences of the nearest

cations A, T1, and T2, is reduced to 1.586(2) Å, as in structures of other milarite group minerals. Within large cavities between the two $[\text{Si}_{12}\text{O}_{30}]$ rings, atoms of K are situated (C site, c. n. = 12). The T2 tetrahedron ($\text{Zn}-\text{O} = 1.959$ Å) is irregular, with angles O-T2-O ranging from 98.70° to 124.36° (Table 2). According to geometrical characteristics, the tetrahedron is well comparable with the (Zn,Li)-tetrahedron in the dusmatovite structure [3]. The A octahedron is predominantly occupied by Ca atoms and represents a regular polyhedron, $\text{A}-\text{O}3 = 2.300(2)$ Å. The B site (c. n. = 9) is exclusively occupied by K atoms (the occupation is only 50%).

(4) Thus, shibkovite with the formula $\text{K}(\text{K}, \square)_2(\text{Ca}, \text{Mn}, \text{Na})_2\text{Zn}_3[\text{Si}_{12}\text{O}_{30}]$, $z = 2$, and sp. gr. *P6/mcc*, is the third (after armenite and milarite proper) mineral in the milarite group, with a predominance of Ca at the A octahedral site and the second (after dusmatovite) mineral with a predominance of Zn at the T2 site. The peculiar combination of the predominant cations at these two sites in the crystal structure has made it possible to distinguish shibkovite as an individual mineral species.

ACKNOWLEDGMENTS

We are grateful to D.I. Belakovskii for access to the MINSPEC data base [8]. This work was supported by the Russian Foundation for Basic Research, project nos. 97-05-64000 and 97-05-65923.

REFERENCES

1. Forbes, W.C., Baur, W.H., and Khan, A.A., *Am. Miner.*, 1972, vol. 57, pp. 463-472.
2. Hawthorne, F.C., Kimata, M., Cerny, P., *et al.*, *Am. Miner.*, 1991, vol. 76, pp. 1836-1856.
3. Sokolova, E.V. and Pautov, L.A., *Dokl. Akad. Nauk*, 1995, vol. 344, no. 5, pp. 607-610.
4. Kabalov, Yu.K., Sokolova, E.V., Pautov, L.A., and Shnaider, Yu., *Kristallografiya*, 1998, vol. 42.
5. North, A.C.T., Phillips, D.C., and Mathews, F.S., *Acta Crystallogr.*, 1968, vol. 24, p. 351.
6. *SDP-USER'S Guide*, Delft: Enraf-Nonius, 1985.
7. Andrianov, V.I., *Kristallografiya*, 1987, vol. 32, pp. 228-231.
8. *Minspec. Vers. 3.2, 1994-1997*, Belakovskii, D.I., Ed., 1997.