GROUTITE, $HMnO_2$, A NEW MINERAL OF THE DIASPORE-GOETHITE GROUP

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ABSTRACT

Groutite, $HMnO_2$ is a new member of the diaspore-goethite group. It resembles manganite in general appearance as in luster, color, streak, hardness and specific gravity. Its structure, crystal forms and habits, cleavage and pleochroism are different. It occurs on the Cuyuna range, Minnesota, associated with iron ores.

INTRODUCTION

In 1942 the writer was presented with a small group of beautiful black crystals of a manganese mineral which had been thought to be manganite. The crystal habit of the mineral was so different, however, that an x-ray powder diagram was prepared which gave a pattern entirely different from any other known manganese mineral. A search for more material revealed that the mineral is not rare in the iron mines of the Cuyuna range of Minnesota. Some very fine specimens were presented to the writer by Mr. George Chamberlin, chief mining engineer of Pickands, Mather and Company at Crosby, Minn. The original sample examined was obtained from Mr. Harvey J. Hakala, mining engineer of the Oliver Iron Mining Company. It came from the Sagamore open pit west of Ironton on the Cuyuna range. Dr. R. B. Ellestad made the analysis. To all these men the writer is greatly indebted. Grants by the Graduate School of the University of Minnesota are gratefully acknowledged.

CRYSTALLOGRAPHY

Very beautiful specimens of hundreds of crystals, up to 5 mm. in greatest dimensions were available. Examination shows that the vast majority of the crystals are wedge or lens-shaped and that their faces are rounded and curved in a way that makes their measurements almost impossible. They have many markings on them similar to those of Fig. 3 which represents a sketch of what is visible of most crystals. The vertical [001] zone is always striated parallel to the c axis. The only usable vertical forms were {110} and {120}, and measurements on them are accurate to only the nearest degree. Form {010} occurs as very narrow faces but the brachypinacoidal cleavage is so perfect that reflections from it were very valuable. Another form in the vertical zone, probably present, is {130}. Form {100} was not observed but cleavage parallel to it may be seen, though interrupted by the perfect cleaving parallel to {010}. The readings on the forms {111} and {021} are usually fair and accurate to the nearest 10 minutes, though they are commonly smaller than shown in Fig. 2. Form (134) was observed only twice, and then only as one face on a crystal. It was large and gave good signals. Vicinal and curved faces precluded any other measurements. The crystals are attached to the walls of the cavities with the plane of the *a* and *b* axes more or less normal to their supports. This occurrence emphasizes their wedge- and lens-like shapes.

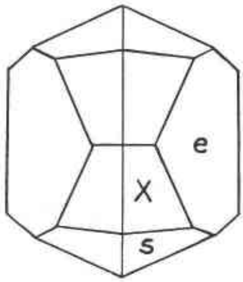

FIG. 1

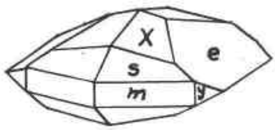

FIG. 2

FIG. 3

In recording the crystal elements and forms, the new edition of the *System of Mineralogy* (1) has been followed. All angles and other calculations are based on the reliable *x*-ray data below. If only two circle goniometric values had been used, the axial ratio would have been 0.440:1: 0.268.

ELEMENTS

Orthorhombic dipyramidal class

$a:b:c \;= 0.4262:1:0.2663$

$p_0:q_0:r_0 = 0.6248:0.2663:1$

$q_1:r_1:p_1 = 0.4262:1.6004:1$

$r_2:p_2:q_2 = 3.7550:2.3463:1$

TABLE 1. FORMS OBSERVED

Form	Indices	ϕ	ρ	ϕ_1	ρ_1	ϕ_2	ρ_2
b	010	0°00′	90°00′	90°00′	90°00′	— —	0°00′
m	110	66 55	90 00	90 00	23 05	0°00′	66 55
y	120	49 33	90 00	90 00	40 27	0 00	49 33
e	021	0 00	28 02	28 02	90 00	90 00	61 58
s	111	66 55	34 12	14 55	58 53	58 00	77 16
x	134	38 02	14 14	11 18	81 17	81 07	78 50

STRUCTURAL DATA

Powder and rotation photographs about the [100] and [001] directions were made. It is planned to make a complete determination of the structure at some later date. There is such similarity in the data of groutite, diaspore and particularly goethite, however, that the new mineral must be isostructural with the other two. The size of the unit cell is $a_0=4.56$ Å, $b_0=10.70$ Å, $c_0=2.85$ Å. It is interesting to observe that the height of the unit cell is 2.85 Å, or possibly twice this value, which is the same as

TABLE 2. POWDER PHOTOGRAPH OF GROUTITE, SAGAMORE MINE, NEAR IRONTON, MINN. Unfiltered Fe radiation. Radius of camera 57.3 mm. Indices obtained from rotation photographs.

No. of line	*d*	*I*	Indices	No. of line	*d*	*I*	Indices
1	5.36	1	020	19	1.465	1	
2	4.17	10+	110	20	1.448	1	
3	3.462	1–2	120	21	1.435	2	
4	2.798	6	130	22	1.398	1	
5	2.675	6	040	23	1.367	.5–1	
6	2.524	1	021	24	1.345	1	
7	2.369	6		25	1.304	.5	
8	2.303	5	140	26	1.286	1	180?
9	2.210	2		27	1.281	1	
10	2.008	1		28	1.267	1	
10*a*	1.959	.5	041	29	1.258	1	
11	1.932	1	150	30	1.220	1	
12	1.798	.5		31	1.212	1	081
13	1.763	2		32	1.202	1	
14	1.732	1		33	1.153	2	
15	1.692	5		34	1.134	1–2	
16	1.603	4		35	1.107	1	
17	1.559	0		36	1.086	.5	
18	1.515	3	061	37	1.077	.5	
				38	1.068	3	0, 10, 0

that of pyrolusite, Ba-psilomelane, cryptomelane and manganite (in the latter 5.70/2). While those minerals have habits of elongation parallel to [001], groutite crystals are very short in this direction. The lines of the powder photograph are included here (Table 2) because in very fine grained specimens it might be impossible to distinguish groutite from manganite by any other means.

PHYSICAL PROPERTIES

Cleavage occurs parallel to {010} and {100}. The former is exceedingly perfect and yields brilliant reflections. The color of the mineral is jet black, and the luster is brilliant submetallic to adamantine. The streak is dark brown like that of manganite. The hardness may be slightly essl than that of manganite, the brittleness seems to be the same. The specific gravity determined on a gram of handpicked material is 4.144 recalculated to 4° C. This determination was made in a fused silica pycnometer. The theoretical density based on the size of the unit cell is 4.172. The optical properties have not been determined except for pleochroism, which is very strong in white light.

TABLE 3. CHEMICAL ANALYSES

	1	1 minus residue	2	Theoretical composition
MnO	78.06	79.97	80.04	80.66
O	8.73	8.94	9.02	9.10
H_2O+	10.14	10.39		10.24
H_2O-	.04	.04		
Al_2O_3	not det.			
Fe_2O_3	.02	.02		
$(Na,K)_2O$	not det.			
BaO	.00			
P_2O_5	.33	.34	.07	
Insoluble residue	2.39			
Total	99.70	99.71		100.00

R. B. ELLESTAD, *analyst.*

Very dark brown to black	[001]
Yellowish brown	[010]

Groutite could be distinguished from manganite by this property since the pleochroism of this mineral is weak.

Groutite is infusible and loses water on heating in air at temperatures above 200° C. Heating at 150° C. in air for five days does not affect it.

CHEMICAL COMPOSITION

Material for the analyses was handpicked very carefully. Analysis 1 is from a specimen from the Mahnomen Mine, according to Mr. George Chamberlin who presented it to the writer. The associated quartz could not be eliminated completely and is recorded as insoluble. Partial analysis 2 is on a sample from the Sagamore Mine, which contains no insoluble residue. Dr. R. B. Ellestad kindly furnished the note* below regarding

* Total manganese was determined by potentiometric titration of manganous ion with permanganate, in a neutral pyrophosphate solution, following the method of Lingane and Karplus (*Ind. and Eng. Chem.*, Analytical Ed. **18**, 191, 1946). Excess oxygen was determined by solution of the sample in a mixture of sulfuric acid and an excess of standard sodium arsenite, followed by the titration of the excess arsenite with permanganate. This method is described by Kolthoff and Sandell (Textbook of Quantitative Inorganic Analysis,

analytical procedure. Dr. W. W. Wetzel of Minnesota Mining and Manuturing Company, St. Paul, Minn., kindly ran a spectrographic analysis for the writer. He reports less than 0.1% CaO, about 0.05 MgO, about 0.05 Na_2O and a trace of Al_2O_3.[1]

Occurrence

Groutite, as stated in the introduction, has been found in at least three mines of the Cuyuna iron range in Minnesota. There is good reason to believe that it is present as minute crystals in other mines of the district. Very fine specimens have been obtained from the Sagamore, Mangan No. 2, and Mahnomen pits. Since these specimens are very attractive even to the layman, it is probable that a number of them, if not many, are in local collections. The crystals always line vugs and nearly always are associated with manganite. The manganite usually is the common variety which forms radiating columnar but compact coatings, occasionally one inch thick. The groutite crystals are attached to the tops of the columns approximately with their (100) planes. In at least one specimen the manganite columns are elongated parallel to the [100] direction, and the attached groutite crystals have their [100] parallel to that of the manganite. Some crystals seem to show oriented growth on the manganite with the plane (100) in common. Since the c_0 and b_0 dimensions are very similar this is not surprising.

In one specimen unusual manganite crystals were observed which may correspond to one of several varieties described by Flink (3). They are very thin and platy in habit and have the shape of the end of a gladiator's sword. The very thin terminal faces are somewhat rounded. Deep striations parallel to the elongation prevent measuring of any faces in the vertical zone.

The only other minerals associated with groutite are colorless quartz crystals, hematite and goethite. A thin coating of calcite may be found on some specimens. These can be dissolved with dilute H_2SO_4 without harming the manganese minerals.

Relationship to Diaspore and Goethite

Until recent years it had been thought that manganite was a member of the diaspore-goethite group. M. J. Buerger (2) has shown, however, that the bonding of hydrogen corresponds more closely to an OH ion in

p. 605; Macmillan, N. Y., 1943). Total water was determined by the Penfield method, using a flux of lead oxide.

[1] A spectrographic analysis was made by Dr. H. C. Harrison in Professor Esper Larsen's laboratory. It was received too late for inclusion above. He reports concentrations 0.1–0.01% of Al, Fe, Mg, Ca, Zr, Mo, Sb, Sn. Concentrations 0.01–0.001% of Na, K, Ti, Ni, Hf, Pb, Y, Gd, Sc, Yb, Cr, V, Cu, Ag, Ba, Li, Sr, Bi.

manganite. Similar bonds exist in boehmite and lepidocrocite. These three minerals can be placed in one group, therefore, though it must be admitted that manganite is not too closely related. It might conceivably be placed between the two groups because the dimensions of its unit cell are close to those of groutite as shown in Table 4.

TABLE 4. COMPARISON OF UNIT CELLS, VOLUMES, AND AXIAL RATIOS

	a_0	b_0	c_0	Volume	Axial ratios
diaspore	4.40	9.39	2.84	117.34	.4689:1:.3019
goethite	4.64	10.00	3.03	140.59	.4593:1:.3034
groutite	4.56	10.70	2.85	139.05	.4262:1:.2663
manganite	8.86	5.24	5.70	—	
manganite*	4.43	10.48	2.85	132.33	.4227:1:.2719
boehmite	3.78	11.08	2.85	119.36	.320:1:.242
lepidocrocite	3.87	12.51	3.06	148.13	.309:1:.245

* The dimensions have been divided or multiplied, respectively, by 2 to conform to other minerals in the table.

The volumes of unit cells containing the same number of chemical molecules are shown in Table 4. The smaller ones would be expected to belong to the minerals with the greater stability. Diaspore and boehmite are similar in stability. Lepidocrocite is considerably larger in volume than goethite and less stable under pressure and elevated temperatures.† For this reason it is also a rare mineral. The same applies to the manganese dimorphs. Groutite probably forms only under unusual conditions as evidenced by its limited occurrence and association.

CONCLUSION

A new manganese oxide monohydrate has been discovered on the Cuyuna range in Minnesota. It has been named groutite for Professor F. F. Grout of the University of Minnesota. The mineral is a member of the diaspore-goethite group and has the formula $HMnO_2$. It forms orthorhombic, black, wedge-shaped crystals with a high submetallic luster. Its streak is dark brown, and it exhibits strong pleochroism. Specific gravity 4.14. The mineral has a highly perfect cleavage parallel (010) and less so parallel (100). Its unit cell dimensions are: a_0 4.56, b_0 10.70, c_0 2.85 Å.

REFERENCES

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4. BRAGG, W. L., *Atomic Structure of Minerals*, 111 (1937).

† According to unpublished recent experiments by the writer.