

Bariopharmacoalumite, a new mineral species from Cap Garonne, France and Mina Grande, Chile

S. J. MILLS^{1,*}, M. S. RUMSEY², G. FAVREAU³, J. SPRATT², M. RAUDSEPP¹ AND M. DINI⁴

¹ Department of Earth and Ocean Sciences, University of British Columbia, 6339 Stores Rd, Vancouver, British Columbia, Canada, V6T 1Z4

² Department of Mineralogy, Natural History Museum, Cromwell Road, London SW7 5BD, UK

³ 421 Avenue Jean Monnet, 13090 Aix-en-Provence, France

⁴ Escuela de Sociología, Universidad Central, Av. Francisco de Aguirre 0405, La Serena, Chile

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ABSTRACT

Bariopharmacoalumite, ideally $\text{Ba}_{0.5}\text{Al}_4(\text{AsO}_4)_3(\text{OH})_4 \cdot 4\text{H}_2\text{O}$, is a new mineral from Cap Garonne, France. It occurs in several places within the mine as colourless to pale yellow interpenetrating cubes up to 0.5 mm across. Bariopharmacoalumite is transparent to translucent, with a white streak, has an adamantine lustre and imperfect cleavage on {001}. The Vickers hardness is 234.35 and the Mohs harness is 3.5. Bariopharmacoalumite is isotropic, with $n = 1.573$ (upper estimate) [calculated from reflectance values at 589 nm using Fresnel Equations]. The empirical formula, based on 20 oxygen atoms, is: $(\text{Ba}_{0.54}\text{Cu}_{0.03}\text{K}_{0.01})_{\Sigma 0.58}(\text{Al}_{3.99}\text{Fe}_{0.02})_{\Sigma 4.01}(\text{AsO}_4)_{3.00}(\text{OH})_{3.85}\text{O}_{0.15} \cdot 4\text{H}_2\text{O}$ and the calculated density (on the basis of the empirical formula and single-crystal unit cell) is 2.580 g/cm³. The four strongest lines in the X-ray powder diffraction pattern are [$d_{\text{obs}}(\text{\AA})$, $I_{\text{obs}}(hkl)$]: 7.759, 100, (001); 5.485, 27, (011); 3.878, 27, (002); 4.454, 18, (011). Bariopharmacoalumite from Cap Garonne is cubic, space group $P43m$ with $a = 7.742(4)$ Å, $V = 464.2(4)$ Å³ and $Z = 1$. The crystal structure was solved by direct methods and refined to $R_1 = 0.0705$ for 215 reflections with $I > 4\sigma(I)$ and is consistent with members of the pharmacosiderite supergroup. Data are also presented from zoned bariopharmacoalumite–bariopharmacosiderite crystals found at the Mina Grande mine, Chile.

KEYWORDS: bariopharmacoalumite, bariopharmacosiderite, crystal structure, Cap Garonne, new mineral, Mina Grande mine, pharmacosiderite supergroup, Chile.

Introduction

THE pharmacosiderite supergroup of minerals (Rumsey *et al.*, 2010) has been thoroughly investigated recently to determine the crystal structure and exchange properties of members of the supergroup (e.g. Mills *et al.*, 2010a,b; Rumsey

et al., 2010). During these investigations, several new species have been discovered: including hydroniumpharmacosiderite (Mills *et al.*, 2010b) and natropharmacoalumite (Rumsey *et al.*, 2010), while several species of “ivanyukites”, also part of the supergroup, were described by Yakovenchuk *et al.* (2009). Here we present the third new member in our series of reports: bariopharmacoalumite. The mineral and name (IMA 2010-041) were approved by the IMA Commission on New Minerals, Nomenclature and Classification prior to publication. The holotype is preserved in the collections of the Natural History Museum, London, under the registration number BM 2010.82. Material removed from this

* E-mail: smills@nhm.org

Present address: Mineral Sciences Department, Natural History Museum of Los Angeles County, 900 Exposition Boulevard, Los Angeles, California 9007, USA

specimen and prepared for optical and chemical analysis is additionally registered as P16907. Further co-type material from the same find is registered as BM 2010,83 and material from the Mina Grande mine (which is not considered type but discussed in this paper) is registered as BM 2010,84.

History

A number of bariopharmacalumite occurrences has been reported in the literature over the past 50 years under different names. These are described briefly below:

'Barium-alumopharmacosiderite'

Walenta (1966) first reported a sample of "barium-alumopharmacosiderite" from the ancient copper mines of Neubulach, Black Forest, Germany. The "barium-alumopharmacosiderite" samples were all Fe-bearing and zoned, but in all instances were Al-dominant. The mineral forms as crusts of pale yellow crystals on mansfieldite and is associated with arsenocrandallite. The crystals form as cubes $\{001\}$ up to 50 μm across, with the form $\{111\}$ rarely observed. Refractive indices show $n = 1.650$ (rim) and $n = 1.62$ (core). Walenta (1966) also observed anomalous bluish to brownish interference colours and noted sector zoning. The cell dimension (determined from powder data) was: $a = 7.89 \text{ \AA}$, with the probable space group $P4_3m$. The mineral and its description were never submitted to the IMA for approval.

Wittern (2001) also reported "barium-alumopharmacosiderite" from the Michael mine, Weiler, Black Forest, Germany.

"Barium-zinc-alumopharmacosiderite"

"Barium-zinc-alumopharmacosiderite" was also published without approval by Sarp *et al.* (1994) from Cap Garonne, France. Sarp *et al.* (1994) reported the ideal formula as: $\text{Ba}_{0.5}\text{Cu}_{0.5}\text{Al}_4(\text{AsO}_4)_3(\text{OH})_5 \cdot 5\text{H}_2\text{O}$, and associated minerals including weilerite, mansfieldite, zeunerite, metazeunerite, cornubite, parnaute and olivenite. The crystals are colourless and pseudocubic, with a maximum dimension of 0.3 mm across. The crystal system was reported as tetragonal, with space group $I4_2m$ and cell $a = 15.476(2)$ and $c = 15.675(4) \text{ \AA}$.

New occurrences

Cap Garonne

The old copper mine of Cap Garonne is located near the town of Le Pradet, Var, France. It was operated between 1862 and 1917 through the technique of 'chambers and pillars'. Two mines were opened – the North and South mines, working sub-horizontal veins of conglomerates and sandstones of Triassic age. The minerals present are mainly secondary species deriving from the breakdown of tetrahedrite/tennantite and galena, usually developing in fractures or more rarely in cavities within the country rock (e.g. perroudit/capgaronnite/iltisite and ktenasite/guarinoite/theresemanganite). Part of the North mine now hosts a museum dedicated to the

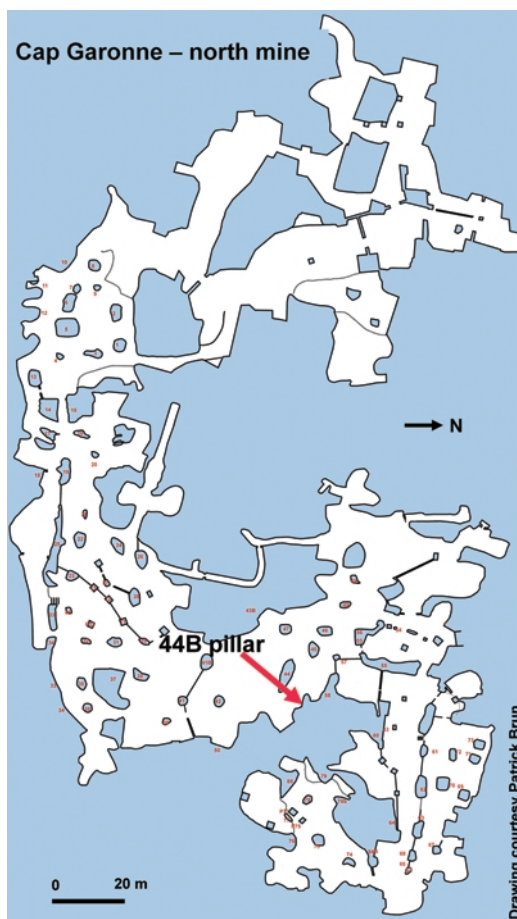


FIG. 1. Schematic map of the North mine, Cap Garonne, showing the position of the type locality (red arrow).



FIG. 2. View of pillar 44b, Cap Garonne mine. Arrow indicates the site where the type specimens were found.

mining history of the site, collaborating with the Association des Amis de la mine de Cap Garonne (AAMCG) to develop knowledge regarding the mineralogy of the mine.

Cap Garonne is the type locality for 12 species (camerolaite, capgaronnite, deloryite, geminite, guarinoite, iltisite, mahnertite, perroudite, pradetite, pushcharovskite, therese-magnanite, and zdenekite), and was the subject of two PhD studies (Guillemin, 1952; Chiappero, 1993). The latter introduced a systematic numbering of the pillars of the North mine, now used to locate accurately the origin of specimens. This numbering was extended by the AAMCG to include the walls at the periphery of the mine.

The type specimen of bariopharmacoalumite was collected in one of these new pillars, named 44b (Fig. 1). A long fracture in the conglomerate extends vertically from the lead-bearing levels (here associated with iron) at the top of the mineralized vein, down to copper-bearing levels at the bottom. Several aluminium-bearing minerals are observed in this fracture, including mansfieldite and philipsbornite. Other minerals present include: beudantite, carminite, duftite, mimetite, and scorodite in the Fe/Pb area, and olivenite and lavendulan in the Cu area (Fig. 2).

The mineral has also been found at four other places in the Cap Garonne mines. One in the North mine, where it was found opposite the pillar that produced the type specimen, in pillar 44, as

small (0.3 mm) white cubes covering fractures of the conglomerate, where it is associated with olivenite, arsesumebite and philipsbornite, and three in the South mine, from pillars that are not yet numbered. One of these South-mine occurrences is already famous among collectors for the discovery of deloryite (Sarp and Chiappero, 1992). At this locality, bariopharmacoalumite was collected in isolated white cubes (to 0.5 mm) in fractures containing zeunerite and mansfieldite. In the other two occurrences of the South mine, bariopharmacoalumite is found with lavendulan, mansfieldite and olivenite.

A bariopharmacoalumite-bearing specimen of unknown origin from within Cap Garonne mine is also present in the collections of the NHM, London registered originally as mansfieldite (BM 1965,346). This is a large 15 cm × 15 cm piece (Fig. 3) of fracture surface that was collected before the pillar numbering system was implemented. It shows rich encrustations of pale yellow bariopharmacoalumite cubes associated with mansfieldite, sky-blue arsenogorceixite and olivenite.

Mina Grande mine

The mine consists of two claims, Mina Grande and San Antonio, both now largely made up of old dumps and rock piles. The Mina Grande was worked for secondary copper ore by artisan

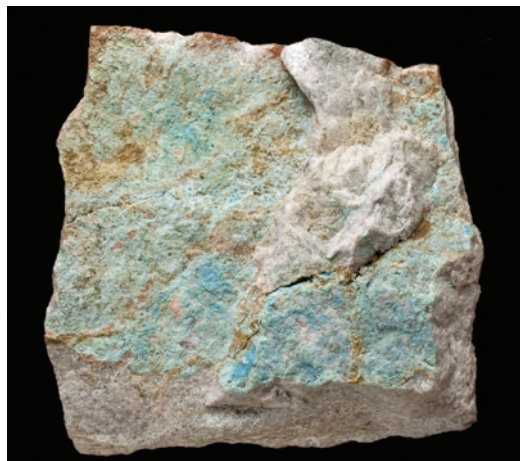


FIG. 3. Sample 1965,346 showing pale yellow bariopharmacoalumite cubes associated with mansfieldite, sky-blue arsenogorceixite and olivenite. Field of view: 16 cm across.

miners known locally as ‘*pirquineros*’¹, and both properties, notably Mina Grande, were worked for primary Cu (bornite and chalcopyrite) and Ag before 1840.

The local geology is dominated by andesitic breccias, which, according to Domeyko (1848), can be described as brecciated porphyric rock (“*porphyre bigarré*”). Geological interpretation of the site shows nearly horizontal mineralized strata (locally called “*mantos*”) that are probably sedimentary or volcanic in origin. This unit consists of bands of finely crystalline siliceous and calcareous rock, alternating with bands of more coarsely crystalline calcareous rock and it is within the latter, that most of the mineralization is found. The *mantos* are cut by vertical fault-related fractures that also carry significant mineralization and both of these mineralized features are cut by later non-mineralized basic dykes (Wilmot, 1960). There are two main veins recognized at Mina Grande – Veta Negra and Veta Blanca, both found in the west fault fracture. The main gangue mineral here is baryte, which is found in large quantities on the outer boundaries of the mineralized veins (Benitez, 1949). Other gangue materials include:

quartz, jasper and other undifferentiated brecciated carbonates. Near the surface, oxidized mineralization can still be observed in the form of secondary copper minerals including carbonates (malachite and azurite), silicates (chrysocolla), sulphates (brochantite) and arsenates (cornubite and olivenite). Domeyko (1848) also reported secondary Pb minerals including mimetite and pyromorphite.

Bariopharmacoalumite occurs here as zones within bariopharmacosiderite crystals. Due to the mode of occurrence, we were unable to determine all the physical properties of the mineral and so this occurrence could not be considered for co-type status. The bariopharmacoalumite–bariopharmacosiderite crystals are associated with quartz and chalcedony on a limonite-goethite matrix, which occurs close to the siliceous–calcareous strata.

Physical and optical properties

Cap Garonne

Bariopharmacoalumite typically occurs as radial growths of colourless to pale yellow interpenetrating cubes up to several millimetres across (Figs 4, 5). Individual cubes are generally <100 μm in size and some exhibit stepped growth features. Some cubes are elongated, giving a rectangular outline. The only form observed is {001}. Bariopharmacoalumite is transparent to translucent, with a white streak, has an adamantine lustre and imperfect cleavage on {001}. The tenacity is brittle, fracture irregular and is non-fluorescent. The Vickers hardness is 234.35 (load 245.75 mN) with a range (10 measurements) of 165.24–327.38, which is equivalent to 3.5 on the Mohs scale. The calculated density (on the basis of the empirical formula and single-crystal unit cell) is 2.580 g/cm³.

Bariopharmacoalumite is isotropic, with $n = 1.573$ (upper estimate) [calculated from reflectance values at 589 nm using Fresnel Equations]. A determination from individual fragments was attempted using refractive index oils; the results proved inconsistent however, probably due to minor chemical zonation. Bariopharmacoalumite shows anomalous extinction, typical of members of the supergroup and deep blue internal reflections probably due to twinning.

Mina Grande mine

Bariopharmacoalumite occurs as thin growth zones within bariopharmacosiderite crystals

¹ Pirquineros is the Chilean word meaning free handcraft miners, who worked together in small cooperatives or informal groups.

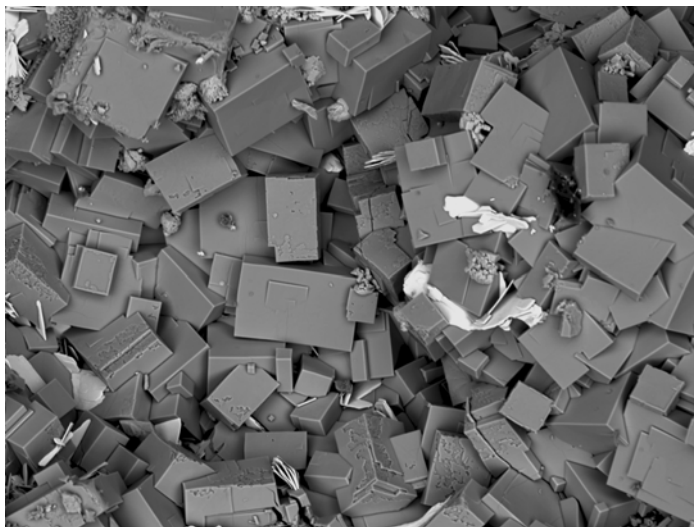


FIG. 4. BSE image of interpenetrating cubes of bariopharmacoalumite from Cap Garonne (South mine). Field of view: $\sim 150 \mu\text{m}$ across.

(Figure 6). The crystals range in colour from yellow to orange to light brown and in size from 0.1 to 0.5 mm across. $\{001\}$ is the only form observed. The crystals are opaque, have an orange streak and a dull lustre.

3 mm $\times$ 2 mm fragment from Cap Garonne consisting of ~ 100 intergrown crystals, using a Cameca SX100 electron microprobe at the Natural History Museum, London. The operating conditions were: 10 kV, 4 nA and a $30 \mu\text{m}$ beam diameter. Si, Ca, Na, P, Ti, Sr, Cl and F were

Chemical composition

Quantitative wavelength-dispersive EMP analyses (sixteen points) were carried out on a

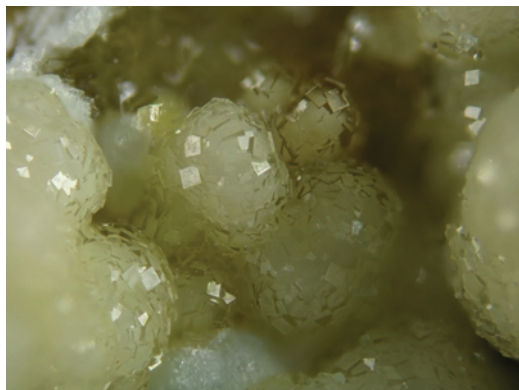


FIG. 5. Radial growths of yellowish interpenetrating cubes of bariopharmacoalumite from Cap Garonne (pillar 44b). Field of view: 1 mm across (photo – Jean-Marc Johannet).

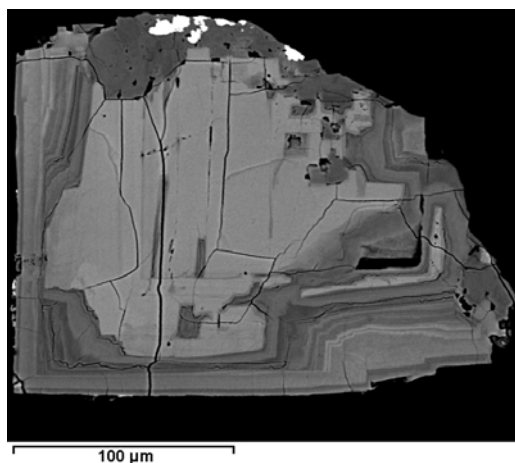


FIG. 6. Backscattered SEM image showing zoning in a single bariopharmacoalumite-bariopharmacosiderite crystal from the Grande mine, Chile. The brighter areas are bariopharmacoalumite. The crystal is $\sim 200 \mu\text{m}$ across.

TABLE 1. Analytical data for bariopharmacoalumite from Cap Garonne.

	Wt.%	Range	SD	Standards
K ₂ O	0.07	0.0–0.19	0.06	KBr
BaO	11.35	10.80–11.91	0.28	Baryte
CuO	0.35	0.26–0.46	0.06	Copper metal
Al ₂ O ₃	27.89	26.72–28.75	0.64	Corundum
Fe ₂ O ₃	0.19	0.0–1.21	0.38	Fayalite
As ₂ O ₅	47.28	46.43–47.83	0.28	GaAs
H ₂ O*	14.58	11.87–13.72	0.54	
Total	101.71			

* Calculated for the tetrahydrate.

sought for but were below the detection limit. The presence of OH and H₂O were confirmed by the crystal-structure analysis, but insufficient material was available for a direct determination of H₂O. H₂O was thus calculated from the results of the crystal-structure determination. Analytical data are given in Table 1. It should be noted that the slightly high total is attributed to the sensitivity of the mineral in the electron beam.

The empirical formula (based on 20 O atoms) is: (Ba_{0.54}Cu_{0.03}K_{0.01})_{Σ0.58}(Al_{3.99}Fe_{0.02})_{Σ4.01}(AsO₄)_{3.00}(OH)_{3.85}O_{0.15}·4H₂O. It is noted that the charge of (Ba_{0.54}Cu_{0.03}K_{0.01}) is 1.15⁺, necessitating the deprotonation of 0.15 p.f.u. of the bridging OH[−] ions. The simplified and ideal end-member formula of bariopharmacoalumite is: Ba_{0.5}Al₄(OH)₄(AsO₄)₃·4H₂O, which requires BaO 10.45, Al₂O₃ 27.87, As₂O₅ 47.00, H₂O 14.74, total 100.00 wt.%.

Crystallography

Cap Garonne

X-ray powder diffraction data for Cap Garonne bariopharmacoalumite were obtained on a Bruker D8 powder diffractometer, utilizing Co-K α radiation at the Department of Earth and Ocean Sciences, University of British Columbia, Canada. Data collected on a flat plate, are shown in Table 2. The refined unit-cell parameters using *Checkcell* (Laugier and Bochu, 2004) were: $a = 7.742(4)$ Å and $V = 464.2(4)$ Å³, which correspond well to the single-crystal data (see below).

The single-crystal study was carried out using a Bruker X8 ApexII single-crystal diffractometer at the Department of Chemistry, University of

British Columbia (Table 3). A single, cube-shaped fragment from a larger crystal mass was used for collection of intensity data at 293 K. The data were processed using the Bruker Apex program suite (Bruker, 2003), with data reduction using the *SAINT* program and absorption correction by the multi-scan method using *SADABS* (Bruker, 2003).

The structure was solved in space group $P\bar{4}3m$ by direct methods using SHELXS-97 and subsequent difference Fourier syntheses followed by full-matrix least-squares refinement on F^2 using SHELXL-97 (Seldrick, 2008). The initial location of the framework ions Fe/Al, As, O1 and O2 revealed that they were located in similar positions to those reported by Zemmann (1947, 1948) and Buerger *et al.* (1967) for the general pharmacosiderite structure. The O atoms of the

TABLE 2. Powder X-ray data for bariopharmacoalumite from Cap Garonne.

<i>hkl</i>	d_{obs}	I_{obs}	d_{calc}	I_{calc}
001	7.759	100	7.738	100
011	5.485	27	5.471	12
111	4.454	18	4.467	24
002	3.878	27	3.869	24
012	3.456	14	3.460	8
112	3.159	16	3.159	34
022	2.738	16	2.736	51
003	2.582	10	2.580	6
103	2.452	12	2.447	44

The four strongest lines are in bold.

BARIOPHARMACOALUMITE, A NEW MINERAL

TABLE 3. Crystallographic data and refinement parameters for bariopharmacoalumite.

	Cap Garonne	Mina Grande
Crystal data		
Ideal formula	Ba _{0.5} (Al,Fe) ₄ (OH) ₄ (AsO ₄) ₃ ·4H ₂ O	Ba _{0.5} (Al,Fe) ₄ (OH) ₄ (AsO ₄) ₃ ·4H ₂ O
Crystal system	cubic	cubic
Space group	<i>P</i> $\bar{4}$ 3 <i>m</i>	<i>P</i> $\bar{4}$ 3 <i>m</i>
Unit-cell parameters, <i>a</i> (Å)	7.772(2)	7.850(2)
Unit-cell volume, <i>V</i> (Å ³)	469.4(2)	483.7(2)
<i>Z</i>	1	1
Calculated density (g/cm ³)	2.58	2.61
Absorption coefficient (mm ⁻¹)	7.827	8.802
Crystal size (mm)	0.15 × 0.15 × 0.15	0.20 × 0.25 × 0.15
Data collection		
Diffractometer	Bruker X8 ApexII	Bruker X8 ApexII
Temperature (K)	293	293
Radiation, wavelength (Å)	Mo- <i>K</i> α, 0.71073	Mo- <i>K</i> α, 0.71073
θ range for data collection (°)	2.62–26.32	2.59–28.77
<i>h</i> , <i>k</i> , <i>l</i> ranges	–7 → 9; –3 → 9; –7 → 7	–8 → 8; –10 → 2; –6 → 7
Total reflections collected	1230	853
Unique reflections	215	266
Unique reflections <i>F</i> > 4σ(<i>F</i>)	168	192
Data completeness to θ _{max} (%)	99.2	98.8
Structure refinement		
Refinement method	Full-matrix least-squares on <i>F</i> ²	Full-matrix least-squares on <i>F</i> ²
No. of refined parameters, restraints	24, 1	26, 1
Weighting coefficients <i>a</i> , <i>b</i> *	0.1424, 0.99	0.163, 0.156
Extinction coefficient	0.12(3)	0
Data/restraints/parameters	215/1/24	266/1/26
<i>R</i> ₁ [<i>F</i> > 4σ(<i>F</i>)], <i>wR</i> ₂ [<i>F</i> > 4σ(<i>F</i>)],	0.0705, 0.1737	0.1004, 0.2459
<i>R</i> ₁ all, <i>wR</i> ₂ all	0.0929, 0.1924	0.1348, 0.2657
Goodness-of-fit on <i>F</i> ²	1.007	1.177
Largest diff. peak and hole (e/Å ³)	3.31, –0.62	1.80, –2.565

* Sheldrick (2008)

fractionally occupied H₂O molecules (O3 and O4) and the hydrogen for the hydroxyl atom (H2) were then added to the structure based on inspection of the difference Fourier map (Table 4). Refinement of the Ba site gave 0.41 a.p.f.u. though attempts to refine K on the site resulted in an unstable refinement. The *R*-factor increased in both cases; therefore we constrained the site at 0.5 a.p.f.u.. Refinement of the Al site gave an Al:Fe ratio of 0.78(4):0.22(4), which is more Fe-rich than the crystals analysed by electron probe – pharmacosiderite supergroup minerals tend to be zoned and can vary greatly from crystal to crystal. With the occupancies for O3 and O4 fixed at their previously refined values and with their thermal parameters constrained to be isotropic, due to the partial occupancy of these

atoms, an anisotropic refinement converged to *R*₁ = 0.0650. The structure reported herein is inverted; however, this gives atomic coordinates which are more easily comparable to all previously reported structures. This treatment is consistent with the structural reports for other members of the pharmacosiderite supergroup.

The average bond lengths (Table 5) for <As–O> and <Al–O> are fairly typical (1.665 and 1.933 Å), while the distance between O2 and O4 is 2.72 Å, which is indicative of H-bonding. The average bond length for the Ba site is 3.197 Å, which is in 12-fold coordination, is also very typical. All these values are consistent with the previous structure reports for the supergroup (e.g. Buerger *et al.*, 1967; Mills *et al.*, 2010a,b; Rumsey *et al.*, 2010).

TABLE 4. Final atom coordinates, site occupancies and atom displacement parameters ($\text{\AA}^2$) for bariopharmacoalumite.

	x/a	y/b	z/c	Occ.	U_{eq} or U_{iso}	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cap Garonne											
AsI	$\frac{1}{2}$	0	0	1	0.0315(13)	0.0258(17)	0.0344(15)	0.0344(15)	0	0	0
AlI	0.1421(5)	0.1421(5)	0.1421(5)	0.78(4)	0.028(3)	0.028(3)	0.028(3)	0.028(3)	-0.0039(17)	-0.0039(17)	-0.0039(17)
Fel	0.1421(5)	0.1421(5)	0.1421(5)	0.22(4)	0.028(3)	0.028(3)	0.028(3)	0.028(3)	-0.0039(17)	-0.0039(17)	-0.0039(17)
O1	0.1259(12)	0.3809(16)	0.1259(12)	1	0.038(4)	0.036(4)	0.036(4)	0.043(7)	0.004(4)	0.004(4)	-0.004(5)
O2	0.8881(13)	0.8881(13)	0.8881(13)	1	0.026(5)						
H2	0.829(2)	0.829(2)	0.829(2)	1	0.031						
Ba1	0	$\frac{1}{2}$	$\frac{1}{2}$	0.17	0.049(3)						
O3	$\frac{1}{2}$	0.120(8)	$\frac{1}{2}$	0.19	0.017(12)						
O4	0.686(5)	0.686(5)	0.686(5)	0.44	0.051(13)						
Mina Grande											
AsI	$\frac{1}{2}$	0	0	1	0.0237(14)	0.019(2)	0.0259(18)	0.0259(18)	0	0	0
AlI	0.1427(5)	0.1427(5)	0.1427(5)	0.58(5)	0.0115(18)	0.0115(18)	0.0115(18)	0.0115(18)	-0.0017(16)	-0.0017(16)	-0.0017(16)
Fel	0.1427(5)	0.1427(5)	0.1427(5)	0.42(5)	0.0115(18)	0.0115(18)	0.0115(18)	0.0115(18)	-0.0017(16)	-0.0017(16)	-0.0017(16)
O1	0.127(2)	0.393(2)	0.127(2)	1	0.040(5)	0.047(8)	0.026(10)	0.047(8)	0.001(6)	-0.009(10)	0.001(6)
O2	0.8878(19)	0.8878(19)	0.8878(19)	1	0.023(8)	0.023(8)	0.023(8)	0.023(8)	-0.006(6)	-0.006(6)	-0.006(6)
H2	0.829(2)	0.829(2)	0.829(2)	1	0.028						
Ba1	0	$\frac{1}{2}$	$\frac{1}{2}$	0.17	0.031(3)						
O3	$\frac{1}{2}$	0.137(13)	$\frac{1}{2}$	0.2	0.02(2)						
O4	0.690(10)	0.690(10)	0.690(10)	0.2	0.02(3)						

TABLE 5. Selected bond distances (Å) for bariopharmacoalumite.

		Cap Garonne	Mina Grande	
As1	O1	1.665(14)	1.64(2)	× 4
Al1	O1	1.864(14)	1.97(2)	× 3
Al1	O2	2.002(9)	2.029(12)	× 3
Ba1	O4	3.183(6)	3.220(6)	× 4
Ba1	O1	3.204(6)	3.205(10)	× 8
O2	H2	0.80(2)	0.80(2)	
O4	H2	1.92(4)	1.89(9)	

Mina Grande mine

A single crystal from the Mina Grande mine was also studied and determined in the same manner as the Cap Garonne sample to $R_1 = 0.1004$ (Table 3). Because of the diffuse nature of the spots, which correspond to the two different minerals, the R -factor is slightly larger than ideal, though refinement of the Al/Fe site can act as a proxy for bariopharmacoalumite:bariopharmacosiderite composition. In the case of the studied ‘crystal’ the refined Al:Fe is 0.58(4):0.42(4) (Table 4), indicating that the zoning seen in Fig. 6 is pervasive throughout the crystals, and that there is roughly an equal proportion of bariopharmacoalumite and bariopharmacosiderite in the bulk crystal.

Discussion

All “barium-alumopharmacosiderite” and “barium-zinc-alumopharmacosiderite” reports constitute legitimate bariopharmacoalumite occurrences in accordance to the nomenclature scheme of the pharmacosiderite supergroup (Rumsey *et al.*, 2010). The tetragonal “barium-zinc-alumopharmacosiderite” from Cap Garonne can be considered bariopharmacoalumite-*Qac* using polytypic nomenclature (where the cubic polytypes are suffixed –*Ca*). It is of note that both polytypes have also been reported for bariopharmacosiderite (Hager *et al.*, 2010). The formula reported by Sarp *et al.* (1994) for “barium-zinc-alumopharmacosiderite” is incorrect, as it is probable that $Ba+Zn = 0.5$ a.p.f.u., and that $(OH) \leq 4$. The instability of the mineral under the microprobe is likely to be the source of the errors in the reported totals. In the case where the total cation charge is $>1+$, deprotonation of OH occurs, therefore $(OH)_5$ is impossible.

We have also confirmed an additional locality for bariopharmacoalumite from the Gambatesa mine, Val Graveglia, Liguria, Italy, where it occurs as very pale greenish cubes on white schistose rock. The occurrence has been confirmed by single-crystal X-ray studies (Uwe Kolitsch/SJM) [$P\bar{4}3m$, $a = 7.7515(10)$] and SEM-EDS analyses (Corrado Balestra).

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References

- Benitez, F. (1949) *Mina Grande*. Sernageomin, Santiago de Chile, 1–2.
- Bruker (2003) *SAINT, SADABS and SHELXTL*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Buerger, M.J., Dollase, W.A. and Garaycochea-Wittke, I. (1967) The structure and composition of the mineral pharmacosiderite. *Zeitschrift für Kristallographie*, **125**, 92–108.
- Chiappero, P.-J. (1993) *Les arsénates de cuivre naturels: systématique et approche des conditions de genèse par les synthèses. Application au gisement plumbocuprifère de Cap Garonne, Var (France)*. PhD thesis, Université d’Orléans, France.
- Domeyko, I. (1848) Sur le plomb vanadaté et le vanadate double de plomb et de cuivre du Chili. *Annales de mines y de recueil de memoires sur l’exploitation de mines et sur le sciences et les arts qui s’y rapportant*, **14**, 145–149.
- Guillemin, C. (1952) Etude minéralogique et métallogénique du gîte plumbocuprifère du Cap Garonne (Var). *Bulletin de la Société Française de Minéralogie et de Cristallographie*, **75**, 1–159.
- Hager, S.L., Leverett, P., Williams, P.A., Mills, S.J., Hibbs, D.E., Raudsepp, M., Kampf, A.R. and Birch, W.D. (2010) The single-crystal X-ray structures of bariopharmacosiderite-C, bariopharmacosiderite-Q and natropharmacosiderite. *The Canadian Mineralogist*, **48**, 1477–1485.
- Laugier, J. and Bochu, B. (2004) *Chekkcell*: Graphical powder indexing cell and space group assignment software: <http://www.ccp14.ac.uk/tutorial/lmgp/>.

- Mills, S.J., Hager, S.L., Leverett, P., Williams, P.A. and Raudsepp, M. (2010a) The crystal structure of H_3O^+ -exchanged pharmacosiderite. *Mineralogical Magazine*, **74**, 487–492.
- Mills, S.J., Kampf, A.R., Williams, P.A., Leverett, P., Poirier, G., Raudsepp, M. and Francis, C.A. (2010b) Hydroniumpharmacosiderite, a new member of the pharmacosiderite supergroup from Cornwall, UK: structure and description. *Mineralogical Magazine*, **74**, 863–869.
- Rumsey, M.S., Mills, S.J. and Spratt, J. (2010) Natropharmacoalumite, $\text{NaAl}_4[(\text{OH})_4(\text{AsO}_4)_3]\cdot 4\text{H}_2\text{O}$, a new mineral of the pharmacosiderite supergroup and the renaming of aluminopharmacosiderite to pharmacoalumite. *Mineralogical Magazine*, **74**, 929–936.
- Sarp, H. and Chiappero, P.-J. (1992) Deloryite, $\text{Cu}_4(\text{UO}_2)(\text{MoO}_4)_2(\text{OH})_6$, a new mineral from the Cap Garonne mine near Le Pradet, Var, France. *Neues Jahrbuch für Mineralogie, Monatshefte*, 58–64.
- Sarp, H., Chiappero, P.-J. and Favreau, G. (1994) Barium-zinc alumopharmacosiderite de la mine de Cap Garonne (Var, France). *Archives des Sciences de Genève*, **47**, 45–50.
- Sheldrick, G. M. (2008) A short history of SHELX. *Acta Crystallographica*, **A64**, 112–122.
- Walenta, K. (1966) Beiträge zur Kenntnis seltener Arsenatminerale unter besonderer Berücksichtigung von Vorkommen des Schwarzwalds. *Tschermaks Mineralogische Petrographische Mitteilungen*, **11**, 121–164.
- Wilmot, A.H. (1960) *Report on the Talcuna group*. Sernageomin, Santiago de Chile, pp. 6–10.
- Wittern, A. (2001) *Mineralfundorte und ihre Minerale in Deutschland*. E. Schweizerbart'sche Verlagsbuchhandlung, Stuttgart, Germany, 286 pp.
- Yakovenchuk, V.N., Nikolaev, A.P., Selivanova, E.A., Pakhomovsky, Y.A., Korchak, J.A., Spiridonova, D.V., Zalkind, O.A. and Krivovichev, S.V. (2009) Ivanyukite-Na-T, ivanyukite-Na-C, ivanyukite-K, and ivanyukite-Cu: New microporous titanosilicates from the Khibiny massif (Kola peninsula, Russia) and crystal structure of ivanyukite-Na-T. *American Mineralogist*, **94**, 1450–1458.
- Zemann, J. (1947) Über die Struktur des Pharmakosiderits. *Experientia*, **3**, 452.
- Zemann, J. (1948) Formel und Struktur des Pharmakosiderits. *Tschermaks Mineralogische und Petrographische Mitteilungen*, **1**, 1–13.