

Bariosincosite, a new hydrated barium vanadium phosphate, from the Spring Creek Mine, South Australia

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ABSTRACT

Bariosincosite is a new barium vanadium phosphate hydrate from the Spring Creek Mine, near Wilmington, South Australia. The new mineral occurs as irregular clusters of pale green, very thin platy crystals up to 250 µm across and 2 to 5 µm thick. The tetragonal crystals are tabular on {001} and the other form present is {100}. Associated with bariosincosite are quartz, cuprite, native copper, fluorapatite, whitlockite, baryte and springcreekite, $\text{BaV}_3^{3+}(\text{PO}_4)_2(\text{OH}, \text{H}_2\text{O})_6$. Bariosincosite appears to have formed under supergene or low-temperature late-stage hydrothermal conditions. Electron microprobe analysis yielded: BaO 23.20; SrO 4.19; CaO 0.36; VO_2 31.55; Fe_2O_3 0.20; Al_2O_3 0.50; P_2O_5 28.15; H_2O 13.93 (calculated). These data give an empirical formula of $(\text{Ba}_{0.77}\text{Sr}_{0.20}\text{Ca}_{0.03})_{\Sigma 1.00}[(\text{V}_{0.96}\text{Al}_{0.03}\text{Fe}_{0.01}^{3+})_{\Sigma 1.00}\text{O}(\text{PO}_4)]_2 \cdot 4\text{H}_2\text{O}$, calculated on the basis of two P atoms. The simplified formula is $\text{Ba}(\text{V}^{4+}\text{OPO}_4)_2 \cdot 4\text{H}_2\text{O}$. The mineral is transparent with a very pale green streak, a vitreous lustre and an estimated Mohs hardness of 3. The strongest lines in the X-ray powder pattern are [d_{obs} (I_{obs}) (hkl)] 6.414 (20) (110, 002); 5.748 (70) (111); 4.552 (30) (112, 200); 3.198 (20) (220, 004); 3.100 (100) (203, 221); 2.847 (40) (222, 114); 2.786 (80) (311); 2.368 (30) (313, 115); and 2.017 (100) (420, 332, 116). These data were indexed on a tetragonal cell, with $a = 9.031(6)$, $c = 12.755(8)$ Å and $V = 1040(1)$ Å³; the space group is probably $P4/n$ or $P4/nmm$. For $Z = 4$ and using the empirical formula, the calculated density is 3.306 gm/cm³. Bariosincosite is uniaxial negative with $\omega = 1.721(2)$ and $\varepsilon = 1.715(2)$ (white light); pleochroism is weak from colourless (E) to pale green (O), absorption $\text{O} > \text{E}$. The mineral is named for the relationship to sincosite, $\text{Ca}(\text{V}^{4+}\text{OPO}_4)_2 \cdot 4\text{H}_2\text{O}$.

KEYWORDS: bariosincosite, new mineral, barium vanadium phosphate, sincosite, Spring Creek Mine, South Australia.

Introduction

THE Spring Creek Mine exploited a small copper deposit near Wilmington, at the southern end of the Flinders Ranges, South Australia. The small mine dumps have yielded a rich suite of secondary minerals, including a number of rare phosphates such as beraunite, chalcosiderite, hentschelite, mitridatite and perloffite (Birch and Mumme, 1988, Beyer and Elliott, 1996). During extensive investigations of the mineralogy of the deposit,

Beyer and Elliott (1996) noted two unknown barium vanadium phosphate minerals. The characterization and description of one of these species, the Ba analogue of sincosite, is the subject of this paper. The new species, bariosincosite, has been named for its relationship to sincosite, $\text{Ca}(\text{VOPO}_4)_2 \cdot 4\text{H}_2\text{O}$. The mineral and the name were approved by the Commission on New Minerals and Mineral Names in 1998 (98-047). The type specimen is held in the collections of the South Australian Museum, Adelaide.

Occurrence

The Spring Creek Mine (32°41'S 137°07'E) is situated ~10 km south of Wilmington and on the eastern flank of Mt Remarkable, at the southern end of the Flinders Ranges, South Australia. The copper deposit was discovered in 1860 (Austin, 1863) and was worked intermittently for its rich cuprite-native copper-bearing ore. Work was finally abandoned in 1918 and the mine was reserved from the operation of the mining act to allow for it to be used as a water supply for the nearby township of Wilmington. In 1996 the Spring Creek Mine and the surrounding area was transferred to the Mt Remarkable National Park and collection of material is now prohibited.

The Spring Creek copper deposit is located within the contact zone of a quartzite unit of the Rhynie Sandstone group and a slate unit of the Tindelpina Shale (part of the Tapley Hill formation), both units being members of the late Proterozoic Adelaide System. The copper mineralization occurs as two intersecting lodes in a fault zone. This zone is severely fractured and has been the locus for copper enrichment (Binks *et al.*, 1968; Preiss, 1987). The mine water is not acidic, indicating the absence of primary sulphides beneath the ore zone and suggesting that the copper may have been transported some distance from its primary source (Jack, 1917). Some small phosphate deposits in the region are also associated with rocks of the Tapley Hill formation, this formation could be the source of the phosphate mineralization at Spring Creek (Summers, 1953; Beyer and Elliott, 1996). Cuprite, the principal copper mineral, and the secondary phosphates occur in vugs and cavities in the quartz-goethite matrix.

The new mineral generally occurs as irregular clusters of very thin platey crystals on the faces of slightly corroded cuprite crystals within cavities in a quartz-goethite matrix. On one specimen, the mineral occurs on native copper. The associated minerals are quartz, native copper, fluorapatite, whitlockite, baryte and springcreekite, $\text{BaV}_3^{3+}(\text{PO}_4)_2(\text{OH}, \text{H}_2\text{O})_6$ (Kolitsch and Pring, 1999). Barriosincosite appears to have formed under supergene or low-temperature late-stage hydrothermal conditions. The close association with cuprite and native copper indicates a slightly oxidizing or neutral environment (Williams, 1990). It is a late-stage secondary mineral which appears to predate only springcreekite in the paragenetic sequence. There is some evidence of

subsequent remobilization of fluorapatite and quartz, as tiny crystal of these minerals, together with crystals of springcreekite, occur on the surface of some of the barriosincosite crystals.

Physical and optical properties

Barriosincosite occurs as irregular, radiating to divergent groups of platey crystals up to 250 μm square and 5 μm thick. The principal form observed is {001} and the SEM image shows that the only other form is {100} (Fig. 1). Possible twinning on {110} was observed during the SEM investigation and the crystals often exhibit subparallel growth of {001}. The crystals have a splintery fracture and a distinct cleavage on {001}. They are transparent and the colour is pale green with a slightly bluish tinge (No. 134D on the Royal Horticultural Society, London, colour chart); the streak is very pale green. The lustre is vitreous and the Mohs hardness is estimated to be 3, based on a test on synthetic $\text{Ba}(\text{VOPO}_4)_2 \cdot 4\text{H}_2\text{O}$. The density could not be measured because of the very thin nature of the crystals; the calculated density, based on the empirical formula and with $Z = 4$, is 3.306 g cm^{-3} , or 3.40 g cm^{-3} for the simplified formula $\text{Ba}(\text{VOPO}_4)_2 \cdot 4\text{H}_2\text{O}$.

The optical parameters of barriosincosite were determined in white light using Cargille immersion liquids. The mineral is uniaxial negative with $\omega = 1.721(2)$ and $\epsilon = 1.715(2)$. However, because of the small crystal size, the extreme thinness of the crystals and the unavoidable, close inter-growth of subparallel plates, it can not be ruled

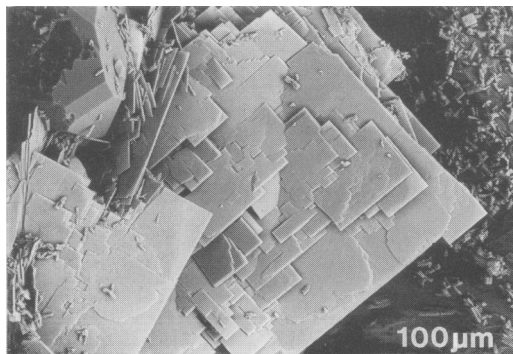


FIG. 1. SEM photomicrograph showing a group of platey barriosincosite crystals.

out that bariosincosite may be biaxial with a very small optical angle. The latter possibility might be suggested by the interference colours which were found to be anomalous bluish grey; however, a dispersion of the optical axes was not observed. Pleochroism is weak, E colourless and O pale greenish, and absorption $O > E$. Extinction is straight both along the plate edges and parallel to $\{001\}$.

For the purposes of comparison, the optical properties of monoclinic (pseudotetragonal) synthetic $\text{Ba}(\text{VOPO}_4)_2 \cdot 4\text{H}_2\text{O}$ were also investigated using the same method. The crystals are biaxial negative, with α 1.716(2), β 1.722(2), γ 1.722(2). The difference between β and γ is estimated to be 0.0005. $2V$ (est.) is $\sim 50 \pm 10^\circ$ and dispersion is strong, $r > v$. The interference colours are anomalous bluish grey and the optical axis plane is parallel to $\{100\}_{\text{tet}}$. Unlike the mineral from the Spring Creek Mine, the extinction is oblique and the angle between plate edges and the extinction position is $13.3 \pm 0.5^\circ$; plates sitting on their edges show straight extinction. The synthetic material also shows prominent twinning on $\{110\}_{\text{tet}}$ which was only rarely observed in the natural material.

Chemistry

Bariosincosite was analysed using a Cameca SX50 electron microprobe at 15 kV with a nominal specimen current of 0.02 μA . The standards used were pure V metal, benitoite (Ba), celestite (Sr), wollastonite (Ca), fluorapatite (P), hematite (Fe) and corundum (Al). Traces of Cu were also detected. As water could not be determined directly due to insufficient material, in the analyses below water was calculated to give $4\text{H}_2\text{O}$ by analogy with sincosite. Initial electron microprobe analyses gave low totals ($\sim 90\%$) but remarkably accurate cation ratios. In order to overcome this problem, thin crystals of natural sincosite (of known composition and similar thickness) were used as a secondary standard and the analysis totals were corrected for the effects of beam penetration through the crystals. The final analyses leave little doubt that the mineral is chemically the Ba analogue of sincosite (Table 1). Some variation in the ratio of Ba:Sr was noted in the analyses. Eight additional partial analyses were undertaken in order to monitor the distribution of Ba and Sr. Although their distribution was found to be somewhat heterogeneous and varying from 7.5:1 to 1.6:1, in all of

the crystals analysed Ba was dominant over Sr. The empirical formula, calculated on the basis of 2 P atoms, is $(\text{Ba}_{0.77}\text{Sr}_{0.20}\text{Ca}_{0.03})_{\Sigma 1.00}[(\text{V}_{0.96}\text{Al}_{0.03}\text{Fe}_{0.01}^{3+})_{\Sigma 1.00}\text{O}(\text{PO}_4)]_2 \cdot 4\text{H}_2\text{O}$, and the simplified formula is $\text{Ba}(\text{V}^{4+}\text{OPO}_4)_2 \cdot 4\text{H}_2\text{O}$.

X-ray crystallography

The X-ray powder diffraction pattern was recorded using a 100 mm diameter Guinier-Hägg camera with monochromated $\text{Cr-K}\alpha_1$ radiation ($\lambda = 2.2896 \text{ \AA}$) and with silicon employed as an internal standard. Line intensities were estimated visually by comparison with a set of standard reflections. Because reflections with d -spacings of $< 2 \text{ \AA}$ tend to be faint and difficult to measure on films recorded using $\text{Cr-K}\alpha_1$ radiation, a second powder pattern was recorded using a 114.6 mm diameter Gandolfi camera with $\text{Co-K}\alpha$ radiation ($\lambda = 1.79021 \text{ \AA}$). The powder patterns for bariosincosite are given in Table 2. The patterns were indexed on the basis of a tetragonal cell similar to that given for sincosite by Zolensky (1985). Least-squares refinement of the cell using the Guinier-Hägg pattern gave a tetragonal unit cell with $a = 9.031(6)$, $c = 12.755(8) \text{ \AA}$, $V = 1040(1) \text{ \AA}^3$. The axial ratio calculated from the unit cell parameters $c:a$ is 1.412:1. Attempts were also made to index the pattern on the basis of the monoclinic unit cell for synthetic $\text{Ba}(\text{VOPO}_4)_2 \cdot 4\text{H}_2\text{O}$ given by Roca *et al.* (1997); however, this gave a cell with higher

TABLE 1. Electron microprobe analysis of bariosincosite (wt.%)

Constituent	Range	Mean	Atoms ³
BaO	17.72–26.80	23.20	0.77
SrO	2.41–7.49	4.19	0.20
CaO	0.17–0.60	0.36	0.03
VO ₂	30.71–32.46	31.55	1.92
Fe ₂ O ₃	0.15–0.23	0.20	0.01
Al ₂ O ₃	0.35–0.62	0.50	0.06
P ₂ O ₅	27.26–29.18	28.15	2.00
H ₂ O		13.93 ¹	
Total		102.08 ²	

1. Water calculated on the basis of $4\text{H}_2\text{O}$ per formula unit.

2. High total due to dehydration in the beam

3. Calculated on the basis of 2 P atoms

No other elements with $Z > 8$ were detected

TABLE 2. X-ray powder diffraction data for bariosincosite $\text{Ba}(\text{VOPO}_4)_2 \cdot 4\text{H}_2\text{O}$

Pattern 1		Pattern 2		<i>d</i> cal	<i>hkl</i>
<i>h</i> / <i>k</i> / <i>l</i>	<i>d</i> obs	<i>h</i> / <i>k</i> / <i>l</i>	<i>d</i> obs		
20	6.414	20	6.362	6.387, 6.378	110, 002
70	5.748	100	5.722	5.712	111
		5	5.366		
30	4.522	40	4.519	4.517, 4.513	112, 200
		5	4.253	4.257, 4.252	201, 003
10	3.695	20	3.690	3.686	202
8	3.553	30b	3.548	3.539	113
5	3.445			3.413	212
20	3.198	60	3.192	3.194	220, 004
100	3.100	40	3.101	3.098	203, 221
10	2.984	10	3.006	3.007	104
		5	2.924	2.930, 2.928	301, 213
40	2.847	50	2.858	2.855, 2.853	222, 114
80	2.786	50	2.794	2.787	311
		10	2.718	2.725	302
		5b	2.614	2.606, 2.605	312, 204
		10	2.556	2.553, 2.551	223, 005
30	2.368	70	2.375	2.371, 2.369	313, 115
		5b	2.338	2.331	322,
8	2.251	10	2.257	2.258, 2.257	224, 400
5	2.226	5	2.224	2.224	401, 205
15	2.124	30	2.130	2.126	006, 314, 402
7	2.100	5	2.104	2.100	331
100	2.017	50	2.022	2.017	420, 332, 116
		5	1.992	1.994, 1.993	225, 403, 421
		5	1.969	1.970	324
		20b	1.927	1.925, 1.923	442, 206
5	1.902	30	1.907	1.903	333, 315
		5	1.846	1.842	404
		10	1.775	1.771, 1.770	510, 334, 226
5	1.752	10	1.754	1.754, 1.752	511, 117
		10b	1.707	1.707, 1.706	424, 316, 512
		10b	1.639	1.635	513, 335
		5b	1.586	1.584, 1.582	441, 425, 227
		10vb	1.550	1.549, 1.548	514, 442, 530
		10b	1.500	1.505, 1.503	208, 336, 532
		20	1.467	1.465	426, 602
		5b	1.458	1.455	515, 533
		20b	1.429	1.428	228, 444, 620
		2b	1.393		

standard deviations than the tetragonal cell. Comparison of the powder patterns of bariosincosite and synthetic $\text{Ba}(\text{VOPO}_4)_2 \cdot 4\text{H}_2\text{O}$ showed them to be almost identical but the reflections for the synthetic monoclinic compound are somewhat broader than those for the mineral. This, taken in conjunction with the optical data, indicates that bariosincosite is probably tetragonal. The space group could not be unambiguously assigned but there are no reflections of the $hk0$ -type with $h+k = 2n+1$ in the powder pattern

suggesting possible space groups $P4/n$ or $P4/nmm$, the latter having been determined for the parent compound, $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$.

Relationship to other minerals and compounds

Bariosincosite is the barium analogue of sincosite, but there has long been some uncertainty about the stoichiometry and the symmetry of sincosite. Schaller (1924) gave the formula for sincosite as $\text{CaO} \cdot \text{V}_2\text{O}_4 \cdot \text{P}_2\text{O}_5 \cdot 5\text{H}_2\text{O}$

TABLE 2. (contd.)

Pattern 1		Pattern 2		dcal	hkl
I/Io	dobs	I/Io	dobs		
		5b	1.358		
		10b	1.305		
		30b	1.272		
		10b	1.253		
		5b	1.229		
		2b	1.182		
		2b	1.165		
		20b	1.143		
		2b	1.128		
		5b	1.112		
		5b	1.094		
		10b	1.080		
		5b	1.065		
		5b	1.049		

Intensities visually estimated for both patterns.

Pattern 1 was recorded using a Guinier-Hägg camera using Cr- $K\alpha_1$ radiation and Si as an internal standard.

Pattern 2 was recorded using a 114.6 mm Gandolfi camera with Co- $K\alpha$ radiation on a polycrystalline sample. b = broad, vb = very broad.

(i.e. $\text{Ca}(\text{VOPO}_4)_2 \cdot 5\text{H}_2\text{O}$), although chemical data on another one of his samples indicates 4 rather than $5\text{H}_2\text{O}$. Zolensky (1985) recorded a full powder diffraction pattern for sincosite, indexed by analogy to the meta-autunite cell, but assumed the composition to be a $(\text{VOPO}_4)_2 \cdot 5\text{H}_2\text{O}$. Shitov *et al.* (1984) reported sincosite from Kazakhstan and showed that the mineral contains only $4\text{H}_2\text{O}$. They also found the mineral to be biaxial negative with α 1.670, β 1.690, γ 1.694 but with pseudotetragonal symmetry, $a = 9.08$, c 12.86 Å and proposed the space group $P4_2/n$. Kang *et al.* (1992) prepared $\text{Ca}(\text{VOPO}_4)_2 \cdot 4\text{H}_2\text{O}$ via hydrothermal methods and determined the crystal structure. They found $\text{Ca}(\text{VOPO}_4)_2 \cdot 4\text{H}_2\text{O}$ to be triclinic, $P1$, with $a = 6.3484$, $b = 6.350$, $c = 6.597$ Å; $\alpha = 106.81^\circ$, $\beta = 94.09^\circ$, $\gamma = 90.02^\circ$. They also noted a second reaction product, $\text{Ca}_x(\text{VOPO}_4)_2 \cdot 4\text{H}_2\text{O}$ with $x < 1$ which was a darker shade of green and crystallized in $Pnma$. Kang *et al.* (1992) reported that a comparison of the calculated powder pattern of their synthetic calcium compound to that of sincosite reported by Zolensky (1985) indicates that the crystal structures are similar and that the naturally occurring mineral has higher symmetry. Franke *et al.* (1997) also synthesized $\text{Ca}(\text{VOPO}_4)_2 \cdot 4\text{H}_2\text{O}$

by hydrothermal methods and checked the identity of the product by X-ray powder diffraction. Single crystal structure analysis of their product also showed only $4\text{H}_2\text{O}$ per formula unit and triclinic symmetry, but with a strong pseudotetragonal cell (Franke *et al.*, 1997).

Roca *et al.* (1997) noted that there is a large family of layered oxovanadium phosphate hydrates, of the type $\text{M}(\text{VOPO}_4)_2 \cdot n\text{H}_2\text{O}$ (M = metal cation). Some of these compounds are employed as catalysts, while others have unusual magnetic interactions and ion exchange behaviour (Ayyappan *et al.*, 1998). The layered vanadium phosphates are also closely related to the layered niobium and zirconium phosphates (NbOPO_4 and ZrOPO_4) which are the subject of considerable interest because of their significant negative thermal expansion (Sleight, 1998).

The following oxovanadium phosphate hydrates have been reported: $\text{M}(\text{VOPO}_4)_2 \cdot n\text{H}_2\text{O}$, $M = \text{Na}, \text{Ca}, \text{Sr}, \text{Ba}, \text{Pb}, \text{Co}, \text{Ni}, \text{Cu}, \text{Ag}$, all have $n = 4$; $M = \text{K}, \text{Rb}, \text{Pb}, \text{Ni}$, all have $n = 3$; $M = \text{Cu}, \text{Zn}$ but with very low stoichiometry $x = 0.1$ to 0.2 , have $n = 5$ (Kang *et al.*, 1992, Roca *et al.*, 1997, Ayyappan *et al.*, 1998). The parent compound, $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$, has the same VOPO_4 layer as sincosite and bariosincosite and is tetragonal, $P4/nmm$, $a = 6.202$, $c = 7.710$ Å.

The layers consist of alternating $V(O,H_2O)_6$ octahedra and PO_4 tetrahedra linked via corners and are joined via H bonding or interlamellar cations (Fig. 2). Kang *et al.* (1992) noted that the insertion of interlamellar cations results in the relative displacement of adjacent $VOPO_4$ layers, the nature of the displacement varying between compounds; in $Ca(VOPO_4)_2 \cdot 4H_2O$ the layers are displaced by $a/2$.

There must remain some doubt about the actual symmetry of barrosincosite and since there is no definitive evidence to suggest a lower symmetry, convention has been followed here and the unit cell with the highest symmetry has been chosen. Given the layered nature of these structures it seems likely that a number of polytypes may exist in nature, their occurrence being controlled by cation stoichiometry and conditions of crystallization.

Roca *et al.* (1997) prepared $Ba(VOPO_4)_2 \cdot 4H_2O$ (Fig. 2) by reacting V metal, V_2O_5 , $Ba(CH_3COO)_2$, H_3PO_4 and water in a teflon acid digestion hydrothermal bomb at $200^\circ C$ for 48 h. The other members of the structural family

have been prepared hydrothermally, under acidic conditions (pH 1–2) (Kang *et al.*, 1992; Roca *et al.*, 1997; Ayyappan *et al.*, 1998) or via direct redox intercalation reactions of $VOPO_4 \cdot 2H_2O$ in metal iodide solutions (Jacobson *et al.*, 1985). At the Spring Creek Mine milder conditions of formation are indicated and supergene or low temperature late-stage hydrothermal conditions are probable. The close association with cuprite and native copper indicates a slightly oxidizing or neutral environment (Williams, 1990) and it is possible that under these conditions the $(VOPO_4)$ layers in $Ba(VOPO_4)_2 \cdot 4H_2O$ stack to give a tetragonal structure.

Acknowledgements

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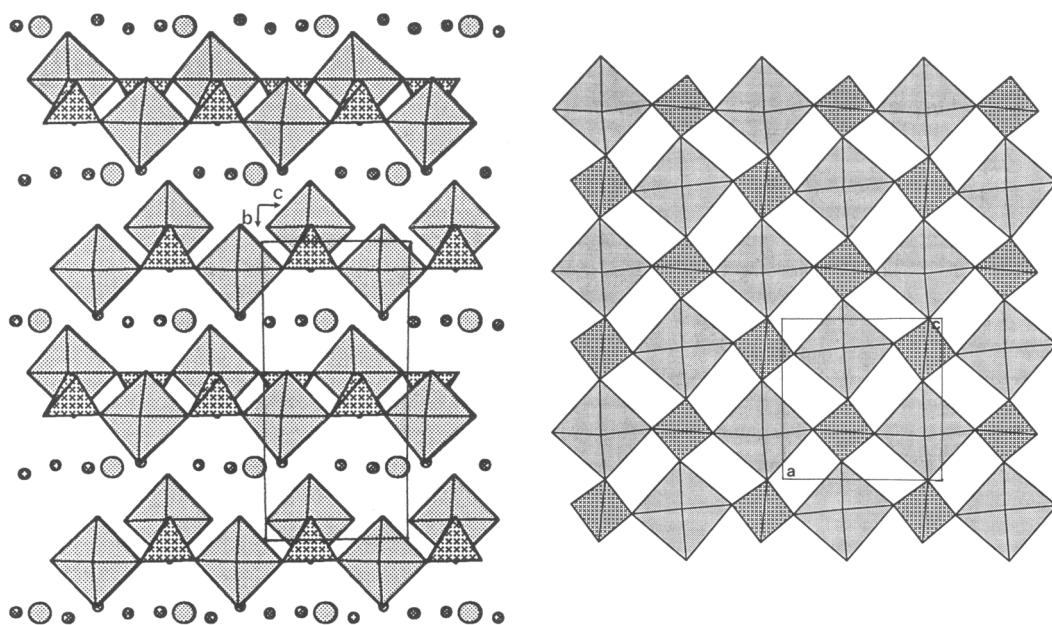


FIG. 2. The structure of synthetic monoclinic $Ba(VOPO_4)_2 \cdot 4H_2O$. (a) View down $\{100\}$ showing the $VOPO_4$ layers and the arrangement of interlayer Ba ions (large circles) and water molecules (small circles) (b) $\{010\}$ view of the $VOPO_4$ layers with Ba cations and water molecules omitted (after Roca *et al.*, 1997).

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