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GEOCHEMISTRY

Crystal Structure of Yegorovite $Na_4[Si_4O_8(OH)_4] \cdot 7H_2O$

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Abstract—Using X-ray analysis, the crystal structure of yegorovite $Na_4[Si_4O_8(OH)_4] \cdot 7H_2O$, a newly-discovered mineral from the Lovozero alkaline complex (Kola Peninsula, Russia), was determined. The mineral is monoclinic, of $P2_1/c$, $a = 9.8744(4)$, $b = 12.3981(5)$, $c = 14.8973(7)$ Å, $\beta = 104.675(5)^o$, $V = 1764.29(13)$Å^3, $Z = 4$. Yegorovite is a representative of a new structure type. Its structure is based upon the zigzag chains $[Si_4O_8(OH)_4]_\infty$ extended along [100]. The Na atoms occupy four nonequivalent crystallographic positions and are located in six-fold polyhedra $[NaO(OH)_2(H_2O)_3]$ and $[NaO(OH)(H_2O)_4]$. The Na polyhedra are joined with each other by vertices and edges to form corrugated layers parallel to (001). To each of these layers, the silicon–oxygen chains adjoin from both sides, and the neighboring Na–Si layers are combined with one another by a system of H-bonds.

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Up to now, among the natural silicates, 11 compounds were known which contained only alkaline-metal cations. Sodium is a specifying element in all these minerals, with potassium added in megacyclite and lithium in silinaite. The purely alkaline natural silicates are distinctive in that they show, in view of simple composition and not wide species diversity as such, most of the topological types of Si, O-complexes. These are the framework (for grumantite $Na[Si_2O_4(OH)] \cdot H_2O$ [1]); various layers for natrosilite $Na_2[Si_2O_5]$ [2], silinaite $NaLi[Si_2O_5] \cdot 2H_2O$ [3], makatite $Na_2[Si_4O_8(OH)_2] \cdot 4H_2O$ [4], kanemite $NaH[Si_2O_4(OH)_2] \cdot 2H_2O$ [5], and magadiite $Na[Si_7O_{13}(OH)_3] \cdot 4H_2O$ [6]); ribbons (for revdite $Na_{16}[Si_4O_6(OH)_5]_2[Si_8O_{15}(OH)_6](OH)_{10} \cdot 28H_2O$ [7]), ring (megacyclite $KNa_8[Si_9O_{18}(OH)_9] \cdot 19H_2O$ [8]), and isolated tetrahedra (for chesnokovite $Na_2[SiO_2(OH)_2] \cdot 8H_2O$ [9]). The crystal structures of kenyaite $Na_2Si_{22}O_{41}(OH)_8 \cdot 6H_2O$ and ertixiite $Na_2Si_4O_9$ are unknown.

In 2008, the Commission on New Minerals, Nomenclature, and Classification of the International Mineralogical Association approved the new mineral yegorovite $Na_4[Si_4O_8(OH)_4] \cdot 7H_2O$ which filled up a substantial gap in the "inventory" of purely alkaline natural silicates because its structure is based upon simple chains of Si-tetrahedra.

Yegorovite was named in memory of the well-known Russian crystallographer and crystallochemist Yu.K. Yegorov-Tismenko (1938–2007). The mineral was identified by the authors in the Palitra peralkaline pegmatite on Kedykverpakhk Mountain of the Lovozero alkaline complex (Kola Peninsula). This is a component of a low-temperature late hydrothermal association together with revdite and megacyclite. The colorless transparent flattened-prismatic crystals of yegorovite (to 1 mm length) are usually split and form, in small cavities, chaotic growths on the surfaces of aggregates of these minerals, as well as of the earlier natrosilite and microcline. In treating this mineral, only Na and Si were found by electron probe analysis. The average composition of yegorovite (wt %) is 23.28 of Na_2O, 45.45 of SiO_2, and 31.27 of H_2O, total 100.00 (the water content was taken as the deficiency of the sum of analysis). The composition corresponds to the empirical formula (calculated for $(O, OH)_{12}$, OH/H_2O ratio was calculated by charge balance): $Na_{3.98}Si_{4.01}O_{8.02}(OH)_{3.98} \cdot 7.205H_2O$. The idealized formula is $Na_4Si_4O_8(OH)_4 \cdot 7H_2O$ [10].

The 3D set of diffraction reflections was obtained for the yegorovite crystal of $0.02 \times 0.05 \times 0.44$ mm dimensions with an Xcalibur S CCD single crystal diffractometer (MoK_α radiation, $\lambda = 0.71073$ Å) at room temperature. On this basis, the parameters of the monoclinic unit cell were specified: $a = 9.8744(4)$, $b = 12.3981(5)$, $c = 14.8973(7)$ Å, $\beta = 104.675(5)°$, $V = 1764.29(13)$ Å^3, $Z = 4$. Absorption correction was applied according to the shape of the crystal ($\mu = 0.527$ mm^{-1}).

The crystal structure of yegorovite was solved, by direct methods, within the $P2_1/c$ space group, and refined using a SHELX 97 program set [11]. The final value of $R_{hkl} = 0.0745$ for 1977 reflections with $I > 2\sigma(I)$.

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Table 1. Coordinates of atoms and parameters of thermal shifts in the structure of yegorovite

Atom	x	y	z	U_{eq}/U^*_{iso}
Si(1)	0.59375(15)	0.82135(13)	0.22737(12)	0.0138(4)
Si(2)	0.85409(15)	0.68222(13)	0.23240(11)	0.0125(4)
Si(3)	0.34122(16)	0.67253(13)	0.23305(12)	0.0138(4)
Si(4)	0.10049(16)	0.83149(13)	0.23761(13)	0.0152(4)
Na(1)	0.0532(3)	0.6184(2)	0.06992(18)	0.0275(6)
Na(2)	0.7635(3)	0.8608(2)	0.05829(19)	0.0286(7)
Na(3)	0.3045(3)	0.8923(2)	0.07159(19)	0.0311(7)
Na(4)	0.4902(2)	0.6251(2)	0.05502(18)	0.0298(7)
O(1) [H_2O]	0.0665(5)	0.4265(4)	0.0859(4)	0.0279(12)
H(1a)	0.033(6)	0.412(5)	0.125(4)	0.005*
H(1b)	0.134(4)	0.463(5)	0.106(5)	0.04(2)*
O(2) [H_2O]	0.6751(5)	0.6900(4)	0.0002(4)	0.0282(11)
H(2a)	0.673(6)	0.675(5)	−0.056(5)	0.03(2)*
H(2b)	0.690(12)	0.640(7)	0.046(6)	0.15(5)*
O(3) [H_2O]	0.9783(5)	0.7937(4)	0.0089(4)	0.0388(13)
H(3a)	0.027(7)	0.851(6)	0.045(5)	0.05(2)*
H(3b)	0.958(6)	0.809(5)	−0.059(5)	0.034(19)*
O(4) [H_2O]	0.3337(6)	0.7544(4)	−0.0283(3)	0.0365(12)
H(4a)	0.252(9)	0.724(8)	−0.062(6)	0.08(3)*
H(4b)	0.389(9)	0.783(8)	−0.064(6)	0.10(4)*
O(5)	0.3959(4)	0.6184(3)	0.3321(3)	0.0195(10)
O(6)	0.9024(4)	0.6274(3)	0.3312(3)	0.0165(9)
O(7)	0.1549(4)	0.8839(3)	0.3376(3)	0.0223(10)
O(8)	0.6507(4)	0.8788(3)	0.3248(3)	0.0249(11)
O(9) [OH]	0.8697(4)	0.6008(3)	0.1481(3)	0.0170(10)
H(9)	0.867(5)	0.540(4)	0.157(4)	0.003(15)*
O(10)	0.9385(4)	0.7913(3)	0.2161(3)	0.0199(10)
O(11)	0.4369(4)	0.7711(3)	0.2109(3)	0.0218(11)
O(12) [OH]	0.5796(5)	0.9035(4)	0.1385(3)	0.0234(10)
H(12)	0.629(8)	0.947(6)	0.170(6)	0.10(4)*
O(13)	0.6876(3)	0.7188(3)	0.2082(3)	0.0181(10)
O(14)	0.1833(4)	0.7219(3)	0.2185(3)	0.0185(10)
O(15) [H_2O]	0.8270(5)	0.0419(4)	0.0922(3)	0.0290(12)
H(15a)	0.908(5)	0.073(4)	0.120(4)	0.005(14)*
H(15b)	0.746(5)	0.058(7)	0.107(6)	0.08(3)*
O(16) [OH]	0.3241(5)	0.5891(4)	0.1458(3)	0.0201(10)
H(16)	0.346(6)	0.5312(16)	0.148(4)	0.018(19)*
O(17) [OH]	0.1186(5)	0.9136(4)	0.1562(3)	0.0210(10)
H(17)	0.123(10)	0.971(3)	0.172(6)	0.09(4)*
O(18) [H_2O]	0.5769(5)	0.4585(4)	0.1060(4)	0.0303(12)
H(18a)	0.658(2)	0.452(6)	0.110(5)	0.04(2)*
H(18b)	0.535(6)	0.428(5)	0.137(4)	0.018(19)*
O(19) [H_2O]	0.3282(6)	0.0756(4)	0.0944(3)	0.0254(12)
H(19a)	0.405(7)	0.095(5)	0.123(5)	0.03(2)*
H(19b)	0.261(10)	0.117(8)	0.117(7)	0.10(4)*

Note: Asterisks mark the isotropic thermal displacement parameters for hydrogen atoms.

Table 2. Interatomic distances (Å) in the structure of yegorovite

Si(1)–O(8)	1.586(4)	Si(2)–O(6)	1.582(4)	Si(3)–O(5)	1.585(4)	Si(4)–O(7)	1.588(4)
O(11)	1.630(4)	O(10)	1.639(4)	O(11)	1.628(4)	O(17)	1.627(5)
O(13)	1.640(4)	O(9)	1.649(5)	O(16)	1.636(5)	O(10)	1.628(4)
O(12)	1.648(5)	O(13)	1.655(4)	O(14)	1.638(4)	O(14)	1.647(4)
Average	1.626	Average	1.631	Average	1.622	Average	1.623
Na(1)–O(1)	2.388(6)	Na(2)–O(15)	2.351(5)	Na(3)–O(19)	2.301(5)	Na(4)–O(18)	2.291(5)
O(1)	2.391(6)	O(19)	2.360(6)	O(4)	2.333(6)	O(2)	2.325(6)
O(3)	2.400(6)	O(2)	2.369(5)	O(17)	2.491(5)	O(4)	2.351(6)
O(9)	2.400(5)	O(12)	2.471(5)	O(15)	2.588(6)	O(16)	2.417(5)
O(14)	2.600(5)	O(3)	2.554(6)	O(11)	2.627(5)	O(18)	2.542(6)
O(16)	2.652(5)	O(10)	2.683(5)	O(12)	2.650(5)	O(13)	2.847(5)
Average	2.472	Average	2.465	Average	2.498	Average	2.462

Table 3. Bond valence sums calculations for yegorovite

	Si(1)	Si(2)	Si(3)	Si(4)	Na(1)	Na(2)	Na(3)	Na(4)	Σ*	H-bonds	Σ
O(1) [H_2O]					0.20; 0.19				0.39	−0.20(O7) −0.17(O8)	0.02
O(2) [H_2O]						0.21		0.24	0.45	−0.23(O8) −0.20(O9)	0.02
O(3) [H_2O]					0.19	0.13			0.32	−0.22(O17) −0.21(O6)	−0.11
O(4) [H_2O]							0.22	0.22	0.44	−0.16(O7) −0.18(O5)	0.10
O(5)			1.13						1.13	0.18(O4) 0.16(O15) 0.23(O12) 0.22(O19)	1.92
O(6)		1.13							1.13	0.21(O3) 0.17(O15) 0.17(O19) 0.24(O17)	1.92
O(7)				1.09					1.09	0.20(O1) 0.16(O4) 0.21(O18) 0.22(O9)	1.88
O(8)	1.10								1.10	0.17(O1) 0.23(O2) 0.16(O18) 0.26(O16)	1.92
O(9) [OH]		0.91			0.20				1.11	0.20(O2) −0.22(O7)	1.09
O(10)		0.96		1.00		0.09			2.05		2.05
O(11)	0.99		0.99				0.11		2.09		2.09
O(12) [OH]	0.95					0.16	0.10		1.21	−0.23(O5)	0.98
O(13)	0.95	0.93						0.06	1.94		1.94
O(14)			0.97	0.92	0.11				2.00		2.00
O(15) [H_2O]						0.22	0.12		0.34	−0.17(O6) −0.16(O5)	0.01
O(16) [OH]			0.95		0.10			0.19	1.24	−0.26(O8)	0.98
O(17) [OH]				1.02			0.15		1.17	0.22(O3) −0.24(O6)	1.15
O(18) [H_2O]								0.25; 0.13	0.38	−0.18(O7) −0.16(O8)	0.04
O(19) [H_2O]						0.22	0.25		0.47	−0.22(O5) −0.17(O6)	0.08
Σ	3.99	3.93	4.04	4.03	0.99	1.03	0.95	1.09			

Note: Σ* is the bond valence sum without hydrogen bonds contribution. In parentheses there are donor and(or) acceptor oxygen atoms (negative and positive values, respectively). The table does not include possible weak bifurcated hydrogen bonds (O(1)–H(1b)–O(16) with O(1)–O(16) distance of 3.19 Å; O(2)–H(2b)–O(13) with O(2)–O(13) distance of 3.09 Å; and O(15)–H(15b)–O(12) with O(15)–O(12) distance of 3.20 Å).

All hydrogen atoms were localized and refined isotropically. The atomic coordinates, displacement parameters, and interatomic distances in yegorovite are given in Tables 1 and 2, respectively. Bond valence sums calculations for yegorovite [12] were performed including the contribution of hydrogen bonds [13] (Table 3).

Yegorovite is a representative of a new structure type; its crystal structure (Fig. 1) is unique; this mineral

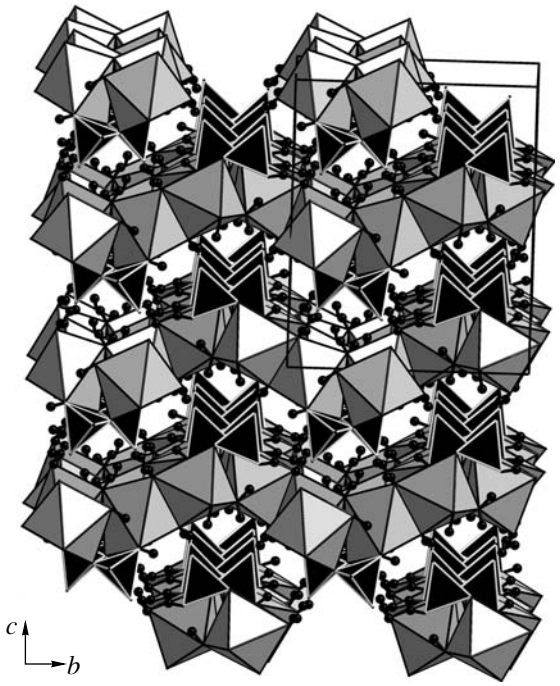

Fig. 1. Crystal structure of yegorovite. Na polyhedra and Si tetrahedra are shown in gray and black, respectively. The small black circles denote hydrogen atoms.

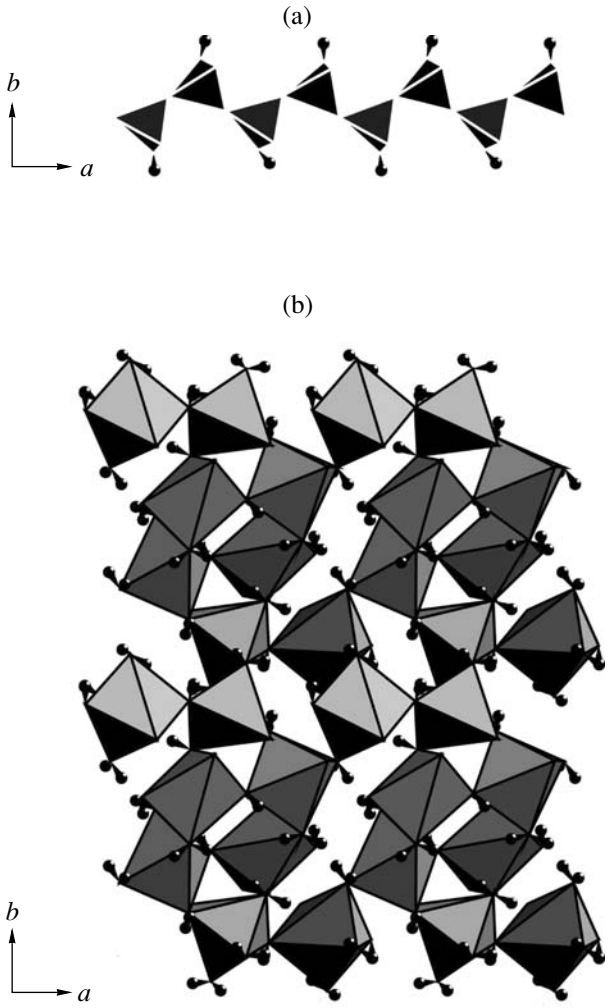

Fig. 2. The chain of Si tetrahedra (a) and the layer of Na six-fold polyhedra (b) in the structure of yegorovite. The small black circles denote hydrogen atoms.

has no structural analogues among natural and synthetic compounds. The main elements of the structure are the zigzag chains $[Si_4O_8(OH)_4]_\infty$ with a period of four tetrahedra, extended along the *a* axis. The degree of chain extension is $f_s = 0.914$. According to F. Liebau, the unbranched tetrahedral silicon–oxygen chain in the structure of yegorovite might be presented in general as $\{uB\,1^1_\infty\}[^4Si_4O_8(OH)_4]^{4-}$. One of the two free vertices of each tetrahedron is presented by an OH group (Fig. 2a). Sodium atoms occupy four nonequivalent crystallographic positions and are situated in six-fold polyhedra of two types: $[NaO(OH)_2(H_2O)_3]$ and $[NaO(OH)(H_2O)_4]$. Na polyhedra are joined to each other by the vertices and edges to form corrugated layers parallel to the *ab* plane (Fig. 2b). Within the layer, one may distinguish the three-, four-, five-, and eight-membered rings of Na-polyhedra. Each layer is adjoined from both sides by silicon–oxygen chains, and the neighboring Na–Si layers are associated with each other by a system of hydrogen bonds.

Note that the location of Si atoms corresponds to the chain with the period equal to 2, but when going to the tetrahedral chain, doubling of the period is required, caused by a slight tilting of tetrahedral and by the geometry of disposition of OH-group hydrogen atoms. At the first stage of the studies, we might select a cell with halved *a* and *c* parameters and another β angle: $a = 4.9341(5)$, $b = 12.3897(16)$, $c = 7.2316(13)$ Å, $\beta = 94.64(3)°$, $V = 440.63(11)$ Å^3 (space group $P2_1/a$). In this simplified model, the silicon–oxygen chains should show the period of 2 but not of 4 tetrahedra, with Na atoms occupying the unified position in the six-fold polyhedra forming the corrugated layers of equitype six-membered rings. However, the presence of significant reflections which doubled the *a* and *c* parameters, the considerably higher value of the divergence factor in the case of the small-cell model ($R_{hkl} = 0.1420$), and the structural validity to increase the cell (the character of the tetrahedral tilting in the chain, the location of H atoms, as well as the different types of Na polyhedra, and, respectively, the configuration of the sodium layers) determined the selection of a cell of quadruple volume corresponding to the chain with a period of a 4-tetrahedra and crystall chemical formula $Na_4[Si_4O_8(OH)_4] \cdot 7H_2O$. The transition from small to large cell is feasible with the matrix [2 0 0/0 –1 0/–1 0 –2].

Yegorovite is the only natural specimen known at present of purely alkaline silicates with a chain silicon–

oxygen motive. As for synthetic Na silicates, a $[Si_2O_5]^{2-}$ chain consisting of four-membered tetrahedral rings was found in the structure of microporous crystals Mu-29 $Na_{32}Si_{64}O_{128}(OH)_{32}$ [14]. The silicon–oxygen chains occur also in the structures of several anhydrous synthetic Na silicates. These are the Na_2SiO_3 metasilicate, the $Na_2Si_3O_7$ phase with a three-layered pack of $[SiO_3]$ metachains, and the $Na_6Si_8O_{19}$ compound, known more than four decades ago but studied structurally only recently, characterized by layers with introduced metachains ($[Si_6O_{15}] + [Si_2O_4] = [Si_8O_{19}]$) [15].

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