

A ferric iron equivalent of hematolite from Sterling Hill, New Jersey and Långban, Sweden

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ABSTRACT. An unnamed Fe^{3+} analogue of hematolite is described from Sterling Hill, New Jersey and Långban, Sweden. Eight microprobe analyses are in good agreement with ratios derived from a prior analysis which yielded: Al_2O_3 0.24, Fe_2O_3 10.85, MgO 10.61, MnO 41.76, As_2O_3 6.65, As_2O_5 15.29, H_2O 13.23 (rem. = 1.63), sum = 100.26%. Single-crystal study indicated that this compound is hexagonal with $a = 8.28 \text{ \AA}$, but the value of c could not be well-defined due to complex polytypism giving rise to diffuse and poorly resolved reflections along c^* . In one case, a value of $c = 72.69 \text{ \AA}$ was dominant. All values that could be determined were multiples of approximately 12 \AA . The strongest lines in the X-ray powder diffraction pattern are: 2.400(100), 1.563(100), 6.09(80), 3.42(50), and 5.13(50). This compound is dark red and occurs as platy hexagonal crystals in clusters associated with a wide variety of species in varied assemblages. It remains unnamed because of the ambiguity arising from polytypism.

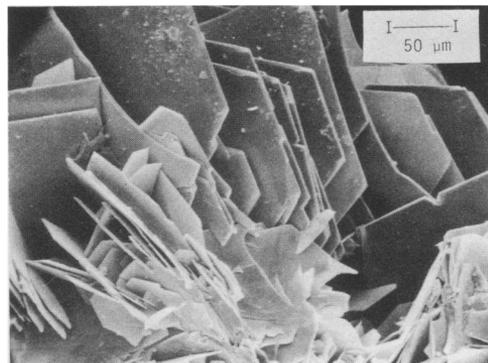
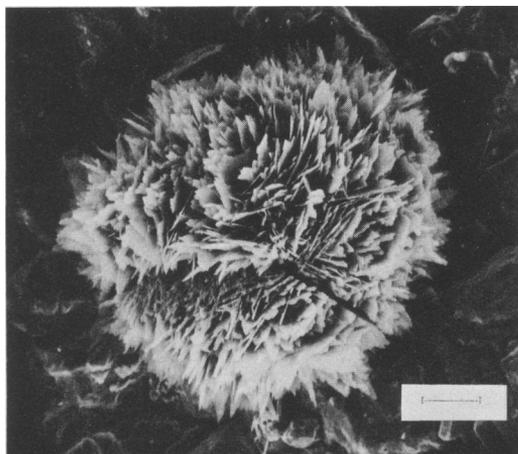
HEMATOLITE was originally described from Nordmarken, Sweden, where it occurs in a fissure assemblage with other basic manganese arsenates. The properties of hematolite are well defined; the original crystallographic work was by Berry and Graham (1948) and the crystal structure was solved by Moore and Araki (1978), who gave the formula $(\text{Mn}^{2+}, \text{Mg}, \text{Al})_{15}(\text{OH})_{23}(\text{AsO}_3)(\text{AsO}_4)_2$.

The hematolite-like mineral described here was originally recorded by the late K. Johansson at Långban, Värmland, Sweden, and an analysis of it was published in a posthumous compilation of his notes by Wickman (1950). Wickman noted that the Al of hematolite was almost completely replaced by Fe^{3+} , but he did not propose species status for this phase. Our discovery of additional specimens of this compound at Sterling Hill, New Jersey, prompted a re-examination of Swedish material to ascertain to what degree it could be characterized. That attempt has been only partially successful due

to the complexity of polytypism (or mixed layering) in the crystals from both occurrences. However, the data strongly imply the existence of an Fe^{3+} analogue of hematolite and related polytypic phases. We have therefore chosen to record our observations but without ascribing a mineral name to the phases in question.

Description. The mineral at Långban occurs in cavities as very crude aggregates of hexagonal crystals, each of which appear to be made up of thin plates stacked along $\{0001\}$. The individual sub-units are slightly offset from each other giving a very serrated appearance to the form, which, if smooth, would correspond to a very steep rhombohedron. Such a habit is not uncommon in other phases characterized by variations in mixed-layer polytypic stacking sequences. There appears to be very little variance in the habit of this mineral on the five specimens studied, with but one exception; sample R5755-1, containing 4.5 wt. % ZnO , consists of dark-red platy crystals on a seam in hausmannite ore. The most striking feature of the paragenesis of the Swedish specimens is the presence and abundance of pyroaurite, $\text{Mg}_6\text{Fe}^{3+}(\text{CO}_3)(\text{OH})_{16} \cdot 4\text{H}_2\text{O}$, which is present as light-brown euhedral crystals surrounding the 'ferric-iron-hematolite' and which occur in an oriented and apparently epitaxial relationship with it, the two species having $\{0001\}$ in common. Although pyroaurite is commonly interlayered with the hematolite-like mineral, there is no systematic periodicity on a megascopic scale. The other commonly associated mineral is calcite.

At Sterling Hill, this compound occurs in a wide variety of assemblages. Analysis No. 1 was obtained from reddish-orange sprays encrusting a serpentine-magnetite ore; they are clearly secondary. Analysis No. 2 was obtained from a 1.0 mm



FIGS. 1 and 2. SEM photographs. FIG. 1 (left). Ragged-edged crystals of hematolite-like mineral from Sterling Hill, New Jersey. Scale bar is 25 μm . FIG. 2 (right). Hexagonal, tabular crystals of hematolite-like mineral from Sterling Hill, New Jersey.

compact spherule, which occurred isolated on willemite–franklinite ore. Both of the above specimens are in the Spex–Gerstmann collection in Franklin, New Jersey. In addition, this hematolite-like mineral also occurs with baryte, chlorophoenicite, franklinite, willemite, and retzian-(Nd) (Dunn and Sturman, 1982) as reddish, platy, ragged-edged crystals (fig. 1). This phase has also been observed associated with allactite and altered covelline at Sterling Hill and in this assemblage it forms as clusters of platy hexagonal crystals (fig. 2). In all of these occurrences, this phase resembles kraisslite or mcgovernite, but is slightly redder in colour.

Crystallography. Single-crystal X-ray diffraction results were obtained for representative crystals of both Swedish (NMNH 143971) and Sterling Hill material using standard precession and Weissenberg techniques. These results indicated that the crystals are hexagonal with $a = 8.28 \text{ \AA}$. The value of c could not be well-defined, however, as the crystals apparently consisted of more than one polytype or mixed-layer structure. The intense diffractions define a lattice which is apparently rhombohedral, with $c = 3 \times 24.23 = 72.69 \text{ \AA}$. All 0001 reflections except those with $l = 6n$ are extinct. Some diffractions also appear to define a primitive cell with $c = 2 \times 24.23 = 48.46 \text{ \AA}$. The value $c = 72.69 \text{ \AA}$ is approximately twice that for hematolite. Precession photographs of other crystals all gave similar results, except that reflections were usually diffuse and poorly resolved along c^* . In no case could definitive results for a single lattice be obtained.

In an attempt to obtain well-defined results for the c -translation, several crystals were mounted for

c -axis rotating crystal photographs. Despite the fact that Fe- $K\alpha$ was used to provide maximum resolution, none of those photographs provided data for the definition of a c -translation. Effectively, there were no well-defined layer lines of the first kind. These results therefore confirm that the crystals are not well-ordered and consist of more than one polytype or mixed-layer structure.

Resolution of the fine detail of the structure of this compound(s) must await further study, probably based on high-resolution TEM techniques. It cannot be resolved using only X-ray techniques. However, all diffraction patterns have one feature in common: the 0001 sequence of reflections is strong and consists only of reflections having $d = 12 \text{ \AA}$ and submultiples thereof. Moore and Araki (1978) showed that hematolite is rhombohedral with space group $R3$, $a = 8.275$ and $c = 36.60 \text{ \AA}$. This structure therefore has a basic repeat unit along c of height 12.2 \AA , which was shown to consist of a five-layer, close-packed sequence. Because the basic repeat of hematolite corresponds to that of the Fe-rich phase described in this paper, it is reasonable to assume that the latter is isostructural with hematolite, except that it is characterized by a variety of polytypic stacking sequences, rather than having a single well-defined sequence as is true of hematolite.

X-ray powder diffraction patterns were obtained for all of the analysed specimens. Data for a representative pattern are listed in Table I, along with data for the powder pattern of hematolite for comparison. All patterns of the hematolite-like phase are very similar, having the same principal lines in common. However, they do differ in having

TABLE I. X-ray powder diffraction data for hematolite-like mineral and hematolite

Fe-hematolite*		Hematolite†	
d (obs.)	I	d (obs.)	I
12.2	30		
6.09	80	6.12	80
		5.63	30
5.13	50	5.20	50
4.10	50	4.14	80
		4.06	20
3.90	20	3.89	30
3.42	50	3.40	40
3.24	30	3.22	40
3.03	10	3.03	20
2.950	20	2.97	20
2.885	10	2.89	10
2.814	30	2.82	30
2.694	30	2.70	10
2.600	30	2.60	40
		2.44	10
2.400	100	2.39	100
2.325	30	2.33	30
2.166	10	2.17	10
2.094	10		
		2.00	20
1.949	5	1.948	20
1.879	10	1.880	40
1.741	20	1.745	40
		1.601	10
1.563	100	1.562	90
1.511	10	1.512	20
		1.369	10
		1.307	10
		1.215	10
		1.143	10

* Powder pattern obtained using a 114.6 mm diameter Gandolfi camera, with polycrystalline sample, Cu-K α X-radiation. Intensities visually estimated.

† Data from Berry and Graham (1948).

some variation in the weaker reflections. The patterns are also generally of poor quality, as reflected in part by broad and smeared-out reflections. This supports the conclusions obtained by the single-crystal studies, in that such features are typical of a phase displaying variations in stacking sequence but having a single basic repeat unit. Because the principal features of the hematolite pattern are almost identical, both structures must be essentially identical.

We note with interest that Araki and Moore

(1981) examined two of the specimens we studied, and implied that they were dixenite. We find that they are not dixenite and not identical to the dixenite Araki and Moore studied (NMNH C4440). There are significant differences in the X-ray powder photographs that permit the identification of dixenite unambiguously.

Analytical procedures. The samples were chemically analysed using an ARL-SEMQ electron microprobe utilizing an operating voltage of 15 kV and a sample current of 0.025 μ A, standardized on brass. The standards used were manganite (Mn), synthetic olivenite (As), synthetic ZnO (Zn), and hornblende (Fe,Al,Mg). The data were corrected using a modified version of the MAGIC-4 program. The samples are chemically homogeneous within the limits of the 10 μ m microprobe beam used. The oxidation state of the Fe was determined by microchemical tests. The oxidation state of the As, for sample R5755 (analysis No. 6) was determined by titration with iodine after distillation with HCl. The full procedure used for this determination was given by Dunn and Nelen (1980). The foregoing analytical procedures have been validated by prior use in Dunn and Nelen (1980) and Dunn *et al.* (1981). There was insufficient material for the direct determination of water; we have calculated it by difference and note that our results are in good agreement with those of the late K. Johanssen and with the theoretical composition of the Fe³⁺ analogue of hematolite. The resultant data are given in Table II.

Although the co-existence of As in two oxidation states is uncommon, there are a number of Mn-arsenates that have mixed-state As. In addition, and most significantly, both of the hematolite-related minerals at Sterling Hill, kraisslite and mcgovernite, have been shown to have As in two oxidation states, albeit with different ratios.

Discussion. The present results confirm the analytical results of K. Johanssen, which were posthumously published by Wickman (1950). The average of the analyses of the Swedish samples is in good agreement with the theoretical composition of the Fe³⁺ analogue of hematolite. Calculation of an empirical formula, based on 15 octahedral cations (other than H), for Johanssen's analysis, yields: (Mn_{8.90}Mg_{3.98}Fe_{2.05}Al_{0.07})_{Σ15.00}(AsO₃)_{1.01}(AsO₄)_{2.01}(OH)_{23.06}, or, ideally, (Mn,Mg,Fe³⁺,Al)₁₅(AsO₃)(AsO₄)₂(OH)₂₃.

The chemical analysis of hematolite (Sjögren, 1885; Moore and Araki, 1978) showed the presence of 2.07 cations with 3+ charge (primarily Al) as noted by Moore and Araki (1978). They proposed that these cations are distributed only on the M(5) and M(7) sites. Site occupancies were proposed to be (0.44 Al + 0.40 Mg + 0.16 Mn) for M(5) and (0.58

TABLE II. Chemical analyses of hematolite-like mineral from New Jersey and Sweden

Analysis	Sample	Al ₂ O ₃	Fe ₂ O ₃ *	MgO	ZnO	MnO	As ₂ O ₃ †	As ₂ O ₅ †	H ₂ O‡	Total	Locality
1.	EG	0.8	8.1	12.7	5.8	39.0	6.2	14.5	14.5	100.0	Sterling Hill
2.	S-G	0.0	9.2	5.7	7.8	45.8	6.0	14.0	11.5	100.0	Sterling Hill
3.	R5755-1	2.2	8.2	13.6	4.8	37.0	6.8	15.9	12.5	100.0	Långban
4.	R5755-1	1.9	8.5	12.8	4.5	37.5	6.4	14.9	13.5	100.0	Långban
5.	94848	0.0	11.1	11.4	1.0	42.5	6.3	14.6	13.1	100.0	Långban
6.	R5755	0.0	10.5	11.5	0.6	43.7	6.8§	14.9§	12.0	100.0	Långban
7.	B20579	1.3	9.7	12.7	4.4	38.5	6.3	14.7	12.4	100.0	Långban
8.	143971	0.0	11.5	11.1	0.5	43.5	6.3	14.7	12.4	100.0	Långban
	(average of 3-8)	0.9	9.9	12.2	2.6	40.4	6.5	14.9	12.6	100.0	Långban
9.	Johanssen	0.24	10.85	10.61	n.g.	41.76	6.65	15.29	13.23	100.26	Långban
10.	Theory		10.68	10.78		42.70	6.62	15.37	13.85	100.00	Theory**
<i>Atoms per 15 octahedrally coordinated cations</i>											
1.	EG	0.22	1.44	4.49	1.02	7.83					
2.	S-G	0.00	1.73	2.13	1.44	9.70					
3.	R5755-1	0.61	1.45	4.76	0.83	7.35					
4.	R5755-1	0.54	1.53	4.56	0.79	7.58					
5.	94848	0.00	2.02	4.10	0.18	8.70					
6.	R5755	0.00	1.90	4.12	0.10	8.88					
7.	B20579	0.36	1.72	4.46	0.76	7.70					
8.	143971	0.00	2.09	4.00	0.01	8.90					
	ave. (3-8)	0.25	1.78	4.34	0.46	8.17					
9.	Johanssen	0.07	2.05	3.98	n.g.	8.90					

* Total Fe calculated as 3+ on the basis of microchemical tests.

† Oxidation state of As calculated as 3+ : 5+ = 1:2.

‡ H₂O by difference except for analyses 9 and 10.

§ Oxidation state of As determined as described in text.

|| Johanssen analysis; total includes 0.09 SiO₂, 0.21 CaO, 0.38 Na₂O, 0.19 K₂O, 0.76 H₂O⁻ (in wt. %).

** Theoretical composition for Fe₃⁺Mn₉Mg₄(AsO₃)(AsO₄)₂(OH)₂₃.

Accuracy of data: ± 4 per cent of the amount present. n.g. = not given.

Al + 0.19 Fe³⁺ + 0.23 Mn) for *M*(7). Although there are uncertainties in site occupancies as noted by Moore and Araki (1978), these results appear to be definitive in the roles for trivalent cations, and show that there is an upper limit of 4 trivalent cations [3 in *M*(5) and 1 in *M*(7)] per formula unit. However, we note that in all analyses of hematolite and the phase described herein, 3+ cations appear to be limited to near 2 per 15 octahedrally co-ordinated cations. Because the analyses of the hematolite-like phase have very low values of Al, and as Fe³⁺ varies from 1.44 to 2.05 cations per formula unit, the analyses show definitively that Fe³⁺ plays the same role in this mineral as Al does in hematolite, but with incomplete occupancy of *M*(5) and *M*(7) by Fe³⁺, the deficiency being made up by Mg.

The role of 3+ ions in hematolite-group minerals remains unclear. Dunn and Nelen (1980) showed that Fe³⁺ is present in both kraisslite and mcgovernite, in nearly constant amounts. Araki and Moore (1981) subsequently indicated that it is an important part of the structure of the related mineral dixenite. It well may be that, as pointed out by Moore and Araki (1978), small amounts of Mg or 3+ ions are necessary for the stability of these

structures. We call attention to the concentration of Mg at approximately 4 atoms per 15 octahedral cations, further supporting the proposition of Moore that hematolite (and thus the Fe³⁺ analogue) may not be able to exist as pure end members without smaller cations. Indeed, Mn does not exceed 10 of the 15 octahedral cations in the phase described herein and does not exceed 10.5 in the only known analysis of hematolite.

Conclusions. The chemical, analytical, and X-ray diffraction data show conclusively that this hematolite-like mineral has the same basic hematolite crystal structure with ferric iron substituting for Al. The X-ray data show that there is not a well-defined *c*-axis repeat, however, although this does serve to explain the serrated morphology of the crystals. Because of this we have decided not to propose species status and a name for this phase, preferring to refer to it only as Fe-hematolite on an informal basis. Further studies, in particular those utilizing TEM techniques, are necessary in order to define the dominant stacking sequences before species status can be proposed.

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