Sodium-pharmacosiderite
a new analog of pharmacosiderite
from Australia
and new occurrences of Barium-pharmacosiderite

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ABSTRACT

Sodium-pharmacosiderite, ideally $Na_2(OH)[Fe_4^{+3}(AsO_4)_3(OH)_4]$ $7H_2O$, is a new mineral from Marda, Western Australia, where it is found associated with arsenopyrite, scorodite, quartz and other species. Sodium-pharmacosiderite is cubic (space group $P\bar{4}3m$, with $a = 8.01(2)$ Å), pale green in color, and occurs in cubic crystals. Additional locality and compositional data are provided for barium-pharmacosiderite, now shown to occur at a number of classic mineral localities.

INTRODUCTION

During a survey of the chemical composition of a large number of specimens of minerals in the pharmacosiderite group, we noted one sample which did not have substantial K or Ba, which are the common large cations in this group. Subsequent study indicated that this sample is Na-rich and our investigation has shown it to be the sodium analog of pharmacosiderite. We have named this new mineral *sodium-pharmacosiderite* in allusion to the composition and the relationship to pharmacosiderite. The species and the name were approved by the Commission on New Minerals and Mineral Names, I.M.A., prior to publication. Type material is preserved at the Smithsonian Institution under catalog #146392.

CRYSTALLOGRAPHY

Sodium-pharmacosiderite occurs as pale green, euhedral, cubic crystals with no modifying forms (Fig. 1). The crystals occur as clusters of randomly oriented crystals. Maximum crystal size is 0.5 mm.

Single-crystal Weissenberg and precession photographs are consistent with space groups $P\bar{4}3m$, $Pm3m$, and $P432$. Buerger *et al.* (1967) reviewed the problems associated with the symmetry of pharmacosiderite and confirmed that it has a substructure with space group $P\bar{4}3m$ and $a \approx 8$ Å. Because pharmacosiderite and sodium-pharmacosiderite are isostructural, we infer that sodium-pharmacosiderite must have space group $P\bar{4}3m$. The lattice parameter ($a = 8.012(1)$ Å) was determined through least-squares refinement of powder diffraction data (Table 1), obtained using FeKα radiation and Si as an internal standard.

Buerger *et al.* (1967) noted that their specimen, which has the pharmacosiderite structure, contains very little K, Na or other large cations, and displays superstructure reflections which require that it

has a symmetry lower than that of a cubic phase, with both *a* and *c* doubled. Mutter *et al.* (1984) studied both natural and ion-exchanged samples, and found that those with alkali ions are generally cubic, some having $a \approx 8$ Å, and some having a superstructure with $a \approx 2 \times 8$ Å. These have space groups $P\bar{4}2m$ and $I\bar{4}2m$, respectively. Barium-dominant samples are generally tetragonal. These fall into one of two groups having $a \approx c \approx 8$ Å, and $a \approx c \approx 2 \times 8$ Å, and space groups $P\bar{4}2m$ and $I\bar{4}2m$, respectively. An ion-exchanged, Na-rich sample, however, displayed powder X-ray diffraction relations indicating a symmetry of the orthorhombic system, or lower symmetry. Given these relations, we carefully examined our powder and single-crystal diffraction photographs for the presence of weak superstructure reflections or subtle deviations of symmetry from those required by space group $P\bar{4}3m$. None was observed. However, as lower symmetries are presumably due to ordering, there may be other samples of naturally occurring sodium-pharmacosiderite which are more highly ordered than ours, and which display some other symmetry.

CHEMICAL COMPOSITION

The samples examined for this study were chemically analyzed using an ARL-SEMQ electron microprobe utilizing an operating voltage of 15 kV and a sample current of 0.025 μa. A wavelength-dispersive microprobe scan indicated the absence of any elements with atomic number greater than 9, except those reported here. The standards used were maricite (Fe,Na), synthetic olivenite (As), barite (Ba) and microcline (K). The resultant analysis yields $As_2O_5 = 39.5$, $Fe_2O_3 = 38.2$, $K_2O = 2.9$, $Na_2O = 6.3$, H_2O (by Penfield method) $= 19.3$, sum $= 106.2\%$. We independently determined that pharmacosiderite can lose substantial H_2O at very low temperatures and presume that our determined weight percent oxides are high due to H_2O loss in sample preparation procedures, and/or under vacuum, and/or under bombardment by the microprobe beam. Accordingly, we have normalized the analysis to sum to 100% with 19.3% H_2O. The normalized analysis yields: $As_2O_5 = 36.7$, $Fe_2O_3 = 35.5$, $K_2O = 2.7$, $Na_2O = 5.8$, $H_2O = 19.3$, sum $= 100.0\%$. The chemical formula, calculated on the basis of Fe = 4 atoms, is (with Z = 1):

$$(Na_{1.68}K_{0.52})_{\Sigma 2.20}Fe_4^{+3}(AsO_4)_{2.87}(OH)_{5.59} \cdot 6.84H_2O.$$

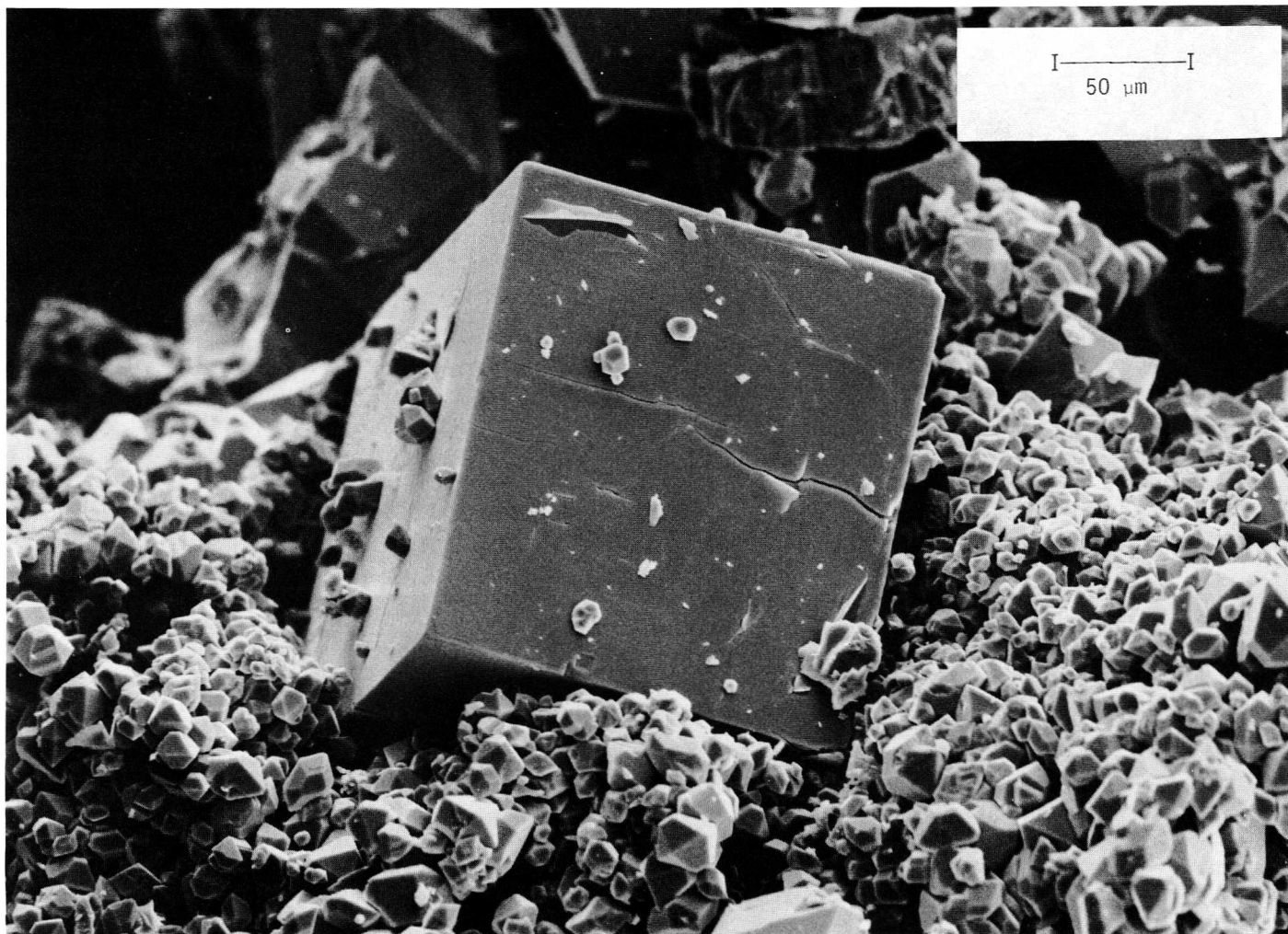This is idealized as $Na_2(OH)[Fe_4^{+3}(AsO_4)_3(OH)_4] \cdot \approx 7H_2O$,
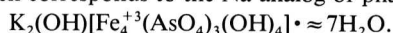
Figure 1. Scanning electron microscope (SEM) image of a cubic crystal of sodium-pharmacosiderite on a druse of scorodite. Smithsonian Institution #146392. Marda, Western Australia.

which corresponds to the Na-analog of pharmacosiderite:

$$K_2(OH)[Fe_4^{+3}(AsO_4)_3(OH)_4] \cdot \approx 7H_2O.$$

The chemical formula for pharmacosiderite has previously been given as $KFe_4^{+3}(AsO_4)_3(OH)_4 \cdot 6\text{-}7H_2O$. Our survey of analyses of the pharmacosiderite group indicates that the large cation site contains either 0.5 Ba or 2K, and that previous analyses of K-bearing species were either low in H_2O values or were of solid solutions with other members wherein Ba substituted in part for K. As our investigation of the new mineral proceeded, we were informed of the independent discovery of these relations by Mutter *et al.* (1984) who confirmed that there are 2 K per 3 As in common pharmacosiderite.

PHYSICAL AND OPTICAL PROPERTIES

Sodium-pharmacosiderite is pale green in color with no obvious color zoning. The hardness (Mohs) is approximately 3. The luster is vitreous on both cleavage and fracture surfaces. The {001} cleavage is very imperfect; the fracture is uneven. The density, determined using heavy liquid techniques, is 2.79 g/cm³ (± 0.04), compared with the calculated value of 2.90 g/cm³ for the end-member. The mineral is brittle. Optically, sodium-pharmacosiderite is isotropic and displays no optical anomalies such as are common to some members of the group and which are presumably tetragonal as shown by Mutter *et al.* (1984). The index of refraction is $n = 1.705(4)$. It is pale green to colorless in thin section and is transparent.

OCCURRENCE

Sodium-pharmacosiderite occurs at Marda, Western Australia, Australia. The occurrence of "pharmacosiderite" here was first noted by Simpson (1952) who reported that it was pale green in color and provided a description of the paragenesis that closely resembles what we have found on the one museum specimen available to us.

The type specimen consists of quartz and arsenopyrite. The arsenopyrite is altered, leaving dissolution vugs. Within these vugs are crystals of green sodium-pharmacosiderite, yellow pharmacosiderite (unanalyzed), scorodite, arseniosiderite, and a yellow powdery member of the jarosite group. All of these minerals were identified using X-ray diffraction.

BARIUM-PHARMACOSIDERITE: NEW DATA

Barium pharmacosiderite was originally described from the Clara mine in the Black Forest, Germany, by Walenta (1966). It has subsequently been found in southern Bohemia by Čech *et al.* (1975), and at Schramberg, Germany (Walenta, 1980). In our search (unsuccessful) for additional samples of sodium-pharmacosiderite, we examined a number of samples simply labeled "pharmacosiderite" from various localities. In the course of this survey, we found additional localities for barium-pharmacosiderite, and we have tabulated these in Table 2. Because of the loss of H_2O during microprobe analysis, our analyses are all high in determined weight

Table 1. X-ray powder diffraction data for sodium-pharmacosiderite.

d(obs)	d(calc)	hkl	I/Io
7.99	8.01	100	100
4.61	4.63	111	50
4.00	4.01	200	40
3.58	3.58	120	5
3.27	3.27	211	80
2.831	2.833	220	60
2.668	2.671	221	30
		300	
2.532	2.534	310	50
2.416	2.416	311	60
2.314	2.313	222	10
2.138	2.142	321	2
1.891	1.889	330	20
		411	
1.838	1.838	331	10
1.791	1.792	420	20
1.749	1.749	421	5
1.709	1.708	332	1
1.604	1.603	500	30
		430	
1.544	1.542	511	20
		333	
1.464	1.463	521	10
1.417	1.416	440	20
1.394	1.395	441	10
		522	
1.375	1.374	530	5
		433	
1.335	1.335	442	5
		600	

Figure 2. SEM image of a rough crystal of barium-pharmacosiderite. Sterling Hill, New Jersey. John Kolic collection.

Table 2. Chemical data for some barium-pharmacosiderites. Calculated on the basis of As = 3 atoms.

Sample #	Fe	Al	As	K	Ba	Locality
28458	4.1	0.0	3.0	0.1	0.6	Robinson's Reef, Port Phillip, Victoria, Australia
80473	4.2	0.1	3.0	0.1	0.4	Tintic district, Utah
B14260	4.0	0.2	3.0	0.0	0.4	Liebenschlehen mine, Neustaedtel-Schneeberg, Germany
R8878	4.3	0.1	3.0	0.0	0.5	Tintic district, Utah
B14242	4.5	0.0	3.0	0.0	0.5	Aschaffenberg, Germany
KOLIC	3.8	0.0	3.0	0.0	0.4	Sterling Hill, New Jersey
B14243	4.2	0.1	3.0	0.0	0.5	Aschaffenberg, Germany
R5621	4.2	0.0	3.0	0.0	0.5	Aschaffenberg, Germany
B14347	4.2	0.3	3.0	0.0	0.5	Tintic district, Utah
C4356	4.3	0.0	3.0	0.0	0.7	Cornwall, England

percent oxides. Because the water content of phases in the pharmacosiderite group may vary, and because it was not feasible to perform water determinations on all these samples, we are unable to normalize our data so as to permit its presentation in the conventional manner. Accordingly, in Table 2 we present the numbers of cations for these barium pharmacosiderites, calculated on the basis of 3 arsenic atoms. The data, although limited, clearly demonstrate that barium-pharmacosiderite has ½ Ba atom per 3 arsenic atoms. Thus, its formula, relative to that of pharmacosiderite, $K_2(OH)[Fe_4^{+3}(OH)_4(AsO_4)_3] \cdot \approx 7H_2O$, is very likely to be $Ba_{0.5}[Fe_4^{+3}(OH)_4(AsO_4)_3] \cdot nH_2O$, where n approximates 7. This formula differs from that of Mutter *et al.* (1984), which they gave as $Ba(H_3O)[Fe_4(OH)_2O_2(AsO_4)_3] \cdot nH_2O$. Their formula is based on analytical results which indicate that there is 1 Ba per 3 As. We have no explanation of why the basic analytical data should be different, especially when the data have been obtained by analyses of several samples from different localities in the cases of both investigations. As noted above, we have carefully analyzed our data for sources of error and have found none. However, there may well be additional complexities of formula for the pharmacosiderite group, reflected by these differences in data.

We present SEM photomicrographs of barium-pharmacosiderite crystals from various localities in Figure 2-4. We wish to emphasize that common (K-dominant) pharmacosiderite may also occur at these localities. Inasmuch as all samples from Tintic district, Utah,
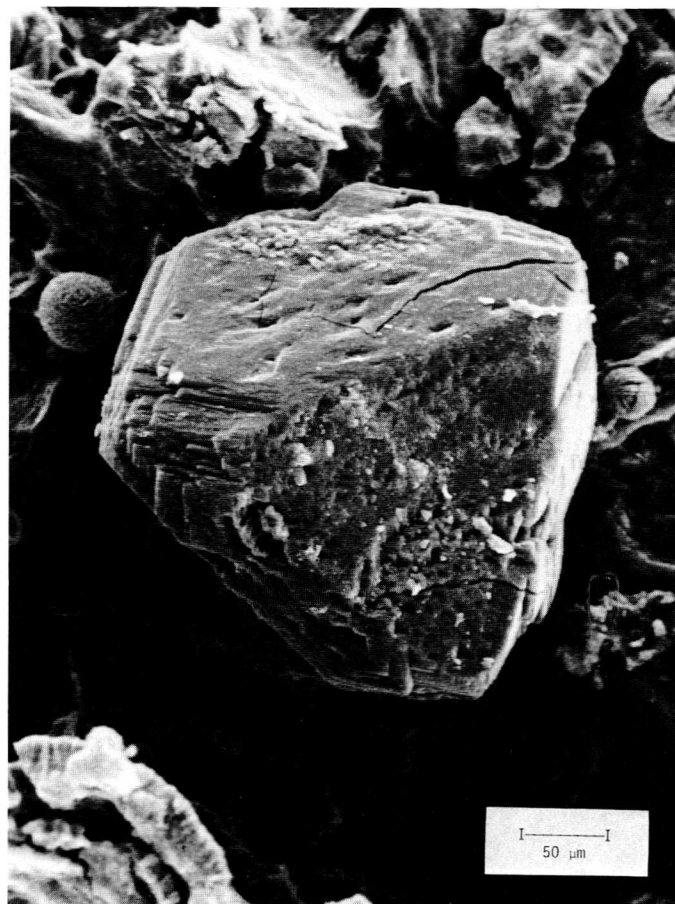
and from Aschaffenberg, Germany, were consistently Ba-dominant, this may be the common member of the pharmacosiderite group at these localities.

As part of our survey, we analyzed several samples from Sterling Hill, New Jersey. One of these (labeled KOLIC in Table 2) is clearly barium-pharmacosiderite, as shown in Figure 2. Another, consisting of medium yellow, prismatic to cubic crystals
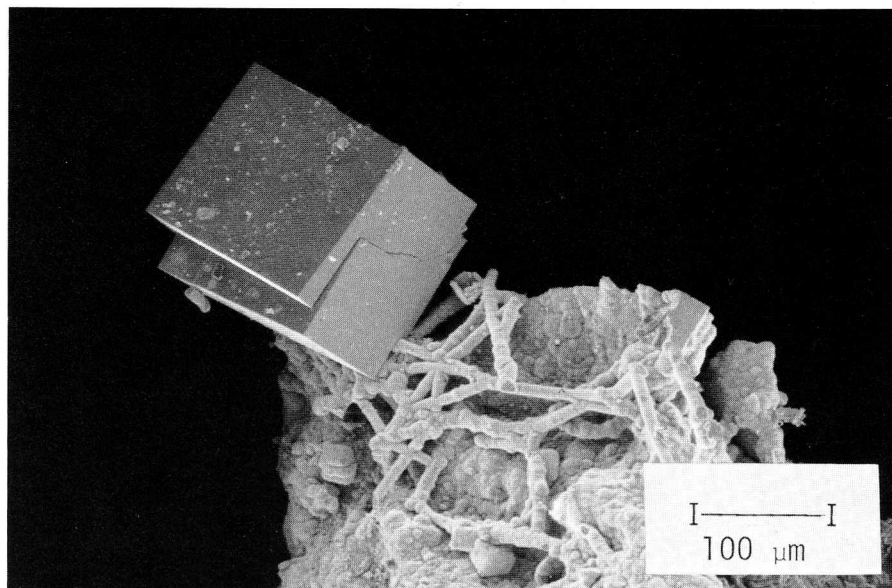
Figure 3. SEM image of a cubic crystal of barium-pharmacosiderite. Tintic district, Utah. Smithsonian collection R8878.
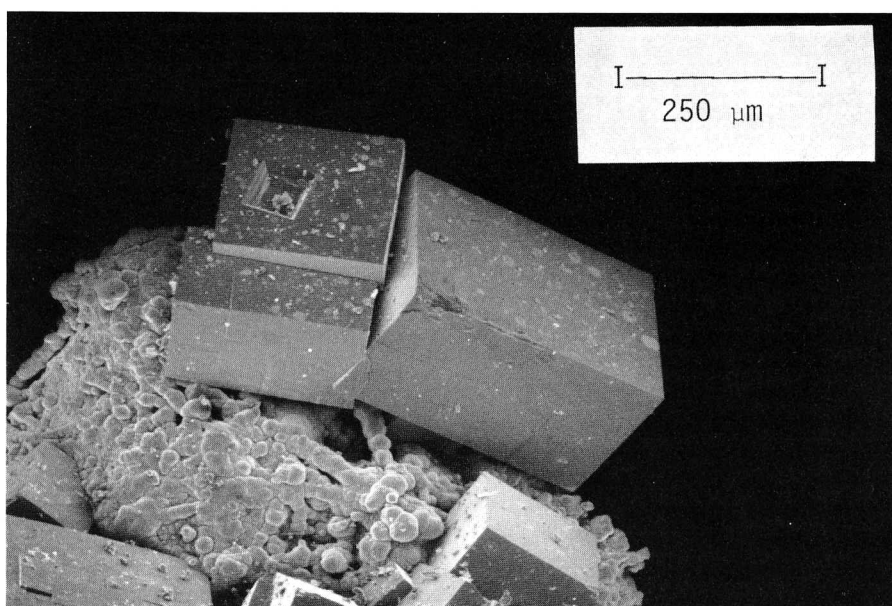

Figure 4. SEM image of a cluster of barium-pharmacosiderite crystals. Tintic district, Utah. Smithsonian collection R8878.

associated with willemite, koettigite and sphalerite in a vein assemblage, is not clearly any one of the known members of the group. It is strontium-dominant for the most part, but is clearly inhomogeneous, containing variable amounts of Pb, Mn, Zn, Ca and other cations. Although a strontium-dominant member of the pharmacosiderite group is predictable, it should be characterized on the basis of better and more homogeneous material than is presently available. For such samples, where nomenclature designations are ambiguous, the use of the general term, "pharmacosiderite-group mineral" is recommended. Members of the pharmacosiderite group commonly exhibit optical anomalies (presumably related to tetragonal symmetry) and also can be easily ion-exchanged in a manner akin to that of zeolites. Based on studies to date, color is not a useful diagnostic feature for discriminating among species in this series.

ACKNOWLEDGMENTS

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