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REFINEMENT OF THE CRYSTAL STRUCTURE AND REVISION OF THE CHEMICAL FORMULA OF OLGITE: $(Ba,Sr)\ (Na,Sr,REE)_2\ Na\ [PO_4]_2$

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Abstract

The crystal structure of olgite, ideally $Ba\ (Na,Sr)_2\ Na\ [PO_4]_2$, hexagonal, sample (I), a 5.5606(2), c 7.0450(6) Å, V 188.65(5) Å^3, and sample (III), a 5.5492(2), c 7.0286(5) Å, V 187.44(4) Å^3, $Z = 1$, D (calc.) = 3.904 (I) and 3.930 (III) g.cm^{-3}, were refined in space group $P\bar{3}m1$ to R_1 indices of 2.73 and 2.58%, respectively, based on 236 and 233 observed [$F_o > 4\sigma F$] unique reflections measured with Mo$K\alpha$ X-radiation. The two samples differ only slightly in Ba and Sr content: $(Ba_{0.76}Sr_{0.20}K_{0.04})_{\Sigma 1.00}\ (Na_{1.15}Sr_{0.68}La_{0.10}Ca_{0.04}Ce_{0.02})_{\Sigma 2.00}\ (Na_{0.97}Mn_{0.03})_{\Sigma 1.00}\ [PO_4]_2$ for sample (I) and $(Ba_{0.88}Sr_{0.12})_{\Sigma 1.00}\ (Na_{1.24}Sr_{0.66}Ce_{0.06}La_{0.04})_{\Sigma 2.00}\ (Na_{0.96}Ca_{0.04})_{\Sigma 1.00}\ [PO_4]_2$ for sample (III), on the basis of 8 atoms of oxygen *pfu*. In the crystal structure, there is one tetrahedrally coordinated P site with $\langle P–O \rangle = 1.526$ and 1.522 Å. There are three M sites: the [12]-coordinated $M(1)$ site is occupied primarily by Ba (with subordinate Sr and minor K), with $\langle M(1)–O \rangle = 2.978$ and 2.969 Å, the [10]-coordinated $M(2)$ site is dominated by Na (with subordinate Sr and REE^{3+}), with $\langle M(2)–O \rangle = 2.806$ and 2.801 Å, and the octahedrally coordinated $M(3)$ site is occupied by Na [with very minor Mn or Ca], with $\langle M(3)–O \rangle = 2.290$ Å. In the crystal structure of olgite, M polyhedra and P tetrahedra link together through common vertices, edges and faces to form a super-densely-packed structure related to glaserite, $K_3\ Na\ (SO_4)_2$. Refinement of the olgite structure indicates that its general chemical formula should be written as $(Ba,Sr)\ (Na,Sr,REE)_2\ Na\ [PO_4]_2$, and its end-member formula is $Ba\ (NaSr)\ Na\ [PO_4]_2$.

Keywords: olgite, Ba–Sr–Na phosphate, crystal-structure refinement, Lovozero, Russia.

SOMMAIRE

La structure cristalline de l'olgite, dont la composition idéale est $Ba\ (Na,Sr)_2\ Na\ [PO_4]_2$, minéral hexagonal, échantillon (I), a 5.5606(2), c 7.0450(6) Å, V 188.65(5) Å^3, et échantillon (III), a 5.5492(2), c 7.0286(5) Å, V 187.44(4) Å^3, $Z = 1$, D (calc.) = 3.904 (I) et 3.930 (III) g.cm^{-3}, a été affinée dans le groupe spatial $P\bar{3}m1$ jusqu'à un résidu R_1 de 2.73 et 2.58%, respectivement, en utilisant 236 et 233 réflexions uniques observées [$F_o > 4\sigma F$] mesurées avec rayonnement Mo$K\alpha$. Les deux échantillons diffèrent légèrement seulement dans leurs teneurs en Ba et Sr: $(Ba_{0.76}Sr_{0.20}K_{0.04})_{\Sigma 1.00}\ (Na_{1.15}Sr_{0.68}La_{0.10}Ca_{0.04}Ce_{0.02})_{\Sigma 2.00}\ (Na_{0.97}Mn_{0.03})_{\Sigma 1.00}\ [PO_4]_2$ dans le cas de l'échantillon (I) et $(Ba_{0.88}Sr_{0.12})_{\Sigma 1.00}\ (Na_{1.24}Sr_{0.66}Ce_{0.06}La_{0.04})_{\Sigma 2.00}\ (Na_{0.96}Ca_{0.04})_{\Sigma 1.00}\ [PO_4]_2$ dans le cas de l'échantillon (III), sur une base de 8 atomes d'oxygène par formule unitaire. Dans la structure, il y a un site P à coordinence tétraédrique, avec $\langle P–O \rangle = 1.526$ et 1.522 Å. Il y a trois sites M: le Ba, avec une proportion subordonnée de Sr et de K, loge au site $M(1)$, à coordinence [12], avec $\langle M(1)–O \rangle = 2.978$ et 2.969 Å; il y a prédominance de Na (Sr et les terres rares sont subordonnées) au site $M(2)$, à coordinence [10], avec $\langle M(2)–O \rangle = 2.806$ et 2.801 Å, et le site octaédrique $M(3)$ contient Na (avec une proportion très mineure de Mn ou Ca), avec $\langle M(3)–O \rangle = 2.290$ Å. Dans la structure de l'olgite, les polyèdres M et les tétraèdres P sont connectés par leurs coins, arêtes et faces communs pour former une structure excessivement dense apparentée à celle de la glaserite, $K_3\ Na\ (SO_4)_2$. D'après les résultats de l'affinement, on devrait écrire sa formule chimique générale $(Ba,Sr)\ (Na,Sr,TR)_2\ Na\ [PO_4]_2$, et la formule du pôle, $Ba\ (NaSr)\ Na\ [PO_4]_2$.

Mots-clés: olgite, phosphate de Ba–Sr–Na, affinement de la structure cristalline, Lovozero, Russie.

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INTRODUCTION

Olgite, Na (Sr,Ba) (PO_4) with Ba varying from 0.34 to 0.42 *apfu*, from the Lovozero alkaline massif, Kola Peninsula, Russia, was described as a new mineral species by Khomyakov *et al.* (1980). The crystal structure of olgite was solved in space group *P*3 (Sokolova *et al.* 1984), who showed that it is related to the glaserite-type structure (Moore 1973, 1976). Sokolova *et al.* (1990) refined the structures of two crystals of barium-rich olgite, designated olgite II and III. Pekov *et al.* (2004) described the new mineral bario-olgite, Ba $(Na,Sr,REE)_2$ Na $(PO_4)_2$, and refined the structure in space group *P*3. The empirical chemical compositions of olgite II, olgite III and bario-olgite are almost identical, and this prompted us to re-examine the crystal structure of the original olgite (olgite I, Sokolova *et al.* 1984) and olgite III (Sokolova *et al.* 1990), particularly as both structures had been refined without proper corrections for absorption.

EXPERIMENTAL

The crystals used here are those originally examined by Sokolova *et al.* (1984), designated olgite I, and Sokolova *et al.* (1990), using their designation of olgite III.

Data collection

Single crystals of olgite I and olgite III were mounted on a Bruker *P*4 automated four-circle diffractometer equipped with graphite-filtered Mo*K*α X-radiation and an APEX 4K CCD detector. The intensities of 2889 (I) and 3159 (III) reflections with $\bar{7} < h < 7$, $\bar{7} < k < 7$, $\bar{9} < l < 9$ were collected to 60.00° 2θ (I) and 59.98° 2θ (III) using 15 s per 0.2° frame, with a crystal-to-detector distance of 4 cm. Empirical absorption-corrections (SADABS, Sheldrick 1998) were applied to both datasets. The unit-cell parameters were obtained by least-squares refinement from the positions of 1192 and 1616 reflections, respectively, with $I > 10\sigma I$, and are given in Table 1.

Crystal-structure refinement

The crystal structures of olgite I and olgite III were refined with the Bruker SHELXTL Version 5.1 system of programs (Sheldrick 1997). Scattering curves for neutral atoms were taken from the International Tables for Crystallography (Ibers & Hamilton 1992). *R* indices are of the form given in Table 1, and are expressed as percentages.

The original solution of the crystal structure of olgite (Sokolova *et al.* 1984) and all subsequent refinements of olgite (Sokolova *et al.* 1990) and bario-olgite (Pekov *et al.* 2004) were done in the space group *P*3. However, the arrangement of atoms in the glaserite structure-type (Moore 1973) is conformable with much higher symmetry, and this encouraged us to try a higher-symmetry space-group. A solution was found in $P\bar{3}m1$ with scattering at 0 0 0 and 0 0 ½ approximately compatible with Na and Ba, respectively. Three cation sites were identified, *M*(1), *M*(2) and *M*(3), and the occupancies of these sites were refined with the

TABLE 1. MISCELLANEOUS STRUCTURE-REFINEMENT INFORMATION FOR OLGITE

	I	III		I	III
a (Å)	5.5606(2)	5.5492(2)	Crystal size (mm)	0.04 × 0.06 × 0.10	0.06 × 0.10 × 0.16
c	7.0450(6)	7.0286(5)	Radiation	Mo*K*α	Mo*K*α
V (Å^3)	188.65(5)	187.44(4)	2θ range for data collection (°)	60.00	59.38
Space group	$P\bar{3}m1$	$P\bar{3}m1$	*R*(int) (%)	1.90	2.12
Z	1	1	Reflections collected	2889	3159
			$\lvert F(obs) \rvert > 4\sigma F$	1767	1821
Absorption coefficient (mm^{-1})	11.59	11.24	Unique reflections	240	238
			$\lvert F(obs) \rvert > 4\sigma F$	236	233
F(000)	203.2	203.0	Refinement method	Full-matrix least-squares on F^2; fixed weights proportional to $1/\sigma(F^2)$	
D(calc) (g.cm^{-3})	3.904	3.930	Goodness of fit on F^2	1.161	1.153
			Final *R* index (%) $[F_o > 4\sigma F]$	2.73	2.58
			R index (%) (all data)	2.77	2.61
			wR_2	6.36	6.38

$R_1 = \Sigma(|F_o| - |F_c|) / \Sigma|F_o|$; $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)^2]^{½}$, $w = 1 / [\sigma^2(F_o^2) + (aP)^2 + bP]$, where $P = (F_o^2 + 2F_c^2) / 3$.
Goodness of fit on $F^2 = [\Sigma w(F_o^2 - F_c^2) / (n - p)]^{½}$, where *n* is the number of reflections and *p* is the number of refined parameters.

scattering curves for Ba, (Sr, Na) and Na, respectively. Refinement of the structures converged to $R_1 = 2.73$ and 2.58%, respectively, for olgite I and III on the basis of 236 and 233 unique observed reflections in the space group $P\bar{3}m1$. Atom positions and anisotropic-displacement parameters for olgite I and III are given in Table 2, selected interatomic distances in Table 3, assigned *M*-site populations in Table 4, and bond valences in Table 5. Observed and calculated structure-factors are available from The Depository of Unpublished Data, CISTI, National Research Council, Ottawa, Ontario K1A 0S2, Canada.

THE STRUCTURE OF OLGITE

Site populations

The site populations were assigned primarily on the basis of the refined site-scattering values (Table 5). The scattering at the *M*(1) site is by far the highest of the three cation sites, requiring that all Ba be assigned to this site. If the remainder of the site is filled with the larger cations, in accord with the size of the coordination polyhedron, the resulting calculated site-scattering values are in close agreement with the refined site-scattering values. The refined site-scattering at the *M*(2) site is considerably larger than the scattering at the *M*(3) site, even allowing for the difference in site multiplicities. Thus all remaining Sr must be assigned to *M*(2), together with the minor amounts of the rare-earth elements (REE), and the balance of the site is filled with Na; the resulting calculated site-scattering values are in close agreement with the refined site-scattering values for *M*(2). The refined scattering at the *M*(3) site is in accord with occupancy by Na with minor Ca or Mn.

TABLE 2. ATOM POSITIONS AND DISPLACEMENT PARAMETERS FOR OLGITE

	x	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	U_{eq}
					Olgite I					
M(1)	0	0	1/2	0.0472(4)	0.0472(4)	0.0140(4)	0	0	0.0236(2)	0.0362(3)
M(2)	1/3	2/3	0.1634(1)	0.0228(5)	0.0228(5)	0.0174(6)	0	0	0.0114(3)	0.0210(4)
M(3)	0	0	0	0.0155(13)	0.0155(13)	0.0125(17)	0	0	0.0078(7)	0.0145(11)
P	2/3	1/3	0.2818(2)	0.0135(6)	0.0135(6)	0.0123(8)	0	0	0.0068(3)	0.0131(5)
O(1)	0.3703(7)	0.18515(4)	0.2039(5)	0.0235(17)	0.0453(17)	0.0415(18)	–0.0085(7)	–0.0171(14)	0.0117(9)	0.0392(10)
O(2)	2/3	1/3	0.4969(7)	0.044(2)	0.044(2)	0.015(2)	0	0	0.0222(11)	0.0345(15)
					Olgite III					
M(1)	0	0	1/2	0.0535(4)	0.0535(4)	0.0145(4)	0	0	0.0268(2)	0.0405(3)
M(2)	1/3	2/3	0.16315(13)	0.0247(5)	0.0247(5)	0.0177(6)	0	0	0.0123(3)	0.0223(5)
M(3)	0	0	0	0.017(1)	0.0173(12)	0.0149(15)	0	0	0.0087(6)	0.0165(10)
P	1/3	2/3	0.7173(2)	0.0150(5)	0.0150(5)	0.0126(7)	0	0	0.0075(3)	0.0142(5)
O(1)	0.3706(7)	0.1853(3)	0.2048(5)	0.0255(15)	0.0499(16)	0.0448(17)	–0.0097(7)	–0.0194(13)	0.0127(8)	0.0428(9)
O(2)	1/3	2/3	0.5023(7)	0.047(2)	0.047(2)	0.016(2)	0	0	0.0234(10)	0.0365(14)

TABLE 3. INTERATOMIC DISTANCES (Å) FOR OLGITE

		I	III
M(1)–O(1)	×6	2.745(4)	2.734(4)
M(1)–O(2)	×6	3.2105(1)	3.2039(1)
<*M*(1)–O>		2.978	2.969
M(2)–O(1)	×6	2.8005(4)	2.7958(4)
M(2)–O(1)a	×3	2.955(4)	2.952(4)
M(2)–O(2)		2.393(5)	2.384(5)
<*M*(2)–O>		2.806	2.801
M(3)–O(1)	×6	2.290(3)	2.290(3)
P–O(1)	×3	1.529(3)	1.525(5)
P–O(2)		1.515(5)	1.511(5)
<*P*–O>		1.526	1.522

a: –*x* + 1, –*y* + 1, –*z*.

TABLE 4. REFINED SITE-SCATTERING VALUES (*epfu*) AND ASSIGNED SITE-POPULATIONS (*apfu*) FOR OLGITE I AND III

		Refined site-scattering	Assigned site-population	Predicted site-scattering	$(M\text{–O})_{calc}$* Å	$(M\text{–O})_{obs}$ Å
M(1)	I	50.5(4)	0.76 Ba + 0.20 Sr + 0.04 K	50.9	2.977	2.978
	III	53.9(4)	0.88 Ba + 0.12 Sr	53.8	2.990	2.969
M(2)	I	47.2(4)	1.15Na + 0.68 Sr + 0.10 La + 0.04 Ca + 0.02 Ce	46.5	2.705	2.806
	III	42.8(4)	1.24 Na + 0.66 Sr + 0.06 Ce + 0.04 La	44.5	2.686	2.801
M(3)	I	11.4(2)	0.97 Na + 0.03 Mn	11.4	2.414	2.290
	III	11.6(2)	0.96 Na + 0.04 Ca	11.4	2.419	2.290

* calculated by summing the constituent radii, values from Shannon (1976).

Coordination of the cations

There is one tetrahedrally coordinated *P* site with <*P*–O> = 1.526 and 1.522 Å for olgite I and III, respectively. These values are somewhat smaller than the grand <P–O> distance of 1.537 Å in minerals, but well within the observed range of <P–O> distances (Huminicki & Hawthorne 2002). There are three *M* sites in the crystal structure of olgite. The *M*(1) site is coordinated by twelve O-atoms with <*M*(1)–O> distances of 2.978 and 2.969 Å, respectively. The *M*(2) site is coordinated by ten O-atoms with <*M*(2)–O> = 2.806 and 2.801 Å, respectively, and is occupied by Na and Sr, together with the REE in the structure (Table 1). The *M*(3) site is octahedrally coordinated, with <*M*(3)–O> distances of 2.290 Å in both structures.

Structure topology

In the crystal structure of olgite, *M*(1) polyhedra link together through common edges to form a (001) sheet at $z \approx 0.5$ (Fig. 1a). Each *M*(1) polyhedron shares common edges with six (PO_4) tetrahedra, three above and three below the plane of the sheet. The *M*(2) polyhedra and *M*(3) octahedra share common faces to form a (001) sheet at $z \approx 0$ (Figs. 1b, c). Each *M*(2) polyhedron shares a face with one (PO_4) tetrahedron and edges with three (PO_4) tetrahedra. These two sheets link through common faces of *M* polyhedra and constitute an *M*–*P*–O framework (Fig. 1d). The crystal structure of olgite is of the super-dense-packed type, and is related to the structure of glaserite, ideally $K_3\,Na\,(SO_4)_2$ (Moore 1973, 1976, 1981). The relations between olgite and glaserite were discussed by Egorov-Tismenko *et al.* (1984).

CHEMICAL FORMULA OF OLGITE

Khomyakov *et al.* (1980) described olgite as a new mineral species, assigned the Laue group $\bar{3}\,m$ (with possible space-groups $P\bar{3}m1$, $P3m1$ and $P321$), and assigned the general formula Na (Sr, Ba) (PO_4) by analogy with the synthetic phases Na Sr (PO_4) and Na Ba (PO_4) that are isostructural with "glaserite", K_3 Na $(SO_4)_2$ (Moore 1973, 1976). Sokolova *et al.* (1984) solved the structure in space group *P*3 and rewrote the general formula as Na (Sr, Ba) (Sr, Na) (Na, Sr) $(PO_4)_2$ in accord with the four *M*-cation sites in the *P*3 structure. Sokolova *et al.* (1990) refined the structures of two crystals of barium-rich olgite in the space group *P*3; the site assignments were as follows: crystal II: (Ba,Sr) (Na,Sr) (Na,Sr) and Na; crystal III: Ba (Na,Sr) (Sr,Na) and (Na,Sr). Chemical compositions for olgite and barium-rich olgite are given in Table 6. The formulae resulting from these assignments are as follows: II: (Ba,Sr) $(Na,Sr)_2$ Na $(PO_4)_2$, and III: Ba (Na,Sr) (Sr,Na) (Na,Sr) $(PO_4)_2$. Pekov *et al.* (2004) wrote the formula of the new species bario-olgite as Ba $(Na, Sr, REE)_2$ Na $(PO_4)_2$, and inspection of their site populations gives the formula (Ba,K) (Na,Sr,REE,Ca) (Na,Sr) Na $(PO_4)_2$.

As noted in the Introduction, the empirical chemical compositions of olgite II and olgite III (Sokolova *et al.* 1990) and bario-olgite (Pekov *et al.* 2004) are almost identical. The general formulae of Sokolova *et al.* (1990) for olgite II (see above) and of Pekov *et al.* (2004) for bario-olgite are also virtually identical, differing only in the minor occupancy of the first cation group by Sr.

A key factor in this issue is that refinement of all these structures was done in too low a symmetry, *P*3 instead of $P\bar{3}m1$. In the former case, there are four distinct cation-sites [*M*1, *M*2, *M*3, *M*4], whereas in the latter case, there are three distinct cation-sites [*M*(1), *M*(2), *M*(3)]. In both olgite and bario-olgite, the *M*(1) and *M*1 sites are analogous and are dominantly occupied by Ba, and the *M*(3) and *M*4 sites are analogous and are dominantly occupied by Na. The principal difference occurs with the *M*(2) and *M*2, *M*3 sites: the latter are distinct in *P*3 but are not distinct in $P\bar{3}m1$. In

TABLE 5. BOND-VALENCE* TABLE FOR OLGITE

	M(1)	*M*(2)	*M*(3)	*P*	Σ
		Olgite I			
O(1)	$0.26^{x6}\downarrow$	$0.13^{x6}\downarrow^{x2}\rightarrow$ $0.10^{x3}\downarrow$	$0.27^{x6}\downarrow$	$1.28^{x3}\downarrow$	2.17
O(2)	$0.09^{x6}\downarrow^{x3}\rightarrow$	0.31		1.33	1.91
Σ	2.10	1.39	1.62	5.17	
		Olgite III			
O(1)	$0.28^{x6}\downarrow$	$0.13^{x6}\downarrow^{x2}\rightarrow$ $0.10^{x3}\downarrow$	$0.26^{x6}\downarrow$	$1.30^{x3}\downarrow$	2.20
O(2)	$0.09^{x6}\downarrow^{x3}\rightarrow$	0.32		1.35	1.94
Σ	2.22	1.40	1.56	5.25	

* bond-valence parameters (*vu*) from Brown (1981).

TABLE 6. CHEMICAL COMPOSITION (wt.%) AND UNIT FORMULA (*apfu*) OF OLGITE AND BARIO-OLGITE

	olgite I*	olgite III**	bario-olgite***		olgite I*	olgite III**	bario-olgite***
P_2O_5	31.60	32.08	31.77	P	1.99	2.02	2.01
SiO_2	–	–	0.08	Si	–	–	–
CaO	0.52	0.50	0.32	Ca	0.04	0.04	0.03
SrO	20.40	17.78	16.57	Sr	0.88	0.77	0.72
BaO	26.50	28.30	31.17	Ba	0.77	0.83	0.91
Na_2O	14.80	15.37	14.78	Na	2.13	2.22	2.14
La_2O_3	3.90	2.21	2.41	La^{3+}	0.11	0.06	0.07
Ce_2O_3	0.77	2.90	1.90	Ce^{3+}	0.02	0.08	0.05
Pr_2O_3	–	–	0.10	Pr^{3+}	–	–	–
Nd_2O_3	–	–	0.16	Nd^{3+}	–	–	–
K_2O	0.46	–	0.87	K	0.04	–	0.08
MnO	0.89	–	0.39	Mn	0.06	–	0.02
Total	99.94	99.74	100.52	Σ	4.05	4.00	4.02

* from Khomyakov *et al.* (1980). ** from Sokolova *et al.* (1990).
*** from Pekov *et al.* (2004).

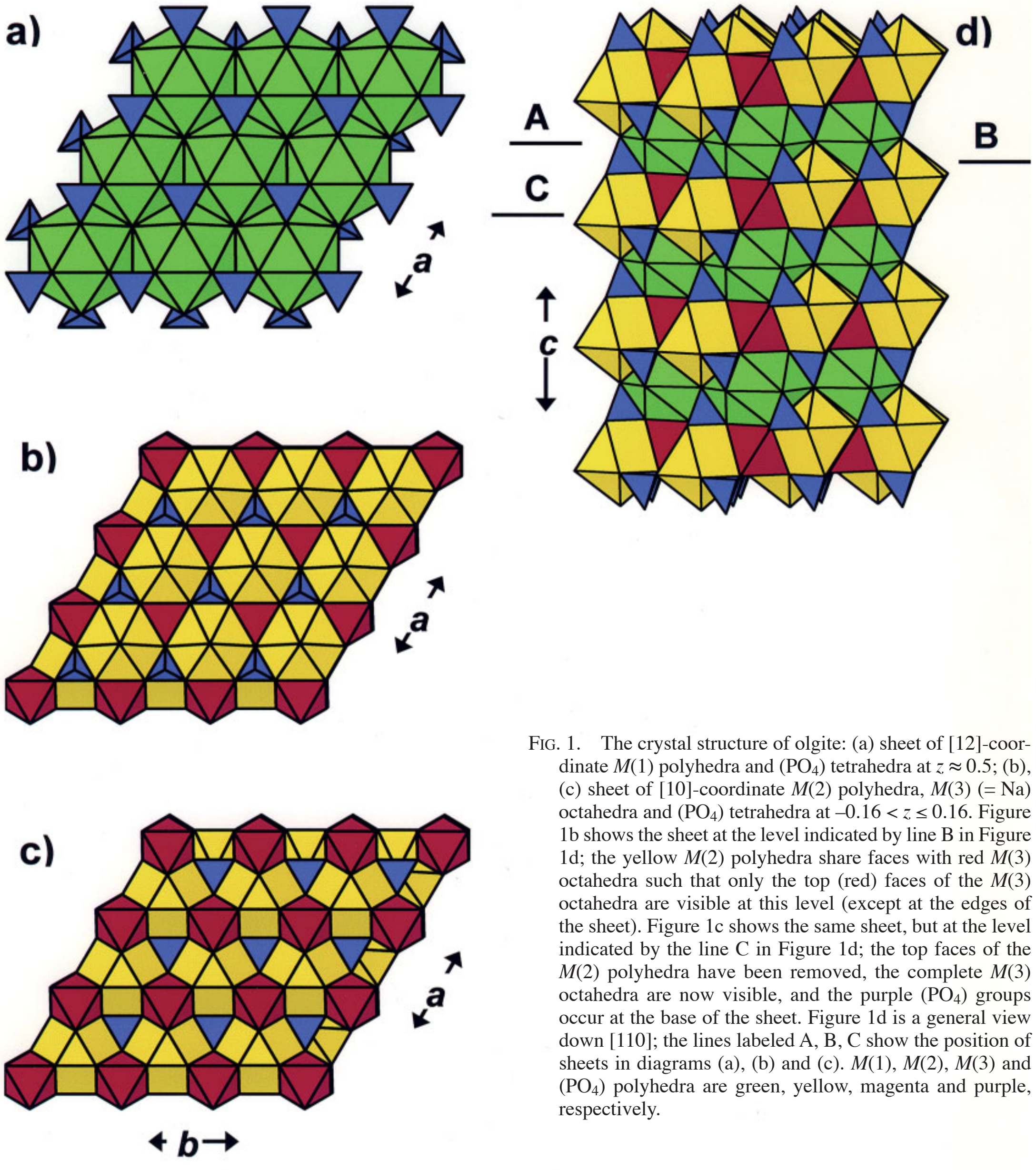

FIG. 1. The crystal structure of olgite: (a) sheet of [12]-coordinate *M*(1) polyhedra and (PO_4) tetrahedra at $z \approx 0.5$; (b), (c) sheet of [10]-coordinate *M*(2) polyhedra, *M*(3) (= Na) octahedra and (PO_4) tetrahedra at $-0.16 < z \leq 0.16$. Figure 1b shows the sheet at the level indicated by line B in Figure 1d; the yellow *M*(2) polyhedra share faces with red *M*(3) octahedra such that only the top (red) faces of the *M*(3) octahedra are visible at this level (except at the edges of the sheet). Figure 1c shows the same sheet, but at the level indicated by the line C in Figure 1d; the top faces of the *M*(2) polyhedra have been removed, the complete *M*(3) octahedra are now visible, and the purple (PO_4) groups occur at the base of the sheet. Figure 1d is a general view down [110]; the lines labeled A, B, C show the position of sheets in diagrams (a), (b) and (c). *M*(1), *M*(2), *M*(3) and (PO_4) polyhedra are green, yellow, magenta and purple, respectively.

this regard, the structure of bario-olgite has since been refined successfully in the space group $P\bar{3}m1$ (D.Yu. Pushcharovsky, pers. commun., 2004).

On the basis of the site populations in Table 4, the general formula of olgite may be written as (Ba, Sr) $(Na, Sr)_2$ Na $(PO_4)_2$, ignoring minor amounts of K, Mn and the REE. However, the requirement of electroneutrality does not allow Na and Sr to vary, as indicated by the term $(Na,Sr)_2$ in the formula; it is clear that for Na and Sr to vary at the *M*(2) site, there must be substitution of additional cations into the structure. In this regard, it is instructive to consider the end-member formula Ba (NaSr) Na $(PO_4)_2$. If Na is to be dominant over Sr at *M*(2), then there must be substitution of a trivalent cation for Sr (or Ba); if Sr is to be dominant over Na at *M*(2), then there must be substitution of a monovalent cation for Ba at *M*(1). A small amount of K does occur in olgite, but is exceeded by the amount of the

REE in all cases, indicating that the substitution Na + REE → Sr + Sr is dominant in all crystals of olgite so far examined. Thus we should probably include this substitution into the general formula of olgite: (Ba,Sr) $(Na,Sr,REE)_2$ Na $(PO_4)_2$.

Summary

The space group of olgite is $P\bar{3}m1$, and there are three distinct large-cation sites in the structure. The general formula is (Ba,Sr) $(Na,Sr,REE)_2$ Na $(PO_4)_2$, and the resulting end-member formula is Ba (NaSr) Na $(PO_4)_2$ for $Z = 1$. Bario-olgite is not distinct from olgite; the former should be considered for discreditation.

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References

Brown, I.D. (1981): The bond-valence method: an empirical approach to chemical structure and bonding. *In* Structure and Bonding in Crystals II (M. O'Keeffe & A. Navrotsky, eds.). Academic Press, New York, N.Y. (1-30).

Egorov-Tismenko, Yu.K., Sokolova, E.V., Smirnova, N.L. & Yamnova, N.A. (1984): The crystal chemistry of the glaserite-type structures. *Mineral. Zh.* **6**(6), 3-9 (in Russ.).

Huminicki, D.M.C. & Hawthorne, F.C. (2002): The crystal chemistry of the phosphate minerals. *In* Phosphates: Geochemical, Geobiological, and Materials Importance (M.L. Kohn, J. Rakovan & J.M. Hughes, eds.). *Rev. Mineral.* **48**, 123-253.

Ibers, J.A. & Hamilton, W.C., eds. (1992): *International Tables for X-ray Crystallography* IV. Kynoch Press, Birmingham, U.K.

Khomyakov, A.P, Semenov, E.I., Shumyatskaya, N.G., Timoshenkov, I.M., Laputina, I.P. & Smol'yaninova, N.N. (1980): Olgite, $Na(Sr,Ba)PO_4$ – a new mineral. *Zap. Vses. Mineral. Obshchest.* **110**, 347-351 (in Russ.).

Moore, P.B. (1973): Bracelets and pinwheels: a topological-geometrical approach to the calcium orthosilicate and alkali sulfate structures. *Am. Mineral.* **58**, 32-42.

________ (1976): The glaserite, $K_3Na[SO_4]_2$ structure type as a "super" dense-packed oxide: evidence for icosahedral geometry and cation–anion mixed layer packings. *Neues Jahrb. Mineral., Abh.* **127**, 187-196.

________ (1981): Complex crystal structures related to glaserite, $K_3Na[SO_4]_2$: evidence for very dense packings among oxysalts. *Bull. Minéral.* **104**, 536-547.

Pekov, I.V., Chukanov, N.V., Kulikova, I.M., Zubkova, N.V., Krotova, O.D., Sorokina, N.I. & Puscharovsky, D.Yu. (2004): The new mineral bario-olgite, $Ba(Na,Sr,REE)_2Na(PO_4)_2$ and its crystal structure. *Zap. Vser. Mineral. Obshchest.* **133**(1), 41-49 (in Russ.).

Shannon, R.D. (1976): Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta Crystallogr.* **A32**, 751-767.

Sheldrick, G.M. (1997): shelx*97*. Program for the solution and refinement of crystal structures. University of Göttingen, Göttingen, Germany.

________ (1998): sadabs *User Guide*. University of Göttingen, Göttingen, Germany.

Sokolova, E.V., Egorov-Tismenko, Yu.K., Yamnova, N.A. & Simonov, M.A. (1984): The crystal structure of olgite $Na(Sr_{0.52}Ba_{0.48})(Sr_{0.56}Na_{0.42})(Na_{0.81}Sr_{0.19})[PO_{3.40}]$ $[P_{0.76}O_{3.88}]$. *Sov. Phys. Crystallogr.* **29**, 633-635.

________, Nadezhina, T.N. & Khomyakov, A.P. (1990): The X-ray diffraction study of highly barium-enriched olgite. *Vestnik MGU, ser. Geology* **N1**, 87-91 (in Russ.).

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