=== **GEOCHEMISTRY** ===

Refinement of Miserite Crystal Structure $(K_{1.29}\square_{0.21})[Ca_{5.51}M^{3+}_{0.49}](Si_6(O,OH)_{15})(Si_2O_7)(F,OH)_2 \cdot 0.25H_2O$ (M = Y, REE, Fe, Ti, Mn, Mg, Na) from the Dara-i-Pioz Occurrence, Pamir, Tajikistan
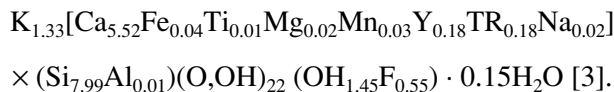
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Miserite is an infrequent alkali Ca-silicate with two types of silicate radicals. The crystal structure of this mineral from carbonatites of the Kipawa Lake deposit, Quebec, Canada, was determined by Scott [1]. This work, based on the photo method, had until recently remained the only structural study of miserite. Some of its results require refinement.

Electron microprobe analysis yielded the following chemical composition (wt %) [2]: SiO_2 50.61, TiO_2 0.16, Al_2O_3 0.05, FeO 0.32, MgO 0.08, CaO 32.66, MnO 0.24, Na_2O 0.06, K_2O 6.59, Y_2O_3 2.11, La_2O_3 0.09, Ce_2O_3 1.06, Pr_2O_3 0.66, Nd_2O_3 1.36, total (REE + Y)$_2O_3$ 5.28, F 1.1, L.O.I. 6.8, H_2O 5.7, $-O=F_2$ 0.46, total 102.85. This composition is close to the miserite composition in [1]. The F and water contents were determined in the Mekhanobr-Analitik Laboratory. Microprobe analyses calculated on the basis of 8 (Si + Al) cations yielded the following crystallochemical formula:

$$K_{1.33}[Ca_{5.52}Fe_{0.04}Ti_{0.01}Mg_{0.02}Mn_{0.03}Y_{0.18}TR_{0.18}Na_{0.02}]$$

$$\times (Si_{7.99}Al_{0.01})(O,OH)_{22}(OH_{1.45}F_{0.55}) \cdot 0.15H_2O \,[3].$$

Chemically, miserite is close to the alkali Ca-silicates canasite [4] and frankamenite [5]. However, miserite contains trivalent cations (mainly REE and Y). The mineral contains water and appreciable K (>1 f.u.).

Miserite structure was refined on the basis of measurements of 2589 X-ray intensity made in a sample $0.08 \times 0.1 \times 0.15$ mm in size using an automatic X-ray single crystal Syntex P2$_1$ diffractometer (2θ_{max} = 70°, MoK_α radiation, graphite monochromator, and scanning rate 2°–30°/min). The unit cell parameters are as follows: $a = 10.120(3)$, $b = 16.079(3)$, $c = 7.378(3)$ Å, $\alpha = 96.62(2)°$, $\beta = 111.15(2)°$, $\gamma = 76.33(2)°$, $V = 1087(1)$ Å^3, $Z = 2$, space group $P\bar{1}$, $d_{meas} = 2.926$, $d_{calc} = 2.87$ g/cm^3. Values of integral intensity were corrected for the LP factor [6]. Site occupancy was refined on the basis of reflections with $\sin\theta/\lambda \leq 0.5$. After refining anisotropic displacement parameters, data were corrected for sample shape using the DIFBAS program [7], WS: $1/[\sigma^2_F + 0.001F^2_{obs}]$, GOF = 1.040. The final value was $R/R_w = 0.0426/0.0429$. The atom coordinates and isotropic displacement parameters are listed in Table 1.

The structure of miserite consists of layers of centrosymmetric tube silicate radicals $[Si_{12}O_{30}]^{12-}$ alternating with walls of M-polyhedra: octahedra and seven-apex polyhedra [8, 9] (Fig. 1). Polyhedral walls contain diorthogroups $[Si_2O_7]^{6-}$. In a given unit cell, the x axis is located inside the layer and links two adjacent tube radicals, the y axis links radicals in the adjacent layers, and the z axis is oriented along the axis of radical elongation.

The *polyhedral wall* of miserite consists of two inversion-related polyhedral layers. Each of the layers consists of three polyhedral columns: octahedra and seven-apex polyhedra (Fig. 2). In each column, two edge-shared polyhedra are translated along the z axis. Columns are linked by shared edges and vertices of polyhedra.

The site occupancy refinement of studied miserite showed that only one Ca$_1$ site is completely occupied by Ca^{2+}, whereas all other sites contain insignificant amounts of trivalent cations (mainly REE and Y) (Table 2). The content of trivalent cations is maximal in the Ca$_6$ site. Such an arrangement of trivalent cations is confirmed by the average bond lengths in polyhedra (Table 3). The average cation–oxygen bond is longest in the seven-

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Table 1. Atomic coordinates and isotropic displacement parameters (Å^{-2})* in miserite structure

Site	x/a	y/b	z/c	$U_{\text{(is/eq)}} \cdot 100$**
K_1	0.3174(2)	0.9949(1)	0.1566(3)	1.83(7)
K_2	0	0	1/2	3.9(2)
Ca_1	0.4004(2)	0.2641(1)	0.5167(2)	0.85(6)
Ca_2	0.4034(2)	0.2596(1)	0.0165(2)	0.74(5)
Ca_3	0.3699(2)	0.6103(1)	0.0838(2)	0.94(5)
Ca_4	0.0065(2)	0.3990(1)	0.3478(2)	1.41(6)
Ca_5	0.6406(2)	0.3808(1)	0.4111(2)	1.28(6)
Ca_6	0.0093(1)	0.60067(7)	0.1524(1)	1.10(4)
Si_1	0.2874(3)	0.4450(1)	0.2843(3)	1.24(8)
Si_2	0.7159(2)	0.5555(1)	0.2758(3)	1.21(8)
Si_3	0.6943(2)	0.9036(1)	0.3271(3)	0.83(7)
Si_4	0.6198(2)	0.1017(1)	0.3356(3)	0.69(7)
Si_5	0.7685(2)	0.1897(1)	0.1424(3)	0.78(7)
Si_6	0.9029(2)	0.8170(1)	0.1169(3)	0.88(7)
Si_7	0.2334(2)	0.8088(1)	0.2814(3)	0.87(7)
Si_8	0.0997(2)	0.1812(1)	0.3009(3)	0.92(7)
O_1	0.1246(7)	0.4530(4)	0.1422(10)	2.8(3)
O_2	0.4004(6)	0.3609(4)	0.2717(9)	1.9(2)
O_3	0.3417(8)	0.5310(4)	0.3049(10)	3.5(3)
O_4	0.7374(8)	0.5712(5)	0.5113(9)	3.3(3)
O_5	0.6048(6)	0.6422(3)	0.1953(8)	1.4(2)
O_6	0.8790(6)	0.5437(4)	0.2923(9)	2.3(3)
O_7	0.6469(7)	0.4747(4)	0.1945(8)	2.2(3)
O_8	0.5903(6)	0.8374(4)	0.2581(8)	1.4(2)
O_9	0.6026(6)	0.0029(3)	0.3016(8)	1.2(2)
O_{10}	0.8017(6)	0.8960(4)	0.1998(8)	1.6(2)
O_{11}	0.2013(6)	0.1029(3)	0.4429(8)	1.5(2)
O_{12}	0.4664(6)	0.1659(3)	0.2767(8)	1.2(2)
O_{13}	0.7159(6)	0.1112(3)	0.2043(8)	1.2(2)
O_{14}	0.7166(6)	0.1127(3)	0.5637(8)	1.4(2)
O_{15}	0.6587(6)	0.2790(3)	0.1428(7)	1.0(2)
O_{16}	0.9348(6)	0.1874(3)	0.2878(8)	1.3(2)
O_{17}	0.2250(6)	0.8406(3)	0.0753(7)	1.3(2)
O_{18}	0.8473(6)	0.7310(3)	0.0914(8)	1.2(2)
O_{19}	0.0692(6)	0.8075(4)	0.2618(8)	1.7(2)
O_{20}	0.3461(6)	0.7212(3)	0.3469(7)	1.1(2)
O_{21}	0.1548(6)	0.2656(4)	0.3746(8)	1.5(2)
O_{22}	0.1077(6)	0.1459(3)	0.0865(8)	1.3(2)
OH	0.8816(5)	0.3589(3)	0.0336(7)	0.5(2)
F	0.8873(6)	0.3635(4)	0.5299(8)	3.3(3)
W	0	0	0	4.5(26)
W_1	0.999(3)	0.002(2)	0.911(4)	0.9(5)

(*) Table of anisotropic displacement parameters is available from the authors.

(**) $U_{\text{eq}} = \frac{1}{3}[U_{11}a^{*2}a^2 + \ldots 2U_{23}b^*c^*bc\cos\alpha]$.

Table 2. Site occupancy in the miserite structure

Site	Repetition factor	Occupancy (at.u.), ion
K_1	2	0.974(5) K$^+$
K_2	1	0.630(8) K$^+$
Ca_1	2	1.009(4) Ca^{2+}
Ca_2	2	0.92(1) Ca^{2+} + 0.08(1) (Fe^{3+} + Mn^{2+} + Mg^{2+})
Ca_3	2	0.959(4) Ca^{2+} + 0.041(4) Y^{3+}
Ca_4	2	0.945(5) Ca^{2+} + 0.055(5) Y^{3+}
Ca_5	2	0.914(5) Ca^{2+} + 0.086(5) Y^{3+}
Ca_6	2	0.770(2) Ca^{2+} + 0.230(2) (Ce^{3+} + Pr^{3+} + Nd^{3+})
W	1	0.11(3) O^{2-}
W_1	2	0.20(2) O^{2-}

apex polyhedron Ca_1 (2.466 Å) and smallest in the octahedron Ca_6 (2.312 Å). The values of bond length are intermediate (2.383–2.386 Å) in Ca_2, Ca_3, and Ca_5 octahedra, which are mainly occupied by Ca^{2+}.

Silicate radicals in the miserite structure are represented by two types. The first type—an infinite $[Si_{12}O_{30}]^{12-}$ tube extended along the z axis with wide channels along two crystallographic axes—consists of four pyroxenoid chains of SiO$_4$ tetrahedra. The second type consists of $[Si_2O_7]^{6-}$ diorthogroups (Fig. 3). Tube silicate $[Si_{12}O_{30}]^{12-}$ radicals are identical to those in frankamenite and canasite [4, 5]. The average Si–O distances in tetrahedra of silicate radicals are similar (1.610–1.630 Å). The average O–Si–O angles are 109.4° (Table 3).

Diorthogroups $[Si_2O_7]^{6-}$ have shared edges with Ca_1- and Ca_4-seven-apex polyhedra and alternate with cavities along the z axis through a 1/2 translation. The average Si–O distances in diorthogroup tetrahedra are less (1.602 Å) than in silicate radical tetrahedra, and Si^{4+} cations in the diorthogroup tetrahedra are significantly shifted from bridging oxygen to the base. The Si–O$_{\text{bridge}}$ distances are equal to 1.668–1.675 Å, whereas Si–O$_{\text{base}}$ = 1.578–1.581 Å. The Si–O–Si angle in diorthogroup (154.4°) significantly exceeds this parameter in chains of tube silicate radicals (Table 3).

K$^+$ cations and H$_2$O molecules occupy the same sites in miserite as in the canasite and frankamenite structures [4, 5]. K$^+$ cations are incorporated in two sites. K_1 located in eight-member rings of silicate radical with an average K–O distance of 2.902 Å links two silicate radicals, while the other K_1, located at the axis of silicate radical with an average K–O distance of 3.12 Å (Table 3) alternates with H$_2$O molecules along the z axis through a 1/2 translation. All sites are incompletely occupied (Table 2). Water in the studied miserite structure is disordered: the occupancy of site W on the silicate radical axis is 0.11, while the occupancy of the W_1
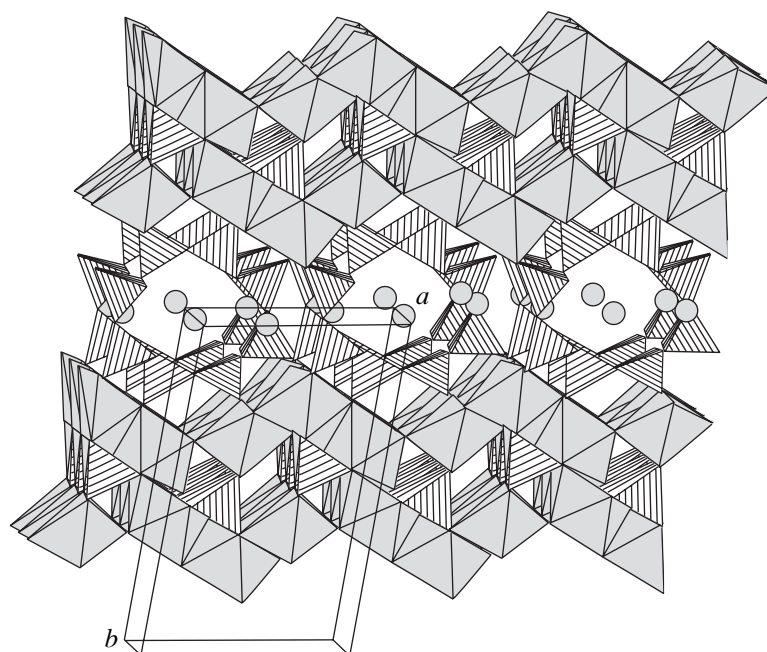
Fig. 1. Crystal structure of miserite (axonometry along [001]). Layers of tube radicals $[Si_{12}O_{30}]^{12-}$ are located between walls formed by Ca-octahedra and seven-apex polyhedra.
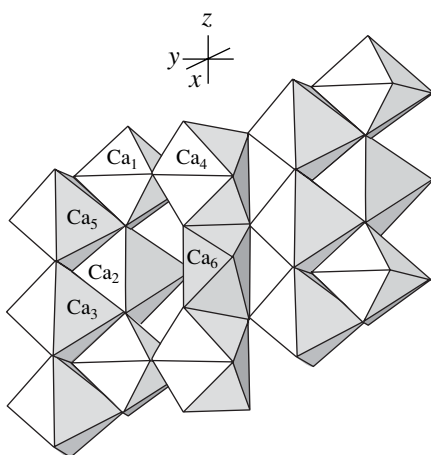

Fig. 2. Arrangement of octahedra and seven-apex polyhedra in the layer of polyhedral walls in the miserite structure.
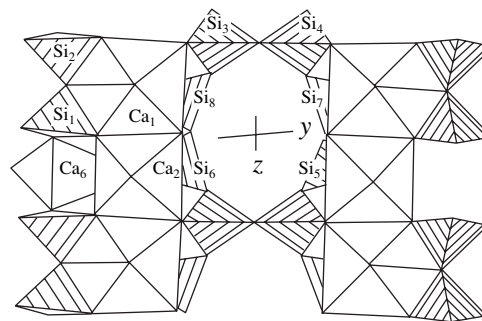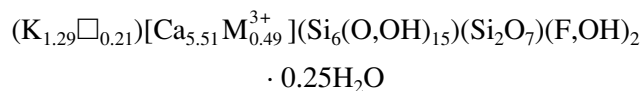

Fig. 3. Position of silicate radicals $[Si_{12}O_{30}]^{12-}$ and diortho-groups $[Si_2O_7]^{6-}$ in the miserite structure. Projection on the (100) plane.

site shifted toward the axis is 0.20. The $W-W_1$ distance is 0.66 Å.

The refined crystallochemical formula of miserite

$$(K_{1.29}\square_{0.21})[Ca_{5.51}M^{3+}_{0.49}](Si_6(O,OH)_{15})(Si_2O_7)(F,OH)_2$$
$$\cdot 0.25H_2O$$

(M = Y, REE, Fe, Ti, Mn, Mg; $\square$ are vacancies in sites of cation K^+) is highly consistent with microprobe data.

Based on recent classifications of silicates [10, 11], miserite should be ascribed to minerals with the tube silicate radical $[Si_{12}O_{30}]^{12-}$. According to [1], silicate radical can contain H_2O molecules and F atoms in one site and K^+ and Ca^{2+} cations in the other site. Our structural study showed that H_2O molecules and F atoms, on the one hand, and K^+ and Ca^{2+} cations, on the other hand, occupy different sites. The large cavity of tube silicate radical contains only K^+ cations and H_2O molecules. Trace elements in miserite from Kipawa Lake are incorporated only in the Ca_6 site [1], whereas trivalent cations in the studied miserite are found in five of six polyhedral sites, with the highest contents in the Ca_6 site.

Table 3. Bond lengths (Å) and valence angles (deg) in the miserite structure

Bond lengths and O–Si–O angles in tetrahedra

Si_1-O_1	1.583(8)	$O_1Si_1O_2$	118.4(4)	Si_5-O_{13}	1.647(7)	$O_{13}Si_5O_{15}$	111.5(4)
$-O_2$	1.572(8)	$O_1Si_1O_3$	112.2(5)	$-O_{15}$	1.594(7)	$O_{13}Si_5O_{16}$	106.7(4)
$-O_3$	1.577(9)	$O_2Si_1O_3$	115.6(4)	$-O_{16}$	1.630(7)	$O_{13}Si_5O_{17}$	103.7(4)
$-O_4$	1.675(8)	$O_1Si_1O_4$	97.7(4)	$-O_{17}$	1.644(7)	$O_{15}Si_5O_{16}$	114.8(4)
Average	1.602	$O_2Si_1O_4$	100.0(4)	Average	1.629	$O_{15}Si_5O_{17}$	112.5(4)
		$O_3Si_1O_4$	110.1(5)			$O_{16}Si_5O_{17}$	107.0(4)
		Average	109.0			Average	109.4
Si_2-O_5	1.592(7)	$O_5Si_2O_6$	119.3(4)	Si_6-O_{10}	1.641(7)	$O_{10}Si_6O_{18}$	111.5(4)
$-O_6$	1.577(9)	$O_5Si_2O_7$	112.1(4)	$-O_{18}$	1.581(7)	$O_{10}Si_6O_{19}$	108.6(4)
$-O_7$	1.575(8)	$O_6Si_2O_7$	115.3(4)	$-O_{19}$	1.619(8)	$O_{10}Si_6O_{22}$	102.4(4)
$-O_4$	1.668(8)	$O_4Si_2O_5$	99.3(4)	$-O_{22}$	1.638(7)	$O_{18}Si_6O_{19}$	112.3(4)
Average	1.603	$O_4Si_2O_6$	98.7(4)	Average	1.620	$O_{18}Si_6O_{22}$	114.3(4)
		$O_4Si_2O_7$	109.3(4)			$O_{19}Si_6O_{22}$	107.2(4)
		Average	109.0			Average	109.4
Si_3-O_8	1.589(7)	$O_8Si_3O_9$	111.7(4)	Si_7-O_{14}	1.645(7)	$O_{14}Si_7O_{17}$	103.7(4)
$-O_9$	1.639(7)	$O_8Si_3O_{10}$	113.8(4)	$-O_{17}$	1.627(7)	$O_{14}Si_7O_{19}$	107.3(4)
$-O_{10}$	1.652(8)	$O_8Si_3O_{11}$	114.1(4)	$-O_{19}$	1.619(8)	$O_{14}Si_7O_{20}$	110.6(4)
$-O_{11}$	1.644(7)	$O_9Si_3O_{10}$	104.1(4)	$-O_{20}$	1.585(7)	$O_{17}Si_7O_{19}$	106.8(4)
Average	1.631	$O_9Si_3O_{11}$	105.4(4)	Average	1.619	$O_{17}Si_7O_{20}$	113.2(4)
		$O_{10}Si_3O_{11}$	106.9(4)			$O_{19}Si_7O_{20}$	114.5(4)
		Average	109.3			Average	109.4
Si_4-O_9	1.619(6)	$O_9Si_4O_{12}$	111.5(4)	Si_8-O_{11}	1.629(7)	$O_{11}Si_8O_{16}$	107.3(4)
$-O_{12}$	1.589(7)	$O_9Si_4O_{13}$	104.9(4)	$-O_{16}$	1.617(8)	$O_{11}Si_8O_{21}$	110.9(4)
$-O_{13}$	1.642(8)	$O_9Si_4O_{14}$	106.4(4)	$-O_{21}$	1.554(7)	$O_{11}Si_8O_{22}$	103.5(4)
$-O_{14}$	1.628(7)	$O_{12}Si_4O_{13}$	112.9(4)	$-O_{22}$	1.641(7)	$O_{16}Si_8O_{21}$	113.8(4)
Average	1.620	$O_{12}Si_4O_{14}$	112.6(4)	Average	1.610	$O_{16}Si_8O_{22}$	106.4(4)
		$O_{13}Si_4O_{14}$	108.1(4)			$O_{21}Si_8O_{22}$	114.2(4)
		Average	109.4			Average	109.4

Si–O–Si angles between tetrahedra

$Si_1O_4Si_2$	154.4(6)	$Si_4O_{14}Si_7$	137.6(5)
$Si_3O_9Si_4$	143.4(5)	$Si_5O_{16}Si_8$	145.4(5)
$Si_3O_{10}Si_6$	135.3(5)	$Si_5O_{17}Si_7$	145.5(5)
$Si_3O_{11}Si_8$	134.7(5)	$Si_6O_{19}Si_7$	145.8(5)
$Si_4O_{13}Si_5$	136.4(4)	$Si_6O_{22}Si_8$	139.7(5)

Ca–O and K–O bond lengths

Ca_1-O_2	2.517(7)	Ca_3-O_3	2.314(8)	Ca_5-O_2	2.356(8)	K_1-O_9	2.724(8)
$-O_4$	2.678(8)	$-O_5$	2.379(8)	$-O_3$	2.366(8)	$-O_{10}$	3.035(7)
$-O_5$	2.468(7)	$-O_7$	2.307(7)	$-O_7$	2.348(7)	$-O_{11}$	2.972(7)
$-O_8$	2.421(7)	$-O_{15}$	2.478(6)	$-O_{15}$	2.451(6)	$-O_{13}$	2.948(6)
$-O_{12}$	2.406(7)	$-O_{20}$	2.520(6)	$-O_{20}$	2.510(7)	$-O_{14}$	2.998(7)
$-O_{20}$	2.452(7)	$-OH$	2.321(7)	$-F$	2.287(8)	$-O_{17}$	2.782(7)
$-O_{21}$	2.321(8)	Average	2.386	Average	2.386	$-O_{22}$	2.780(7)
Average	2.466	Ca_4-O_1	2.567(8)	Ca_6-O_1	2.391(7)	$-W$	2.979(4)
Ca_2-O_2	2.347(7)	$-O_4$	2.558(9)	$-O_1$	2.303(8)	$-W_1*$	3.05(3)
$-O_5$	2.313(7)	$-O_6$	2.380(7)	$-O_6$	2.327(8)	Average of 8	2.902
$-O_8$	2.419(6)	$-O_6$	2.637(7)	$-O_{18}$	2.312(7)	$K_2-O_{10}*$	3.043(7)
$-O_{12}$	2.385(6)	$-O_{21}$	2.291(7)	$-OH$	2.273(6)	$-O_{11}*$	3.073(7)
$-O_{15}$	2.494(7)	$-OH$	2.306(6)	$-F$	2.264(7)	$-O_{13}*$	3.189(7)
$-O_{18}$	2.341(8)	$-F$	2.292(7)	Average	2.312	$-O_{14}*$	3.171(7)
Average	2.383	Average	2.433			$-W_1*$	3.03(3)
						Average of 8	3.119

* Repetition factor of the bond is 2.

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