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## THE SINGLE-CRYSTAL X-RAY STRUCTURES OF BARIOPHARMACOSIDERITE-C, BARIOPHARMACOSIDERITE-Q and NATROPHARMACOSIDERITE

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### ABSTRACT

The crystal structures of two polymorphic forms of bariopharmacosiderite have been determined. Bariopharmacosiderite-C, from Robinson's Reef, Clunes, Victoria, Australia,  $(\text{Ba}_{0.47}\text{K}_{0.04}\text{Na}_{0.02})(\text{Fe}_{3.97}\text{Al}_{0.03})[(\text{As}_{0.72}\text{P}_{0.28})\text{O}_4]_3(\text{OH})_4 \cdot 2.52\text{H}_2\text{O}$ , is cubic, space group  $P\bar{4}3m$ ,  $a$  7.942(1) Å,  $Z = 1$ ,  $R = 0.089$ . Bariopharmacosiderite-Q, from the Sunny Corner mine, Sunny Corner, New South Wales, Australia,  $\text{Ba}_{0.5}\text{Fe}_4(\text{OH})_4(\text{AsO}_4)_3 \cdot 6.16\text{H}_2\text{O}$ , is tetragonal, space group  $P\bar{4}2m$ ,  $a$  7.947(1),  $c$  8.049(2) Å,  $Z = 1$ ,  $R = 0.050$ . In the cubic polymorph, Ba ions are disordered over all faces of the unit cell, whereas in the tetragonal polymorph, Ba ions are centered on the 001 face. In both cases, the Ba ions are 12-coordinate, with eight bonds to arsenate oxygen atoms; four H<sub>2</sub>O groups complete the coordination sphere, with longer bonds to Ba in the cubic polymorph. Additional H<sub>2</sub>O groups are hydrogen-bonded to each other and to the H<sub>2</sub>O groups that coordinate Ba. Some of these exhibit "zeolitic" behavior. By analogy to the properties of synthetic pharmacalumite,  $\text{KAl}_4(\text{AsO}_4)_3(\text{OH})_4 \cdot n\text{H}_2\text{O}$ , the cubic polymorph appears to be more stable than the tetragonal one, although two further body-centered polymorphs are known. In addition, the crystal structure of natropharmacosiderite from the Gold Hill mine, Utah, has been determined. Natropharmacosiderite,  $(\text{Na}_{0.75}\text{K}_{0.14}\text{Ba}_{0.11})_{\Sigma 1.00}\text{Fe}_4(\text{AsO}_4)_3(\text{OH})_{3.89}\text{O}_{0.11} \cdot 4\text{H}_2\text{O}$ , is cubic, space group  $P\bar{4}3m$ , with  $a$  7.928(9) Å,  $Z = 1$  and  $R = 0.0654$ . The Na position is displaced by ~0.2 Å from the Wyckoff 3c site, and is coordinated by four H<sub>2</sub>O groups and eight oxygen atoms of arsenate groups. A new general formula for "excess cation" pharmacosiderite is proposed, involving deprotonation of bridging hydroxide ions.

**Keywords:** bariopharmacosiderite, natropharmacosiderite, crystal structure.

### SOMMAIRE

Nous documentons la structure cristalline de deux formes polymorphiques de la bariopharmacosidérite. La bariopharmacosidérite-C, provenant de Robinson's Reef, Clunes, Victoria, en Australie,  $(\text{Ba}_{0.47}\text{K}_{0.04}\text{Na}_{0.02})(\text{Fe}_{3.97}\text{Al}_{0.03})$

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