Hydroniumpharmacosiderite, a new member of the pharmacosiderite supergroup from Cornwall, UK: structure and description

S. J. MILLS^{1,*}, A. R. KAMPF², P. A. WILLIAMS³, P. LEVERETT³, G. POIRIER⁴, M. RAUDSEPP¹ AND C. A. FRANCIS⁵

¹ Department of Earth and Ocean Sciences, University of British Columbia, Vancouver BC, Canada V6T 1Z4

- ² Mineral Sciences Department, Natural History Museum of Los Angeles County, 900 Exposition Boulevard, Los Angeles, California 90007, USA
- ³ School of Natural Sciences, University of Western Sydney, Locked Bag 1797, Penrith South DC, NSW 1797, Australia
- ⁴ Mineral Sciences Division, Canadian Museum of Nature, PO Box 3443, Station D, Ottawa, Ontario, Canada K1P 6P4
- ⁵ Harvard Mineralogical Museum, 24 Oxford Street, Cambridge, Massachusetts 02138, USA

[Received 29 July 2010; Accepted 30 September 2010]

ABSTRACT

Hydroniumpharmacosiderite, ideally (H₃O)Fe₄(AsO₄)₃(OH)₄·4H₂O, is a new mineral from Cornwall, UK, probably from the St. Day group of mines. It occurs as a single yellowish green, slightly elongated cube, measuring 0.17 mm × 0.14 mm × 0.14 mm. The mineral is transparent with a vitreous lustre. It is brittle with a cleavage on {001}, has an irregular fracture, a white streak and a Mohs hardness of 2–3 (determined on H₃O-exchanged pharmacosiderite). Hydroniumpharmacosiderite has a calculated density of 2.559 g cm⁻³ for the empirical formula. The empirical formula, based upon 20.5 oxygen atoms, is: [(H₃O)_{0.50}K_{0.48}Na_{0.06}]_{1.04}(Fe_{3.79}Al_{0.22})_{4.01}[(As_{2.73}P_{0.15})_{2.88}O₁₂](OH)₄·4H_{2.14}O. The five strongest lines in the X-ray powder diffraction pattern are [d_{obs} (Å), I_{obs} ,(hkl)]: 8.050,100,(001); 3.265,35,(112); 2.412,30,(113); 2.830,23,(202); 4.628,22,(111). Hydroniumpharmacosiderite is cubic, space group $P\bar{4}3m$ with a = 7.9587(2) Å, V = 504.11(2) Å³ and Z = 1. The crystal structure was solved by direct methods and refined to $R_1 = 0.0481$ for 520 reflections with $I > 2\sigma(I)$. The structure is consistent with determinations for H₃O-exhchanged pharmacosiderite and the general pharmacosiderite structure type.

KEYWORDS: hydronium, pharmacosiderite, crystal structure, Cornwall, new mineral, hydroniumpharmacosiderite, UK.

Introduction

THE pharmacosiderite supergroup of minerals (Rumsey *et al.*, 2010) and related synthetic compounds have attracted much interest, especially because their ion exchange properties make them candidates for use as molecular sieves (Mutter *et al.*, 1984; Harrison *et al.*, 1995;

* E-mail: smills@eos.ubc.ca DOI: 10.1180/minmag.2010.074.5.863 Dadachov and Harrison, 1997; Behrens *et al.*, 1998). Also of interest are symmetry variants (Mutter *et al.*, 1984; Peacor and Dunn, 1985). Recently, detailed studies of members of the supergroup have provided new crystal-structure determinations (bariopharmacosiderite-C and -Q and natropharmacosiderite-C: Mills *et al.*, submitted; H₃O-exchanged pharmacosiderite: Mills *et al.*, 2010), as well as new members (natropharmacoalumite: Rumsey *et al.*, 2010) and group nomenclature (Rumsey *et al.*, 2010).

The structure of pharmacosiderite was originally reported by Zemann (1947, 1948), but the K^+

ion could not be located. Subsequently, Buerger et al. (1967) reported the crystal structure of pharmacosiderite from Cornwall, UK, but also noted that they were unable to locate the K^+ ion. They postulated that the charge imbalance could be rectified by the presence of a hydronium ion. Mills et al. (2010) re-evaluated the structure and found it to be consistent with the H_3O^+ -exchanged structure. Herein, we describe the hydronium analogue of pharmacosiderite, hydroniumpharmacosiderite, based upon a single mounted crystal of dimensions $0.17 \text{ mm} \times 0.14 \text{ mm} \times 0.14 \text{ mm}$. This crystal, from the collection of Harvard University, is recorded as having been studied by Buerger, Dollase and Garaycochea-Wittke and evidence suggests that it may be the one used in their crystal-structure determination of pharmacosiderite (Buerger et al., 1967). The mineral and name (IMA 2010-014) were approved by the IMA Commission on New Minerals, Nomenclature and Classification prior to publication. The holotype crystal, now embedded in epoxy in an electron microprobe mount, is housed in the collections of the Harvard Mineralogical Museum (24 Oxford Street, Cambridge, Massachusetts 02138, USA), catalogue number 142784.

Occurrence

Phillips (1811) first reported a mineral from Wheal Gorland in the St. Day group of mines, Cornwall that later became known as pharmacosiderite. Subsequently, Hartley (1899) reported analyses of green pharmacosiderite from what he noted as "certainly old Cornish specimens". He demonstrated K to be present, although he noted the pharmacosiderite to be K-deficient. Embrey and Symes (1987) provide details of the mineralogy and locations of these mines.

The locality for the type crystal is specified by Buerger *et al.* (1967) simply as "Cornwall". The original specimen from which that crystal came was apparently not deposited in a public institution and efforts to locate it have been unsuccessful. All 'green' pharmacosiderites from Cornwall residing in the Harvard mineral collection have been examined and determined to be K-dominant. The collections of the Massachusetts Institute of Technology (the institution of Martin Buerger) and the University of Chile (the institution of Isabel Garaycochea-Wittke) have also been examined for material from Cornwall and/or from the authors. The aforementioned crystal appears to be the only remaining sample ascribable to their study. Although the type crystal could originate from any of the dozens of pharmacosiderite localities in Cornwall, it probably comes from one of the more famous localities, such as Wheal Gorland.

Physical and optical properties

Hydroniumpharmacosiderite occurs as a single yellowish green, slightly elongated cube, (Fig. 1), which is now embedded in epoxy in a mount used for electron microprobe analysis (EMPA). The only form observed was {001}. Hydroniumpharmacosiderite is transparent, with a light green streak (based on H₃O-exchanged pharmacosiderite), has a vitreous lustre and cleavage on {001} (by analogy with other pharmacosiderite group minerals). The tenacity is brittle, fracture irregular and the hardness is 2-3 on the Mohs scale (determined on H₃O-exchanged pharmacosiderite). Hydroniumpharmacosiderite is nonfluorescent. The density could not be measured because of the paucity of available material; however, the calculated density (on the basis of the empirical formula and single-crystal unit cell) is 2.559 g/cm³.

Hydroniumpharmacosiderite is isotropic; however, it displays anomalous birefringence with $n_{\min} = 1.690(2)$ and $n_{\max} = 1.692(2)$, determined in white light (Fig. 2). Anomalous birefringence is typical of members of the



FIG. 1. The single crystal $(0.17 \text{ mm} \times 0.14 \text{ mm} \times 0.14 \text{ mm})$ of hydroniumpharmacosiderite.



FIG. 2. Anomalous birefringence shown in hydroniumpharmacosiderite (crossed polars).

pharmacosiderite group and is often ascribed to strain-induced anisotropy (Buerger *et al.*, 1967). The majority of the crystal studied extinguishes at the same time; however, the extinction is not uniform, suggesting the presence of multiple domains with indistinct boundaries.

Chemical composition

Quantitative wavelength-dispersive EMP analyses (four points) were carried out using a JEOL733 electron microprobe with Geller automation at the Mineral Sciences Division, Canadian Museum of Nature. Operating conditions were 15 kV and 10 nA with a 10 μ m beam diameter. No elements other than those reported were detected. H₂O could not be measured due to lack of material. The EMPA results and the standards used are listed in Table 1.

The empirical formula for hydroniumpharmacosiderite (based on 20.5 O atoms) is: $[(H_3O)_{0.50}K_{0.48}Na_{0.06}]_{1.04}(Fe_{3.79}Al_{0.22})_{4.01}$ [(As_{2.73}P_{0.15})_{2.88}O₁₂](OH)₄·4H_{2.14}O. The simplified formula is (H₃O,K,Na)(Fe,Al)₄[(As,P)O₄]₃ $(OH)_4 \cdot 4H_2O$, or $(H_3O,K)Fe_4(AsO_4)_3(OH)_4$ ·4H₂O. The amount of K noted in the EMPA data is slightly greater than that observed in the single-crystal data (see below); however, both clearly show that H₃O is dominant within the structure. In their study of the structure of pharmacosiderite, Buerger et al. (1967) could not locate the K ion (pharmacosiderite, sensu stricto, is KFe₄(AsO₄)₃(OH)₄·nH₂O). A spectroscopic analysis showed that only traces of alkalis were present in the crystal. In an earlier description of the structure using material from Cornwall, Zemann (1948) also failed to locate the K ion. The end-member formula for hydroniumpharmacosiderite is (H₃O)Fe₄(AsO₄)₃(OH)₄ ·4H₂O, but it is noted that water of crystallization is partly zeolitic in nature (Mutter et al., 1984).

Powder X-ray diffraction

Powder X-ray diffraction (XRD) data (Table 2) were collected using a Rigaku R-Axis Rapid II curved-imaging-plate microdiffractometer utilizing monochromatized Mo- $K\alpha$ radiation at the Natural History Museum of Los Angeles County, USA. Data were collected on the cube-shaped crystal using rotation on two arcs to randomize its orientation. Unit-cell parameters

TABLE 1. Analytical data for hydroniumpharmacosiderite.

Constituent	Wt.%	Range	s.d.	Probe standard
Na ₂ O	0.25	0.0-0.44	0.23	Albite
$\tilde{K_2O}$	2.84	2.62-3.27	0.26	Sanidine
Al ₂ O ₃	1.45	1.33-1.59	0.12	Sanidine
Fe ₂ O ₃	38.33	37.16-39.12	0.96	Hematite
P_2O_5	1.30	1.24-1.38	0.06	Fluorapatite
As ₂ O ₅	39.80	39.38-40.36	0.36	GaAs
H ₂ O*	16.03			
Total	100.00			

*Calculated

I _{obs}	$d_{\rm obs}$	$d^*_{ m calc}$	hkl
100	8.050	7.993	001
22	4.628	4.615	111
14	4.005	3.997	002
4	3.574	3.575	012
35	3.265	3.263	112
23	2.830	2.826	202
10	2.666	2.664	003
19	2.528	2.528	013
30	2.412	2.410	113
6	2.309	2.307	222
3	2.135	2.136	123
2	2.000	1.998	004
5	1.938	1.939	223
9	1.884	1.884	114
3	1.833	1.834	133
14	1.787	1.787	024
4	1.744	1.744	124
2	1.705	1.704	233
7	1.631	1.632	224
9	1.598	1.599	304
8	1.538	1.538	333
6	1.459	1.459	215
10	1.412	1.413	044
6	1.391	1.391	144

TABLE 2. Powder X-ray data for hydroniumpharmacosiderite.

*Calculated using *PowderCell* (Kraus and Nolze, 1996). The eight strongest lines are in bold.

refined from the powder data using *Chekcell* (Laugier and Bochu, 2004) are a = 7.993(6) Å and V = 510.7(6) Å³, which are in good agreement with those obtained from the single-crystal study (see below).

Structure determination

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). The cube-shaped crystal was used for collection of intensity data at 293 K. The data were processed with 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 (Sheldrick, 2008). The initial location of the framework ions Fe, As, O1 and O2 revealed that they were located in similar positions to those reported by Buerger et al. (1967) for the general pharmacosiderite structure. At this stage, refinement using isotropic displacement parameters for all framework atoms converged to $R_1 = 0.069$. Inspection of the difference Fourier map showed three significant residues at $(\frac{1}{2}, 0, \frac{1}{2})$, $(\frac{1}{2}, 0.100, \frac{1}{2})$ and $(0.693, \frac{1}{2})$ 0.693, 0.693) which could be attributed to fractionally occupied K and O sites (K, O3 and O4; Fig. 3, Table 4). The O sites contribute to both water and hydronium. Refinement of the K site led to an occupancy of 0.4 a.p.f.u. similar to that observed in the EMP analyses, which indicated 0.6 of the total 1.6 O atoms generated by O4 is hydronium. This distribution of H₃O + H₂O is consistent with the structure of H₃Oexchanged pharmacosiderite (Mills et al., 2010). These distributions lead to a charge-balanced formula (H₃O_{0.6}K_{0.4})Fe₄(AsO₄)₃(OH)₄ ·2.5H₂O. At this stage the difference Fourier map revealed the position of the expected hydroxyl H atom (H2) on O2 and this was included in the final refinement. With the occupancies for K, 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 = 0.0481. A small residual at ($\frac{1}{2}$, 0.06, $\frac{1}{2}$), which would correspond to the position for Na (c.f.natropharmacosiderite: Mills et al., submitted), could not be added to the structure model and refined due to very low occupancy. A possible H atom at (0.63, 0.63, 0.76), ~0.60 Å from O4, was observed; however, as noted for H₃O-exchanged pharmacosiderite, the positions about O4 made no geometrical sense and it was concluded that the peak was an artefact produced by the disordered joint occupancy of H₃O and H₂O at the O4 site. The structure reported herein is inverted; however, this gives atomic coordinates which are more easily comparable to all previously reported structures. A table of cif data has been deposited with the Principal Editor and is available from http://www.minersoc.org/pages/ e journals/dep mat mm.html

The bond distances (Table 5) for hydroniumpharmacosiderite are consistent with those for both H₃O-exchanged pharmacosiderite and the reevaluated "pharmacosiderite" structure (Mills *et al.*, 2010). Of note in this structure description are

Structural formula	(H ₃ O _{0.6} K _{0.4})Fe ₄ (AsO ₄) ₃ (OH) ₄ ·2.5H ₂ O
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system	Cubic
Space group	P43m
Unit-cell dimensions	a = 7.9587(2) Å
Volume $(Å^3)$	504.11(2)
Ζ	1
D _{calc}	2.552 mg m^{-3}
Absorption coefficient	7.869 mm^{-1}
F(000)	368
Crystal size (mm)	$0.17 \times 0.14 \times 0.14$
θ range for data collection	3.62 to 38.57°
Index ranges	$-13 \le h \le 2, -12 \le k \le 7, -11 \le l \le 11$
Reflections collected	$1814 \ (R_{\rm int} = 0.0488)$
Independent reflections	540
Refinement method	Full-matrix least-squares on F^2
Goodness-of-fit on F^2	1.14
Final R indices $[I > 2\sigma(I)]$	0.0481, wR2 = 0.1358
R indices (all data)*	0.0496, wR2 = 0.1371
Largest diff. peak and hole	1.568 and $-1.173 \text{ e} \text{ Å}^{-3}$

TABLE 3. Crystal-data and -structure refinement details for hydroniumpharmacosiderite.

*The weighting scheme used was: $w = 1/[\sigma^2(F_o)^2 + (0.051P)^2 + 3.19P]$, where $P = [Max(F_o)^2 + 2(F_c)^2]/3$ as defined by *SHELX-97*.



FIG. 3. Crystal structure of hydroniumpharmacosiderite viewed down [110]. AsO₄ tetrahedra (yellow), FeO₆ octahedra (orange), K atom (blue), O atoms of water/hydronium molecules (large grey spheres) and H atoms (small grey spheres).

U_{13} U_{13} U_{13}	16(2) - 0.0016(2) - 0.001	0 0	04(10) - 0.0004(10) - 0.008	23(9) -0.0023(9) -0.002				
U_{33} U	0.0123(2) -0.00	0.0277(4) 0	0.0118(15) -0.00	0.0116(10) -0.00				
U_{22}	0.0123(2)	0.0277(4)	0.0338(15)	0.0116(10)				
• U ₁₁	0.0123(2)	0.0070(4)	0.0338(15)	0.0116(10)				
$U_{ m eq}$ or $U_{ m is}$	0.0123(2)	0.0208(3)	0.0265(10)	0.0116(10)	0.014	0.046(6)	0.050(9)	0.047(7)
Occ.	1	1	1	1	1	0.13	0.25	0.4
z/c	0.14345(8)	0.0	0.3837(6)	0.8857(5)	0.8283(15)	0.5	0.5	0.693(2)
y/b	0.14345(8)	0.0	0.1245(5)	0.8857(5)	0.8283(15)	0.0	0.106(5)	0.693(2)
х/а	0.14345(8)	0.5	0.1245(5)	0.8857(5)	0.8283(15)	0.5	0.5	0.693(2)
	e	S	1	2	2		33	4

TABLE 4. Final atom coordinates, site occupancies and atom displacement parameters (\mathring{A}^2) for hydroniumpharmacosiderite.

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

As-O1	1.680(6)	$\times 4$
Fe-O1 Fe-O2 <fe-o></fe-o>	1.924(5) 2.078(3) 2.001	$\times 3 \times 3$
K-01 K-04 <k-0></k-0>	3.282(3) 3.270(4) 3.278	$\times 8 \times 4$
O2O4 O3O4	2.66(3) 2.70(3)	

long K–O bonds of ~3.3 Å, which, while a little longer than usual, are in line with the ease with which the K ions can be ion exchanged from the lattice. It is possible that the crystal initially crystallized as hydroniumpharmacosiderite devoid of K, but slowly incorporated K over time during interaction with ground and meteoric water. Alternatively, the crystal may have crystallized as pharmacosiderite *senso stricto* and then lost K during interaction with acidic waters.

Discussion

While it is likely that the type locality for hydroniumpharmacosiderite will never be confirmed, the St. Day region of Cornwall may very well yield other examples of hydroniumpharmacosiderite. In the meantime, we have uncovered a second locality for hydroniumpharmacosiderite at the Wendy pit, Tambo mine, Elqui Province, Coquimbo Region, Chile.

Acknowledgements

Fernando Cámara, Daniel Atencio and an anonymous referee are acknowledged for providing helpful comments on the manuscript. NSERC Canada is thanked for a Discovery Grant to Mati Raudsepp. Part of this study was funded by the John Jago Trelawney Endowment to the Mineral Sciences Department of the Natural History Museum of Los Angeles County. Maurizio Dini is thanked for help with the search for the original specimen at the University of Chile and Timothy Grove at MIT.

References

- Behrens, E.A., Poojary, D.M. and Clearfield, A. (1998) Syntheses, X-ray powder structures, and preliminary ion-exchange properties of germanium-substituted titanosilicate pharmacosiderites: HM₃(AO)₄(BO₄)₃ ·4H₂O (M = K, Rb, Cs; A = Ti, Ge; B = Si, Ge). *Chemistry of Materials*, **10**, 959–967.
- 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. *Zeitsschrift für Kristallogrphie*, **125**, 92–108.
- Dadachov, M.S. and Harrison, W.T.A. (1997) Synthesis and crystal structure of Na₄[(TiO)₄(SiO₄)₃]·6H₂O, a rhombohedrally distorted sodium titanium silicate pharmacosiderite analogue. *Journal of Solid State Sciences*, **134**, 409–415.
- Embrey, P.G. and Symes, R.F. (1987) *Minerals of Cornwall and Devon*. Natural History Museum, London.
- Harrison, W.T.A, Gier, T.E. and Stucky, G.D. (1995) Single-crystal structure of Cs₃HTi₄O₄(SiO₄)₃·4H₂O, a titanosilicate pharmacosiderite analog. *Zeolites*, **15**, 408–412.
- Hartley, E. (1899) Communications from the Oxford Mineralogical Laboratory. On the constitution of the natural arsenates and phosphates. *Mineralogical Magazine*, **12**, 152–158.
- Kraus, W. and Nolze, G. (1996) POWDER CELL a program for the representation and manipulation of crystal structures and calculation of the resulting X-ray powder patterns. Journal of Applied Crystallography, 29, 301–303.
- Laugier, J. and Bochu, B. (2004) Chekcell: 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. (2010) The structure of H₃O⁺exchanged pharmacosiderite. *Mineralogical Magazine*, 74, 487–492.
- Mills, S.J., Raudsepp, M., Kampf, A.R., Hager, S.L., Leverett, P., Williams, P.A., Hibbs, D.E. and Birch, W.D. (2010) The crystal chemistry of natropharmacosiderite-*C*, bariopharmacosiderite-*C* and bariopharmacosiderite-*Q*. The Canadian Mineralogist (submitted).
- Mutter, G., Eysel, W., Greis, O. and Schmetzer, K. (1984) Crystal chemistry of natural and ion-exchanged pharmacosiderites. *Neues Jahrbuch für Mineralogie, Monatshefte*, 183–192.
- Peacor, D.R. and Dunn, P.J. (1985) Sodium-pharmacosiderite, a new analog of pharmacosiderite from Australia and new occurrences of barium-pharmacosiderite. *Mineralogical Record*, 16, 121–124.
- Phillips, W. (1811) A description of the Red Oxyd of Copper, the production of Cornwall, and the varieties of its crystal, and observations of the Lodes which principally produced it: and on the crystallization of the arseniated iron. *Transactions of the Geological Society of London*, 1, 23–37.
- Rumsey, M.S., Mills, S.J. and Spratt, J. (2010) Natropharmacoalumite, NaAl₄[(OH)₄(AsO₄)₃] .4H₂O, a new mineral of the pharmacosiderite supergroup and the renaming of aluminopharmacosiderite to pharmacoalumite. *Mineralogical Magazine*, 74, 929–936.
- Sheldrick, G.M. (2008) A short history of SHELX. *Acta Crystallographica*, A64, 112–122.
- 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.