

CATOPTRITE AND YEATMANITE—STUFFED
PYROCHROITE STRUCTURES?

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ABSTRACT

Catoptrite and yeatmanite are two peculiar silicoantimonates of manganese which can be described by the general formula $X_{2+}^{2+}{}_{14}V^{3+4+}{}_{4}Sb_{2}^{5+}Z_{2}^{2+4+}O_{29}$. The catoptrite structure cell contains two such molecules, with $a=5.65 \pm 0.01$, $b=22.92 \pm 0.06$, $c=9.06 \pm 0.01$ Å, $\beta=101^{\circ}30' \pm 15'$. The triclinic cell of yeatmanite is easily related to catoptrite.

Catoptrite has a remarkable substructure, pronounced on hk0 photographs, obeying the condition $h=3n$ and $k=7n$, where $n=0,1,2, \dots$, and the space group criteria. The substructure can be easily satisfied by an equation describing about 77% of the total structure cell scattering matter, distributed in unperturbed pyrochroite-like sheets.

INTRODUCTION

Catoptrite was described as a new species by Flink (1917). Type material occurred at the Brattfors Mine, Nordmark, Sweden, as jet-black crystals embedded in crystalline limestone containing grains of ganet, magnetite, and manganosite. I have studied the "manganostibiite" of Igelström (1884) from Moss Mine, Nordmark and have found some of the specimens to be identical with catoptrite. Furthermore, the "hematostibiite" of Igelström (1885) occurring at the Sjö Mine, Grythytte Parish, Sweden is identical with catoptrite.² Thus, catoptrite may be a more widespread mineral than previously suspected.

Yeatmanite, added to the list of new species by Palache, *et al.* (1938), is a very rare mineral occurring at Franklin, New Jersey associated with green willemite and sarkinite in thin veins cutting granular ore.

Both minerals are closely related; unfortunately, Palache *et al.* did not realize this and no detailed studies were undertaken on catoptrite. Both minerals may be regarded as complex silicoantimonates of general composition $X_{14}Y_4Sb_2Z_2O_{29}$ where $X=Mn^{2+}$, Mg^{2+} , Fe^{2+} ; $Y=Al^{3+}$, Fe^{3+} ; $Z=Si^{4+}$ in catoptrite, and $X=Mn^{2+}$, Zn^{2+} ; $Y=Si^{4+}$; $Z=Zn^{2+}$ in yeatmanite. The general composition is unique among minerals. Catoptrite is monoclinic, and yeatmanite is triclinic. Results of studies offered here indicate that the pot-pourri of elements reported in the analyses for the two minerals is the true state of affairs.

Detailed structure cell studies on catoptrite, reported in this article, not only demonstrate a close structural relationship between the two but also suggest that their structures are built of the simple motif of rather regular pyrochroite-like octahedral sheets.

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² "Hematostibiite," chronologically, has priority. However, it was poorly studied material and the more frequently used *catoptrite* should be retained.

THE STRUCTURE CELL OF CATOPTRITE

Excellent single crystals of type catoptrite were available for study. Flink (1917) established the mineral as monoclinic prismatic, with $a:b:c=0.3981:1:0.2450$, $\beta=101^\circ 13'$, point symmetry $2/m$.

A prism of dimensions $0.2 \times 0.2 \times 0.4$ mm was subjected to rotation and Weissenberg x -ray studies using filtered copper radiation; the derived structure cell parameters are listed in Table 1 along with the data of Palache *et al.* (1938) for yeatmanite in a new orientation.

The agreement between morphological data and structure cell data is

TABLE 1. STRUCTURE CELL DATA FOR CATOPTRITE AND YEATMANITE

| | Catoptrite | Yeatmanite ¹ |
|--------------|--|--|
| a | $5.65 \pm .01 \text{ \AA}$ | 5.52 \AA |
| b | $22.92 \pm .06$ | 11.56 |
| c | $9.06 \pm .01$ | 9.029 |
| α | $90^\circ 0'$ | $92^\circ 48'$ |
| β | $101^\circ 30' \pm 15'$ | $101^\circ 45'$ |
| γ | $90^\circ 0'$ | $76^\circ 11'$ |
| S.G. | $C2/m$ | $P\bar{1}$ or $P1$ |
| Z | 2 | 1 |
| ρ obs | 4.56 | $5.02 \pm .1$ |
| ρ calc. | 4.65 | 5.37 |
| formula | $(\text{Mn, Mg, Fe})_{14}(\text{Al, Fe})_4\text{Sb}_2\text{Si}_2\text{O}_{29}$ | $(\text{Mn, Zn})_{14}\text{Si}_4\text{Sb}_2\text{Zn}_2\text{O}_{29}$ |
| $a:b:c$ | .246:1:.395 ² | .477:1:.781 |

¹ Structure cell data of Palache *et al.* (1938), reoriented so that $a_{\text{new}}=c_{\text{old}}$, $b_{\text{new}}=-b_{\text{old}}$, $c_{\text{new}}=a_{\text{old}}$.

² Flink (1917) gives morphological .245:1:.398, $\beta=101^\circ 13'$, his a and c axes interchanged.

excellent, requiring the simple transformation $(001/0\bar{1}0/100)$. The density of 4.56 was determined with a Mettler balance cup suspension system using air and CCl_4 as weighing media.

There is no need to reproduce the analysis of Flink (1917) which can be conveniently found in Palache *et al.* (1951) as it seems to be essentially correct,¹ even considering the peculiar composition of catoptrite. The analysis computes to very nearly $(\text{Mn}_{.86}, \text{Mg}_{.10}, \text{Fe}_{.04})_{14}^{2+} (\text{Al}_{.83}, \text{Fe}_{.17})_4^{3+} \text{Sb}_2\text{Si}_2\text{O}_{29}$, yielding a calculated density of 4.65 for two formula units in the structure cell. Considering the complexity of the substance, the agreement between densities is good.

Little need be added to the physical data of Flink (1917), except to

¹ I have just received a probe analysis of catoptrite, kindly undertaken by Prof. J. V. Smith, which verifies Flink's analysis.

mention that in the course of this study, catoptrite crystals were found to be magnetic.

Partly indexed powder data for type catoptrite appear in Table 2,

TABLE 2. POWDER DATA FOR CATOPTRITE, "HEMATOSTIBITE" AND "MANGANOSTIBITE" (IN PART). Fe/Mn RADIATION, CALIBRATED FILMS, INTENSITIES VISUAL

| Catoptrite (114.6 mm camera) | | | | Hematostibiite ¹ | | Manganostibiite ^{1,2} | |
|------------------------------|------------------|-------------------|----------|-----------------------------|------------------|--------------------------------|------------------|
| I/I ₀ | d _{obs} | d _{calc} | hkl | I/I ₀ | d _{obs} | I/I ₀ | d _{obs} |
| 6½ | 8.88 | 8.88 | 001 | 7 | 8.7 | 7 | 8.8 |
| 1 | 5.73 | 5.73 | 040 | | | | |
| 4½ | 4.43 | 4.44 | 002 | 4½ | 4.46 | 5 | 4.45 |
| 2 | 3.49 | 3.51 | 042 | | | 1 | 3.47 |
| 1 | 3.43 | 3.43 | 151 | | | | |
| | | 3.44 | 132 | | | | |
| 10 | 2.957 | 2.952 | 152 | 10 | 2.95 | 10 | 2.94 |
| | | 2.960 | 003 | | | | |
| 4 | 2.810 | 2.806 | 201 | 5 | 2.79 | 5 | 2.80 |
| 2 | 2.768 | 2.768 | 171 | | | | |
| | | 2.768 | 200 | | | | |
| 5 | 2.600 | 2.611 | 171 | 6 | 2.60 | 5 | 2.60 |
| | | 2.606 | 152 | | | | |
| | | 2.592 | 202 | | | | |
| 2 | 2.553 | | ? | | | | |
| 4½ | 2.488 | 2.496 | 172 | 4½ | 2.48 | 4 | 2.48 |
| | | 2.492 | 240 | | | | |
| 2 | 2.276 | 2.276 | 172 | 1 | 2.27 | 1 | 2.28 |
| 1 | 2.220 | 2.220 | 004 | 1 | 2.22 | | |
| 3 | 2.146 | 2.153 | 173 | 3 | 2.15 | 3½ | 2.15 |
| | | 2.138 | 153 | | | | |
| 3½ | 1.944 | 1.944 | 173 | 3 | 1.945 | 3 | 1.946 |
| 2 | 1.916 | 1.918 | 064 | 2 | 1.916 | 1 | 1.916 |
| 2 | 1.6635 | 1.6646 | 174 | 2 | 1.666 | 2 | 1.665 |
| 2 | 1.6340 | 1.6371 | 0, 14, 0 | 2 | 1.634 | | |
| 3 | 1.6147 | 1.6112 | 065 | 3 | 1.615 | 2 | 1.614 |
| 3 | 1.5740 | 1.5762 | 175 | 3 | 1.573 | 2 | 1.575 |
| 2 | 1.4802 | | | | | | |
| 2 | 1.4298 | | | | | | |
| 2½ | 1.4092 | | | | | | |
| 1 | 1.3744 | | | | | | |
| 2 | 1.3656 | | | | | | |
| 2 | 1.2429 | | | | | | |
| 2 | 1.1541 | | | | | | |
| 3 | 1.0978 | | | | | | |
| 2 | 1.0700 | | | | | | |

¹ From 57.3 mm cameras.

² Some, but not all, manganostibiites are identical with catoptrite.

along with data for "manganostibiite" (in part) and "hematostibiite" of Igelström. No discussion is offered on the latter two materials as the results of more detailed studies on Igelström's poorly described antimonates including the aforementioned two shall appear in a separate paper. The optical data offered in Palache *et al.* (1951) for "manganostibiite" and "hematostibiite" (p. 1027) properly refer to catoptrite. Unfortunately, the chemical analysis cited under "manganostibiite" refers to a different material (manganostibiite proper) which is presently under investigation and is not related to catoptrite, but appears to be a new polymorph of the braunite-långbanite group.

DISCUSSION ON CATOPTRITE AND YEATMANITE CRYSTAL STRUCTURES

The $hk0$ and $0kl$ Weissenberg photographs for catoptrite demonstrate a very pronounced substructure. The appearance of very strong intensi-

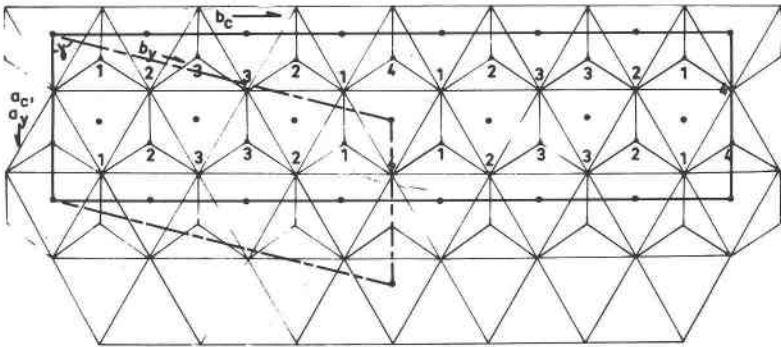


FIG. 1. A regular pyrochroite sheet with the catoptrite (c) and yeatmanite (y) a and b axes superimposed. Numbers refer to oxygen positions.

ties fulfills the condition that $k = 7n$, noticeable if b -axis rotation photographs are taken.

The reason became apparent when the relationship $b/7 = a/\sqrt{3}$ was discovered. The identity of 3.27 \AA suggests a Mn-centered oxygen octahedral edge distance and the relationship between the a and b axes can be satisfied by a regular unperturbed pyrochroite sheet. The projection of the a and b axes of catoptrite upon an unperturbed pyrochroite sheet with metal-metal repeat of 3.27 \AA is shown in Fig. 1. The octahedral centers along b for $X/a = 0$ fulfill the condition $p/7$ where $p = 0, 1, 2, \dots, 6$. At $X/a = \frac{1}{2}$, the centers repeat along b according to the condition $(2p+1)/14$, where $p = 0, 1, 2, \dots, 6$. One such sheet contains 14 Mn-centered octahedra in the structure cell. Assuming another identical sheet resides in the cell, oriented in the same fashion with respect to a and b but translated

along c^* , all 28 Mn atoms in the structure cell can be accounted for. This represents roughly 43% of the total scattering matter. Furthermore, there are constraints upon the oxygen atoms. The oxygen atoms labelled 1, 2, 3, and 4 in Fig. 1, repeat according to the conditions for $X/a \approx \frac{1}{3}$, $Y/b = p/7$, where $p=0,1,2, \dots, 6$. This accounts for 56 oxygen atoms or roughly 34% of the scattering matter. *In toto*, from the model presented here, 77% of the total scattering matter is defined for an $hk0$ projection.

On the $hk0$ Weissenberg photograph, the following reflections are so intense that they render all other reflections relatively weak: 0, 14, 0;

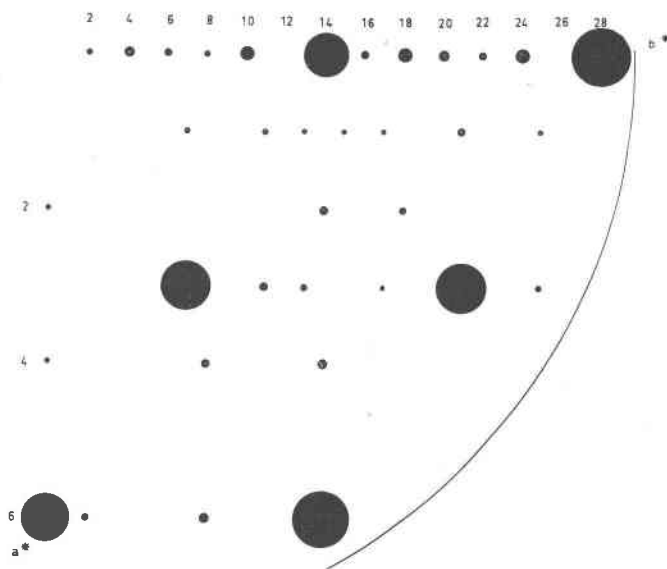


FIG. 2. Reciprocal net (a^*b^*) for catoptrite with approximate intensities represented as circular areas. The quadrant of circular arc represents the limits of the copper sphere.

0, 28, 0; 600; 370; 3, 21, 0; 6, 14, 0. To display this phenomenon, the reciprocal net is shown in Fig. 2 with the circle areas approximating the relative intensities. Extremely intense reflections, from a relative sense, also appear on $0kl$ photographs for $k = 14n$.

The geometrical structure factor accommodating the manganese and oxygen criteria as defined above for the $hk0$ projection (and scaled as to the scattering density percentages 'S') can be stated in the form $S \cos 2\pi hx \cos 2\pi ky$ for $h+k=2n$. The "S" values, as given above were obtained by dividing the total number of electrons attributed to manganese and oxygen respectively by the total number of electrons assigned to all atoms in an asymmetric unit of structure. To a crude approximation (since the

scattering curves for manganese and oxygen are not congruent to each other), the value of 23 electrons was assigned to Mn^{2+} and 9 electrons to O^{1-} .

The manganese contributions are

$$43 \sum_{p=0}^6 (\cos 2\pi h(0) \cos 2\pi k(2p/14) + \cos 2\pi h(\frac{1}{2}) \cos 2\pi k((2p+1)/14)).$$

The oxygen contributions are

$$34 \sum_{p=0}^6 \cos 2\pi h(1/3) \cos 2\pi k(2p/14).$$

This condenses to

$$43 \sum_{p=0}^6 \{\cos 2\pi kp/7 + \cos \pi h \cos \pi k(2p+1)/7\} + 34 \sum_{p=0}^6 \cos 2\pi h/3 \cos 2\pi kp/7.$$

Clearly, complete "in phase" diffraction is assured if $h=3n$ and $k=7n$, where $n=0,1,2, \dots \infty$. These are just the conditions noted on the $hk0$ Weissenberg photograph. No other reflections of this type were observed due to the limitations of the copper sphere.

For two such pyrochroite-like sheets in the structure cell, their separation is expected to be $(c/2) \sin \beta = 4.47 \text{ \AA}$. This is similar to the pyrochroite interlayer distance of 4.69 \AA . The metal-metal distances within the layers and the distance between the layers are apparently shorter than those for pyrochroite due to the presence of the more tightly bound O^{2-} in place of OH^- .

Catoptrite appears to be a stuffed derivative of the pyrochroite structure. The added "stuffing" consists of the remaining Al, Sb, Si and O atoms' apparently between the pyrochroite-like layers. Assuming 4-coordinate Al and Si and 5-coordinate Sb, all oxygen atoms in the structure could conceivably be related to these ligand centers. As yet, the positions for Al, Si, Sb and the remaining O atoms¹ are not known, so no further discussion shall be offered.

Yeatmanite and catoptrite appear to be closely related. Catoptrite has a perfect $\{001\}$ cleavage which is the plane of the pyrochroite-like layers. The perfect cleavage for yeatmanite is parallel to (001) for the orientation in Table 1. Hence, it should be possible to fit the a and b axes and the angle γ upon the pyrochroite sheet. An excellent fit is made if a yeatmanite = a catoptrite and b yeatmanite = $(a+b)/2$ catoptrite. The angle γ calculated from an unperturbed pyrochroite sheet is $76^{\circ}06'$, in excellent agreement with the observed data. The metal-metal distance for yeatmanite is 3.19 \AA , shorter than the 3.27 \AA displacement computed for

¹ If Sb is trivalent, then there are 56 oxygen atoms in the structure cell. Since these are accounted for *in* the sheets, there may be no oxygen atoms *between* the sheets.

catoptrite from the structure cell data. This is consistent with the high zinc content of yeatmanite. The pyrochroite, $\text{Mn}(\text{OH})_2$, metal-metal distance is 3.34 Å (Aminoff, 1918), whereas the hexagonal $\text{Zn}(\text{OH})_2$ metal-metal distance is about 3.19 Å (Lotmar and Feitknecht, 1936). Thus, by comparison, one would expect a foreshortening of the metal-metal distance within octahedral layers for yeatmanite relative to catoptrite.

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