

## A mcgovernite-like mineral and leucophoenicite from the Kombat mine, Namibia

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### ABSTRACT

A mcgovernite-like mineral from the Kombat mine, Namibia, occurs with alleghanyite, calcite, and ribbeite. It has the approximate formula  $(\text{Mn,Mg,Fe}^{3+})_{273}\text{As}^{2+}_{12}\text{As}^{5+}_{30}\text{Si}_{\sim 42}\text{O}_{324}(\text{OH})_{252}$ . It is hexagonal,  $R\bar{3}2/c$  or  $R3c$ , with  $a = 8.224(4)$  and  $c = 204(5)$  Å. Comparison of its chemical composition with that of mcgovernite provides a tentative formula for mcgovernite-like minerals:  $(\text{M}^{2+},\text{M}^{3+})_{273}\text{As}^{3+}_{12}\text{As}^{5+}_{30}\text{Si}_{\sim 42}\text{O}_{324}(\text{OH})_{252}$ , wherein  $\text{M}^{2+} = \text{Mn,Mg,Zn}$ , and  $\text{M}^{3+} = \text{Fe}^{3+},\text{Al}$ . The Kombat mine material differs from true mcgovernite in the absence of Zn, and the substitution of Al for most of the  $\text{Fe}^{3+}$ .

Analytical data for two new occurrences of leucophoenicite, from the Kombat mine and from the Italian Alps, show that this mineral is Ca-bearing, does not contain essential Zn, and has not yet been found as the ideal end member,  $\text{Mn}_7(\text{SiO}_4)_3(\text{OH})_2$ .

### INTRODUCTION

The Kombat mine in Namibia has recently produced a number of assemblages of rare materials including a number of new species such as johninnesite, holdawayite, asisite, ribbeite, and others. The occurrence is of particular interest inasmuch as some assemblages mimic some from Långban, Sweden, and Franklin and Sterling Hill, New Jersey. In this paper we compare data for both a mcgovernite-like mineral from Kombat with Sterling Hill mcgovernite and leucophoenicite from Kombat and Italy with Franklin leucophoenicite.

### CHEMICAL COMPOSITION

The minerals described were chemically analyzed using an ARL-SEMQ electron microprobe with an operating voltage of 15 kV, and a sample current of  $0.025 \mu\text{A}$  measured on brass. The data were corrected using a modified version of the MAGIC-4 program. The standards used for analysis of the mcgovernite-like mineral were Kakanui hornblende (Si, Fe, Al, Mg, Ca), synthetic ZnO (Zn), synthetic olivene (As), and manganite (Mn). The standards used for analysis of leucophoenicites were synthetic tephroite (Mn, Si) and hornblende for the other elements. The oxidation state of As was not directly determined; it was calculated using the  $\text{As}^{3+}:\text{As}^{5+}$  ratio determined for mcgovernite (Dunn and Nelen, 1980). The compositions are presented in Table 1.

### MCGOVERNITE

Mcgovernite was first described from Sterling Hill, Sussex County, New Jersey, by Palache and Bauer (1927).

The crystallography of this species was subsequently investigated by Wuensch (1960, 1968) and Moore and Araki (1978). Mcgovernite has the largest cell translation (other than some polytypes) of any known mineral species (203.15 Å), and the unit cell contains over 1150 atoms. A detailed study of its chemistry was published by Dunn and Nelen (1980), but no formula was proposed. The chemistry of mcgovernite is exceedingly complex; it is a layer structure, with possible solid-solution relations among  $\text{As}^{5+}$ , Si, and  $\text{Fe}^{3+}$ , together with the unknown role of  $\text{As}^{3+}$ . These factors, combined with the absence of a crystal-structure determination, have left mcgovernite as a mineral without a certain chemical formula. True mcgovernite remains known only from Sterling Hill; it has not been found at the close-by, genetically related deposit at Franklin.

### Occurrence

The mcgovernite-like mineral was found in the Kombat mine in Namibia in 1982, in the E15-11 south stope, 11 level, at the 1241-m elevation, in the Asis West sector of the mine. Examination of textures and the rock fabric shows that the flakes and nests of this mcgovernite-like phase are crudely aligned in a foliation or along zones of mineral banding. This foliation or banding is obviously deformed as evidenced from in situ observations made at Asis West. The foliation and mineral layering are tectonically transposed with development of boudins of the separate mineral phases together with rootless fold hinges and intrafolial folds. A steeply plunging mineral lineation is also developed, especially in the associated silicate minerals. The mcgovernite-like mineral flakes and lamellae are also strongly distorted into curved lamella.

## Description

The mcgovernite-like mineral occurs as light to bright yellow platy aggregates up to 1.5 cm in diameter, associated with alleghanyite, chlorite, pyrochroite, several spinels, and ribbeite. The mcgovernite-like mineral occurs in apparent equilibrium with these phases. However, the humite-related minerals, alleghanyite and ribbeite, are segregated on the observed specimens, and the mcgovernite-like mineral is associated preferentially with ribbeite rather than alleghanyite. The rock has a typical metamorphic granular texture. The crystals have vitreous luster, perfect {0001} cleavage, and  $\omega = 1.749 (\pm 0.003)$ ;  $\epsilon$  was not determined. The specimen studied is catalogued as no. 127869 in the Harvard Mineralogical Museum and as NMNH no. 163208 in the Smithsonian Institution.

## Crystallography

This mcgovernite-like mineral from Kombat was investigated by both the powder and single-crystal X-ray diffraction methods. The mineral was first identified by matching its powder pattern (Table 2, column 1) with Powder Diffraction File (PDF) card 25-531 for Sterling Hill mcgovernite. Zero-level [11 $\bar{2}$ 0] axis and *c*-axis precession photographs recorded with MoK $\alpha$  radiation are virtually identical to those illustrated by Wuensch (1960), which suggests that the Kombat mineral and mcgovernite are structurally similar. Additional powder data (Table 2, column 3) were recorded on a Norelco diffractometer over the range 14–45° 2 $\theta$  using monochromatized CuK $\alpha$  radiation and quartz C-105 (Fron del and Hurlbut, 1955) as an internal standard, for the purpose of refining the unit-cell parameters. However, indexing of the powder pattern cannot be done uniquely. The mcgovernite structure, although known to be related to that of hematolite (Wuensch, 1968; Moore and Araki, 1978), has not yet been solved. Thus, structure factors are unavailable to guide the selection of the numerous, closely spaced, possible diffraction maxima that results from the enormous *c* dimension (~205 Å). The large variation in unit-cell values cited in the literature for Sterling Hill mcgovernite (Table 3) is a function of indexing, not of inconsistent data. The diffraction

TABLE 1. Chemical data for mcgovernite, the mcgovernite-like mineral, and leucophoenicite

	Mcgovernite		Leucophoenicite	
	Sterling Hill*	Kombat mine	Kombat mine	Italian Alps
FeO	n.d.	n.d.	0.3	0.3
MgO	11.5	10.2	5.5	2.7
MnO	42.2	53.4	62.8	64.7
CaO	0.0	0.0	2.4	2.8
ZnO	9.3	0.0	0.0	0.0
Fe <sub>2</sub> O <sub>3</sub>	1.7	0.3	n.d.	n.d.
Al <sub>2</sub> O <sub>3</sub>	0.0	1.0	n.d.	n.d.
As <sub>2</sub> O <sub>3</sub>	4.6	5.0	n.d.	n.d.
As <sub>2</sub> O <sub>5</sub>	12.5	13.5	n.d.	n.d.
SiO <sub>2</sub>	9.2	9.0	26.7	26.7
H <sub>2</sub> O	8.49**	8.49**	2.3†	2.8†
Total	99.5	100.9	100.0	100.0
	Cations per 576 oxygens		Cations per 3 silicons	
Fe <sup>2+</sup>	n.d.	n.d.	0.03	0.03
Mg	76.62	66.85	0.92	0.45
Mn	159.73	198.82	5.98	6.16
Ca	0.00	0.00	0.29	0.34
Zn	30.67	0.00	0.00	0.00
Fe <sup>3+</sup>	5.69	0.98	n.d.	n.d.
Al	0.00	5.18	n.d.	n.d.
As <sup>3+</sup>	12.49	13.34	n.d.	n.d.
As <sup>5+</sup>	29.19	31.01	n.d.	n.d.
Si	41.11	39.56	3.00	3.00
H	253.03	248.88	1.72	2.10

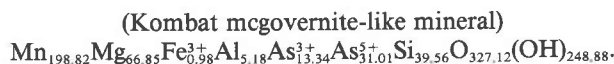
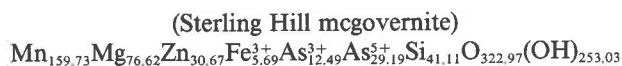
\* Average of five analyses (Dunn and Nelen, 1980).

\*\* Water content from Palache and Bauer (1927).

† Water content calculated by difference.

## Composition

Calculations of unit-cell contents for mcgovernite from Sterling Hill and approximate calculations for the Kombat mine material suggest there are 570 oxygens in the unit cell. However, Moore and Araki (1978) have shown that mcgovernite is very closely related to hematolite and that mcgovernite has an 84-layer structure. Given that hematolite has seven anions per layer, a more structurally sound basis for calculation of a formula is 576 oxygens (588 less 12 for vacancies occupied by lone-pair electrons associated with the AsO<sub>3</sub> groups), which yields the following full-cell formulas:



pattern in Table 2 was indexed by matching observed *d* values with those generated from the cell parameters and space-group extinctions reported by Wuensch (1960). Refinement of these data and the larger data set recorded on film gave results (Table 3) that are indistinguishable (i.e.,  $\Delta < 1\sigma$ ). The differences in unit-cell parameters (Table 3, columns 2 and 6) between the Kombat and Sterling Hill mcgovernites are too small to be ascribed to or correlated with the chemical differences observed.

These formulas permit the proposal of a tentative general formula for mcgovernite-like minerals:  $(\text{M}^{2+}, \text{M}^{3+})_{273}\text{As}_{12}^{3+}\text{As}_{30}^{5+}\text{Si}_{42}\text{O}_{324}(\text{OH})_{252}$ .

The Kombat mine material differs from true mcgovernite in several respects: it is Zn-free, and has Al substituting for much of the Fe<sup>3+</sup>. In the Kombat material, Mn apparently substitutes for the Zn present in Sterling Hill mcgovernite. This substitution is in itself noteworthy inasmuch as Zn is principally in tetrahedral coordination

TABLE 2. X-ray powder data for the mcgovernite-like mineral from the Kombat mine

<i>hkl</i>	<i>d</i> <sub>obs</sub> <sup>*</sup>	<i>d</i> <sub>calc</sub> <sup>**</sup>	<i>d</i> <sub>obs</sub> <sup>†</sup>
0 0 18	11.4	11.385	
0 0 33	6.21	6.210	
0 0 36	5.69	5.693	
0 1 26	5.27	5.284	
1 0 28	5.12	5.104	
0 1 32	4.78	4.762	4.735
1 0 34	4.61	4.601	
0 0 48	4.29	4.269	
1 1 0	4.11	4.112	
0 1 44	3.91	3.898	
1 0 46	3.75	3.777	
0 2 7	3.53	3.535	3.544
0 2 16	3.44	3.431	
0 2 22	3.32	3.326	
2 0 26	3.25	3.245	3.250
0 2 31	3.14	3.135	
0 2 34	3.06	3.066	
0 2 37		2.995	2.998
0 2 40	2.92	2.924	2.928
1 1 51	2.87	2.874	2.874
2 0 44	2.83	2.830	2.829
0 2 46	2.78	2.782	
2 1 7	2.68	2.681	
1 1 60	2.63	2.627	
0 1 74	2.58	2.581	
1 1 63	2.55	2.551	
1 2 29		2.517	2.554
0 1 80	2.41	2.411	2.518
0 2 64	2.38	2.381	
	1.896		
	1.818		
	1.727		
	1.702		
	1.652		

\* Film data recorded with FeK $\alpha$  radiation.\*\* Calculated from  $a = 8.224(4)$  and  $c = 204(5)$  Å, refined from data in column 1.† Diffractometer data recorded with CuK $\alpha$  radiation and quartz internal standard.

in Zn-bearing minerals at Sterling Hill and Franklin. If this Kombat material is completely isostructural with mcgovernite, it would suggest that Zn might be in octahedral coordination in mcgovernite and that there are no zincosilicate layers in the structure of mcgovernite.

The sum of (Al,Fe<sup>3+</sup>) in the Kombat mcgovernite-like mineral approximates six atoms. We have presumed that both Fe<sup>3+</sup> and Al are in octahedral coordination because they have been shown to be so in hematolite by Moore and Araki (1978). There is some indirect evidence to sug-

gest that Fe<sup>3+</sup> (and Al by analogy) might be essential to the crystal structure of these minerals. Moore and Araki (1978) found Al in hematolite, and Dunn and Peacor (1983) described an unnamed Fe<sup>3+</sup> equivalent of hematolite. Additionally, Fe<sup>3+</sup> was shown to be essential to the related mineral, dixenite (Araki and Moore, 1981; Dunn, unpub. data), and present in kraisslite, another mineral very closely related to mcgovernite (Dunn and Nelen, 1980). Fe<sup>3+</sup> is also present in all samples of schallerite, a structurally unrelated Mn-bearing arsenosilicate that occurs at Franklin (Dunn et al., 1981). Therefore, by implication, Fe<sup>3+</sup> or Al might be essential components of the structure of many Mn-bearing arsenosilicates, including those of the hematolite group.

Additional insight into the composition of mcgovernite can be gained by comparing the data in Table 1. The Si content of the mcgovernite-like minerals is relatively invariant as is the As content. Total As appears to vary from 42 to 44 atoms per 576 oxygens, but this apparent variance is most likely due to analytical error. Mg is present in substantial and comparable amounts in both samples and may be essential to mcgovernite-like minerals.

If a future structure determination of mcgovernite shows Zn or Fe<sup>3+</sup> to be essential to the structure of this mineral, then the mineral from the Kombat mine may be a new member of the mcgovernite group.

### LEUCOPHOENICITE

Leucophoenicite, (Mn,Ca,Mg,Zn)<sub>7</sub>(SiO<sub>4</sub>)<sub>3</sub>(OH)<sub>2</sub>, has long been known from the Franklin Mine at Franklin, New Jersey, although it has not been found at the close-by, genetically related deposit at Sterling Hill. Until very recently, it was only known from Franklin, but White and Hyde (1983) found it at Pajsberg, Sweden, and Winter et al. (1983) noted an occurrence in the Valsesia-Val-tournanche area in the Italian Alps, which was originally described as alleghanyite by Dal Piaz et al. (1979). The leucophoenicite from the Italian Alps was found in a small hand sample of black oxidized material, consisting largely of vesuvianite and leucophoenicite (NMNH no. 163193). However, there were no good analytical data given for these latter occurrences. The known chemical composition, and variance thereof, for leucophoenicite was established by analyses of Franklin samples (Dunn, 1985). The occurrence at the Kombat mine provided a reason to gather additional data (Table 1). The Italian sample of Dal Piaz et al. (1979) was obtained through the courtesy of D. R. Peacor, who had verified its identity using single-crystal

TABLE 3. Unit-cell parameters (in Å) for mcgovernite (nos. 1–4) and the mcgovernite-like mineral (nos. 5–8)

	1	2	3	4	5	6	7	8
<i>a</i>	8.22	8.22(2)	8.22	8.16	8.23	8.230(9)	8.228(5)	8.224(4)
<i>c</i>	205.5	203.15(8)	18.7	203.2	205.5	204.9(4)	205(7)	204(5)

Note: Sterling Hill: (1) Measured from precession films (Wuensch, 1960). (2) Moore and Araki (1978), Moore and Ito (1978). (3) PDF card 25-531. (4) PDF card 27-1279. Kombat mine: (5) Measured from precession films. (6) Refined from data in Table 1, column 3, using program LCLSQ (Burnham, 1962). (7) Refined from data in Table 1, column 3, using program LSUCR (Appleman and Evans, 1973). (8) Refined from data in Table 1, column 1, using program LSUCR.

methods. Samples from both occurrences were verified by X-ray powder-diffraction by one of us (P.J.D.).

The Kombat mine leucophoenicite was found in the W1150 stope, 10 level, on the 1288-m elevation, and about 45 m up-plunge from the occurrence of the mcgovernite-like mineral, in the Asis West sector of the mine. A hand specimen consists of a slice of a banded ore sample. The dominant phase is calcian barysilite, which is adjacent to a zone of spessartine + vesuvianite + barite + copper; this zone is adjacent to one containing hausmannite, copper, and leucophoenicite in a gneissic texture (GSC no. 64566). The association with copper is replicated at Franklin as well.

These new analyses indicate clearly that Zn, found in all samples of Franklin leucophoenicite in nearly constant proportions (Dunn, 1985), is not essential to leucophoenicite. Ca, found in the great majority of Franklin leucophoenicite analyses, is present in these two samples as well, further supporting the suggestion (Dunn, 1985) that it might be a cationic substituent of preference for leucophoenicite, rather than for humite-group minerals. The Kombat leucophoenicite has the highest reported Mg content for the species. The Mn content falls within the limits reported previously and further supports the suggestion that leucophoenicite might not be stable as an Mn end member.

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