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THE SINGLE-CRYSTAL X-RAY STRUCTURES OF BARIOPHARMACOSIDERITE-*C*, BARIOPHARMACOSIDERITE-*Q* and NATROPHARMACOSIDERITE

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ABSTRACT

The crystal structures of two polymorphic forms of bariopharmacosiderite have been determined. Bariopharmacosiderite-*C*, from Robinson's Reef, Clunes, Victoria, Australia, $(Ba_{0.47}K_{0.04}Na_{0.02})(Fe_{3.97}Al_{0.03})[(As_{0.72}P_{0.28})O_4]_3(OH)_4 \bullet 2.52H_2O$, is cubic, space group $P\bar{4}3m$, a 7.942(1) Å, $Z = 1$, $R = 0.089$. Bariopharmacosiderite-*Q*, from the Sunny Corner mine, Sunny Corner, New South Wales, Australia, $Ba_{0.5}Fe_4(OH)_4(AsO_4)_3 \bullet 6.16H_2O$, is tetragonal, space group $P\bar{4}2m$, a 7.947(1), c 8.049(2) Å, $Z = 1$, $R = 0.050$. In the cubic polymorph, Ba ions are disordered over all faces of the unit cell, whereas in the tetragonal polymorph, Ba ions are centered on the 001 face. In both cases, the Ba ions are 12-coordinate, with eight bonds to arsenate oxygen atoms; four H_2O groups complete the coordination sphere, with longer bonds to Ba in the cubic polymorph. Additional H_2O groups are hydrogen-bonded to each other and to the H_2O groups that coordinate Ba. Some of these exhibit "zeolitic" behavior. By analogy to the properties of synthetic pharmacoalumite, $KAl_4(AsO_4)_3(OH)_4 \bullet nH_2O$, the cubic polymorph appears to be more stable than the tetragonal one, although two further body-centered polymorphs are known. In addition, the crystal structure of natropharmacosiderite from the Gold Hill mine, Utah, has been determined. Natropharmacosiderite, $(Na_{0.75}K_{0.14}Ba_{0.11})_{\Sigma 1.00}Fe_4(AsO_4)_3(OH)_{3.89}O_{0.11} \bullet 4H_2O$, is cubic, space group $P\bar{4}3m$, with a 7.928(9) Å, $Z = 1$ and $R = 0.0654$. The Na position is displaced by ~0.2 Å from the Wyckoff 3*c* site, and is coordinated by four H_2O groups and eight oxygen atoms of arsenate groups. A new general formula for "excess cation" pharmacosiderite is proposed, involving deprotonation of bridging hydroxide ions.

Keywords: bariopharmacosiderite, natropharmacosiderite, crystal structure.

SOMMAIRE

Nous documentons la structure cristalline de deux formes polymorphiques de la bariopharmacosidérite. La bariopharmacosidérite-*C*, provenant de Robinson's Reef, Clunes, Victoria, en Australie, $(Ba_{0.47}K_{0.04}Na_{0.02})(Fe_{3.97}Al_{0.03})$

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$[(As_{0.72}P_{0.28})O_4]_3(OH)_4$•$2.52H_2O$, est cubique, groupe spatial $P\bar{4}3m$, a 7.942(1) Å, $Z = 1$, $R = 0.089$. La bariopharmacosidérite-Q, provenant de la mine Sunny Corner, à Sunny Corner, Nouveau Pays de Galles, en Australie, $Ba_{0.5}Fe_4(OH)_4(AsO_4)_3$•$6.16H_2O$, est tétragonal, groupe spatial $P\bar{4}2m$, a 7.947(1), c 8.049(2) Å, $Z = 1$, $R = 0.050$. Dans le polymorphe cubique, les ions Ba sont désordonnés sur toutes les faces de la maille élémentaire, tandis que dans le polymorphe tétragonal, les ions Ba sont centrés sur la face 001. Dans les deux cas, les ions Ba possèdent une coordinence 12, dont huit liaisons aux atomes d'oxygène de groupes arsenate; quatre groupes H_2O viennent compléter la sphère de coordinence, avec des liaisons plus longues au Ba dans le polymorphe cubique. Des groupes H_2O additionnels sont rattachés par liaisons hydrogène l'un à l'autre et aux groupes H_2O entourant le Ba. Certains de ceux-ci font preuve d'un comportement "zéolitique". Par analogie avec les propriétés de la pharmacoalumite synthétique, $KAl_4(AsO_4)_3(OH)_4$•nH_2O, le polymorphe cubique semble être plus stable que le polymorphe tétragonal, quoique l'on connaisse deux autres formes polymorphiques à maille centrée. De plus, nous décrivons la structure cristalline de la natropharmacosidérite provenant de la mine Gold Hill, au Utah. La natropharmacosidérite, $(Na_{0.75}K_{0.14}Ba_{0.11})_{\Sigma 1.00}$ $Fe_4(AsO_4)_3(OH)_{3.89}O_{0.11}$•$4H_2O$, est cubique, groupe spatial $P\bar{4}3m$, avec a 7.928(9) Å, $Z = 1$ et $R = 0.0654$. La position Na est déplacée d'environ 0.2 Å de la position Wyckoff 3c, et l'atome est coordonné à quatre groupes H_2O et huit atomes d'oxygène des groupes arsenate. Nous proposons une nouvelle formule générale pour les membres du groupe de la pharmacosidérite ayant un excédent de cations; cette formule implique une déprotonation des ponts d'hydroxyle.

(Traduit par la Rédaction)

Mots-clés: bariopharmacosidérite, natropharmacosidérite, structure cristalline.

Introduction

Pharmacosiderite, $KFe_4(AsO_4)_3(OH)_4$•nH_2O, n = 5–6 (*sensu stricto*), has been known for more than 200 years, but until recently, several of its structural peculiarities have remained to be elucidated. It was originally proposed to be cubic, although anomalous optical properties have been noted for many samples of the mineral (Palache *et al*. 1951) and its congeners. In line with early observations that it could be cation-exchanged (Hartley 1899), bariopharmacosiderite (Walenta 1966), natropharmacosiderite [renamed by Burke (2008); originally described as sodium pharmacosiderite; Peacor & Dunn (1985)], and hydroniumpharmacosiderite (Mills *et al*. 2010a, 2010b) have since been described. In addition, an Al-analogue of pharmacosiderite, pharmacoalumite, is known (Schmetzer *et al*. 1981; for nomenclature, see Rumsey *et al*. 2010), as are the Al-analogue of bariopharmacosiderite (Walenta 1966) and natropharmacoalumite (Rumsey *et al*. 2010).

Zemann (1947, 1948) reported the first structure of cubic pharmacosiderite, space group $P\bar{4}3m$; whereas the study established the overall framework of the structure, the K atoms could not be located. Similarly, Buerger *et al*. (1967) reported a single-crystal structural study confirming the basic lattice structure, but noted that the structure in space group $P\bar{4}3m$ is averaged, and the K atoms could not be found. Furthermore, a spectrographic analysis failed to reveal the presence of any alkali metals; it may be that the crystal studied was in fact the hydronium analogue, known previously from ion-exchange studies (Hartley 1899, Heide 1928, Mutter *et al*. 1984). The careful study by Mutter *et al*. (1984) did resolve ambiguities associated with reported anomalous optical properties and showed that pharmacosiderite and its congeners could crystallize in four related space groups; two are cubic, $P\bar{4}3m$ and $I\bar{4}3m$, with $a \approx 8$ and 16 Å, respectively, and two are tetragonal, $P\bar{4}2m$ and $I\bar{4}2m$, with $a \approx c \approx 8$ and 16 Å, respectively. We note that bariopharmacosiderite, as originally described, is tetragonal, $a = 7.97$, $c = 8.10$ Å; the optical character is uniaxial negative with $\varepsilon = 1.718$ and $\omega = 1.728$ (Walenta 1966). Whereas single-crystal X-ray structures for a number of synthetic AlP, MoP, TiSi, TiGe, (TiNb)Si and GeGe analogues of (FeAs) pharmacosiderite have been reported (Xu *et al*. 2004, and references therein), no satisfactory structure of any pharmacosiderite-group minerals has appeared in the literature, save for that of hydroniumpharmacosiderite. However, the structure of a synthetic cubic phase with the pharmacosiderite structure, $\{[Rb_{1.94}(H_2O,OH)_{3.84}](H_2)_{0.1}\}\{Al_4(OH)_4[PO_4]_3\}$, was recently described (Yakubovich *et al*. 2008). Here we report the structures of cubic natropharmacosiderite, space group $P\bar{4}3m$, bariopharmacosiderite-C and bariopharmacosiderite-Q, space groups $P\bar{4}3m$ and $P\bar{4}2m$, respectively. The suffixes -C and -Q refer to cubic and tetragonal polymorphs, respectively.

Experimental

Pale yellow crystals of bariopharmacosiderite from the Sunny Corner mine, Sunny Corner, New South Wales, Australia, were analyzed (SEM, EDS, standardless) and gave Ba:Fe:As proportions very close to the ideal stoichiometry, 0.5:4:3. Only traces of Al and other cations (Na, K) were detected. The crystals changed from pale yellow to green when left exposed to the atmosphere for two weeks, and the pale yellow color was restored upon heating at 100°C for 24 hours. Immersion in water for five minutes caused them to become green again, indicating that at least part of the water of crystallization is "zeolitic" in nature. Pale orange-brown, optically isotropic crystals of bariopharmacosiderite from Robinson's Reef, Clunes, Victoria, Australia (Museum Victoria specimen number

M7966) were analyzed (n = 5) with an electron microprobe (EMP) (WDS mode, 15 kV, 20 nA, 5 μm beam diameter). We used as standards albite (Na), synthetic $KTaO_3$ (K), anandite (Ba), hematite (Fe), corundum (Al), fluorapatite (P) and arsenopyrite (As). Analytical results [average, (range, SD)] were Na 0.07 (0.01–0.26, 0.10), K 0.18 (0.05–0.54, 0.18), Ba 8.55 (7.96–10.0, 0.75), Fe 26.16 (24.58–27.02, 1.01), Al 0.08 (0.07–0.09, 0.02), As 19.96 (19.55–20.39, 0.34), P 3.21 (2.80–3.60, 0.27), total 85.39 wt%. Insufficient material was available for the direct determination of H_2O. Normalization to (P + As) = 3 and setting (Fe + Al) = 4 gives $(Ba_{0.51}K_{0.04}Na_{0.02})_{\Sigma 0.57}(Fe_{3.97}Al_{0.03})[(As_{0.72}P_{0.28})O_4]_3(OH)_4 \bullet nH_2O$. If H_2O is calculated by difference, $n \approx 5$. However, the crystal-structure refinement indicates that there is less H_2O present. The slight excess positive charge of $(Ba_{0.51}K_{0.04}Na_{0.02})$, alternatively, could be accommodated by deprotonation of a small proportion of the bridging OH groups. It is also worth noting that the range of analytical data indicates that the crystals are chemically inhomogeneous, a feature of a number of naturally occurring members of the pharmacosiderite group (Hartley 1899, Heide 1928, Mutter *et al*. 1984, Mills *et al*. 2010b). In the structure refinement, the Ba site was fixed at $(Ba_{0.47}K_{0.04}Na_{0.02})$ with total charge equal to 1+, but this has no effect on the structural conclusions that are reached.

The sample of natropharmacosiderite used in this study is from the Gold Hill mine, Gold Hill, Tooele County, Utah, USA; it is composed of translucent to transparent orange to brown cubes and modified tetrahedra, which show the forms {001} and {111} and range in size up to 2 mm on edge. Globules of translucent conichalcite and transparent olivenite crystals forming clusters and radiating sprays up to 0.5 mm across are associated with the natropharmacosiderite. The sample has been deposited in the collections of Mineral Sciences Department, Natural History Museum of Los Angeles County, catalogue number LACMNH 61590.The sample was originally studied by Wise & Kokinos (1993), and confirmed as natropharmacosiderite by EMP (WDS) methods. The sample shows no substitution of Al for Fe, nor of P for As. The exchangeable cation contents are $(Na_{0.75}K_{0.14}Ba_{0.11})_{\Sigma 1.00}$.

Bariopharmacosiderite-Q from Sunny Corner

For the single-crystal analysis of the structure, a cleavage fragment was mounted on a Bruker SMART CCD diffractometer and data collected at 150(2) K with graphite-monochromatized Mo$K\alpha$ radiation. Data were corrected for Lorentz and polarization effects, and an absorption correction (Sheldrick 2008) was applied in each case. Unit-cell dimensions were determined by least-squares refinement of the complete datasets and are listed in Table 1 together with associated crystal data and structure-refinement details. The structures were solved by direct methods using SHELXS and subsequent difference-Fourier syntheses, starting with the coordinates of Zemann (1947, 1948) and Buerger *et al*. (1967) and refined on F^2 by full-matrix least-squares methods using SHELXL (Sheldrick 2008).

The unit cell of bariopharmacosiderite-*Q* is pseudocubic; we expected to find the Fe, As and O atoms in similar positions to those in the cubic pharmacosiderite-type structure of Buerger *et al*. (1967). This was confirmed, and the model refined isotropically to an $R1$ value of 0.21. A difference-Fourier map then revealed the remaining contents of the structure in the tunnels formed by the [Fe–As–O] lattice. A Ba^{2+} ion with a population parameter of *ca*. 50% was located at (½,½,0), *i.e*., *C*-face-centered, and a number of partially occupied H_2O molecule positions were found in tunnel sites at positions controlled by bonding to the Ba^{2+} ion or by hydrogen bonding. In addition, small amounts of H_2O are located in or near the faces unoccupied by Ba ions. Not all H_2O and Ba sites can be simultaneously occupied, and this is accommodated by their fractional occupancies. Isotropic refinement proceeded with a site occupancy of 50% for the Ba^{2+} ion and occupancies for the H_2O molecules being adjusted to give acceptable displacement-parameters. Refinement was continued using anisotropic displacement parameters for all atoms except the oxygen atoms of the partially occupied H_2O molecule, which were refined isotropically. This converged smoothly and resulted in acceptable displacement parameters for all atoms. A difference-Fourier map revealed the location of the hydroxyl hydrogen atom (on O2), but owing to the low population-parameters of the H_2O molecules in tunnel sites, no further hydrogen atoms could be reliably located. Refinement converged to an $R1$ of 0.0501 and $wR2$ of 0.1337. The weighting scheme used was $w = 1/(\sigma^2 F_o^2 + 0.0396P^2 + 9.76P)$, where $P = (F_o^2 + 2F_c^2)/3$, as defined by SHELXL97 (Sheldrick 2008). Final atom parameters are listed in Table 2, anisotropic displacement parameters in Table 3 and selected bond lengths and angles in Table 4. The refined stoichiometry of bariopharmacosiderite-*Q* from Sunny Corner is $Ba_{0.5}Fe_4(OH)_4(AsO_4)_3 \bullet 6.16H_2O$.

Bariopharmacosiderite-C from Clunes

The single-crystal structure analysis of the mineral was performed in the same way as above. The starting set of coordinates for Fe, As and O atoms of Buerger *et al*. (1967) refined isotropically to an $R1$ value of 0.22. A difference-Fourier map then revealed the positions of the contents of the tunnels formed by the framework of polyhedra. A Ba^{2+} ion with a population parameter of *ca*. 50% was located at (0,½,½), *i.e*., all faces are centered, as were two partially occupied H_2O molecule positions in tunnel sites at positions controlled by hydrogen bonding. Isotropic refinement then took into account the compositions of the Fe(Al), As(P) and Ba(K,Na) sites as determined by analysis, and with site occupancies for the Ba^{2+} ion and lattice

TABLE 1. BARIOPHARMACOSIDERITE: CRYSTAL DATA AND STRUCTURE-REFINEMENT DETAILS

	Bariopharmacosiderite-*Q*	Bariopharmacosiderite-*C*
Empirical formula*	$Ba_{0.5}Fe_4(OH)_4(AsO_4)_3$•$6.16H_2O$	$Ba_{0.5}Fe_4(OH)_4(AsO_4)_3$•$2.52H_2O$
Formula weight	886.33	778.82
Temperature	150 K	150 K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	Tetragonal	Cubic
Space group	$P\bar{4}2m$	$P\bar{4}3m$
Unit-cell dimensions	a = 7.947(1) Å c = 8.049(2) Å	a = 7.942(1) Å
Volume	508.3(1) Å^3	500.9(1) Å^3
Z	1	1
Density (calculated)	2.90 g cm^{-3}	2.58 g cm^{-3}
Absorbtion coefficient	9.63 mm^{-1}	7.37 mm^{-1}
F(000)	429	371
Crystal size	0.15 × 0.15 × 0.10 mm	0.15 × 0.15 × 0.10 mm
2θ range for data collection	5.06 to 57.48°	5.12 to 55.98°
Index ranges	$-10 \le h \le 10$, $-10 \le k \le 10$, $-10 \le l \le 10$	$-10 \le h \le 9$, $-10 \le k \le 10$, $-10 \le l \le 10$
Reflections collected	4686	4345
Independent reflections	704	269
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	704 / 1 / 50	269 / 1 / 23
Goodness-of-fit on F^2	1.29	1.45
Final R indices [$I > 2\sigma(I)$]	0.050, $wR2$ = 0.138	0.089, $wR2$ = 0.254
R indices (all data)	0.051, $wR2$ = 0.138	0.090, $wR2$ = 0.254
Extinction coefficient	0.011(6)	0.14(4)
Largest diff. peak and hole	1.39 and –2.50 e Å^{-3}	2.85 and –3.56 e Å^{-3}

* Simplified empirical formulae neglecting substitution at the Ba, As and Fe sites in bariopharmacosiderite-*C*. The refined model chemical formula for the latter sample is $(Ba_{0.47}K_{0.04}Na_{0.02})(Fe_{3.97}Al_{0.03})[(As_{0.72}P_{0.28})O_4]_3(OH)_4$•$2.52H_2O$ (see experimental section for a comment on fractionally occupied H_2O sites).

H_2O molecules being adjusted to give acceptable displacement-parameters. Refinement then converged with anisotropic displacement parameters for all atoms except the oxygen atoms of the partially occupied H_2O molecules, which were refined isotropically. However, we noted that the anisotropic tensors for Ba gave an unrealistic displacement-model, and subsequently it was refined isotropically. Attempts to split the Ba site with the ion disordered at *ca*. 0.025, ½, ½ resulted in an unstable model. It is possible that the Ba ion does sit at 0, ½, ½, and minor amounts of K and Na in the cell are sited at *ca*. 0.025, ½, ½. In natropharmacosiderite, the Na ions are indeed located at the latter site (see below). At present, with the quality of data as it is, we are unable to resolve this detail, and so the exchangeable cation site must be taken to be an average for Ba, K and Na. A difference-Fourier map revealed the location of the hydroxyl hydrogen atom (on O2), but again owing to the low population-parameters of the two H_2O molecules in the tunnel sites, no other hydrogen atoms could be reliably located. There was evidence in difference maps of several additional, partially occupied, H_2O molecule positions, but population parameters were quite low, and attempts to include them in the final model resulted in an unstable refinement. Refinement converged to an $R1$ of 0.089 and $wR2$ of 0.254. The weighting scheme used was $w = 1/(\sigma^2F_o^2 + 0.1131P^2 + 12.70P)$, where $P = (F_o^2 + 2F_c^2)/3$, as defined by SHELXL97 (Sheldrick 2008). The relatively high final R value may be attributed in part to merohedral twinning in the crystal studied (refined twin-ratio 0.69:0.31). Final atom parameters are listed in Table 2, anisotropic displacement parameters in Table 3 and selected bond lengths and angles in Table 4. The refined stoichiometry of bariopharmacosiderite-*C* from Clunes is $Ba_{0.5}Fe_4(OH)_4(AsO_4)_3$•$2.52H_2O$.

Natropharmacosiderite-C from Gold Hill

Single-crystal data were collected using a Bruker X8 Apex II diffractometer (Table 5). A cube-shaped crystal of dimensions 0.1 × 0.1 × 0.1 mm was used for collection of intensity data at 293 K. Data were processed with the Bruker Apex suite of programs; data reduction was performed using SAINT, and an absorption correction was made by the multi-scan method using SADABS. Unit-cell dimensions were determined by least-squares refinement of the complete dataset and are given in Table 5, together with associated crystal data

and structure-refinement details. The crystal structure of natropharmacosiderite was solved in space group $P\bar{4}3m$ starting with the coordinates of the framework atoms of Buerger *et al.* (1967). Subsequent difference-Fourier syntheses and least-squares refinement on F^2 using SHELXL (Sheldrick 2008) revealed the remainder of the unit-cell contents. The non-framework ions sited in the channels of the structure (Na, O3, O4 and H) were not refined anisotropically owing to the split nature of some sites and their low occupancies. Aside from the proton of the bridging OH group, other H atoms could not be reliably located. Refinement converged to an $R1$ of 0.065 and $wR2$ of 0.153. The slightly high R-factors are primarily due to the presence of twinning. However, the quality of the data is still good, and the final goodness-of-fit is 1.04. The weighting scheme used was $w = 1/(\sigma^2F_o^2 + 0.1233P^2)$, where P $= (F_o^2 + 2F_c^2)/3$, as defined by SHELXL97 (Sheldrick 2008). Final atom-parameters are listed in Table 6, and selected bond-lengths, in Table 7. The refined stoichiometry of natropharmacosiderite-*C* from Gold Hill is $(Na_{0.75},K_{0.14},Ba_{0.11})_{\Sigma 1.00}Fe_4(AsO_4)_3(OH)_{3.89}O_{0.11}\bullet 4H_2O$. This formula implies some deprotonation of the bridging hydroxide ions for charge balance.

TABLE 2. FINAL COORDINATES[a], SITE-OCCUPANCY FACTORS, AND EQUIVALENT ISOTROPIC-DISPLACEMENT PARAMETERS (Å²) OF ATOMS IN BARIOPHARMACOSIDERITE

Atom	*x*/*a*	*y*/*b*	*z*/*c*	sof	U_{eq}
Bariopharmacosiderite-*Q* from Sunny Corner					
Fe	0.1422(2)	0.1422(2)	0.1437(2)	1	0.0078(4)
As1	0	0	½	1	0.0112(5)
As2	½	0	0	1	0.0148(5)
O1A	0.1248(9)	0.1248(9)	0.3830(12)	1	0.016(2)
O1B	0.1252(9)	0.3855(7)	0.1214(8)	1	0.012(1)
O2	0.8858(9)	0.8858(9)	0.8868(11)	1	0.011(2)
H	0.828(9)	0.828(9)	0.821(16)	1	0.020
Ba	½	½	0	0.50	0.0330(9)
W1A	0.333(2)	0.333(2)	0.740(2)	0.50	0.017(4)
W1B	0.326(5)	0.255(6)	0.673(5)	0.145	0.015(9)
W2A	½	0	½	0.70	0.020(4)
W2B	0.160(4)	½	½	0.30	0.022(6)
W2C	½	½	0.129(8)	0.20	0.016(12)
Bariopharmacosiderite-*C* from Clunes					
Fe[b]	0.1431(4)	0.1431(4)	0.1431(4)	1	0.016(1)
As[c]	½	0	0	1	0.019(1)
O1	0.124(2)	0.387(2)	0.124(2)	1	0.031(4)
O2	0.888(2)	0.888(2)	0.888(2)	1	0.010(4)
H	0.831(2)	0.831(2)	0.831(2)	1	0.014
Ba[d]	0	½	½	0.176	0.016(3)
W1	0.688(12)	0.688(12)	0.688(12)	0.18	0.03(4)
W2	0.198(9)	½	½	0.3	0.03(2)

[a] Atoms designated W are oxygen atoms of H_2O molecules. [b] The Fe site was refined as $(Fe_{3.97}Al_{0.03})$, with displacement parameters for Fe and Al constrained to be equal. [c] The As site was refined as $(As_{0.72}P_{0.28})$, with displacement parameters for As and P constrained to be equal. [d] The Ba site was refined as $(Ba_{0.47}K_{0.04}Na_{0.02})$ so that the total charge is 1+, with displacement parameters for Ba, K and Na constrained to be equal.

Results and Discussion

The general structural framework (Fig. 1) in both bariopharmacosiderite-*C* and bariopharmacosiderite-*Q* conforms to that proposed by Zemann (1947, 1948) and Buerger *et al.* (1967), and in both cases the Ba^{2+} ions are located in the faces of the unit cell, as has been found for a number of related synthetic phases related to pharmacosiderite (Xu *et al.* 2004, and references therein). In the tetragonal structure, the cell is *C* face-centered

TABLE 3. BARIOPHARMACOSIDERITE: ANISOTROPIC DISPLACEMENT PARAMETERS (Å²)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Bariopharmacosiderite-*Q* from Sunny Corner						
Fe	0.0064(5)	$=U_{11}$	0.0110(7)	-0.0004(4)	$=U_{23}$	$=U_{23}$
As1	0.0110(7)	$=U_{11}$	0.012(1)	0	0	0
As2	0.0077(8)	0.019(1)	0.0175(9)	0	0	0
Ba1	0.033(1)	$=U_{11}$	$=U_{11}$	0	0	0
O1A	0.016(3)	$=U_{11}$	0.015(4)	0.000(3)	$=U_{23}$	-0.002(3)
O1B	0.014(3)	0.004(3)	0.016(3)	0.002(2)	-0.004(2)	-0.002(2)
O2	0.014(3)	$=U_{11}$	0.007(4)	-0.001(2)	$=U_{23}$	-0.001(3)
Bariopharmacosiderite-*C* from Clunes[a]						
Fe	0.016(1)	$=U_{11}$	$=U_{11}$	-0.0018(9)	$=U_{23}$	$=U_{23}$
As	0.008(2)	0.025(2)	$=U_{22}$	0	0	0
O1	0.029(5)	0.036(8)	$=U_{11}$	0.005(5)	0.003(7)	$=U_{23}$
O2	0.010(4)	$=U_{11}$	$=U_{11}$	0.000(4)	$=U_{23}$	$=U_{23}$

[a] Ba was refined isotropically (see text).

TABLE 4. BARIOPHARMACOSIDERITE: SELECTED BOND-DISTANCES (Å) AND ANGLES (°)

Bariopharmacosiderite-*Q*			Bariopharmacosiderite-*C*		
Fe–O1A	1.937(10)		Fe–O1	1.95(2)	×3
Fe–O1B	1.948(6)	×2	Fe–O2	2.06(1)	×3
Fe–O2	2.091(9)		<Fe–O>	2.01	
Fe–O2	2.064(6)	×2			
<Fe–O>	2.01				
O1A–Fe–O1B	99.0(3)		O1–Fe–O1	98.4(7)	
O1A–Fe–O2	92.4(4)		O2–Fe–O1	91.9(6)	
O1B–Fe–O1B	97.4(4)		O2–Fe–O2	75.6(9)	
O1B–Fe–O2	91.6(3)		<O–Fe–O>	89.5	
O1B–Fe–O2	90.4(3)				
O2–Fe–O2	76.8(4)				
O2–Fe–O2	76.4(4)				
<O–Fe–O>	89.5				
Ba–W1A	2.82(2)	×4	Ba–W1	3.26(2)	×4
Ba–O1B	3.258(7)	×8	Ba–O1	3.27(1)	×8
As1–O1A	1.69(1)	×4	As–O1	1.66(2)	×4
As2–O1B	1.670(7)	×4			

* For bariopharmacosiderite-*Q*, symmetry-related atoms with respect to *x*, *y*, *z* are #1: *y*, *x*, *z*; #2: -*y* + 1, *x* - 1, -*z* + 1; #3: *y* - 1, -*x* + 1, -*z* + 1; #4: -*x* + 1, -*y* + 1, *z* - 1.

by Ba^{2+} ions, which is 12-coordinated. Eight equivalent Ba–O bonds (3.26 Å) involve arsenate oxygen atom O1B, and the coordination sphere is completed by four shorter Ba–O bonds (2.82 Å) to the H_2O molecule W1A (Table 4). This situation is not maintained in the cubic structure, although the eight Ba–O bonds to arsenate oxygen are identical within error. In this instance, coordination is completed by four Ba–O bonds to H_2O molecules (W1), and these are substantially longer (3.26 Å) than those in bariopharmacosiderite-*Q*. The reason for this is not readily apparent.

The Fe^{3+} ion in both structures possesses a somewhat distorted octahedral coordination geometry completed by a *facial* arrangement of three hydroxide ions and three arsenate oxygen atoms; hydroxide ions each bridge three Fe^{3+} ions. The degree of distortion of the coordination sphere varies only slightly for the cubic and tetragonal structures, and average Fe–O bond lengths and O–Fe–O angles are the same in both structures, within error. The hydrogen atom of the bridging hydroxide group is hydrogen-bonded to the H_2O molecule coordinated to Ba in both structures (Table 8). The O2–H…W1 angle in bariopharmacosiderite-*C* is linear, but the corresponding angle in bariopharmacosiderite-*Q*, O2–H…W1A is 163(2)° as a consequence of the longer Ba–W1B bond. In the tetragonal structure, another lattice H_2O site (W1B) is found to hydrogen-bond to O2, with O2–H…W1B equal to 166(3)°. Atom W1B does not bond to Ba, and the siting of W1A and W1B is made possible by fractional occupancies of the atoms concerned, together with Ba; both H_2O groups cannot be present at the same time. Other possible hydrogen-bond contacts are listed in Table 8. Some of

TABLE 5. NATROPHARMACOSIDERITE: CRYSTAL DATA AND STRUCTURE-REFINEMENT DETAILS

Empirical formula	$(Na_{0.75}K_{0.14}Ba_{0.11})_{\Sigma 1.00}Fe_4(AsO_4)_3(OH)_{3.89}O_{0.11}\cdot 4H_2O$		
Formula weight	854.11	Temperature	273(2) K
Wavelength	0.71073 Å	Crystal system	Cubic
		Space group	$P\bar{4}3m$
Unit-cell dimension *a*	7.928(9) Å		
Volume	498.3(9) Å^3	*Z*	1
Absorption coefficient	8.16 mm^{-1}	*F*(000)	412
Crystal size		0.1 × 0.1 × 0.1 mm	
2θ range for data collection		5.14 to 65.84°	
Index ranges		$-11 \le h \le 4$, $-11 \le k \le 7$, $-5 \le l \le 11$	
Reflections collected		2312	
Independent reflections		385	
Refinement method		Full-matrix least-squares on F^2	
Goodness-of-fit on F^2		0.945	
Final *R* indices [$I > 2\sigma(I)$]		0.0683, *wR*2 = 0.1643	
R indices (all data)		0.1401, *wR*2 = 0.1963	
Extinction coefficient		0.00	
Largest diff. peak and hole		1.56 and -0.80 e Å^{-3}	

TABLE 6. FINAL COORDINATES, SITE OCCUPANCIES, AND DISPLACEMENT PARAMETERS (Å^2) OF ATOMS IN NATROPHARMACOSIDERITE-*C*

Atom	*x*/*a*	*y*/*b*	*z*/*c*	sof	U_{eq}
Fe	0.1429(3)	0.1429(3)	0.1429(3)	1	0.0229(8)
As	½	0	0	1	0.0201(7)
O1	0.1261(9)	0.1261(9)	0.3826(12)	1	0.026(3)
O2	0.8861(12)	0.8861(12)	0.8861(12)	1	0.018(4)
H	0.8283(19)	0.8283(19)	0.8283(19)	1[a]	0.021
Na[b]	0.050(13)	½	½	0.167	0.023(17)
O3	0.692(3)	0.692(3)	0.692(3)	0.5	0.041(9)
O4	0.130(9)	½	½	0.33	0.037(14)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Fe	0.0229(8)	= U_{11}	= U_{11}	-0.0001(9)	= U_{23}	= U_{23}
As	0.0163(12)	0.0220(9)	= U_{22}	0	0	0
O1	0.029(3)	0.029(3)	0.019(5)	0.002(3)	= U_{23}	-0.010(4)
O2	0.018(4)	= U_{11}	= U_{11}	0.001(3)	= U_{23}	= U_{23}

[a] For the refined stoichiometry $(Na_{0.75}K_{0.14}Ba_{0.11})_{\Sigma 1.00}Fe_4(AsO_4)_3(OH)_{3.89}O_{0.11}\cdot 4H_2O$, the sof is 0.97. [b] The Na site was refined as $(Na_{0.75}K_{0.14}Ba_{0.11})$ in line with results of electron-microprobe analyses, with displacement parameters for Na, K and Ba constrained to be equal.

TABLE 7. SELECTED BOND-DISTANCES (Å) IN NATROPHARMACOSIDERITE

As–O1	1.694(11)	×4	Na–O1	3.15(3)	×4
			Na–O1	3.41(3)	×4
Fe–O1	1.910(10)	×3	Na–O4	2.97(3)	×2
Fe–O2	2.061(8)	×3	Na–O4	3.56(3)	×2
<Fe–O>	1.99		<Na–O>*	3.27	
O2–H	0.79(2)		H...O3	1.87(2)	

* Includes contributions from Ba and K.

TABLE 8. HYDROGEN BONDING DETAILS AND OTHER O–O CONTACTS POSSIBLY INVOLVED IN HYDROGEN BONDING (Å, °)

Bariopharmacosiderite-*C*		Bariopharmacosiderite-*Q*	
O2–H	0.78(2)	O2–H	0.84(2)
H…W1	1.97(16)	H…W1B	1.84(5)
O2–H…W1	180(2)	O2–H…W1B	166(3)
		O2–H	0.84(2)
		H…W1A	1.92(6)
		O2–H…W1A	163(2)
W2–O1	3.17(2)	W2A–O1A	3.28(1)
		W2B–O1A	3.14(1)
		W2B–O1B	3.19(1)
W1–W2	2.30(9)	W1B–W2A	2.82(5)
		W1A–W2B	2.72(2)
		W1B–W2C	2.88(6)
W1–O1	3.19(3)	W1A–O1B	3.20(3)
		W1B–O1A	3.01(4)
		W1B–O1B	2.97(1)

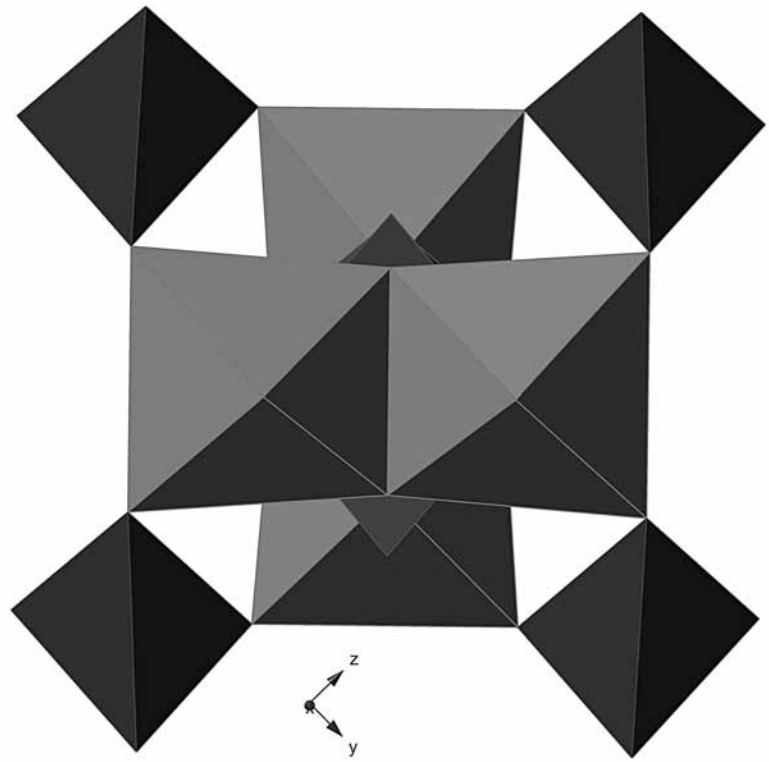

FIG. 1. The basic framework of the pharmacosiderite structure. The AsO_4 tetrahedra are dark grey, and the FeO_6 octahedra are lighter.

the water of crystallization is "zeolitic" in nature, a fact noted by earlier workers (Hartley 1899, Heide 1928, Mutter *et al*. 1984).

The two polymorphs described here are so similar in structure that there is no perceivable reason for the fact that they should form at all. Nevertheless, an unusual Ostwald effect (Ostwald 1897) has been discerned during the preparation of synthetic alumopharmacosiderite (S.L. Hager, unpubl. results). Initially, unstable monoclinic or tetragonal $KAl_4(AsO_4)_3(OH)_4 \bullet nH_2O$ is obtained, and these decompose in the solid state at room temperature to cubic alumopharmacosiderite result. This suggests that bariopharmacosiderite-*C* may well be the stable polymorph, but no such inference can be made with respect to the body-centered polymorphs that also exist (Mutter *et al*. 1984).

The structural framework of natropharmacosiderite also conforms to that of the general pharmacosiderite structure-type (Zemann 1947, 1948, Buerger *et al*. 1967). The crystal studied is cubic, space group $P\bar{4}3m$, but in line with the observations of Mutter *et al*. (1984), other polymorphs of natropharmacosiderite are possible. The structure differs from that of pharmacosiderite by having the Na ion displaced from Wyckoff 3*c* site at 0, ½ ,½ by ~0.2 Å. This phenomenon has been noted in the Cs titanosilicate analogues of pharmacosiderite (Harrison *et al*. 1995) and a synthetic Rb phosphate analogue of pharmacosiderite (Yakubovich *et al*. 2008). In natropharmacosiderite, the Na (+ K,Ba) atom is 12-coordinate, with eight bonds to arsenate oxygen atoms, four of 3.21 and four of 3.33 Å. The coordination sphere is completed by two bonds (3.11 Å) and two longer contacts (3.41 Å) to the H_2O molecule (O3). For the cation placed at the Wyckoff 3*c* site, the 12-fold coordination sphere involves four equivalent bonds to O3, whereas the remaining eight equivalent bonds are all to O1. If placed on this site, the *R* factor and displacement parameter both increase.

As is the case with the two structures of bariopharmacosiderite above, the hydrogen atom of the bridging hydroxide group bonds to O3, and forms a linear bond. In natropharmacosiderite, the H...O3 distance is slightly shorter (1.87 *versus* 1.97 Å), reflecting the bonding scheme of Na to O3. Further hydrogen atoms have thus far been unaccounted for in the pharmacosiderite structure.

Detailed investigations of the difference-Fourier maps provided one possible candidate for hydrogen bonding to O4. The possible hydrogen position was located in difference-Fourier maps at (0.0926, 0.4876, 0.3555) with an intensity of 0.5 *e* Å^{-3}, sitting ~1.1 Å from O4 within the channels. If left unrefined, the O4–H distance is slightly long for an H_2O molecule, and displacement parameters and site occupancies for both atoms are unstable or unrealistic (the hydrogen atom is required to be partially occupied). Using restraints and allowing the position and occupancy to refine yield a position at [0.078(19), 0.47(3), 0.394(13)], with a U_{eq} = 0.061 and a site occupancy of 0.7. In this position, the O4–H distance is 0.96 Å, and H...O1 is 3.11 Å, both reasonable values. However, the final *R* factor increased slightly because of the uncertainty in the position and associated increase in the displacement parameter of O4, and hence this hydrogen atom was left out of the final model.

It is appropriate to consider the general formula for pharmacosiderite-group minerals. Peacor & Dunn (1985) reported the simplified formula of natropharmacosiderite as $Na_2(OH)Fe_4(AsO_4)_3(OH)_4$•~$7H_2O$, but their analytical total was 106.2 wt%, and the formula was normalized to 100 wt% with H_2O kept at 19.3 wt% (determined by the Penfield method). Assuming that this composition represents the true formula of the crystal studied, the formula is more properly $Na_2Fe_4(AsO_4)_3(OH)_3O$•~$7H_2O$, where a bridging hydroxyl ion is deprotonated, rather than postulating additional hydroxyl ions. Thus, natropharmacosiderite from the type locality represents a stoichiometric variant of the general pharmacosiderite formula. The natropharmacosiderite from Gold Hill, on the other hand, has a more typical formula, $(Na_{0.75}K_{0.14}Ba_{0.11})_{\Sigma 1.00}Fe_4(AsO_4)_3(OH)_{3.89}O_{0.11}$•$4H_2O$, but with less H_2O than pharmacosiderite. We note that the structure is still maintained with significantly less H_2O (*e.g.,* bariopharmacosiderite-*C* with 2.52 H_2O), so that there is no absolute quantity required for the formation of natropharmacosiderite. Because of this factor, we recommend that the general formula for natropharmacosiderite be written as $Na_{1+x}Fe_4(AsO_4)_3(OH)_{4-x}O_x$•$nH_2O$, but we note that the exact range for *x* and *n* are not well constrained owing to the rarity of the mineral. Each occurrence is likely to have a slightly different stoichiometry.

Both Ba-dominant structures reported here are close to the "ideal" stoichiometry, $Ba_{0.5}Fe_4(AsO_4)_3(OH)_4$•$nH_2O$. Bariopharmacosiderite-*Q* was first reported from the Clara mine in Black Forest, Germany by Walenta (1966), who gave the formula $BaFe_4(AsO_4)_3(OH)_5$•nH_2O. Various amounts of Ba *pfu* have been found in a number of specimens including 1.0 Walenta (1966, 1994), 0.8–1 (Mutter *et al.* 1984) and 0.4–0.7 (Peacor & Dunn 1985). Charge compensation was dealt with explicitly by Walenta (1966, 1994) by introducing an extra hydroxyl ion in the formula, derived by the deprotonation of a H_2O molecule. Similar patterns of substitution of monovalent cations in amounts greater than 1.0 have been reported for other members of the pharmacosiderite group (Mutter *et al.* 1984). More recently, Sejkora *et al.* (2006) reported a series of compositions of pharmacosiderite with K^+ contents ranging up to 3.35 *pfu*. It is unlikely that these formulae can be accounted for by increasing the number of hydroxyl ions in the structure, and Mutter *et al.* (1984) have shown by Mössbauer spectroscopy that there is no replacement of Fe^{3+} by Fe^{2+} in pharmacosiderite. It is likely that charge compensation is achieved in these cases by deprotonation of the bridging OH. Thus for Ba = 1.0 *pfu*, a stoichiometry of $BaFe_4(AsO_4)_3(OH)_3O$•nH_2O is derived, with a potential series of substitutions to an end-member composition $Ba_{2.5}Fe_4(AsO_4)_3O_4$•nH_2O. With pharmacosiderite itself, further substitution of $K^+ \rightarrow H^+$ may proceed until all cell faces are fully occupied, resulting in the formula $K_3Fe_4(AsO_4)_3(OH)_2O_2$•$nH_2O$. Thus it is clear that the pharmacosiderite group hosts a family of stoichiometries, as well as a range of structures. Finally, it is noted that color variation in the group is well known, ranging from pale yellow or green to deep orange, red and red-brown (Hartley 1899, Heide 1928, Palache *et al.* 1951, Mutter *et al.* 1984). This must arise by a change of the Fe^{3+} ion chromophore, and this cannot be achieved by deprotonating lattice H_2O molecules in the structure. However, changing the chromophore from $FeO^{As}_3(OH)_3$ to $Fe\ O^{As}_3O^{OH}(OH)_2$ (O^{As} and O^{OH} represent arsenate and deprotonated OH oxygen atoms, respectively) would explain the change of color of pharmacosiderite-group minerals from pale greenish yellow for "ideal" stoichiometries to orange and red for "excess cation" stoichiometries. The change is akin to that observed for $[Fe(H_2O)_6]^{3+}$ (pale lavender) to $[Fe(H_2O)_5OH]^{2+}$ (orange). As more exchangeable cations are added to the lattice, charge balance is simply maintained by further deprotonation of available Fe_3OH centers.

Supplementary Data

Full lists of crystallographic data excluding structure-factor tables have been deposited with the Inorganic Crystal Structure Database (ICSD), Fachinformationszentrum, Karlsruhe, Germany; CRYSDATA@FIZ-Karlsruhe.DE. Any request to the ICSD for this material should quote the full literature citation and the CSD number 420545 for bariopharmacosiderite-*C*, CSD number 420544 for bariopharmacosiderite-*Q* and CSD number 422350 for natropharmacosiderite. Tables of structure factors are available from the Depository of Unpublished Data on the MAC website [document Bariopharmacosiderite CM48_1477 and Natropharmacosiderite CM48_1477].

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