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PLUMBOPHARMACOSIDERITE, $Pb_{0.5}Fe^{3+}_4(AsO_4)_3(OH)_4{\cdot}5H_2O$, A NEW MINERAL SPECIES FROM THE MONTE FALÒ Pb-Zn MINE NEAR THE VILLAGE OF COIROMONTE IN THE ARMENO MUNICIPALITY, NOVARA PROVINCE, ITALY

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ABSTRACT

Plumbopharmacosiderite, $Pb_{0.5}Fe^{3+}_4(AsO_4)_3(OH)_4{\cdot}5H_2O$, is a new hydrated and hydroxylated arsenate of Fe^{3+} and Pb belonging to the pharmacosiderite group, pharmacosiderite supergroup of minerals. It was found at the Monte Falò Pb-Zn mine near the village of Coiromonte in the Armeno municipality, Novara province, Italy. The mineral occurs on the surfaces of brittle fissures in a mica schist cross-cut by arsenopyrite veins as minute cubes up to 50 μm in size. Plumbopharmacosiderite is a product of oxidation of primary Pb-, Fe-sulfide minerals due to weathering of the primary ore and is found in close association with arsenopyrite, scorodite, beudantite, rare segnitite, marcasite, galena, sphalerite, and mimetite. Its color is pale green to yellowish-green, transparent with a vitreous to resinous luster. The streak is white. Plumbopharmacosiderite is brittle with an irregular fracture. The Mohs hardness is 2.5–3 and the calculated density is 2.89 g/cm^3. The mineral is optically isotropic with refractive index $n = 1.73(1)$. Plumbopharmacosiderite is non-fluorescent under 254 nm (short wave) and 366 nm (long wave) UV light. The empirical formula is: $(Pb_{0.42}K_{0.20}Ba_{0.15}Na_{0.03}Ca_{0.01})_{\Sigma 0.81}(Fe^{3+}_{3.69}Al_{0.22})_{\Sigma 3.91}(As_{2.95}Si_{0.01})_{\Sigma 2.96}O_{12}(OH)_{\Sigma 3.90}{\cdot}5H_2O$. The simplified formula is $Pb_{0.5}Fe^{3+}_4(AsO_4)_3(OH)_4{\cdot}5H_2O$. Plumbopharmacosiderite is cubic, with space group $P\bar{4}3m$ and unit-cell parameters a 7.9791 (2) Å and V 508.00(6) Å^3 for $Z = 1$. Its crystal structure was refined and conforms with that of bariopharmacosiderite. The new mineral and the name plumbopharmacosiderite were approved by the Commission on New Minerals, Nomenclature, and Classification (CNMNC) of the International Mineralogical Association (IMA) under the number IMA 2016-109.

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Introduction

The pharmacosiderite group of minerals belongs to the pharmacosiderite supergroup, together with the pharmacoalumite and ivanyukite groups. Pharmacosiderite now consists of eight hydrated and hydroxylated arsenate mineral species characterized by the presence of Fe^{3+} at the M2 site and both monovalent (Na, K, Cs, Tl, and H_3O^+) and divalent cations (Ba, Sr, and Pb for this new species) at the M1 site. Except for strontiopharmacosiderite, which is tetragonal with space group $P\bar{4}2m$ and $a \cong c$, all members are cubic with space group $P\bar{4}3m$. The crystal structure of pharmacosiderite was first described by Zemann (1948). Subsequently,

TABLE 1. COMPARISON OF THE PHYSICAL PROPERTIES FOR MINERALS OF THE PHARMACOSIDERITE GROUP

Mineral	Plumbo-pharmacosiderite	Bario-pharmacosiderite	Strontio-pharmacosiderite	Pharmacosiderite
Type locality	Monte Falò, Italy	Robinson'e Reef, Australia, and Clara Mine, Germany	La Plâtriére, Switzerland	Tincroft Mine, United Kingdom
Reference	This work	[1,2]	[3]	[4]
Ideal formula	$Pb_{0.5}Fe^{3+}{}_4(AsO_4)_3(OH)_4{\cdot}5H_2O$	$Ba_{0.5}Fe^{3+}{}_4(AsO_4)_3(OH)_4{\cdot}5H_2O$	$Sr_{0.5}Fe^{3+}{}_4(AsO_4)_3(OH)_4{\cdot}4H_2O$	$KFe^{3+}{}_4(AsO_4)_3(OH)_4{\cdot}6–7H_2O$
Space group	$P\bar{4}3m$	$P\bar{4}3m$	$P\bar{4}2m$	$P\bar{4}3m$
a (Å)	7.9791	7.942	8.084	7.98
c (Å)			8.151	
Z	1	1	1	1
	—	—	—	—
Strong X-ray lines	8.024 (100)	8.050 (55)	—	7.982 (100)
	—	7.940 (60)	—	—
	5.859(15)	—	—	—
	4.558(12)	4.600 (65)	—	4.608 (17)
	—	4.017 (75)	—	—
	3.980 (18)	3.962 (100)		3.991 (8)
	3.252 (23)	3.240 (75)	3.309 (55)	3.258 (16)
	2.830 (18)	2.821 (75)	2.874 (100)	2.822 (11)
	—	2.801 (60)	—	—
	—	—	—	—
	2.535 (12)	2.509 (70)	2.574 (45)	2.524 (8)
	—	2.393 (65)	2.456 (40)	2.406 (9)
	—	2.298 (65)	—	—
	—	—	2.332 (55)	—
	—	—	1.908 (50)	—
	1.879 (30)	—	1.808 (60)	—
	—	—	—	—
Density	2.89	3.05	—	2.797
Hardness	—	2½ Mohs	—	2½ Mohs
Color	Pale yellowish green	Reddish brown, yellow, yellowish green	—	Green and brown different tinges
Morphology	{100}	{100},{111}	—	{100},{111}

[1] Hager *et al.* (2010), [2] Greis *et al.* (1981), [3] Mills *et al.* (2014), [4] Buerger *et al.* (1967), [5] Peacor & Dunn (1985), [6] Mills *et al.* (2010a, b), [7] Mills *et al.* (2013), [8] Rumsey *et al.* (2014).

Buerger *et al*. (1967) refined the crystal structure of pharmacosiderite using a specimen from Cornwall. They found that the pharmacosiderite structure is characterized by strongly distorted FeO_6 octahedra, which share corners with AsO_4 tetrahedra to form large zeolite-like channels in the center of the unit cell. Buerger *et al*. were not able to find alkalis in the chemical composition of their samples. Mills *et al*. (2010a) solved the structure of H_3O^+-exchanged pharmacosiderite, finding a close correspondence with the experimental results obtained by Buerger *et al*. (1967), and locating the H_3O^+ ion displaced from the center of the unit-cell face. Hager *et al*. (2010) described the crystal structure of bariopharmacosiderite and natropharmacosiderite, confirming the general framework described by Buerger *et al*. (1967), but locating the heavy cation Ba exactly at the center of the unit-cell face, while the lighter Na atom is located in the same position as described by Mills *et al*. (2010a) for H_3O^+ groups.

The general characters of the eight arsenate minerals belonging to the pharmacosiderite group are summarized in Table 1. In this paper we describe the Pb analogue of this group of minerals. The new species and its name have been approved by the IMA

TABLE 1. CONTINUED.

Natro-pharmacosiderite	Hydronium-pharmacosiderite	Cesium-pharmacosiderite	Thallium-pharmacosiderite
Marda, Australia	St Day, Cornwall, United Kingdom	Wendy pit, Tambo mine, Chile	Crven Dol Canyon, Macedonia
[5]	[6]	[7]	[8]
$(Na,K)Fe^{3+}_4(AsO_4)_3(OH)_4{\cdot}6–7H_2O$	$(H_3O)Fe^{3+}_4(AsO_4)_3(OH)_4{\cdot}4H_2O$	$CsFe^{3+}_4(AsO_4)_3(OH)_4{\cdot}4H_2O$	$TlFe^{3+}_4(AsO_4)_3(OH)_4{\cdot}4H_2O$
$P\bar{4}3m$	$P\bar{4}3m$	$P\bar{4}3m$	$P\bar{4}3m$
8.012	7.9587	7.9637	7.987
1	1	1	1
7.99 (100)	8.050 (100)	8.04 (100)	—
—	—	—	—
—	—	—	—
4.61 (50)	4.628 (22)	4.627 (23)	—
4.00 (40)	4.005 (14)	4.009 (17)	—
—	—	—	—
3.27 (80)	3.265 (35)	3.270 (40)	3.266 (67)
2.831 (60)	2.830 (23)	2.831 (31)	2.832 (100)
—	—	—	—
2.668 (30)	—	—	2.665 (53)
2.532 (50)	2.528 (19)	2.532 (22)	2.525 (87)
2.416 (60)	2.412 (30)	2.415 (22)	2.414 (60)
—	—	—	—
—	—	—	2.309 (60)
—	—	—	1.882 (53)
—	1.787 (14)	1.790 (14)	1.784 (73
1.604 (30)	—	—	—
2.794	—	—	—
3 Mohs	—	—	—
Pale green, dull orange	—	—	—
{100}	—	—	—

TABLE 2. AVERAGED (8 POINTS) ELECTRON MICROPROBE COMPOSITION OF PLUMBOPHARMACOSIDERITE

	wt.%	range	esd		*apfu***
As_2O_5	38.41	(32.86–44.56)	3.94	As	2.953
P_2O_5	0.07	(0.00–0.17)	0.07	P	0.009
SO_3	0.03	(0.00–0.06)	0.03	S	0.003
SiO_2	0.04	(0.00–0.09)	0.07	Si	0.005
Al_2O_3	1.30	(1.08–1.44)	0.12	Al	0.225
Fe_2O_3	33.37	(31.35–34.97)	1.45	Fe^{3+}	3.692
CaO	0.03	(0.00–0.09)	0.03	Ca	0.005
BaO	2.61	(2.28–2.93)	0.23	Ba	0.150
ZnO	0.05	(0.00–0.23)	0.08	Zn	0.005
PbO	10.59	(9.63–11.62)	0.69	Pb	0.419
Na_2O	0.12	(0.01–0.36)	0.14	Na	0.034
K_2O	1.08	(0.48–1.36)	0.34	K	0.203
H_2O*	14.17			H	13.900
Total	101.87				

Notes: * calculated for total = 100.00 wt.%; ** *apfu* on the basis of 14 anhydrous O atoms *pfu*.

Commission on New Minerals, Nomenclature, and Classification (IMA2016-109, Vignola *et al*. 2017). The mineral is named as the Pb-rich member of the pharmacosiderite group.

Occurrence, General Appearance, and Physical Properties

Plumbopharmacosiderite was found by one of the authors (CA) in the dumps of the Monte Falò Pb-Zn mine near the village of Coiromonte in the Armeno municipality, Novara province, Italy (45°50′52.37″N, 8°29′1.13″E). Mining for Pb and Zn lasted from 1920 to 1953 and the mine tunnels (now collapsed) attained a total length of about 340 m. Galena was the most important extracted mineral, with minor sphalerite and small amounts of arsenopyrite, pyrite, and marcasite recovered as well. The ore is hosted by quartz veins crosscutting mica schist belonging to the Serie dei Laghi formation. Plumbopharmacosiderite occurs on the surfaces of brittle fissures in a mica schist cross-cut by arsenopyrite veins as minute cubes up to 50 μm in size. It is a product of oxidation of primary Pb-,Fe-sulfide minerals due to weathering of the primary ore and was found in close association with arsenopyrite, scorodite, beudantite, rare segnitite, marcasite, galena, sphalerite, and mimetite. Its color is pale green to yellowish-green, transparent with a vitreous to resinous luster. The streak is white. Plumbopharmacosiderite is brittle with an irregular fracture. The hardness could not be measured due to the small size of the crystals, but the Mohs hardness is inferred to be 2.5–3 by analogy with the other species belonging to the pharmacosiderite group. The density, calculated from the formula weight and single crystal unit-cell parameters, is 2.89 g/cm^3. The mineral is optically isotropic with a measured refractive index $n = 1.73(1)$. Plumbopharmacosiderite is non-fluorescent under 254 nm (short wave) and 366 nm (long wave) UV light. The Gladstone-Dale compatibility index, calculated with the calculated density and measured refractive index, is –0.089 (poor). This poor compatibility index may be due to problems in measuring refractive index using tiny, colored, and imperfectly clear crystals.

The type sample used for the complete characterization of the new species plumbopharmacosiderite is stored in the Mineralogical Collection of the Laboratoire de Minéralogie, University of Liège, Belgium (number 20392).

Chemical Composition

Quantitative chemical analyses were performed using a polished and carbon-coated section of plumbopharmacosiderite and a JEOL JXA-8200 electron microprobe working in wavelength-dispersion mode at the laboratory of the Department of Earth Sciences, University of Milan. The system was operated using an accelerating voltage of 15 kV, a beam current of 5 nA, a spot size of 5 μm, and a counting time of 30 s on the peaks and 10 s on the backgrounds. The following minerals were used as standards: realgar (As*L*α, S*K*α), graftonite KF16 (P*K*α, Fe*K*α, Mn*K*α, and Ca*K*α), anorthite An 137 (Si*K*α and Al*K*α), baryte (Ba*L*α), celestine (Sr*L*α), galena (Pb*M*α), omphacite USNM 110607 (Na*K*α), and orthoclase PSU OR 1A (K*K*α). Sulfur, Si, Mn, and Sr were below the detection limit. The raw data were corrected for matrix effects using the ΦρZ method from the JEOL series of programs. The H_2O content was calculated for a total of 100 wt.%, OH groups were calculated to maintain charge balance. The averaged (eight points) electron microprobe composition of plumbopharmacosiderite is reported in Table 2. The empirical formula, calculated on the basis of 28 positive charges per formula unit, is: $(Pb_{0.42}K_{0.20}Ba_{0.15}Na_{0.03}Ca_{0.01})_{\Sigma 0.81}(Fe^{3+}_{3.69}Al_{0.22})_{\Sigma 3.91}(As_{2.95}P_{0.01})_{\Sigma 2.96}O_{12}(OH)_{3.90}\cdot 5H_2O$. The simplified formula is $Pb_{0.5}Fe^{3+}_4(AsO_4)_3(OH)_4\cdot 5H_2O$, which theoretically requires PbO 12.37, Fe_2O_3 35.41, As_2O_5 38.23, and H_2O 13.98 wt.% for a total of 100.00 wt.%.

X-Ray Diffraction Data and Crystal Structure Refinement

The X-ray powder diffraction pattern of plumbopharmacosiderite was collected with an Agilent Xcalibur 4-circle diffractometer, equipped with an EOS CCD detector, using Mo*K*α radiation (λ =

TABLE 3. X-RAY POWDER DIFFRACTION DATA OF PLUMBOPHARMACOSIDERITE

I/I_0	d_{obs}	d_{calc}	h	k	l
100	8.024	7.979	0	0	1
15	5.859	5.642	0	1	1
12	4.558	4.607	1	1	1
18	3.980	3.989	0	0	2
23	3.252	3.257	1	1	2
18	2.83	2.821	2	0	2
6	2.666	2.660	1	2	2
12	2.535	2.523	1	0	3
9	2.403	2.406	1	1	3
6	2.286	2.303	2	2	2
3	2.130	2.133	2	1	3
9	2.00	1.995	0	0	4
29	1.879	1.881	3	0	3
3	1.837	1.831	1	3	3
6	1.783	1.784	0	2	4
6	1.692	1.701	3	2	3
3	1.63	1.629	2	2	4
3	1.594	1.596	0	0	5
3	1.539	1.536	3	3	3
3	1.458	1.457	2	1	5
6	1.409	1.411	0	4	4
3	1.384	1.389	4	1	4

TABLE 4. DETAILS OF THE DATA COLLECTION AND STRUCTURE REFINEMENT OF PLUMBOPHARMACOSIDERITE

Crystal shape	Cube
Crystal size (μm)	30 × 30 × 30
Crystal color	Pale green, transparent
T (K)	298
Unit-cell constants	a = 7.9791 (2) Å V = 508.00 (6) Å^3
Reference chemical formula	$Pb_{0.5}Fe^{3+}_4(AsO_4)_3(OH)_4{\cdot}5H_2O$
Space Group	$P\bar{4}3m$
Z	1
Radiation type	Synchrotron light source
Wavelength (Å)	0.800381
Diffractometer	XRD1 beamline (Elettra-Trieste)
Data-collection method	ω scan
Step size (°)	1
Max. θ (°)	32.85
h_{min}, h_{max}	–9, +9
k_{min}, k_{max}	–10, +10
l_{min}, l_{max}	–10, +10
No. measured reflections	3384
No. unique reflections	287
No. unique refl. with $I > 3\sigma(I)$	284
No. refined parameters	16
Refinement on	F
Req	12.98
R_1 (obs/all)(%)	10.07/10.08
Final $wR2$	14.89/14.89
Residuals (e$^-$ / Å^3)	+2.01/–3.26

$R_{int} = \sum|F^2_{obs} - F^2_{obs}(mean)|/\sum(F^2_{obs})$;
$R_1 = \sum(|F_{obs} - F_{calc}|)/\sum|F_{obs}|$;
$wR2 = (\sum(w(F^2_{obs} - F^2_{calc})^2)/\sum(w(F^2_{obs})^2)^{0.5}$,
$w = 1/(\sigma^2(F^2_{obs}))$.

0.71073 Å) and working in Debye-Scherrer geometry, at the Geology Department of the University of Liège, Belgium. Operating conditions were 50 kV, 30 nA, and a sample-to-detector distance of 40 mm. The very small amount of specimen was mounted on a glass fiber (50 μm diameter). Refinement of unit-cell parameters was performed using the LCLSQ 8.4 program (Burnham 1991), starting with the unit-cell parameters described for bariopharmacosiderite by Hager *et al*. (2010). The powder pattern reflections were found to be consistent with the space group $P\bar{4}3m$. The complete list of indexed reflections is reported in Table 3. The refined unit-cell parameters are a 7.972(25) Å and V 507(2) Å^3 (with $Z = 1$), in good agreement with those obtained by the single-crystal study. The complete list of indexed reflections is reported in Table 2. The eight strongest measured lines are [d in Å, (I/I_0), (hkl)]: 8.024 (**100**) (001), 1.879 (**29**) (033), 3.250 (**24**) (112), 3.980 (**18**) (002), 2.830 (**18**) (202), 5.859 (**15**) (011), 4.558 (**12**) (111), and 2.535 (**12**) (103).

Intensity data were collected from a 0.03 × 0.03 × 0.03 mm single crystal of plumbopharmacosiderite at XRD1 beamline (Elettra) using monochromatic radiation (λ = 0.800381 Å) by omega rotation, collecting on 360° with a step scan of 1°, and integrating each step in 1 s. The data were collected with the Dectris 2M area detector and processed first with the Crysalis software for absorption and Lorentz-polarization corrections. Details pertaining to the data collection and structure refinement are summarized in Table 4. Space group tests led to the $P\bar{4}3m$ space group with the following unit-cell parameters: a 7.9791(2) and V 508.00(6) Å^3 for $Z = 1$. The crystal structure of plumbopharmacosiderite was solved using the SUPERFLIP program (based on the charge flipping algorithm, Palatinus & Chapuis 2007) implemented in JANA2006 (Petricek *et al*. 2014). The atomic positions (Table 5) were found to be in good agreement with those described by Hager *et al*. (2010) for bariopharmacosiderite. Lead was found from the difference Fourier map showing a maximum of about 8 e$^-$ in the special position 0,½,½. Further residuals in the Fourier map were detected around the

TABLE 5. REFINED POSITIONAL AND ANISOTROPIC DISPLACEMENT PARAMETERS (Å^2) FOR PLUMBOPHARMACOSIDERITE

	ai	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	U_{iso}/U_{eq}
Fe	1	0.1431(3)	0.1431(3)	0.1431(3)	0.0206(11)	0.0206(11)	0.0206(11)	–0.0047(8)	–0.0047(8)	–0.0047(8)	0.0206(6)
As	1	0.5	0	0	0.0143(17)	0.0404(17)	0.0404(17)	0	0	0	0.0317(10)
Pb	0.13(2)	0	0.5	0.5							0.12(2)
O1	1	0.1243(15)	0.381(2)	0.1243(15)							0.035(4)
O2	1	0.8865(13)	0.8865(13)	0.8865(13)							0.008(3)
Ow1	0.6739	0.685(7)	0.685(7)	0.685(7)							0.100(18)
Ow2	0.5671	0.219(10)	0.5	0.5							0.100(18)

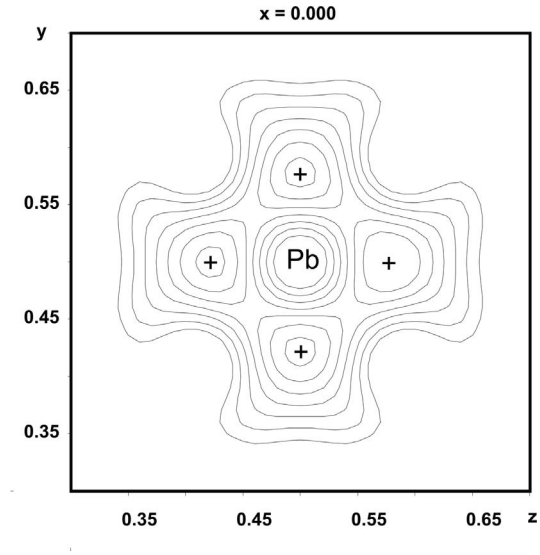

FIG. 1. Fourier map of the residuals close to the Pb position.

Pb position. These peaks are located in the plane of the unit-cell face (Fig. 1). These maxima are due to a slight disorder caused by the presence of K and Na located not exactly in the center of the unit-cell face but in the position *ca*. 0.025,½,½ as described by Hager *et al*. (2010) for natropharmacosiderite. Tests for possible merohedral twinning, as described in Hager *et al*. (2010), gave no improvements to the crystal-structure refinement. We finalized the refinement using anisotropic thermal parameters for Fe and As and isotropic thermal parameters for Pb and oxygen atoms. Moreover, the thermal parameters for Ow1 and Ow2 were constrained to be equal. During the last refinement cycles the occupancies of Ow1 and Ow2 were fixed in order to obtain an overall oxygen content close to that calculated from the chemical analysis. When convergence was achieved, no peaks greater than +2.01 and less than –3.26 e$^-$/Å^3 were present in the final difference-Fourier map. The general framework of the plumbopharmacosiderite structure conforms to that proposed by Buerger *et al*. (1967) for pharmacosiderite. In our structure the Ow2 atom is slightly offset from the position described by Buerger *et al*. (1967) due to the presence of Pb. Indeed, the positions of Pb and Ow2 are mutually exclusive in plumbopharmacosiderite. The plumbopharmacosiderite structure is characterized by strongly distorted FeO_6 octahedra, which share corners with AsO_4 tetrahedra to form large zeolite-like channels that are consistent with the pharmacosiderite structure-type as described by Buerger *et al*. (1967). Lead ions are

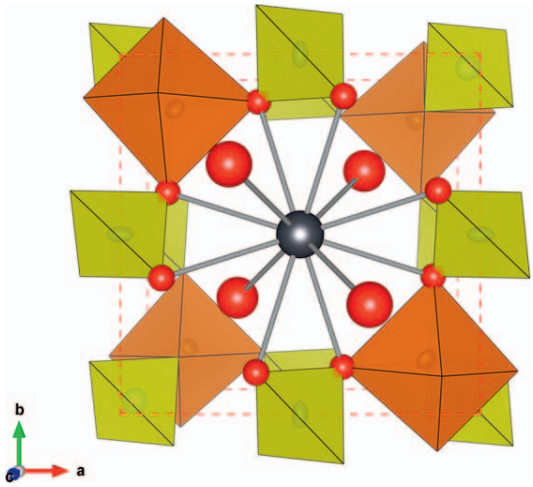

FIG. 2. The crystal structure of plumbopharmacosiderite along **c**. AsO_4 tetrahedra in yellow, FeO_6 octahedra in brown. The Pb ion (dark grey) is located at the center of the channel on the unit-cell face. The large red spheres represent oxygen atoms of OH groups (figure drawn using VESTA, Momma & Izumi 2011).

located in the center of the unit-cell face on the zeolitic channel (Fig. 2). Lead with minor K and H_2O and further water are sited within these channels. The average bond lengths for <As–O> and <Fe–O> are fairly typical (1.695 and 1.991 Å), while the contact between O2 and O4 is 2.78 Å, which is indicative of H bonding (Table 6). The average bond length for the Pb site is 3.289 Å, which is also very typical.

DISCUSSION

The mineral is named plumbopharmacosiderite since it corresponds to the Pb-rich term in the pharmacosiderite group of minerals. Plumbopharmacosiderite is a hydrated and hydroxylated lead-iron arsenate belonging to the pharmacosiderite supergroup, pharmacosiderite group. The Dana classification is 42.08.01, hydrated phosphates, arsenates, and vanadates containing hydroxyl or halogen, pharmacosiderite supergroup, pharmacosiderite group. The Strunz classification is 8.DK, phosphates, arsenates, and vanadates with large and medium-sized cations (OH *etc*.). Its crystal structure conforms very well to that described by Hager *et al*. (2010) for bariumpharmacosiderite, confirming the dominance of Pb at the center of the unit-cell face with some disorder due to the presence of alkalis.

TABLE 6. SELECTED BOND DISTANCES (Å) AND ANGLES (°) IN THE STRUCTURE OF PLUMBOPHARMACOSIDERITE

Fe–O1	1.908(16)	×3	O1–Fe–O1	98.6(5)
Fe–O2	2.074(11)	×3	O2–Fe–O1	91.5(5)
Fe–O	**1.991**		O2–Fe–O2	76.2(4)
Pb–Ow1	3.27(5)	×4		
Pb–O1	3.298(13)	×8		
Pb–O	**3.289**			
As–O1	1.695(14)	×4		
O2–Ow1	2.78(6)			

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