

Natropharmacoalumite, $\text{NaAl}_4[(\text{OH})_4(\text{AsO}_4)_3]\cdot 4\text{H}_2\text{O}$, a new mineral of the pharmacosiderite supergroup and the renaming of aluminopharmacosiderite to pharmacoalumite

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ABSTRACT

Natropharmacoalumite, ideally $\text{NaAl}_4[(\text{OH})_4(\text{AsO}_4)_3]\cdot 4\text{H}_2\text{O}$, is a new mineral from the Maria Josefa Gold mine, Rodalquilar, Andalusia region, Spain. It occurs as colourless, intergrown cubic crystals with chenevixite, kaolinite, jarosite and indeterminable mixtures of Fe and Sb oxyhydroxides. Individual crystals are up to 0.5 mm on edge, although crystals are more commonly ~0.25 mm across and occur in patchy aggregates several millimetres across. The mineral is transparent with a vitreous to adamantine lustre. It is brittle with an imperfect cleavage, irregular fracture and a white streak. The Mohs hardness is ~2.5 with a calculated density of 2.56 g cm^{-3} for the empirical formula. Electron microprobe analyses yielded Na_2O 2.52%, K_2O 1.49%, Al_2O_3 29.50%, As_2O_5 48.84% and H_2O was calculated in line with the structural analysis as 16.28% totalling 98.63%. The empirical formula, based upon 20.21 oxygen atoms, is $[\text{Na}_{0.57}\text{K}_{0.22}(\text{H}_3\text{O})_{0.21}]_{\Sigma 1.00}\text{Al}_{4.05}(\text{As}_{2.97}\text{O}_{12})(\text{OH})_4\cdot 4\text{H}_2\text{O}$. The five strongest lines in the X-ray powder diffraction pattern are $[d_{\text{obs}}(\text{\AA}), I_{\text{obs}}, (hkl)]: 7.759, 100, (100); 4.473, 40, (111); 3.870, 50, (200); 2.446, 9, (301); 2.331, 12, (311)$. Natropharmacoalumite is cubic, space group $P\bar{4}3m$ with $a = 7.7280(3) \text{ \AA}$, $V = 461.53(3) \text{ \AA}^3$ and $Z = 1$. The crystal structure was solved by direct methods and refined to $R_1 = 0.063$ for 295 reflections with $F > 4\sigma(F)$. The structure conforms broadly to that of the general pharmacosiderite structure type, with Na as the dominant cation in cavities of strongly distorted Al octahedra and As tetrahedra. A new group nomenclature system for minerals with the pharmacosiderite structure has been established, including the renaming of aluminopharmacosiderite to pharmacoalumite.

KEYWORDS: natropharmacoalumite, pharmacosiderite group, new mineral species, sodium aluminium arsenate, Maria Josefa mine, Rodalquilar, Spain, mineral nomenclature, redefinition, aluminopharmacosiderite, pharmacoalumite.

Introduction

NATROPHARMACOALUMITE was fortuitously discovered during a confirmatory energy dispersive X-ray (EDX) analysis of a specimen purchased at the 2009 Munich Mineral show labelled as aluminopharmacosiderite from Maria Josefa mine, Rodalquilar in Spain. The specimen was

offered by mineral dealer Christian Rewitzer who had originally identified the material on the basis of XRD analysis alone. The specimen was entered into the collections at the Natural History Museum (NHM) in London as BM 2009,161. In accordance with the NHM acquisition strategy and to satisfy curatorial protocol, the specimen identity has to be verified by EDX, and, where applicable, powder XRD analysis. It was during this confirmatory EDX analysis, using a rough fragment, that the material was first shown to be dominant in Na rather than K, corresponding to the Na-analogue of aluminopharmacosiderite.

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During discussions on a suitable name for the mineral, MSR and SJM noted that in order to follow the prefix nomenclature scheme which has been used for Fe-dominant pharmacosiderites, the new mineral would logically be named 'natroaluminopharmacosiderite'. Not only is this name long and unwieldy, it is also misleading as "sider" indicates the presence of iron, which is not a major constituent in this Al-dominant mineral. As a result, a proposal (Proposal 2010-A) to rename aluminopharmacosiderite and to establish a formal group nomenclature (see below) following the rules of Mills *et al.* (2009) was submitted and approved.

The new mineral is named natropharmacoalumite, and follows the already established prefix-based nomenclature of the pharmacosiderite supergroup. The name is in allusion to the cation dominance of Na and Al. The new mineral name and its characteristic data have been approved by the IMA Commission on New Minerals, Nomenclature and Classification (IMA 2010-009). The specimen, registered as BM 2009,161 at the Natural History Museum in London and probe block (P16713) derived from it represent the only holotype material.

Occurrence

Natropharmacoalumite occurs at the Maria Josefa mine (36°51'30"N, 2°5'2"W), near the town of Rodalquilar in the Andalusia region of Spain. The mine is one of a number in the region that work quartz veins in an epithermal Au-bearing alunite deposit within the Rodalquilar caldera. Gold was first found in the region in the 1880s but mining production had largely stopped by 1966 and now the mine lies abandoned (Arribas *et al.*, 1995).

The area is important mineralogically being the type locality for rodalquilarite (Sierra Lopez *et al.*, 1968), and is now visited mainly by mineral collectors due to its rich suite of secondary species. The specimen that contains natropharmacoalumite was removed from a large Fe-rich silicified boulder in the western area of the dumps.

Physical and optical properties

Natropharmacoalumite forms colourless, transparent cubes up to 0.5 mm on edge, although most crystals are ~0.25 mm across. The cubes are often intergrown irregularly to form crystalline patches several mm across (Fig. 1). Although not entirely

clear from the one sample studied, the intergrowth of the cubes would suggest that penetration twins and stepped growth features upon the cube surface are common. No other crystallographic forms apart from {100} were observed. The crystal patches occur in cavities and fracture surfaces within a greenish-brown vuggy quartz gossan, coloured mainly by powdery green chenevixite, yellow-brown jarosite and earthy white kaolinite. Small isolated regions of dark orange-brown Fe-Sb oxyhydroxides exist, but were too small to characterize. Natropharmacoalumite is non-fluorescent, has a white streak, a vitreous to adamantine lustre and an average VHN of 267 (load 98.3 mN), with a range of 214–329 (load 98.3 mN). The hardness and physical properties are similar to other pharmacosiderite-type minerals (Zemann, 1948; Schmetzer *et al.*, 1981; Peacor and Dunn, 1985; Mills *et al.*, 2011). The mineral is brittle, shows an irregular fracture and imperfect cleavage on {100}. The density could not be measured due to lack of sufficient sample but was calculated as 2.564 g cm⁻³ using structural considerations and



0.5 mm

FIG. 1. Colourless intergrown cubes of natropharmacoalumite associated with undifferentiated yellow-brown Fe-Sb-oxide/hydroxides.

the empirical formula. Approximate refractive index measurements were obtained using several rough fragments, immersion oils and white light; a determination close to the Cargille certified index of refraction liquids oil $n = 1.556$ was obtained. White internal reflections can be observed. More indicative refractive index tests proved difficult due to the irregular morphology of the tiny fragments used and a lack of material upon the specimen. Natropharmacoalumite is assumed to be anomalously biaxial, anomalous birefringence is typical in members of the pharmacosiderite group and is often ascribed to strain-induced anisotropy and twinning which single-crystal XRD studies show to be present in this material.

Chemical composition

Two grains of natropharmacoalumite were removed from two patches on either side of the small specimen, in order to ascertain the range of compositional variation between different areas. The grains were mounted in epoxy, polished, carbon coated and analysed using a Cameca SX100 electron microprobe at the Department of Mineralogy, Natural History Museum, London, UK, operating in wavelength-dispersive mode initially with an accelerating voltage of 20 kV, probe current of 20 nA and a 10 μm beam diameter; however, this showed significant decomposition of the sample under the electron beam and possible migration of Na. To minimize the migration of Na and loss of water, less intense analytical conditions were used; an accelerating voltage of 10 kV, probe current of 4 nA and a beam diameter of 30 μm . Elements detected included: Na (Jadeite reference standard), Al (Corundum reference standard), K (KBr reference standard) and As (Gallium Arsenide reference standard), P, Ti, Cu, Ba, Ca, Fe, Sr and Si were sought, but found to be below detection limits. All analyses were calculated using the 'PAP' matrix correction (Pouchou and Pichoir, 1988) with the inclusion of H_2O . Direct determination of H_2O was impossible due to a lack of sample. However, the presence of OH and H_2O were confirmed by the structural analysis. Analytical results are given in Table 1.

Calculation of an empirical formula was reliant on two assumptions: (1) OH = 4 and H_2O = 4, in line with the general formula for the majority of members of the pharmacosiderite supergroup; (2) the sum of exchangeable cations = 1. If the

TABLE 1. Analytical data for natropharmacoalumite.

Constituent	Wt.%	Ideal	Analytical range
Na_2O	2.52	4.51	2.01–2.66
K_2O	1.49	0	1.29–1.64
Al_2O_3	29.50	29.65	28.17–29.61
As_2O_5	48.84	50.13	45.57–49.54
H_2O	16.28	15.72	
Total	98.63	100	

sum of the charges of the exchangeable cations other than H_3O^+ is $<1+$, the remainder of the positive charge must be accounted for by the presence of the appropriate amount of hydronium ion (see also Mills *et al.*, 2010a,b).

The empirical formula calculated on the basis of 20.21 O atoms (based on crystallographic assumptions, see below) is: $(\text{Na}_{0.57}\text{K}_{0.22}(\text{H}_3\text{O})_{0.21})_{\Sigma 1.00}\text{Al}_{4.05}(\text{As}_{2.97}\text{O}_{12})(\text{OH})_4 \cdot 4\text{H}_2\text{O}$. The simplified formula is $(\text{Na},\text{K},\text{H}_3\text{O})\text{Al}_4(\text{AsO}_4)_3(\text{OH})_4 \cdot 4\text{H}_2\text{O}$ and the end-member formula is $\text{NaAl}_4(\text{AsO}_4)_3(\text{OH})_4 \cdot 4\text{H}_2\text{O}$, which requires Na_2O 4.51 wt.%, Al_2O_3 29.65 wt.%, As_2O_5 50.13 wt.% and H_2O 15.72 wt.%, total 100.00 wt.%.

Crystallography

X-ray powder diffraction data were obtained on a Bruker D8 powder diffractometer, utilizing

TABLE 2. Powder XRD data for natropharmacoalumite.

I_{obs}	d_{obs}	I_{calc}	d_{calc}	hkl
100	7.759	100	7.740	100
40	4.473	36	4.469	111
50	3.870	12	3.870	200
6	3.459	6	3.462	201
6	3.158	15	3.160	112
6	2.736	22	2.737	202
6	2.581	38	2.580	300,122
9	2.446	38	2.448	301
12	2.331	25	2.334	113
3	1.879	6	1.877	401,223
3	1.826	6	1.824	033,411

The intensities of the $h00$ reflections are enhanced due to preferred orientation effects.

Co-K α radiation at the Department of Earth and Ocean Sciences, University of British Columbia, Canada. Data were collected on a flat plate and are shown in Table 2. The refined unit-cell parameters were $a = 7.740(3)$ Å and $V = 463.723$ Å³, which correspond well with the single-crystal data (see below).

The single-crystal study was carried out using a Bruker X8 ApexII single-crystal diffractometer at the Department of Chemistry, University of British Columbia (Table 3). A single cube-shaped fragment from a larger, twinned natropharmacoalumite crystal was used for collection

of intensity data at 293 K. Single-crystal studies revealed that all measured examples were twinned with domains at 90° to each other, corresponding to twinning on {100}. The data were processed with the Bruker Apex program suite (Bruker, 2003), with data reduction using the *SAINTE* 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

TABLE 3. Crystallographic data and refinement parameters for natropharmacoalumite by single-crystal XRD.

Crystal data	
Empirical formula	[(Na _{0.57} K _{0.22} (H ₃ O) _{0.21}] _{Σ1.00} Al ₄ (AsO ₄) ₃ (OH) ₄ ·4H ₂ O
Crystal system	cubic
Space group	$P\bar{4}3m$
Unit-cell parameter a (Å)	7.7280(3)
Unit-cell volume (Å ³)	461.53(3)
Z	1
Calculated density (g/cm ³)	2.564
Absorption coefficient (mm ⁻¹)	5.76
Crystal size (mm)	0.15 × 0.15 × 0.15
Data collection	
Diffractometer	Bruker X8 ApexII
Temperature (K)	293
Radiation, wavelength (Å)	Mo-K α , 0.71073
θ range for data collection (°)	2.64–30.52
h, k, l ranges	–7 → 11, –9 → 8, –9 → 11
Total reflections collected	2437
Unique reflections (R_{int})	305 (0.035)
Unique reflections $F > 4\sigma(F)$	295
Data completeness to θ_{max} (%)	98.4
Absorption correction method	SADABS
Structure refinement	
Refinement method	Full-matrix least-squares on F^2
Weighting coefficients a, b^*	0.0767, 0.0457
Extinction coefficient	0.031(11)
Data/restraints/parameters	305/1/23
R_1 [$F > 4\sigma(F)$], wR_2 [$F > 4\sigma(F)$],	0.0592, 0.1657
R_1 all, wR_2 all	0.0613, 0.1685
Goodness-of-fit on F^2	1.861
Largest diff. peak and hole (e/Å ³)	1.33, –1.09

$$R_{int} = (n/n - 1)^{1/2} [F_o^2 - F_o(\text{mean})^2] / \Sigma F_o^2$$

$$R_1 = \Sigma |F_o| - |F_c| / \Sigma |F_o|; wR_2 = \{ \Sigma [w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o^2)^2] \}^{1/2};$$

$$* \text{weight} = 1 / [\sigma^2(F_o^2) + (aP)^2 + bP], \text{ where } P = (\max(F_o^2, 0) + 2F_c^2) / 3;$$

$$\text{GooF} = \{ \Sigma [w(F_o^2 - F_c^2)^2] / (n - p) \}^{1/2}$$

where n is the number of reflections and p is the number of refined parameters.

location of the framework ions Al, 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.

Inspection of the difference Fourier map showed two significant residuals at (0.686, 0.686, 0.686) and (0.0, 0.122, 0.0) which could be attributed to a fractionally occupied O site (water and hydronium ions). Refinement of the Na (+K) site led to an occupancy of 0.79 a.p.f.u., similar to that observed in the EMP analyses, which indicated that 0.21 of the total 2.00 O atoms generated by O4 is hydronium. This distribution of H₃O + H₂O is consistent with the structure of H₃O-exchanged pharmacosiderite and hydroniumpharmacosiderite (Mills *et al.*, 2010*a,b*). These distributions lead to the charge-balanced formula (Na_{0.57}K_{0.22}H₃O_{0.21})Al₄(AsO₄)₃(OH)₄·2.89H₂O. 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 Na(+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 = 0.0592.

Inspection of the difference Fourier map for the H atoms associated with the (H₂O + H₃O) molecules showed evidence of a possible H atom at (0.603, 0.603, 0.751) placing it ~1.04 Å from O3. Despite this, and the fact that symmetry elements produced a further two H positions, attempts to refine the partially occupied H atom position were unsuccessful and the arrangement of H atom positions about O3 made no geometrical sense. As was the case for H₃O-rich pharmacosiderites (Mills *et al.*, 2010*a,b*) it was concluded that the peak was spurious and it was not included in the final model. The structure reported herein is inverted; however, this gives atomic coordinates which are more easily comparable to all previously reported structures. Details of data collection and refinement are given in Table 3. The refined atomic coordinates, site occupancies and displacement parameters are given in Table 4 and polyhedral bond distances in Table 5.

The natropharmacoalumite structure is characterized by strongly distorted AlO₆ octahedra, which share corners with AsO₄ tetrahedra to form large zeolite-like channels which are consistent with the pharmacosiderite structure-type as described by Buerger *et al.* (1967). H₂O with

TABLE 4. Refined atomic coordinates, site occupancies and displacement parameters of natropharmacoalumite.

	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U</i> _{eq} or <i>U</i> _{iso}	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₂₃	<i>U</i> ₁₃	<i>U</i> ₁₂
As1	0.5	0	0	0.0122(6)	0.0096(7)	0.0135(6)	0.0135(6)	0	0	0
Al1	0.1391(4)	0.1391(4)	0.1391(4)	0.0114(10)	0.0114(10)	0.0114(10)	0.0114(10)	0.0016(10)	0.0016(10)	0.0016(10)
O1	0.1266(6)	0.1266(6)	0.3758(8)	0.0148(15)	0.0171(19)	0.0171(19)	0.010(3)	0.0015(16)	0.0015(16)	-0.007(2)
O2	0.8858(9)	0.8858(9)	0.8858(9)	0.013(3)	0.013(3)	0.013(3)	0.013(3)	0.002(2)	0.002(2)	0.002(2)
H2	0.8259(18)	0.8259(18)	0.8259(18)	0.016						
Na1*	0.5	0.052(5)	0.5	0.031(7)						
O3	0.5	0.122(8)	0.5	0.030(10)						
O4	0.685(3)	0.685(3)	0.685(3)	0.047(7)						

* Na:K fixed at 0.57:0.22 after refinement.

TABLE 5. Selected bond lengths (Å) in natropharmacoalumite.

As1	O1	1.684(7)	× 6
Al1	O1	1.834(7)	× 3
	O2	1.977(6)	× 3
<Al–O>		1.906	
Na1	O3	2.86(2)	× 2
	O1	3.09(2)	× 4
		3.33(2)	× 4
<Na–O>		3.14	
O2	O4	2.68(4)	
O2	H2	0.80(2)	

minor H₃O, and Na with minor K, and further water are sited within these channels (Fig. 2). The average bond lengths for <As–O> and <Al–O> are fairly typical (1.684 and 1.906 Å), while the contact between O2 and O4 is 2.68 Å, which is indicative of H bonding. The average bond length for the Na/K site is 3.14 Å, which is also very typical. All these values are consistent with the previous structure reports for the supergroup.

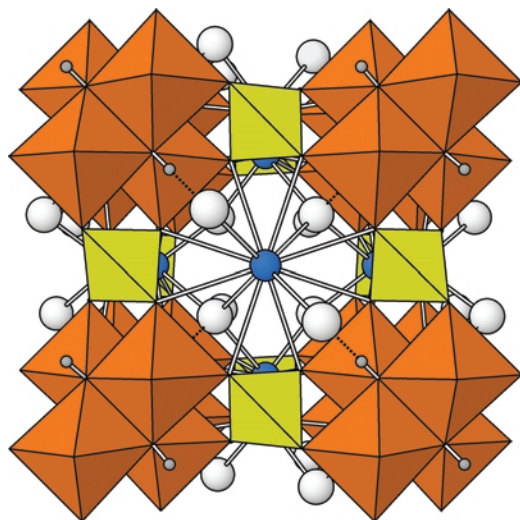


FIG. 2. Crystal structure of natropharmacoalumite. AsO₄ tetrahedra (yellow), FeO₆ octahedra (orange), Na atom (blue), O atoms of water/hydronium molecules (large grey spheres) and H atoms (small grey spheres).

Renaming of aluminopharmacosiderite

Aluminopharmacosiderite, KAl₄[(AsO₄)₃(OH)₄]·6.5H₂O, was described by Schmetzer *et al.* (1981) from Guanaco, Chile and has since been described from a number of localities worldwide (Anthony *et al.*, 2000). The name was an allusion to its composition, containing aluminium and being related to pharmacosiderite. In Greek, *pharmacōn* = poison and *sideros* = iron. Consequently, aluminopharmacosiderite is somewhat of an enigma, in that its end-member ideal composition contains no iron despite a name that would have reflected that. Note also that the prefix nomenclature which has been applied to other ‘pharmacosiderites’ denotes the change in the alkali cation, i.e. natro and bario. To make the nomenclature for Al-dominant species consistent with those of the Fe-dominant species and to continue with the use of prefix nomenclature based on changing of the alkali cation, aluminopharmacosiderite is renamed to pharmacoalumite where ‘alum’ is derived from the element aluminium; this replaces ‘sider’, to reflect the dominance of Al in the mineral.

Nomenclature

With the characterization of natropharmacoalumite, it becomes sensible to revisit the nomenclature of the pharmacosiderite-type minerals and to establish a formal mineral group and a systematic naming scheme for further members of the group that may be discovered in the future.

The minerals of this group have a generalized formula of $AB_4[(OH)_4(TO_4)_3]_nH_2O$, where *A* is commonly a large cation, e.g. K, Na, Ba or H₃O; *B* is Fe, Al or Ti (Ge and other elements are known synthetically); *T* is As with minor P, and *n* varies from about 1 to ~9. It should be noted that pharmacosiderites have been reported from the Czech Republic where the cation contents exceeded 1 a.p.f.u., up to a maximum of almost 4 a.p.f.u. (Sejkora *et al.*, 2006, Sejkora *et al.*, 2009). Both cubic and quadratic polytypes of the crystal structure are known (Mutter *et al.*, 1984) though the cubic polytypes appear to be more common.

Following the group nomenclature of Mills *et al.* (2009), minerals with the pharmacosiderite structure type (pharmacosiderite, bariopharmacosiderite, natropharmacosiderite, ivanyukite-Na, ivanyukite-K, ivanyukite-Cu, pharmacoalumite and natropharmacoalumite) can be placed into groups according to the *B* and *T* sites (Table 6). In

accordance with Mills *et al.* (2009), the group name is based on the first member discovered within the group; pharmacosiderite, $KFe_4[(AsO_4)_3(OH)_4] \cdot nH_2O$, was named “Pharmakosiderite” by Hausmann (1813) and has historical priority over all the other structurally related minerals. Pharmacosiderite can thus be used to define the supergroup name for all species, the group name for Fe-dominant members and the K-dominant, Fe-dominant mineral. For Al-dominant members, the new term pharmacalumite will be used as the group name and the K-dominant, Al-dominant mineral, in accordance with the revised dominant constituent rule (Hatert and Burke, 2008). This name replaces aluminopharmacosiderite, a name which becomes obsolete.

Recently Yakovenchuk *et al.* (2009) described a series of titanosilicates (“ivanyukites”) with the pharmacosiderite structure type. Ivanyukite can thus be used to describe members where Si replaces As and Ti replaces Fe or Al. The complete pharmacosiderite supergroup and individual groups are outlined in Table 6.

It should be noted that there now exists both prefix-based and suffix-based nomenclature within this new supergroup. While it would be ideal to have consistency across the supergroup, it is our view that having double suffixes with the form (-cation-polytype) is potentially confusing and rather unwieldy, although we can appreciate that prefix nomenclature gives very long names. We also feel that renaming the “ivanyukites” is not ideal, as these species have just been approved by the CNMNC. In light of all of these factors, we have decided to leave the names unchanged.

Summary

Natropharmacoalumite is a new secondary mineral from Rodalquilar in Spain, with the

same structure as all pharmacosiderite supergroup minerals which share similar physical, chemical and optical properties. They are placed within the Nickel-Strunz grouping system at 8.DK. Interestingly, the Gladstone-Dale compatibility relationship for natropharmacoalumite using the empirical formula is poor at -0.091 . We do not know the reason for this poor compatibility, but note that Yakovenchuk *et al.* (2009) suggested that a similarly poor compatibility index for ivanyukite-K might arise from high levels of cation deficiency. This phenomenon may also affect natropharmacoalumite with respect to cation distribution. Alternatively, it is quite possible that the crystal fragments used for the determination of the refractive index had a slightly different composition to the two that were used for the chemical analysis. The accuracy of the refractive index measurements could be improved, but not to the extent that the compatibility would be altered significantly.

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TABLE 6. Members of the pharmacosiderite supergroup.

A site	B = Fe (Pharmacosiderite group)	B = Al (Pharmacoalumite group)	B = Ti, T = Si (Ivanyukite group)
K	Pharmacosiderite	Pharmacoalumite	Ivanyukite-K
Na	Natropharmacosiderite	Natropharmacoalumite	Ivanyukite-Na
Ba	Bariopharmacosiderite	Bariopharmacoalumite ²	
H ₃ O	Hydroniumpharmacosiderite ¹		
Cu			Ivanyukite-Cu

¹ Mills *et al.* (2010b); ² IMA 2010-041

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