NEW MANGANESE OXIDES: HYDROHAUSMANNITE AND WOODRUFFITE*

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ABSTRACT

Hydrohausmannite occurs at Franklin, New Jersey, and at Långban and Pajsberg, Sweden, as an oxidation product of pyrochroite, $Mn(OH)_2$. It is identical with synthetic material prepared by Feitknecht and Marti (1945) and others by the oxidation of synthetic $Mn(OH)_2$. Chemically, hydrohausmannite is a variable hydrated oxide of Mn^2 and Mn^3, based on the structure of hausmannite, $MnMn_2O_4$, in which variation in the ratio of Mn^2 to Mn^3 is compensated by a concomitant substitution of (OH) for O. Tetragonal, with $a_0=5.79$ Å, $c_0=9.49$; optically uniaxial negative with ω 2.055, ϵ 1.95 (Franklin). Color brownish black to iron-black.

Woodruffite occurs at Sterling Hill, New Jersey, as botryoidal masses associated with chalcophanite and zincian cryptomelane in secondary zinc ores. Dense types have $G=3.71$ and a hardness of $4\frac{1}{2}$, with an iron-black color; also pulverulent and chocolate-brown in color. Chemical composition $(Zn, Mn^2)_2Mn_5^4O_{12}\cdot 4H_2O$, with $Zn:Mn^2=1.54:1$.

HYDROHAUSMANNITE

Feitknecht and Marti (1945) have shown that a variable, hydrated oxide of divalent and trivalent manganese related in crystal structure to hausmannite, $MnMn_2O_4$, is formed during the oxidation of synthetic manganous hydroxide. The same substance has been obtained by Dubois (1934) and others. The composition of the phase is found analytically to range at least between the limits given by the empirical formulae $MnO_{1.15}\cdot nH_2O$ and $MnO_{1.43}\cdot nH_2O$, where n is about 0.5 and includes non-essential water. Feitknecht and Marti, following the earlier work of Starke (1939) on hydrated magnetite, consider that the mechanism of compositional variation involves a variation in the Mn^2 to Mn^3 ratio in a hausmannite-like structure with valence compensation effected by a concomitant substitution of (OH) for O. The synthetic hydrated oxide is distinguished from anhydrous hausmannite by the appearance of a very strong extra line in the *x*-ray powder pattern. The two patterns otherwise are identical, although the high order lines of the hydrated phase are relatively diffuse. The extra line appears adjacent to and on the high-θ side of the first line, (101), in the hausmannite pattern and it is stated that it can be indexed as (002) in the hausmannite cell. The *x*-ray powder spacing data are not given, however, and only a line drawing of the pattern has been published.

A mineral identical with the synthetic material has been recognized

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from three localities as an alteration product of natural manganous hydroxide, pyrochroite. The name hydrohausmannite is here adopted for the natural mineral. This name was first proposed by Feitknecht and Marti for the synthetic material. It was earlier used by Boldyrev (1928) for what appears to be the same substance; his name, however, was proposed on theoretical grounds and a specific description of a mineral was not offered.

Altered Pyrochroite and Backstromite. Synthetic $Mn(OH)_2$ when freshly formed is transparent and colorless. The natural mineral, pyrochroite, always is more or less oxidized. It is then brownish black or black in color and in the final stages of alteration becomes virtually opaque. *X*-ray powder patterns taken in iron radiation of a number of pyrochroite specimens from Långban and Pajsberg, Sweden, and Franklin, New Jersey, show an admixture in varying proportions of two phases. One of these has a brucite-type pattern and is $Mn(OH)_2$ proper; the other phase is hydrohausmannite. Completely altered crystals and, usually, the surficial parts of incompletely altered crystals give the pattern of hydrohausmannite only. The pure hydrohausmannite is iron-black to brownish black in color and affords a brown powder. It gives a distinct water test when heated in a closed tube. The material often shows a lamellar parting derived from the cleavage of the original pyrochroite. The gravity and hardness cannot be measured accurately because of the fragile and porous nature of the pseudomorphs. The small particle size and near opacity of the material precludes optical measurements. Translucent grains are dichroic in brown and dark brown.

Backstromite also gives the *x*-ray pattern of hydrohausmannite. The name backstromite was proposed by Aminoff (1919) for a hypothetical orthorhombic dimorph of $Mn(OH)_2$ found at Långban as pseudomorphs supposedly consisting largely of manganite. The manganite had formed by the alteration of pyrochroite which itself was presumed to have formed from the original supposititious backstromite. A chemical analysis by Mauzelius of the material, cited in Table 2, was interpreted as a mixture of manganite and pyrochroite, although the presence of these substances was not shown directly. *X*-ray patterns of backstromite from Långban (not type material) are identical with that of hydrohausmannite.

An occurrence of what appears to be a primary crystallization of hydrohausmannite was noted on a specimen from Franklin, New Jersey. The original label of the specimen, dated August, 1911, from the F. A. Canfield collection, reads: *Unknown crystals and calcite from Franklin Furnace. These contain lots of Mn, but other tests were not made. Colonel [Colonel W. A. Roebling] or Hancock never saw a specimen like it. Price $5.00.* The specimen shows bundles and fan-like groupings of tiny dark-brown needles lining solution cavities a few millimeters wide in a matrix of calcite, sussexite and zincite. Optically, the mineral is uniaxial negative with indices of refraction much lower than those of hausmannite (Table 3). There is strong absorption in brown, with E > O, and the elongation is negative. Only about 100 mg. of material were available on the specimen. A spectrographic analysis by Dr. H. C. Harrison established that Mn was the only major cationic constituent and that Fe, Zn and other elements were present in amounts less than 0.1 per cent. The unheated sample gave an *x*-ray pattern identical with that of the hydrohausmannite described above. After heating in air to 500°, the extra line (002) in the pattern became very weak and the pattern then was identical with that of hausmannite with the exception of a few faint extra lines that corresponded in position to the strongest lines of the manganese spinel jacobsite.

X-ray Powder Data. X-ray powder spacing data for hydrohausmannite

TABLE 1. *X*-RAY POWDER DATA FOR NATURAL HYDROHAUSMANNITE AND HAUSMANNITE
Fe radiation, Mn filter, 114 mm. diameter camera

Hydrohausmannite			*hkl*	Hausmannite	
I	*d meas.*	*d calc.*		*d meas.*	*I*
	Å	$a_0=5.79$ Å, $c_0=9.49$		(Aminoff, (1926))	
2	4.95	4.94	101	4.90	2
10	4.65	4.74	002	—	—
3	3.10	3.10	112	3.09	3
2	2.89	2.90	200	2.88	1
5	2.78	2.78	103	2.75	6
6	2.50	2.50	211	2.48	10
4	2.38	2.37	004	2.35	2
3	2.05	2.05	220	2.04	2
1	1.844	1.835	204	1.824	1
2	1.803	1.804	105	1.793	2
1	1.710	1.708	312	1.702	1
1	1.655	1.648	303	1.641	1
4	1.586	1.583	321	1.577	5
5	1.549	1.550	224	1.543	5
2	1.447	1.447	400	1.441	2
—	—	—	305	1.345	1
1	1.283	1.283	413	1.278	1
1	1.231	1.236	404	1.231	1
—	—	—	127	1.197	2
—	—	—	008	1.185	2
—	—	—	415	1.122	2

indexed in terms of a tetragonal cell with $a_0 = 5.79$ Å, $c_0 = 9.49$, are given in Table 1. The data differ from those of anhydrous hausmannite only in the presence of a very strong extra line that indexes as (002). The cell dimensions are virtually identical with those of hausmannite, for which Aminoff (1926) found $a_0 = 5.76$ Å, $c_0 = 9.44$.

Chemical Composition. Starke (1939) has shown that a hydrated type of magnetite can be synthesized in which a serial increase in the ratio of Fe^2 to Fe^3 is compensated by a concomitant entrance of both vacancies in the cation positions and a substitution of (OH) for O. This mechanism is a variant of the well known series extending between magnetite, $FeFe_2O_4$, and maghemite, γ-Fe_2O_3. These two types of variation can be represented by the following formulae, in which cation vacancies are indicated by V and the subscripts indicate the unit cell contents.

Magnetite (x=0) Maghemite ($x = 2\frac{2}{3}$)

$$Fe_8^2Fe_{16}^3O_{32} \rightleftarrows (Fe_{8-3x}^2Fe_{2x}^3V_x)_8Fe_{16}^3O_{32} \rightleftarrows V_{2\,2/3}Fe_{21\,1/3}^3O_{32} = \gamma\text{-}Fe_2O_3$$

Hydromagnetite ($x = 2\frac{2}{3}$)

$$Fe_8^2Fe_{16}^3O_{32} \rightleftarrows (Fe_{8-x}^2V_x)_8Fe_{16}^3O_{32-2x}(OH)_{2x} \rightleftarrows (Fe_{5\,1/3}^2V_{2\,2/3})_8Fe_{16}^3O_{26\,2/3}(OH)_{5\,1/3}$$

In the hydrated series, other numerical relations that afford valence compensation also can be derived between the three variables, Fe^2/Fe^3, V/total cations, and OH/O, and in general the particular mechanism, if this is fixed, can be identified only by chemical analysis.

Feitknecht and Marti suggest that this general type of variation obtains in hydrohausmannite, but do not discuss specific mechanisms. Hausmannite, $MnMn_2O_4$, has a distorted spinel structure and, as shown by Verwey and de Boer (1936), forms an anhydrous series to the tetragonal phase, γ-Mn_2O_3:

Hausmannite (x=0) γ-Mn_2O_3 ($x = 1\frac{1}{3}$)

$$Mn_4^2Mn_8^3O_{16} \rightleftarrows (Mn_{4-3x}^2Mn_{2x}^3V_x)Mn_8^3O_{16} \rightleftarrows V_{1\,1/3}Mn_{10\,2/3}^3O_{16}$$

The ratio of Mn^2 to Mn^3 in synthetic hydrohausmannite is known analytically, and extends on both sides of the hausmannite ratio, $Mn^2:Mn^3 = 1:2$, but the content of essential water is not known accurately. This prevents the specific mechanism of variation from being identified. On the high Mn^2 side of the ratio, a mechanism such as $Mn^2(Mn_{2-x}^3\text{-}Mn_x^2)_2\,O_{4-x}(OH)_x$ may be operative. A similar mechanism apparently operates in the gamma polymorph of MnO_2, and may be expressed $(Mn_{1-x}^4Mn_x^3)\,O_{2-x}(OH)_x$. On the high Mn^3 side of the ratio, the excess of positive valence requires either the coupled development of vacancies in the cation positions, to give the anhydrous series to γ-Mn_2O_3, or the simultaneous coupling of both vacancies and of an OH/O substitution to give a hydrated series.

The unit cell contents of the hydrohausmannite from Långban have

TABLE 2. ANALYSIS OF BACKSTROMITE (HYDROHAUSMANNITE) FROM LÅNGBAN, CITED FROM AMINOFF (1919)

		Atomic Quotients	Cell Contents (M.W.=927)	
CaO	0.14			
PbO	0.04			
MgO	1.68	Mg = .014	.132	1.647
MnO	11.59	Mn^2 = .1634	1.515	
Mn_2O_3	77.80	Mn^3 = .9856	9.138	9.155
Fe_2O_3	0.14	Fe^3 = .0018	.017	
Sb_2O_3	0.07			
H_2O +130°	5.16	H+ = 5.31	5.31	
H_2O −130°	3.24	H− = 3.33	3.33	
		O = 2.125	19.70	

been calculated on the basis of Mauzelius' analysis of backstromite (Table 2), using the specific gravity, 4.84, of hausmannite. The cell contents then are approximately represented by a value $x=1.155$ in the formula

$$(Mn_{4-2x}^{2}Mn_{x}^{3}V_{x})Mn_{8}^{3}O_{16-x}(OH)_{x}$$

but there is a large analytical excess of H_2O even if the water below 130° is regarded as non-essential. New analyses of coarsely crystallized synthetic or natural material of known specific gravity and unit cell dimensions are needed in order to resolve the problem of the composition of hydrohausmannite.

TABLE 3. OPTICAL PROPERTIES OF HYDROHAUSMANNITE AND RELATED MINERALS

		ω	ϵ	Reference
Hausmannite	$MnMn_2O_4$	2.46	2.15	Larsen (1921)
Hydrohausmannite	$(Mn^2, Mn^3)_3(O, OH)_4$	2.055	1.95	(Present study)
Hetaerolite	$ZnMn_2O_4$	2.34	2.14	Larsen (1921)
Hydrohetaerolite	$(Zn, Mn^3)_3(O, OH)_4$	2.26	2.10	Larsen (1921)

Hetaerolite, $ZnMn_2O_4$, is isostructural with hausmannite, $MnMn_2O_4$, and similarly has a hydrated analogue that has been known for many years as hydrohetaerolite (Table 3). An account of this mineral has been given by Frondel and Heinrich (1942). Hydrohetaerolite appears to be a valid species, and its composition may be determined by the same general type of mechanism obtaining in hydrohausmannite.

WOODRUFFITE

The neighboring zinc deposits of Sterling Hill and Franklin, New Jersey, are known chiefly for the primary zinc and manganese minerals that they afford in abundance and great variety. When the Sterling Hill mine was first opened about 1870, however, a large body of secondary zinc minerals was mined in shallow pits in the limestone adjacent to the outcroppings of the primary ore. These oxidized ores consisted chiefly of hemimorphite, and magnificent drusy specimens of this mineral have been preserved in collections. The hemimorphite was associated with a zinc-rich clay called vanuxemite (a mixture according to Faust (1951)) together with minor amounts of chalcophanite and hydrohetaerolite. Both of the latter species were first described from this place. Hydrous oxides of iron and manganese also occurred as botryoidal crusts and layers and as dense to earthy masses cementing corroded fragments of franklinite and other primary minerals. Specimens of the latter material that have been preserved in mineral collections are usually found labelled as wad or psilomelane—the latter name being used in the broad, indefinite sense formerly obtaining. *X*-ray study of a number of such specimens has shown that at least two different minerals are present. One is a variety of cryptomelane containing a small amount of zinc in solid solution, and the other is a hydrated oxide of manganese and zinc that is here described as a new species under the name of woodruffite. The latter mineral occurs chiefly as masses and crusts with a botryoidal surface and a concentric, coarsely layered internal structure. The material is very fine-grained and

TABLE 4. *X*-RAY POWDER SPACING DATA FOR WOODRUFFITE AND TODOROKITE
Fe radiation, Mn filter. 114 mm. diameter camera

Woodruffite		Todorokite	
I	*d* (in Å)	*I*	*d* (in Å)
5	9.51	10	9.65
4	6.99	½	7.2
10	4.77	8	4.81
3	4.40	3	4.46
1	4.08		
2	3.48		
1	3.33		
2	3.13	4	3.20
1	3.05		
½	2.84		
2	2.63		
1	2.56		
4	2.466	3	2.45
5	2.404	4	2.40
5	2.225	4	2.216
1	2.152	1	2.150
2	2.131		
3	1.984	1	1.981
1	1.922		
2	1.895		
2	1.747		
1	1.680		
2	1.660		
½	1.636		
1	1.592		
5	1.423	4	1.419
		1	1.392
		5	1.331

TABLE 5. CHEMICAL ANALYSES OF WOODRUFFITE, TODOROKITE AND A SYNTHETIC ZN, MN OXIDE

	1	2	3	4
Na_2O	0.06		0.21	
K_2O	0.55		0.54	
CaO			3.28	
BaO	0.12		2.05	
MgO	0.62		1.01	
ZnO	13.89	14.92		14.8
MnO	7.88	8.45	12.38	12.3
MnO_2	64.27	65.73	65.58	65.9
Fe_2O_3	0.26		0.20	
Al_2O_3	0.14		0.28	
SiO_2	0.86			
H_2O	10.48	10.90	11.28	6.0
Rem.			2.43	
Total	99.13	100.00	99.24	99.0
G	3.71		3.67	

1. Woodruffite. Sterling Hill, New Jersey. Lee C. Peck, analyst, August, 1948.
2. Theoretical Composition, $(Zn, Mn)_2Mn_5O_{12}.4H_2O$ with $Zn:Mn^2=1.54:1$.
3. Todorokite. Todoroki mine, Hokkaido, Japan. Yoshimura (1934). Rem. is SiO_2 0.45, P_2O_5 0.42, SO_3 0.28, insol. 1.28, TiO_2 tr., CO_2 tr. H_2O includes $H_2O+9.72$, $H_2O-1.56$.
4. Synthetic hydrated zinc manganese oxide described by Wadsley (1950*a*, 1950*b*).

is opaque in crushed grains. Occasionally, corroded crystals of franklinite are found embedded in the masses, and certain of the layers, usually the outermost, may contain disseminated, platy crystals of chalcophanite. Some specimens are rather hard, about 4½, with an iron-black color and brownish streak, but the mineral also occurs as soft, almost pulverulent coatings of a chocolate-brown color. The hard material has a specific gravity of 3.71, and the fracture is smooth-conchoidal with a dull luster.

The *x*-ray powder spacing data, obtained in iron radiation, are given in Table 4. The *x*-ray pattern is rather similar to those of todorokite (Table 4) and cryptomelane. There are marked differences, however, in the relative intensities of the first few lines in these patterns. Todorokite affords a relatively diffuse pattern, as a consequence of small particle size, and a number of lines, especially in the region from *d* 1.98 to 1.41, which are seen visually to correspond approximately to lines in the woodruffite pattern, were too weak and diffuse to measure accurately. The todorokite pattern was obtained from an authentic specimen kindly loaned by Dr. W. F. Foshag of the U. S. National Museum, that answered exactly the original description of this mineral by Yoshimura (1934).

A chemical analysis of woodruffite by L. C. Peck is cited in Table 5, together with the reported analyses of todorokite and a synthetic hydrated oxide of zinc and manganese described by Wadsley (1950*a*, 1950*b*). Peck's analysis as originally reported gave total Mn as MnO 60.32 and oxygen 11.83 per cent. The actual valence state of the Mn in the mineral is not known, and the analysis is here given with the MnO and O recalculated as MnO and MnO_2. A spectrographic examination of the analysis sample by Dr. H. C. Harrison showed Mn and Zn as the only major cations present, with Na, K, Ba, Mg, Si, Al and Fe present in amounts less than 1 per cent and Ca, Sr, Co, Ni, Sn, Cr, Mo, V and Ti present in trace amounts. The ratios of the analysis are very close to the formula $(Zn, Mn^2, Mg, Na, K, Ba)_2(Mn^4, Fe^3, Al)_5O_{12}\cdot 4H_2O$ or, essentially,

$$(Zn, Mn^2)_2Mn_5^4O_{12}\cdot 4\ H_2O, \text{ with } Zn{:}Mn^2=1.54{:}1.$$

The ratios of the analysis of todorokite are slightly different, and are between those of the formula cited and the formula $(Mn^2, Ca, Mg, Ba)Mn_3^4O_7\cdot 2H_2O$. If todorokite and woodruffite are isostructural, as is suggested by the *x*-ray patterns, the formulae should be analogous. The observed differences may be due to analytical error or to impurities in the analyzed sample of todorokite. The presence of 2.43 per cent total P_2O_5, SO_3, SiO_2 and insoluble in the analysis of todorokite indicates that this material was relatively impure.

Synthetic hydrated zinc manganese oxides (or hydrated zinc manganites) have been prepared recently by Feitknecht and Marti (1945) and Wadsley (1950*a*, 1950*b*). The material of Wadsley (1950*a*) was obtained by base exchange of synthetic $(Na, Mn)Mn_3O_7\cdot nH_2O$ (with $Na{:}Mn=1{:}1$) with a solution of $ZnCl_2$. Wadsley gives the formula as $(Zn, Mn)Mn_3O_7\cdot 2H_2O$, but the analysis, cited in Table 5, is somewhat closer to $(Zn, Mn)Mn_2O_5\cdot H_2O$ with $Zn{:}Mn=1{:}1$. An *x*-ray powder pattern was indexed in terms of a hexagonal cell with $a_0=8.41$ Å, $c_0=9.8$, containing four formula-units. The actual *d*-spacings are not cited, but the pattern is said to closely resemble that of $(Na, Mn)Mn_3O_7\cdot nH_2O$ for which *d*-values are given. Wadsley (9950*b*) attempted to recrystallize the material by heating it in a dilute solution of Zn and Mn chlorides in a bomb. *X*-ray powder study showed that at 80° a mixture of hetaerolite with some chalcophanite was formed, at 160° a mixture of hetaerolite with some hydrohetaerolite (?) and at 300° hetaerolite only. Wadsley (1950*b*) also described a synthetic calcium derivative of $(Na, Mn)Mn_3O_7\cdot nH_2O$ with the composition $(Ca, Mn)Mn_4O_9\cdot 5H_2O$, together with Ba, Cu and Al derivatives. The Ca compound apparently is hexagonal with the cell dimensions $a_0=8.44$, $c_0=9.87$ Å. Samson and Wadsley (1948) have described a natural occurrence at Buchan, Victoria, of a mineral apparently identical with synthetic (Na, Mn)$Mn_3O_7 \cdot nH_2O$. The *x*-ray powder data indicate that woodruffite is distinct from all of the above mentioned substances. The pattern of woodruffite is quite unlike that of chalcophanite. The composition of this mineral usually is given as (Zn, Mn) $Mn_2O_5 \cdot 2H_2O$, but Samson and Wadsley (1948) have indicated that it may be $ZnMn_3O_7 \cdot 3H_2O$.

The name woodruffite is proposed for this species after Samuel Woodruff (deceased), for many years employed as a miner by the New Jersey Zinc Company. The detailed mineralogy of Franklin and Sterling Hill is known to science very largely through the activity of local collectors in finding and preserving unusual material. Some of the famous collections from these places are those associated with the names of Canfield, Hancock, Roebling, Fowler, Losey, Kemble, and Gage. According to F. A. Canfield,[1] ". . . Woodruff worked harder to collect, and did collect more fine specimens than all the others put together. My father came next, then the two Loseys and then the Kembles." Among the specimens known with some certainty to have come from Woodruff are the giant franklinite crystals measuring up to 7 inches on an octahedral edge that are preserved in the Canfield collection of the U. S. National Museum and also the very realistic plaster duplications of such crystals in the Harvard collection.

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[1] Letter to Professor Charles Palache, January 28, 1907.