

## The structure of $\text{H}_3\text{O}^+$ -exchanged pharmacosiderite

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### ABSTRACT

The crystal structure of  $\text{H}_3\text{O}^+$ -exchanged pharmacosiderite (pharmacosiderite is  $\text{KFe}_4(\text{AsO}_4)_3(\text{OH})_4 \cdot n\text{H}_2\text{O}$ , *sensu stricto*) has been determined by single-crystal X-ray diffraction and refined to  $R_1 = 0.0418$ .  $\text{H}_3\text{O}^+$ -exchanged pharmacosiderite,  $(\text{H}_3\text{O}^+)\text{Fe}_4(\text{AsO}_4)_3(\text{OH})_4 \cdot 4.5\text{H}_2\text{O}$ , is cubic, space group  $P\bar{4}3m$ , with  $a = 7.982(9)$  Å,  $V = 508.5(9)$  Å<sup>3</sup> and  $Z = 1$ . The structure broadly conforms to that of the general pharmacosiderite structure type, with the hydronium ion generated by partial protonation of a site corresponding to a molecule of water of crystallization and its symmetry-related equivalents. In addition, the structure of a “pharmacosiderite” from Cornwall, United Kingdom, in which no alkali metals could be detected, has been re-evaluated and found to be consistent with that of the  $\text{H}_3\text{O}^+$ -exchanged structure. Its composition is  $(\text{H}_3\text{O}^+)\text{Fe}_4(\text{AsO}_4)_3(\text{OH})_4 \cdot 4\text{H}_2\text{O}$ , with the partially occupied water found for the exchanged structure at  $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$  being absent in this case.

**KEYWORDS:** hydronium, pharmacosiderite, crystal structure, exchange, Cornwall.

### Introduction

THE pharmacosiderite group of minerals and synthetic variants have attracted much interest due to a number of factors including ion exchange properties, changes in symmetry (Mutter *et al.*, 1984; Peacor and Dunn, 1985) and their potential use as molecular sieves (Mutter *et al.*, 1984; Harrison *et al.*, 1995; Dadachov and Harrison, 1997; Behrens *et al.*, 1998). One of the main drives for the latter is the capacity of pharmacosiderite to readily exchange alkali or alkaline earth ions for heavier ions such as  $\text{Cs}^+$  (Harrison *et al.*, 1995; Xu *et al.*, 2004). Phases structurally related to pharmacosiderite have also been shown to be useful in the separation of the <sup>90</sup>Y from <sup>90</sup>Sr (Sylvester, 2003) and the recovery of <sup>82</sup>Sr from irradiated targets (Sylvester *et al.*, 2006). Recently, there has been interest in developing structural models for the various polymorphs of

pharmacosiderite variants. This has seen the description of bariopharmacosiderite-*C* and -*Q* and natropharmacosiderite-*C* (Mills *et al.*, 2010). Alkali pharmacosiderites are usually cubic, space group  $P\bar{4}3m$  with  $a \approx 8$  Å (Buerger *et al.*, 1967), or space group  $I\bar{4}3m$  with  $a \approx 16$  Å (Mutter *et al.*, 1984). However, some members exhibit ordering, which reduces the cubic symmetry to tetragonal, space group  $P\bar{4}2m$  with  $a \approx c \approx 8$  Å (Mills *et al.*, 2010), or space group  $I\bar{4}2m$  with  $a \approx c \approx 16$  Å (Mutter *et al.*, 1984).

The structure of pharmacosiderite was originally reported by Zemann (1947, 1948), but the  $\text{K}^+$  ion could not be located. Subsequently, Buerger *et al.* (1967) reported the crystal structure of pharmacosiderite from Cornwall, UK. In their structural description, they pointed out that they too were unable to locate the  $\text{K}^+$  ion and postulated that the charge imbalance could be accounted for by the presence of a hydronium ion. In this connection, a spectrographic analysis of their crystal found that alkali metals were absent. To evaluate these suggestions, we have re-evaluated the crystal structure of Buerger *et al.* (1967) and here we report our findings, together with a description of a

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single-crystal X-ray structure of an  $\text{H}_3\text{O}^+$ -exchanged natropharmacosiderite.

## Experimental

### Sample description

For the exchange experiment, several orange-brown, cubic, single crystals of natropharmacosiderite  $[(\text{Na}_{0.75}, \text{K}_{0.14}, \text{Ba}_{0.11})_{\Sigma 1.00} \text{Fe}_4(\text{AsO}_4)_3(\text{OH})_{3.89} \text{O}_{0.11} \cdot 4\text{H}_2\text{O}]$ ; Mills *et al.* 2010] from the Gold Hill mine, Gold Hill, Tooele County, Utah, USA, were placed in  $10 \text{ cm}^3$  of distilled water, to which were added four drops of 10% aqueous HCl. Within  $\sim 10 \text{ s}$  the colour of the crystals changed from orange-brown to pale green, then more slowly to a pale greenish grey. The crystals were kept in the solution for four days before being examined by single-crystal X-ray diffraction methods. Chemical analysis confirmed the absence of Na, K and Ba in the final exchanged

crystals. Similar methods to prepare  $\text{H}_3\text{O}^+$ -exchanged pharmacosiderite have been reported by Mutter *et al.* (1984). The sample used is housed in the collections of Mineral Sciences Department, Natural History Museum of Los Angeles County, catalogue number LACMNH 61590. A complete sample description can be found in Mills *et al.* (2010).

### Data collection

The single-crystal study of an  $\text{H}_3\text{O}^+$ -exchanged crystal was carried out using a Bruker X8 ApexII single-crystal diffractometer at the Department of Chemistry, University of British Columbia (Table 1). A cubic crystal of dimensions  $0.15 \text{ mm} \times 0.15 \text{ mm} \times 0.15 \text{ mm}$  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

TABLE 1. Crystal data and structure-refinement details.

	$\text{H}_3\text{O}^+$ -exchanged pharmacosiderite	"pharmacosiderite" (Buerger <i>et al.</i> , 1967)
Empirical formula	$(\text{H}_3\text{O}^+) \text{Fe}_4(\text{AsO}_4)_3(\text{OH})_4 \cdot 4.5\text{H}_2\text{O}$	$(\text{H}_3\text{O}^+) \text{Fe}_4(\text{AsO}_4)_3(\text{OH})_4 \cdot 4\text{H}_2\text{O}$
<i>M</i>	808.29	799.28
Temperature	296(2) K	Room temperature
Wavelength	0.71073 Å	1.5418 Å
Crystal system	Cubic	Cubic
Space group	$P\bar{4}3m$	$P\bar{4}3m$
Unit-cell dimensions	$a = 7.982(9) \text{ Å}$	$a = 7.980(10) \text{ Å}$
Volume	$508.5(9) \text{ Å}^3$	$508.2(11) \text{ Å}^3$
<i>Z</i>	1	1
$D_{\text{calc}}$	$2.639 \text{ mg m}^{-3}$	$2.612 \text{ mg m}^{-3}$
Absorption coefficient	$7.73 \text{ mm}^{-1}$	$28.78 \text{ mm}^{-1}$
$F(000)$	391	386
Crystal size	$0.15 \text{ mm} \times 0.15 \text{ mm} \times 0.15 \text{ mm}$	$0.17 \text{ mm} \times 0.17 \text{ mm} \times 0.17 \text{ mm}$
$\theta$ range for data collection	$2.55$ to $27.28^\circ$	$7.65$ to $69.49^\circ$
Index ranges	$-5 \leq h \leq 9, -8 \leq k \leq 1, -7 \leq l \leq 6$	$1 \leq h \leq 9, 0 \leq k \leq 6, 0 \leq l \leq 5$
Reflections collected, $R_{\text{int}}$	329, 0.021	128
Independent reflections	171	128
Refinement method	Full-matrix least-squares on $F^2$	Full-matrix least-squares on $F^2$
Goodness-of-fit on $F^2$	1.33	1.31
Final <i>R</i> indices [ $I > 2\sigma(I)$ ]	$R_1 = 0.0418, wR_2 = 0.1119$	$R_1 = 0.0539, wR_2 = 0.1482$
<i>R</i> indices (all data)*	$R_1 = 0.0431, wR_2 = 0.1122$	$R_1 = 0.0539, wR_2 = 0.1482$
Extinction coefficient	0.020(6)	0.004(2)
Largest diffraction peak and hole	1.62 and $-0.57 \text{ e.Å}^{-3}$	1.34 and $-0.69 \text{ e.Å}^{-3}$

\* The weighting schemes used were:

$w = 1/[\sigma^2(F_o)^2 + (0.051P)^2 + 3.19P]$  for  $\text{H}_3\text{O}^+$ -exchanged pharmacosiderite and;

$w = 1/[\sigma^2(F_o)^2 + (0.071P)^2 + 7.54P]$  for "pharmacosiderite" of Buerger *et al.* (1967),

where  $P = [\text{Max}(F_o)^2 + 2(F_c)^2]/3$  as defined by SHELX-97

*SAINT* program and absorption correction by the multi-scan method using *SADABS* (Bruker, 2003). Lists of observed and calculated structure factors are deposited at [http://www.minersoc.org/pages/e\\_journals/dep\\_mat\\_mm.html#2010](http://www.minersoc.org/pages/e_journals/dep_mat_mm.html#2010).

### Description and discussion of the H<sub>3</sub>O<sup>+</sup>-exchanged pharmacosiderite structure

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 and a subsequent isotropic refinement converged to  $R_1 = 0.079$  at this stage. Inspection of a difference Fourier map showed two significant residues at  $(\frac{1}{2}, 0, \frac{1}{2})$  and  $(0.685, 0.685, 0.685)$  which could be attributed to fractionally occupied O atoms (water or hydronium ion), O3 and O4

respectively, and it was noted that they were in similar positions to those reported by Buerger *et al.* (1967) for the general pharmacosiderite structure. With thermal parameters for O3 and O4 constrained to be isotropic, due to the partial (50%) occupancy of these atoms, an anisotropic refinement converged to  $R_1 = 0.050$ . The resulting difference map and the thermal parameter for O3 clearly indicated that this atom was more appropriately positioned at  $(\frac{1}{2}, \sim 0.05, \frac{1}{2})$ , i.e. statistically distributed across the centre of the cell face. Further, there was a significant residual in the difference map at  $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$  which could be attributed to another partially occupied (50%) O atom, O5. This final model (Figure 1) converged to  $R_1 = 0.0418$ , where acceptable isotropic thermal parameters resulted for O3, O4 and O5 when each of these atoms was assigned a population parameter of 50%.

Inspection of the final difference map revealed no evidence of the expected hydroxyl H atom on O2, as found in bariopharmacosiderite and natropharmacosiderite (Mills *et al.*, 2010), despite O2 having a close contact of 2.70 Å

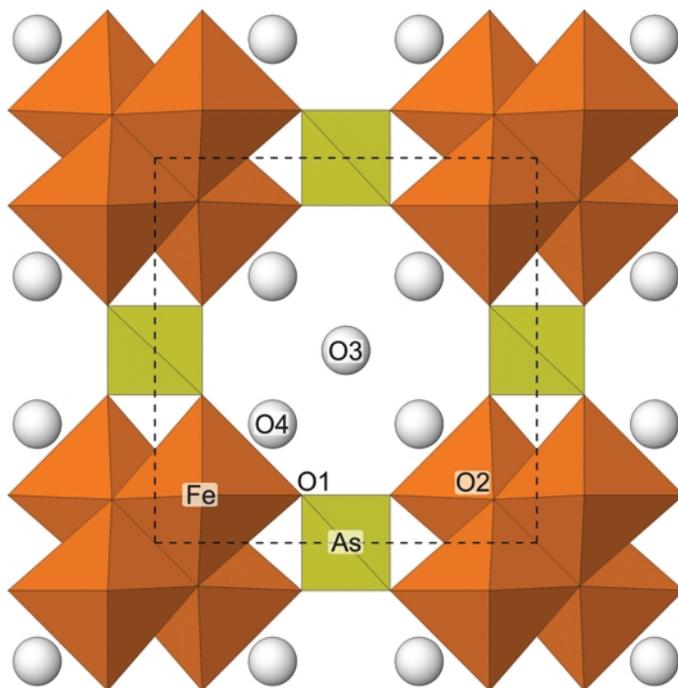


FIG. 1. Crystal structure of H<sub>3</sub>O-exchanged pharmacosiderite. AsO<sub>4</sub> tetrahedra (yellow), FeO<sub>6</sub> octahedra (orange) and oxygen atoms of water molecules (grey).

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

	$x/a$	$y/b$	$z/c$	Occ.	$U_{\text{eq}}$ or $U_{\text{iso}}$	$U_{11}$	$U_{22}$	$U_{33}$	$U_{23}$	$U_{13}$	$U_{12}$
H <sub>3</sub> O <sup>+</sup> -exchanged pharmacosiderite											
Fe	0.1433(3)	0.1433(3)	0.1433(3)	1	0.0097(9)	0.0099(9)	0.0099(9)	0.0099(9)	-0.0004(8)	-0.0004(8)	-0.0004(8)
As	$\frac{1}{2}$	0	0	1	0.0123(8)	0.0065(15)	0.0153(11)	0.0153(11)	0	0	0
O1	0.1239(9)	0.1239(9)	0.3842(12)	1	0.019(2)	0.022(4)	0.022(4)	0.015(6)	0.001(3)	0.001(3)	-0.007(4)
O2	0.8867(10)	0.8867(10)	0.8867(10)	1	0.005(4)	0.005(4)	0.005(4)	0.005(4)	-0.002(3)	-0.002(3)	-0.002(3)
O3	$\frac{1}{2}$	0.0500(40)	$\frac{1}{2}$	$\frac{1}{2}$	0.048(11)						
O4	0.6913(28)	0.6913(28)	0.6913(28)	$\frac{1}{2}$	0.028(9)						
O5	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	0.035(20)						
Bueger <i>et al.</i> (1967) "pharmacosiderite"											
Fe	0.1429(3)	0.1429(3)	0.1429(3)	1	0.015(1)	0.015(1)	0.015(1)	0.015(1)	-0.002(1)	-0.002(1)	-0.002(1)
As	$\frac{1}{2}$	0	0	1	0.023(1)	0.012(2)	0.029(2)	0.029(2)	0	0	0
O1	0.1230(12)	0.1230(12)	0.3829(16)	1	0.025(3)						
O2	0.8868(14)	0.8868(14)	0.8868(14)	1	0.013(4)						
O3	$\frac{1}{2}$	0.069(6)	$\frac{1}{2}$	$\frac{1}{2}$	0.057(12)						
O4	0.694(4)	0.694(4)	0.694(4)	$\frac{1}{2}$	0.048(14)						

with O4. There was also no evidence of H atoms associated with two of the three partially occupied O atom sites, O3 and O5, despite contacts between O4 and O3 and between O4 and O5 of 2.99 and 2.64 Å, respectively, which again seemed to be clear evidence of H-bonding. However, there was evidence of a possible H atom at (0.65, 0.65, 0.76) placing it ~0.80 Å from O4. Despite this, attempts to refine the partially occupied H atom position were unsuccessful and the arrangement of H atom positions about O4 made no geometrical sense; it was concluded that the peak was spurious and it was not included in the final model. Assuming that the H<sub>3</sub>O<sup>+</sup> ion required for charge balance in the structure is associated with O4, with the remainder of that site occupancy due to H<sub>2</sub>O, and that the O3 and O5 sites are both partially occupied only by H<sub>2</sub>O molecules, the formula for H<sub>3</sub>O<sup>+</sup>-exchanged pharmacosiderite studied here is (H<sub>3</sub>O<sup>+</sup>)Fe<sub>4</sub>(AsO<sub>4</sub>)<sub>3</sub>(OH)<sub>4</sub>·4.5H<sub>2</sub>O. We note that the proton required for charge balance may in fact be distributed over all water molecules, in line with the observation that the mineral acts as a proton conductor (Mutter *et al.*, 1984). Crystal data and structure-refinement details are given in Table 1 and final atom and thermal displacement parameters are given in Table 2.

*Re-evaluation of the crystal structure of pharmacosiderite by Buerger et al. (1967)*

Using their published structure factor data ( $F_o$ , all 128 reported reflections being observed), the crystal structure of pharmacosiderite reported by Buerger *et al.* (1967) was re-evaluated by difference Fourier techniques and full-matrix least-squares refinement on  $F^2$  using SHELXL-97. The positions of the framework ions Fe, As, O1 and O2 together with the two partially occupied O atom positions O3 and O4 reported by Buerger *et al.* (1967) were used in an initial refinement with all atoms ascribed isotropic thermal parameters. This converged to  $R_1 = 0.063$  and resulted in acceptable thermal parameters for both O3 and O4, the population parameters of which had been held at 50% in line with the findings of Buerger *et al.* (1967) and also the structure of H<sub>3</sub>O<sup>+</sup>-exchanged pharmacosiderite reported above. The structure originally reported by Buerger *et al.* (1967) was therefore fully confirmed. At this stage the difference Fourier map indicated some anisotropy about the Fe and As atoms and a further refinement step

with anisotropic thermal parameters for Fe and As was performed, where for 128 reflections the data to parameters ratio was still just acceptable at 8:1. This final refinement converged to an  $R_1 = 0.054$ . An examination of the resulting difference map showed no residual at ( $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ ) as found for O5 in H<sub>3</sub>O<sup>+</sup>-exchanged pharmacosiderite. It also revealed no evidence of H atoms on O2 or O3 despite these atoms having contacts of 2.67 and 2.89 Å, respectively with O4, and which are indicative of H-bonding. However, as for the H<sub>3</sub>O<sup>+</sup>-exchanged pharmacosiderite structure, there was evidence of a possible H atom at (0.65, 0.65, 0.77) placing it ~0.80 Å from O4 but again with unacceptable geometry about the O atom resulting. It may be that the H<sub>3</sub>O<sup>+</sup> ion is preferentially associated with the O4 site, but this remains to be confirmed. For charge balance the overall formula (H<sub>3</sub>O<sup>+</sup>)Fe<sub>4</sub>(AsO<sub>4</sub>)<sub>3</sub>(OH)<sub>4</sub>·4H<sub>2</sub>O results, indicating slightly less water than with the H<sub>3</sub>O<sup>+</sup>-exchanged pharmacosiderite. This is not surprising as it is known that at least some of the water content of pharmacosiderite is zeolitic in nature (Mutter *et al.*, 1984). Crystal data and structure-refinement details are given in Table 1 and final atom and thermal displacement parameters are given in Table 2.

Selected bond lengths in the two structures are given in Table 3, including O...O (water) contacts. The two structures are essentially identical save for the different amount of water of crystallization. Slight differences are associated with the positions of O3 and O4 in the two structures, no doubt occasioned by the different

TABLE 3. Selected bond distances (Å).

	H <sub>3</sub> O <sup>+</sup> -exchanged pharmacosiderite	"pharmacosiderite" (Buerger <i>et al.</i> 1967)
As—O1	1.675(10) × 4	1.673(14)
Fe—O1	1.938(10) × 3	1.928(14)
Fe—O2	2.071(7) × 3	2.071(9)
<Fe—O>	2.005	2.000
O2...O4	2.70(4)	2.67(6)
O3...O4	2.99(2)	2.89(3)
O4...O5	2.65(4)	

H-bonding array possible for the more-or-less hydrated crystals. The results of this study indicate that the specimen studied by Buerger *et al.* (1967) was, as they suggested, in fact the natural  $\text{H}_3\text{O}^+$  analogue of pharmacosiderite. Unfortunately, the mine in Cornwall from which the specimen came from was not reported, but investigations are currently underway to locate the specimens (and/or the locality) used in the earlier study.

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