

Ba–Cu ordering in bariopharmacoalumite-*Q2a2b2c* from Cap Garonne, France

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ABSTRACT

Bariopharmacoalumite-*Q2a2b2c*, $\text{Ba}_{0.5}(\text{Cu}, \text{ZnO})_{0.1}\text{H}_{0.6}[\text{Al}_4(\text{OH})_4(\text{As}_{0.9}\text{Al}_{0.1}\text{O}_4)_3] \cdot 5.5\text{H}_2\text{O}$, from the south mine of the old copper mine at Cap Garonne, France, has a $2 \times 2 \times 2$ *I*-centred tetragonal superstructure of the basic pharmacosiderite-type structure. Cell parameters are $a = 15.405(2)$ Å and $c = 15.553(3)$ Å. The structure was determined and refined in $I\bar{4}2m$ to $R_1 = 0.057$ for 2697 reflections with $I > 2\sigma(I)$, using synchrotron X-ray data on a twinned crystal. The origin of the superlattice cell doubling was determined to be due predominantly to the ordering of Ba atoms in half of the $[0\ 0\ 1]$ channels, centred at $(0, 0, 0)$ and $(\frac{1}{2}, \frac{1}{2}, 0)$. The other channels, centred at $(\frac{1}{2}, 0, 0)$ and $(0, \frac{1}{2}, 0)$, were found to be occupied by corner-connected chains of Cu/Zn-centred square planar units.

KEYWORDS: pharmacosiderite, crystal structure, supercell, synchrotron, Cap Garonne, France.

Introduction

THE pharmacosiderite group of microporous minerals and synthetic equivalents is of considerable interest because of their ionic conductivity (Feng and Greenblatt, 1992) and ion exchange properties (Mutter *et al.*, 1984; Behrens and Clearfield, 1997; Tripathi *et al.*, 2004). According to a recent review of nomenclature for the minerals (Rumsey *et al.*, 2010), pharmacosiderite, $\text{K}[\text{Fe}_4(\text{OH})_4(\text{AsO}_4)_3] \cdot 6-7\text{H}_2\text{O}$ (Hausmann, 1813; Zemann, 1948) is used to define the mineral supergroup, with member groups including the pharmacosiderite, pharmacoalumite and ivanyukite groups, referring to the Fe–As, Al–As and Ti–Si members. The group members are further distinguished by suffixes indicating the symmetry and periodicity of the unit cell (*C* for cubic, *Q* for tetragonal or *T* for trigonal; Rumsey *et al.*, 2010; Hager *et al.*,

2010; Yakovenchuk *et al.*, 2009). The great flexibility of the structure to accommodate a large variety of substituting elements and valence states at all cation sites is indicated in published compositions for synthetic and ion-exchanged equivalents, which can be described by the general formula $A_{4-x}[B_4O_{4-y}(\text{OH})_y(\text{TO}_4)_3] \cdot n\text{H}_2\text{O}$, with $A = \text{K}^+, \text{Na}^+, \text{Li}^+, \text{Rb}^+, \text{Cs}^+, \text{H}_3\text{O}^+, \text{Ti}^+, \text{NH}_4^+, \text{Ag}^+, \text{Ba}^{2+}$ or Cu^{2+} ; $B = \text{Fe}^{3+}, \text{Al}^{3+}, \text{Mo}^{3+}, \text{Mo}^{4+}, \text{Ti}^{4+}$ or Ge^{4+} ; and $T = \text{As}^{5+}, \text{P}^{5+}, \text{Si}^{4+}, \text{Ge}^{4+}$ or Al^{3+} . Although the maximum value of $A = 4$ occurs for the synthetic phases $\text{Na}_4[\text{Ti}_4\text{O}_4(\text{SiO}_4)_3] \cdot 6\text{H}_2\text{O}$ (Dadachov and Harrison, 1997) and $\text{Ag}_4[\text{Ge}_4\text{O}_4(\text{GeO}_4)_3] \cdot 6\text{D}_2\text{O}$ (Roberts and Fitch, 1991), the majority of pharmacosiderite-type structures contain 1–2 *A* cations per formula unit (p.f.u.) (Rumsey *et al.*, 2010).

The structure for cubic ($a \approx 7.9$ Å) pharmacosiderite in space group $P\bar{4}3m$ was first determined by Zemann (1948) and confirmed by Buerger *et al.* (1967). Although some doubt existed over the location of the K^+ ion, subsequently found to be due to H_3O^+ exchange

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for K^+ in the samples studied (Mills *et al.*, 2010*a,b*), the details of the microporous framework were well established. It comprises cubane-like clusters of four edge-shared, Fe-centred octahedra, centred at the cell corners and interconnected *via* corner-sharing with AsO_4 tetrahedra located at the centres of the cell edges. The polyhedra form a 3-D open framework encasing spherical cavities that are interconnected along $\langle 1\ 0\ 0 \rangle$ *via* 8-member ring windows (four octahedral edges alternating with four tetrahedral edges). The large *A* cations can be located at or close to the centres of the windows (cell face centres) or within the cavities. Baur and Fischer (2013) have recently presented an alternative description of the pharmacosiderite structure as a rock-salt derivative structure based on a cubic close-packed anion lattice and with ordered vacancies at both anion and cation positions. The cubane cluster of four edge-shared octahedra in pharmacosiderite is a small element of the MgO rock-salt structure.

From a careful crystal chemical analysis of diffraction data for natural pharmacosiderite and pharmacalumite group minerals, Mutter *et al.* (1984) identified four polytypes. In addition to the archetype cubic phase there are three polytypes with space groups that are subgroups of $P\bar{4}3m$. They are tetragonal primitive, $P4_2m$, with $a \approx c \approx 7.9\text{ \AA}$; body-centred cubic, $I\bar{4}3m$, with $a \approx 15.8\text{ \AA}$ and body-centred tetragonal, $I\bar{4}2m$, with $a \approx c \approx 15.8\text{ \AA}$. In the primitive cubic polytype the *A* cations are distributed over the 3(*a*) sites at the cell-face centres. Mutter *et al.* (1984) proposed that in tetragonal polytypes ordering of *A* cations occurs on only one of the face centre sites, giving $c/a > 1$, or on two face centres for which $c/a < 1$. An additional polytype with space group $R\bar{3}m$, a trigonal subgroup of $P\bar{4}3m$, was found for ivanyukite-Na-*T* by Yakovenchuk *et al.* (2009). In all cases the distortion from cubic symmetry is very small. Crystal structure refinements have been conducted for examples of the trigonal (Yakovenchuk *et al.*, 2009) and primitive tetragonal (Hager *et al.*, 2010) polytypes, but no refinement of tetragonal mineral structures with doubled axes has been reported.

A pharmacalumite mineral with a tetragonal body-centred double cell was found at the Cap Garonne mine in Var, France and reported by Sarp *et al.* (1994). The mineral has Ba as the main *A* cation, together with a few percent of Cu and Zn, with a reported ideal formula $Ba_{0.5}(Zn,Cu)_{0.5}(Al,Fe)_4(AsO_4)_3(OH)_5 \cdot 5H_2O$. Sarp *et al.* (1994)

reported the unit-cell parameters $a = 15.476(2)$ and $c = 15.675(4)$ and space group $I\bar{4}2m$. According to the nomenclature for pharmacosiderite supergroup minerals (Rumsey *et al.*, 2010) coupled with IUCr conventions for polytypes (Guinier *et al.*, 1984), the mineral can be described as bariopharmacalumite- $Q2a2b2c$. In this study the structure of this mineral has been determined and refined using synchrotron data collected on a twinned crystal.

Experimental

The sample used for study was a hand specimen collected by one of us (G.F.) at the South mine of the Cap Garonne old copper mine near the town of Le Pradet, Var, France, close to the deloryite occurrence (Sarp and Chiappero, 1992). Cu/Zn-bearing bariopharmacalumite forms as mm-scale aggregates of colourless to pale yellow crystals, associated with quartz, baryte, mansfieldite, olivenite and bulachite. They form as interpenetrating cubes showing $\{1\ 0\ 0\}$ faces and are typically 50 to 200 μm across, as shown in fig. 1 of Sarp *et al.* (1994). In other parts of the hand specimen, clusters of elongated cubes are associated with fibres of bulachite as shown in Fig. 1. The specimen in the present study is not from the same part of the South mine as the specimen described by Sarp *et al.* (1994), which was found at Annex S, the type locality for

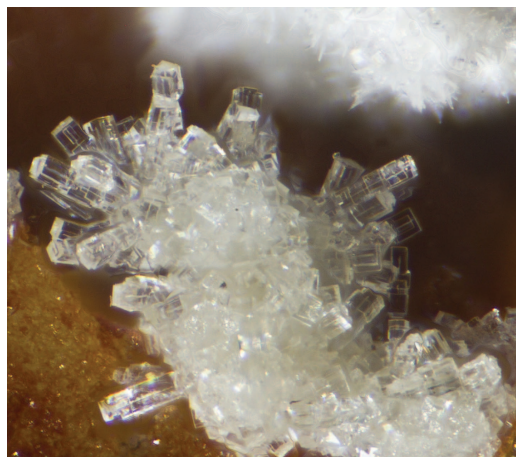


FIG. 1. Elongated colourless crystals of bariopharmacalumite with fibrous bulachite from the South Mine. Field of view: 0.5 mm. Museum Victoria specimen M52929.

forêtite (Mills *et al.*, 2012). It has been deposited in the collections of Museum Victoria, registration number M52929.

A portion of the hand specimen was mounted in a C-doped epoxy block, polished and carbon-coated for electron microprobe (EMP) analysis (JEOL Hyperprobe JXA-8500F, WDS mode, 15 kV accelerating voltage, 3 nA beam current and 5–10 μm defocused beam). Standards used were scorodite, $\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$ (Fe and As), adularia, KAlSi_3O_8 (K), chalcopyrite, CuFeS_2 (Cu), AlPO_4 (Al), benitoite, $\text{BaTiSi}_3\text{O}_9$ (Ba) and ZnS (Zn). The results are given in Table 1.

Individual crystals were screened for quality using oscillation photos. The patterns commonly showed streaking of the reflections and splitting due to twinning, particularly for those with a yellow colour. Eventually a small colourless crystal was found for which the oscillation photos showed relatively sharp reflections. The crystal was mounted at the end of a thin quartz rod for X-ray data collection on the macromolecular beam line MX2 of the Australian Synchrotron. Data were collected at 100 K using an ADSC Quantum 315r detector and monochromatic radiation with a wavelength of 0.7093 Å. A ϕ scan was employed with framewidths of 1° and a counting time per frame of 1 s. The intensity data sets were processed using *XDS* (Kabsch, 2010) without scaling and with absorption correction and scaling using *SADABS* (Bruker, 2001) giving 36,742 reflections with a mean I/σ of 7.6. The reflections were indexed with a triclinic cell, $a = 13.394$ Å, $b = 13.390$ Å, $c = 13.383$ Å, $\alpha = 109.72^\circ$, $\beta = 109.78^\circ$ and $\gamma = 109.00^\circ$. A search for higher symmetry gave a low figure-of-merit (FOM) for an *I*-centred tetragonal cell with $a = 15.405(2)$ Å and $c = 15.553(3)$ Å, similar to that reported by Sarp *et*

al. (1994). A reconstruction of the reciprocal lattice from the data frames showed the presence of non-fitted reflections due to twinning. Data collection and processing information are given in Table 2. The *WinGX* suite of programs (Farrugia, 1999) was used for the structure analysis, including *SHELX97* (Sheldrick, 2008) for the refinements.

The structure study began with an analysis of the subcell reflections corresponding to the tetragonal subcell with $a = 7.702$ Å and $c = 7.776$ Å. The starting model was that reported for bariopharmacosiderite-*Q* in space group $P\bar{4}2m$ by Hager *et al.* (2010). The model was refined to $R_1 = 0.09$ for 920 unique subcell reflections, using anisotropic thermal parameters. This is larger than the R_{merge} for equivalent reflections of 0.07, so *ROTAX* (Cooper *et al.*, 2002) was used to check for possible twin laws. Twinning by rotation about a pseudocubic 3-fold axis, coupled with racemic twinning, was effective and resulted in a lowering of R_1 to 0.048. The Ba atom was confirmed to be ordered in the *C* face-centred site 1(*d*) ($\frac{1}{2}$, $\frac{1}{2}$, 0), as proposed by Mutter *et al.* (1984). The only significant new structural feature to emerge from the subcell reflection refinement was a partially occupied site at ($\frac{1}{2}$, $\frac{1}{2}$, 0.229), located at only 1.8 Å from the Ba atom. For convenience of reference in the later discussion we will refer to this as the *X* site.

A starting model in the doubled supercell, space group $I\bar{4}2m$, was then generated from the subcell model. An important factor to be considered in the building of the supercell model was the strong likelihood that the axis doubling was due to ordering of the Ba atoms (which have only 50% occupancy of the 1(*d*) site in the subcell). Using the bariopharmacoalumite-*Q* subcell coordinates as a basis, the Ba 1(*d*) site

TABLE 1. EMP results (wt.%) for bariopharmacoalumite-*Q2a2b2c*.

Oxide	Range	Average (15 analyses)	Sarp <i>et al.</i> (1994)
Al_2O_3	24.7–28.4	26.1	26–30.5
Fe_2O_3	2.13–6.66	4.29	0–6.74
As_2O_5	39.7–44.2	41.5	34.4–41.7
BaO	8.04–9.89	8.83	5.73–9.87
K_2O	0.01–0.15	0.07	0.06–1.99
CuO	0.00–1.88	0.38	0.33–2.03
ZnO	0.15–1.03	0.70	0.73–4.68
Analysis Total	79.0–85.8	82.0	75.8–83.3
H_2O (by difference)	14.2–21.0	18.0	16.6–24.2

becomes the 8(i) site located at $(\frac{1}{4}, \frac{1}{4}, 0)$ in the $I\bar{4}2m$ supercell, so that ordering of four Ba atoms is not possible. Locating the origin of the subcell to $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, however, allows the Ba atom, now at $(0, 0, \frac{1}{2})$, to be split into two 4-fold sites, 4(*d*) at $(0, \frac{1}{2}, \frac{1}{4})$ and 4(*e*) at $(0, 0, z)$, where $z = \frac{1}{4}$, in the supercell. Refinement of the Ba occupancy for these two sites confirmed that Ba was ordered into the 4(*e*) site. Additionally, the *X* site was found to be located near the 4(*d*) site, unoccupied by Ba. Difference Fourier maps showed that an atom at this site is 4-coordinated with distances in the range 1.75 to 2.12 Å. The scattering curve for Cu was used for this site. As the microprobe analyses in the present study and earlier reported analyses by Sarp *et al.* (1994) both showed a deficiency of As, refinements were conducted with partial substitution of As by Al. Such incorporation of Al in both octahedral and tetrahedral sites of pharmacosiderite-type structures has been reported previously for synthetic aluminogermanates by Shin *et al.* (2011).

Refinement with anisotropic atomic displacement parameters for the framework atoms and Ba

and isotropic parameters for Cu/Zn and intra-channel water molecules converged at $R_1 = 0.057$ for 2697 observed reflections. Further refinement details are given in Table 2. The refined coordinates and equivalent isotropic atomic displacement parameters are given in Table 3. Tables of anisotropic atomic displacement parameters and observed and calculated structure factors have been deposited with the Principal Editor of *Mineralogical Magazine* and are available from www.minersoc.org/pages/e_journals/dep_mat_mm.html.

Results and discussion

The EMP analyses are given in Table 1. The ranges lie within those reported by Sarp *et al.* (1994), also given in Table 1 [averages not reported by Sarp *et al.* (1994)]. No clear element-element correlations are evident. They are probably masked by variations in analysis totals due to the strong sensitivity of the sample to beam damage, a point also noted by Sarp *et al.* (1994) and common in all pharmacosiderite and

TABLE 2. Crystal data and structure refinement for bariopharmacoalumite-*Q2a2b2c*.

Empirical formula	Ba _{0.5} (Cu,ZnO) _{0.1} H _{0.6} [Al ₄ (OH) ₄ (As _{0.9} Al _{0.1} O ₄) ₃]·5.5H ₂ O
Formula weight	754.5
Temperature	100 K
Wavelength	0.7093 Å
Crystal system	cubic
Space group	$I\bar{4}2m$
Unit-cell dimensions	$a = 15.405(5)$ Å, $c = 15.553(5)$ Å
Volume	3691(2) Å ³
Z	8
Density (calculated)	2.72 g/cm ³
Absorption coefficient	6.52 mm ⁻¹
<i>F</i> (000)	2942
Crystal size	0.05 mm × 0.03 mm × 0.015 mm
Collection mode	Phi scan, 360°, $\Delta\Phi = 1^\circ$, 1 s count time
Theta range for data collection	1.86 to 29.99°
Index ranges	$-21 \leq h \leq 21$, $-21 \leq k \leq 21$, $-21 \leq l \leq 21$
Reflections collected	36,742
Independent reflections	2824 [$R_{\text{int}} = 0.075$]
Completeness to $\theta = 29.99^\circ$	99.6%
Twinning	$\pm 120^\circ$ rotation about $[\bar{1} \ 1 \ 1] + \text{racemic}$
Refinement method	Full-matrix least-squares on F^2
Data / observed / parameters	2824 / 2697 / 154
Gof on <i>F</i> ²	1.074
Final <i>R</i> indices [$I > 2\sigma(I)$]	$R_1 = 0.057$, $wR_2 = 0.146$
<i>R</i> indices (all data)	$R_1 = 0.064$, $wR_2 = 0.158$
Extinction coefficient	0.0037(3)

TABLE 3. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for bariopharmacoalumite-Q2a2b2c.

Atom	Site	Occupancy	x	y	z	U(eq)
As1	8(i)	0.945(15)	2452(1)	2452(1)	-6(3)	22(1)
Al1		0.055(15)	2452(1)	2452(1)	-6(3)	22(1)
As2	16(j)	0.945(15)	5(2)	2502(1)	2550(1)	21(1)
Al2		0.055(15)	5(2)	2502(1)	2550(1)	21(1)
Al3	8(i)	1.0	3212(3)	3212(3)	3169(4)	19(1)
Al4	16(j)	1.0	8187(2)	3223(2)	3203(3)	19(1)
Al5	8(i)	1.0	8175(3)	8175(3)	3222(4)	19(1)
O1A	8(i)	1.0	3179(4)	3179(4)	4358(7)	29(2)
O1B	16(j)	1.0	8091(5)	3190(5)	4386(5)	25(1)
O1C	8(i)	1.0	8104(4)	8104(4)	4399(7)	31(2)
O2A	16(j)	1.0	3182(5)	4399(5)	3059(5)	23(1)
O2B	16(j)	1.0	8146(5)	4401(5)	3094(6)	29(2)
O2C	16(j)	1.0	3138(5)	9386(5)	3178(5)	29(2)
O2D	16(j)	1.0	8144(5)	9368(5)	3165(5)	27(2)
O3A	8(i)	1.0	1919(5)	1919(5)	1956(9)	19(2)
O3B	16(j)	1.0	6946(6)	1928(6)	1925(6)	21(2)
O3C	8(i)	1.0	6946(7)	6946(7)	1894(10)	27(3)
Extra-framework atoms						
Ba1	4(e)	0.812(9)	0	0	2501(1)	18(1)
Ba2	8(g)	0.042(4)	2525(19)	5000	0	60
Ba3	8(f)	0.042(4)	2520(19)	5000	5000	60
Cu	8(g)	0.100(9)	5000	0	3637(17)	73(9)
O4	4(d)	0.100(9)	5000	0	2500	73(9)
O5	4(c)	0.100(9)	5000	0	5000	73(9)
W1A	8(i)	1.0	847(6)	847(6)	6133(8)	34(2)
W1B	8(i)	1.0	5844(6)	5844(6)	6153(7)	31(2)
W1C	16(j)	0.54(2)	5789(17)	1392(17)	5721(16)	69(5)
W1D	16(j)	0.46(2)	5770(20)	900(20)	6180(18)	69(5)
W2A	8(g)	0.81(2)	3077(7)	5000	0	30(2)
W2B	8(f)	0.81(2)	3094(7)	5000	5000	30(2)
W3	2(a)	0.21(9)	0	0	0	60(40)

pharmacoalumite minerals (e.g. Rumsey *et al.*, 2010; Mills *et al.*, 2010b). The variable Fe content is considered to be due to μm -scale zoning with bariopharmacosiderite, as shown in Fig. 2. Attempts to include Fe at the Al sites in the refinement led to increased *R* values, so in calculating the empirical formula minor bariopharmacosiderite has been removed from the analyses.

The measured As_2O_5 levels are consistently lower than the value of 47.0 wt.% calculated for bariopharmacoalumite, $\text{Ba}_{0.5}\text{Al}_4(\text{OH})_4(\text{AsO}_4)_3 \cdot 4\text{H}_2\text{O}$ (Mills *et al.*, 2011). Similar low levels of As_2O_5 were reported by Sarp *et al.* (1994). An interpretation of this result, supported by subsequent refinements, is that there is partial substitution of Al^{3+} for As^{5+} in the tetrahedral

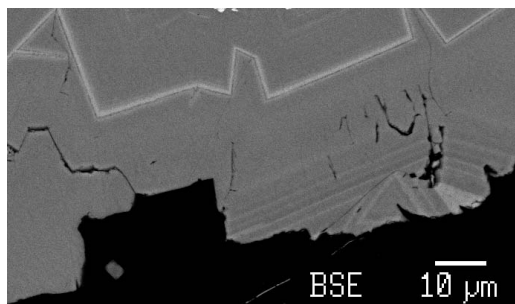


FIG. 2. Backscattered electron photomicrograph of bariopharmacoalumite-Q2a2b2c showing fine-scale zoning of bariopharmacosiderite (white).

sites. A precedent for Al^{3+} occupying both octahedral and tetrahedral sites in pharmacosiderite-type phases is given in the study of synthetic aluminogermanate phases reported by Shin *et al.* (2011). These authors used ^{27}Al nuclear magnetic resonance spectroscopy to confirm directly minor substitution of Al^{3+} for Ge at the tetrahedral sites. With the $\text{Al}^{3+}/\text{As}^{5+}$ substitution taken into account, the empirical formula for bariopharmacoalumite-*Q2a2b2c*

from the EMP analyses is $\text{Ba}_{0.5}(\text{Cu},\text{ZnO})_{0.1}\text{H}_{0.6}[\text{Al}_4(\text{OH})_4(\text{As}_{0.9}\text{Al}_{0.1}\text{O}_4)_3]\cdot 5.5\text{H}_2\text{O}$. The 0.6H in the formula is required for charge balance.

Substitution of a trivalent ion at the tetrahedral sites has not been reported previously for pharmacosiderite or pharmacoalumite minerals. The location of Al^{3+} at the As^{5+} sites was supported by the results of the structure refinement and the calculated bond lengths (Table 4). The refined Al^{3+} content of the As^{5+} sites is

TABLE 4. Polyhedral bond lengths and possible H-bonded anion–anion distances (Å) for bariopharmacoalumite-*Q2a2b2c*.

As1–O1A	1.693(10)	W1A–O2D	2.964(9)
–O1B	1.696(8)	–O2D	2.967(8)
–O1B	1.696(8)	–O3C	2.67(2)
–O1C	1.696(10)	–W2A	2.75(1)
		–W2A	2.75(1)
As2–O2A	1.696(7)		
–O2B	1.681(8)	W1B–O2A	2.952(9)
–O2C	1.680(7)	–O2A	2.953(9)
–O2D	1.685(7)	–O3A	2.66(2)
		–W2B	2.75(1)
Al3–O1A	1.85(1)	–W2B	2.75(1)
–O2A	1.837(8)	–W3	2.57(1)
–O2A	1.837(8)		
–O3B	1.97(1)	W1C–O1B	2.72(3)
–O3B	1.97(1)	–O2B	2.91(2)
–O3C	2.01(2)	–O3B	2.70(3)
		–O5	2.71(3)
Al4–O1B	1.85(1)		
–O2B	1.824(9)	W1D –O2B	2.80(3)
–O2C	1.850(9)	–O3B	2.67(4)
–O3A	1.982(9)	–O4	2.74(3)
–O3B	2.013(9)	–O5	2.58(3)
–O3C	1.99(1)		
Al5 –O1C	1.84(1)	W2B–O1A ($\times 2$)	2.982(7)
–O2D	1.841(9)	–W3	2.94(1)
–O2D	1.843(9)		
–O3A	1.98(1)	Split atoms	
–O3B	1.94(1)	W1C–W1D	1.04(3)
–O3B	1.94(1)		
		Metal–Metal	
Ba1–O2A ($\times 4$)	3.077(7)	Al3–Al4 ($\times 2$)	3.075(6)
–O2D ($\times 4$)	3.190(8)	–Al5	3.024(8)
–W1A ($\times 2$)	2.81(1)	–As1	3.185(4)
–W1B ($\times 2$)	2.79(1)	–As2 ($\times 2$)	3.175(4)
		Al4–Al4	3.072(7)
Cu–O4	1.77(3)	–Al5	3.054(6)
–O5	2.12(3)	–As1	3.198(6)
–W1D ($\times 2$)	1.84(4)	–As2	3.155(5)
		–As2	3.177(5)
		Al5–As1	3.173(8)
		–As2 ($\times 2$)	3.170(4)

5.6(1.5)%, which is smaller than the 10% Al from the average EMP analysis but within the range of individual analyses. The average As–O distances of 1.695(5) and 1.685(4) Å are longer than reported for cubic bariopharmacoalumite from Cap Garonne (1.665(14) Å; Mills *et al.*, 2011) and for cubic bariopharmacosiderite (1.66(2) Å; Hager *et al.*, 2010), as would be expected for partial Al^{3+} substitution, although the increases are barely significant. The Al–O bonds for the three independent octahedral sites, given in Table 4, show the same variations as reported for other phases containing cubane-type $[\text{Al}_4(\text{OH})_4\text{O}_8]^{4-}$ clusters with three short and three long bonds. The distances to μ_3 hydroxyls, shared between three octahedra, are considerably longer (1.94–2.01 Å) than the distances to the peripheral oxygens of the clusters that are shared with AsO_4 tetrahedra (1.82–1.85 Å). Confirmation that the μ_3 anions, O3A, O3B and O3C are predominantly hydroxyls comes from bond-valence calculations (Bresle and O’Keeffe, 1991), giving values of 1.23, 1.26 and 1.19 respectively.

A projection of the structure of bariopharmacoalumite- $Q2a2b2c$ along the c axis is shown in Fig. 3. This illustrates the ordering of Ba atoms in alternate [0 0 1] channels along [1 0 0] and [0 1 0]. The intervening channels contain the Cu and Zn atoms. A view of the Cu/Zn coordination and linkage is shown in Fig. 4a. The Cu/Zn atoms have slightly distorted square planar coordination. The individual square planar units are corner connected to form chains along [0 0 1] and are rotated by $\sim 90^\circ$ with respect to their corner-connected neighbours. The short average Cu/Zn–O distance of 1.89 Å is suggestive of Cu^{3+} . For comparison, $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ has chains of corner-connected square planar Cu^{3+} with an average Cu–O distance of 1.89 Å (David *et al.*, 1987) and $\text{KCu}^{3+}\text{O}_3$ has chains of edge-shared square planar units with Cu–O = 1.84 Å (Hestermann and Hoppe, 1969). The refined occupancy of the square planar metal atom site gives 0.100(8) atoms per formula unit (a.p.f.u.), which matches the sum of Cu+Zn from the EMP analyses. Zinc has been reported with square planar coordination in $\text{Ba}_3\text{Zn}_3\text{As}_2\text{O}_2$ (Brock and Kauzlarich, 1994).

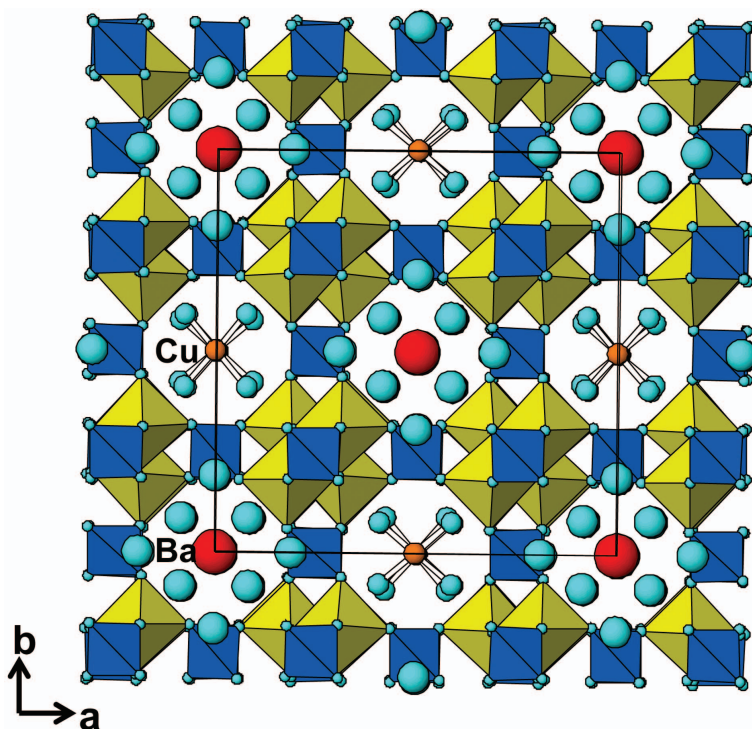


FIG. 3. Polyhedral framework of bariopharmacoalumite- $Q2a2b2c$, viewed along [0 0 1]. Large blue circles are water molecules, small blue circles are oxygen atoms.

The Ba atoms occupy the centres of 8-member ring windows connecting spherical cages that are stacked to form $[0\ 0\ 1]$ channels at the origin and C-centre of the supercell. The atoms are 8-coordinated to framework oxygens in the form of flattened rectangular antiprisms, with distances $\text{Ba1-O2A} = 3.08\ \text{\AA}$ ($\times 4$) and $\text{Ba1-O2D} = 3.19\ \text{\AA}$ ($\times 4$). Barium is also coordinated to a tetrahedron of water molecules, W1A and W1B, which sit above the centres of the long edges of the antiprisms as shown in Fig. 4*b* at shorter distances of $2.79\ \text{\AA}$ ($\times 2$) and $2.81\ \text{\AA}$ ($\times 2$). The same coordination is reported for tetragonal bariopharmacosiderite-*Q*, with eight long distances of $3.26\ \text{\AA}$ to framework oxygens and four shorter distances of $2.82\ \text{\AA}$ to water molecules (Hager *et al.*, 2010). In contrast, cubic bariopharmacoalumite has much longer distances to four water molecules of $3.18\ \text{\AA}$ (Mills *et al.*, 2011). This can be understood in terms of H bonding to other water molecules. In bariopharmacoalumite-*Q2a2b2c*, the W1A/W1B molecules form angles of $106\text{--}107^\circ$ with pairs of W2A/W2B water molecules at distances of $2.75\ \text{\AA}$, conducive to H bonding. In the cubic

phase, however, with disordered Ba atoms and water molecules, the water molecules equivalent to W2A/W2B (= O4 in Mills *et al.*, 2011) are located only $0.9\ \text{\AA}$ from Ba atoms and so cannot be present when the Ba site is occupied. This means that the water molecules bonding to Ba (= O3 in Mills *et al.*, 2011) are not constrained by H bonding to O4 water molecules and so are free to take up a different (longer) bond to Ba.

The ordering of Ba preferentially in one set of face-centred sites is not complete. The refined site occupancy for Ba1 in the 4(*e*) site at $\sim(0, 0, \frac{1}{4})$ gives only 0.4 atoms p.f.u., whereas the average EMP analysis corresponds to 0.48 Ba p.f.u. The remaining 0.08 Ba atoms were located at the other face-centred sites over which Ba is distributed statistically in the cubic $7.7\ \text{\AA}$ phase (Mills *et al.*, 2011). These correspond to the 8(*f*) site ($x, 0, 0$) and the 8(*g*) site, ($x, 0, \frac{1}{2}$), with $x \approx \frac{1}{4}$, in the $I\bar{4}2m$ supercell. Refinement using the scattering curve for Ba at these sites and with the thermal parameter fixed because of the small fractional occupancy, gave occupancies that agreed with the shortfall of 0.08 Ba p.f.u., as shown by the refinement results in Table 3. These minor Ba

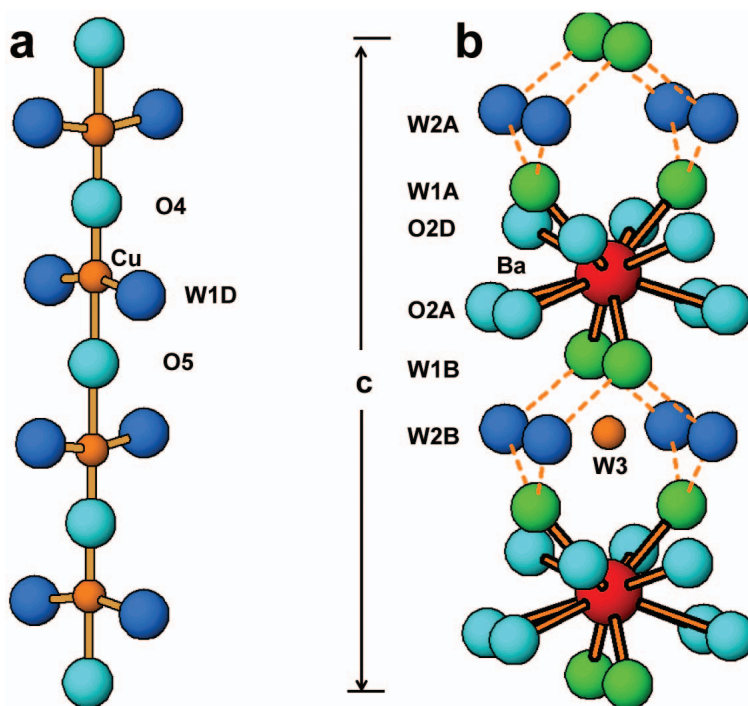


FIG. 4. (a) Columns of corner-sharing Cu/Zn-centred square planar units, occupying $[0\ 0\ 1]$ channels centred at $(\frac{1}{2}, 0, 0)$ and $(0, \frac{1}{2}, 0)$. (b) Ba1 and other extra-framework atoms in the $[0\ 0\ 1]$ channels centred at $(0, 0, 0)$ and $(\frac{1}{2}, \frac{1}{2}, 0)$.

sites are located only ~ 0.9 Å from water molecules W2A and W2B and in the early stages of the refinement they were considered to be split water sites. Similarly, the partially occupied Cu/Zn site was assigned initially as a water molecule site. Pharmacosiderite-type microporous phases present particular difficulties in assigning extra-framework cations and anions because of the occurrence of partially occupied and apparently split water molecule sites. In their structural study of $\text{Na}_3\text{H}_x(\text{H}_2\text{PO}_4)_x[(\text{Ge}_4\text{O}_4(\text{GeO}_4)_3)\cdot 4\text{H}_2\text{O}]$ using both X-ray and neutron diffraction data, Nenoff *et al.* (1994) noted that neither the Na^+ nor HPO_4^- ions could be located unambiguously by difference Fourier maps and were assumed to be disordered over the fractionally occupied water molecule sites.

The number of extra-framework water molecules from the structure refinement sum to 5.7 p.f.u., quite close to the value inferred from the EMP analyses. Distances between water molecules and to framework anions below 3 Å, indicative of H bonding, are given in Table 4. The W1A/W1B water molecules, bonded to Ba1, are probably donor atoms for H bonds to W2A/W2B and acceptor atoms for bonds from the hydroxyl ions O3A/O3C. The split W1C/W1D water molecules are in the channels containing the Cu/Zn atoms. They are acceptors for H bonds from the hydroxyl ion O3B and donors to the framework oxygens O1B/O2B and the O atoms O4 and O5 bonded to Cu/Zn. The W3 site at the origin is interesting. It sits at the centre of spherical cavities in the channels containing the Ba1 atoms and is surrounded by a tetrahedron of W1B molecules at 2.57 Å to W1B and four longer equatorial distances of 2.94 Å to W2B. The location of W3 is shown in Fig. 4b. It is possible that a hydronium ion, H_3O^+ , occupies this site. Mills *et al.* (2010a) have found this site in the centre of the spherical cages to be occupied in H_3O^+ -exchanged natropharmacosiderite but it is not occupied in the natropharmacosiderite used for the exchange experiment (Hager *et al.*, 2010).

There are no published studies of tetragonal, doubled-cell pharmacosiderite-type structures to compare with the results of the present study. Bialek and Gramlich (1992) have reported a single-crystal refinement of a synthetic germanate, $\text{K}_3\text{HGe}_7\text{O}_{16}\cdot 4\text{H}_2\text{O}$, with a body-centred cubic, doubled cell ($a = 15.418$ Å). In this case the superstructure was found to be predominantly due to small displacements of the Ge atoms, rather than to ordering of the extra-framework K^+

cations. Shin *et al.* (2011) obtained similar results from refinement of an Al-substituted K germanate using synchrotron powder X-ray diffraction data. Single-crystal studies are warranted on cubic and tetragonal superstructures of bariopharmacosiderite (Mutter *et al.*, 1984) to determine if Ba/vacancy ordering is a more general phenomenon in these minerals.

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