

What is the pharmacosiderite group?

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The pharmacosiderite group of secondary minerals is complex. The first mineral of the group described, pharmacosiderite, $\text{KFe}_4(\text{AsO}_4)_3(\text{OH})_4 \cdot n\text{H}_2\text{O}$, is cubic, space group $P43m$, and the general structure of the group was established by Zemann (1947, 1948) and Buerger *et al.* (1967). Mutter *et al.* (1984) established that synthetic members may have larger I – type cubic cells. Bariopharmacosiderite, of composition $\text{Ba}_{0.5}\text{Fe}_4(\text{AsO}_4)_3(\text{OH})_4 \cdot n\text{H}_2\text{O}$, is tetragonal. A number of other members of the group have been subsequently described, including a primary Ti-Si analogue. For the secondary species a general stoichiometry $\text{AB}_4(\text{AsO}_4)_3(\text{OH})_4 \cdot n\text{H}_2\text{O}$ ($A = \text{K}, \text{Na}, \text{H}_3\text{O}, 0.5\text{Ba}; B = \text{Fe}, \text{Al}$) could be written (some water is zeolitic in nature). Many other cations may be exchanged for A in synthetic preparations and solid-solution phenomena are pronounced.

Nevertheless, the general formula remains unsatisfactory because A may in fact be satisfied by a combination of cations whose total positive charge sums to a maximum of 5. This is achieved by the simultaneous, stepwise deprotonation of the hydroxide ions in the lattice. This mechanism serves to explain the red colour of members of the group with apparently anomalous contents at the A site.

This complex solid solution is noted in a number of natural phases, including K-rich species that approach the composition $\text{K}_{3.5}\text{Fe}_4(\text{AsO}_4)_3\text{O}_{2.5}(\text{OH})_{1.5} \cdot n\text{H}_2\text{O}$. The end-member of this series, $\text{K}_4\text{Fe}_4(\text{AsO}_4)_3\text{O}_3(\text{OH}) \cdot 4\text{H}_2\text{O}$, may be synthesised, as may be many other congeners containing mono- and divalent cations. End-member formulae are different in both cases. One consequence of the substitution is that any H_3O^+ -bearing member is limited to a total charge at the A site of 1+. Yet a further complication concerns the fact that the replacement of water molecules in the lattice by chloride ions can be accompanied by further substitution of A cations. These may be situated in the faces of the unit cell, slightly displaced from the faces, or at the centre of the cubic unit cell. The presence of chloride in natural material has not been reported.

These phenomena introduce a nomenclature problem for the group that remains to be formally resolved, both in terms of structure and composition. A number of suggestions for a resolution are explored.

Finally, hydroniumpharmacoalumite, $(\text{H}_3\text{O})\text{KAl}_4(\text{AsO}_4)_3(\text{OH})_4 \cdot n\text{H}_2\text{O}$, has been synthesised and its stability determined at 25°C. This has enabled the geochemical conditions under which members of the group form to be explored in relation to other simpler secondary arsenate minerals. It is noted in this connection that secondary members of the pharmacosiderite group are widespread in the oxidised zones of As-bearing base metal deposits.

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