NEW DATA ON HETAEROLITE, HYDROHETAEROLITE, CORONADITE, AND HOLLANDITE

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ABSTRACT

Hetaerolite, $ZnMn_2O_4$, is isostructural with hausmannite, $MnMn_2O_4$. Weissenberg x-ray study of type hetaerolite gave: $a_0=5.74$, $c_0=9.15$; $a_0:c_0=1:1.594$, $a:c=1.5952$ (morph.); cell contents $Zn_4Mn_8O_{16}$. The hetaerolite described by Palache in 1928 from Sterling Hill and Franklin, New Jersey, is identical with the original hetaerolite of Moore (1877) from Sterling Hill.

The so-called hetaerolite from Sterling Hill described by Palache and Schaller in 1910 apparently is the same as that from Leadville, Colorado, described by Ford and Bradley in 1913. The Leadville mineral, for which the name hydrohetaerolite has been proposed, differs from type hetaerolite in its fibrous character, in x-ray cell dimensions ($a_0=5.71$, $c_0=9.04$; body-centered tetragonal (?)), in slightly lower indices of refraction, and in apparently containing a few per cent each of SiO_2 and H_2O. Proof of tetragonal symmetry and of homogeneity is lacking. The status of the mineral is uncertain.

Coronadite is a valid species and is isostructural with hollandite. Hollandite has been thought to be tetragonal from uncertain morphological evidence, but x-ray powder study suggests that it and coronadite are only pseudotetragonal. Coronadite has the composition $MnPbMn_6O_{14}$. The composition of hollandite is uncertain, but the mineral appears to be the barium analogue, $MnBaMn_6O_{14}$, of coronadite. Psilomelane (17% BaO) and hollandite are distinct species.

HETAEROLITE

The name hetaerolite was given by Moore in 1877 to a massive mineral found with chalcophanite at Sterling Hill, New Jersey. Moore stated that the mineral had the composition $ZnMn_2O_4$, analogous to hausmannite, $MnMn_2O_4$, but he did not quote the figures of his analysis nor did he describe the physical and chemical properties in sufficient detail to adequately characterize the substance. In 1910, Palache published an analysis made by Schaller in 1906 of a fibrous mineral from Sterling Hill that was thought to be identical with the original hetaerolite of Moore. The water reported in the analysis (column 2, Table 1) was regarded as due to admixed chalcophanite and the formula $ZnMn_2O_4$, originally suggested by Moore, was assigned to the mineral. A few years later, in 1913, Ford and Bradley described a fibrous mineral found with chalcophanite in the Wolftone mine, Leadville, Colorado. The analysis by Bradley (column 3, Table 1) gave the formula $Zn_2Mn_4O_8 \cdot H_2O$, after the deduction of about 10 per cent hemimorphite which was supposed to be present in order to account for the SiO_2 reported. The name hetaerolite was retained for this mineral by Ford and Bradley on the belief that the original

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TABLE 1. ANALYSES AND CELL CONTENTS OF HETAEROLITE, HYDROHETAEROLITE, CORONADITE, AND HOLLANDITE

	1	2	3	4	5	6	7
Mn_2O_3	64.21	60.44	56.00	54.63			
MnO_2					59.60	60.80	65.63
MnO	1.86				8.02	7.12	5.12
ZnO	32.46	33.43	37.56	37.66		0.11	
PbO					28.68	28.66	
BaO					0.23		17.59
Fe_2O_3	0.24	0.77		0.67	0.60	1.10	10.56
Al_2O_3					0.10	0.68	0.94
SiO_2	0.18	1.71	2.69	2.91	0.26		
H_2O	0.19	3.89	4.36	3.78	1.80	1.11	
Rem.	0.49				0.52	0.42	
Total	99.63	100.24	100.61	99.65	99.81	100.00	99.84
G.	5.18	4.85	4.6		5.505 (5.44)	5.246	4.95

CALCULATED ATOMIC CONTENTS OF UNIT CELL

Mn^4					6.25	6.38	6.23
Mn^3	7.71	7.54	6.99	6.82			
Fe^3	0.38	0.09		0.08			1.24 (+Al)
Si	0.03	0.28	0.44	0.48			
Mn^2	0.25				1.03	0.92	0.59
Zn	3.78	4.05	4.52	4.56			
Pb					1.17	1.17	
Ba							0.95
O	15.70	16.06	15.88	15.86			
H_2O	0.10	2.13	2.39	2.07	0.91	0.56	

1. Hetaerolite. Sterling Hill, New Jersey. Rem. is MgO. Bauer's anal. in Palache (1928).

2. Hydrohetaerolite. Sterling Hill, New Jersey. H_2O+ 1.42, H_2O- 2.47. Schaller's anal. in Palache (1910).

3. Hydrohetaerolite. Wolftone mine, Leadville, Colorado. Average of two analyses. Bradley's anal. in Ford and Bradley (1913).

4. Hydrohetaerolite. Leadville, Colorado. Palmer's anal. in Wells (1937).

5. Coronadite. Bou Tazoult, Morocco. Rem. is CaO 0.05, CuO 0.14, P_2O_5 0.03, As_2O_5 0.04, V_2O_5 0.20, CO_2 0.04. Campredon's anal. in Orcel (1933).

6. Coronadite. Coronado vein, Clifton-Morenci, Arizona. Rem. is MoO_3 0.37, CuO 0.05. Recalculated to 100 after deduction of 7.22 insol. and 0.45 alkalies, CaO, MgO, and loss of wt. Hillebrand's anal. in Lindgren and Hillebrand (1904).

7. Hollandite. Kajlidongri, India. Winch's anal. in Fermor (1909).

hetaerolite of Moore was not anhydrous but contained water. Moore said that his mineral yielded a little water in the closed tube. These writers also considered that the water in Schaller's analysis was essential and not due to admixed chalcophanite. A recent re-analysis (column 4, Table 1) by Palmer of the mineral from Leadville is cited by Wells (1937), and this also shows about 4 per cent of water.

In 1928, Palache described a mineral found as pyramidal crystals in the unoxidized ore at Sterling Hill and Franklin, New Jersey. This material was analyzed by Bauer and proved to be anhydrous $ZnMn_2O_4$. Goniometric measurement proved that the mineral was tetragonal and morphologically related to hausmannite. It was then proposed by Palache to adopt Moore's name hetaerolite for the anhydrous mineral, analogous to hausmannite, here recognized, since this was the sense of the original definition. The actual material of Moore, together with the apparently hydrous mineral analyzed by Schaller was separated under the name hydrohetaerolite as a distinct species. The hydrous mineral from Leadville, described by Ford and Bradley, also is to be classed as hydrohetaerolite.

Part of the original specimen of hetaerolite described by Moore and the original specimens of so-called hetaerolite measured and analyzed by Palache and Bauer were available to the writers for study. *X*-ray powder patterns, taken in Fe radiation, of these specimens proved to be identical. The nomenclature used by Palache is, therefore, entirely proper. A Weissenberg *x*-ray examination was made of a measured crystal of hetaerolite. The data obtained are summarized in Table 2, and com-

TABLE 2. COMPARISON OF HETAEROLITE AND HAUSMANNITE

	Cell Contents	Space Group	a_0	c_0	$a_0:c_0$ (*x*-ray)	$a:c$ (morph.)	G. (obs.)	G (calc.)	ω	ϵ	Cleavage
Hetaerolite	$Zn_4Mn_8O_{16}$	$I4_1/amd$	5.74	9.15	1.594	1.5952	5.18	5.23	2.35	2.10	{001} imperfect; also {011} and {112}(?)
Hausmannite	$Mn_4Mn_8O_{16}$	$I4_1/amd$	5.75	9.42	1.638	1.6364	4.84	4.84	2.455 ±0.02	2.15 ±0.02	{001} good, {112} and {011} indistinct

pletely confirm the supposed isostructural relation to hausmannite. The *x*-ray data given for hausmannite are from the powder and rotation study of Aminoff (1936). The specific gravity, given in the original description as 4.85, was re-determined on the microbalance and found to be 5.18. An imperfect cleavage on {001} was observed on macroscopic crystals, and one and possibly two additional cleavages were noted in crushed grains under the microscope. The latter cleavages probably correspond to the {011} and {112}, cleavages of hausmannite. The morphological

TABLE 3. *X*-RAY POWDER DIFFRACTION DATA FOR HYDROHETAEROLITE, HETAEROLITE, CORONADITE, AND HOLLANDITE. Fe RADIATION

Hydrohetaerolite				Hetaerolite			Coronadite		Hollandite	
d	*I*	*hkl*	a_0	*d*	*I*	*hkl*	*d*	*I*	*d*	*I*
3.188	1			4.871	1	101	3.466	6	4.957	2
3.006	7	112	5.700	3.045	7	112	3.104	10	3.459	6
2.855	3	200	5.709	2.855	4	200	2.400	4	3.113	10
2.660	9	103	5.700	2.698	9	103	2.205	4	2.475	1
2.455	10	211	5.703	2.460	10	211	2.155	2	2.409	3
2.250	3	004	5.686	2.300	3	004	2.001	1	2.198	3
2.173	1			2.017	3	220	1.960	1	2.173	2
2.019	3	220	5.710	1.792	3	204	1.919	1	1.988	1
1.771	3			1.752	5	105	1.836	2	1.952	1
1.717	5	105	5.690	1.683	4	312	1.742	1	1.916	1
1.677	4	312	5.712	1.616	3	303	1.691	1	1.842	2
1.612	2	303	5.719	1.560	5	321	1.642	2	1.829	2
1.553	5	321	5.686	1.518	8	224	1.591	1	1.747	1
1.506	8	224	5.711	1.430	4	400	1.542	5	1.694	1
1.430	4	400	5.720	1.350	1	206	1.432	1	1.657	3
1.408	2	314	5.700	1.323	3	305	1.400	1	1.631	3
1.311	2	305	5.712	1.277	2	107	1.374	2	1.583	1
1.294	1	332	5.728	1.263	3	413	1.356	2	1.544	5
1.278	1	420	5.717	1.212	1	404	1.298	1	1.435	1
1.261	4	413	5.724	1.169	5	127	1.237	1	1.419	1
1.210	1	404	5.727	1.151	4	008	1.218	1	1.404	1
1.181	1			1.107	4	415	1.148	1	1.363	2
1.159	3	316	5.723	1.089	3	335	1.116	1	1.351	2
1.151	3	334	5.684	1.053	2	521			1.306	2
1.127	3	008	5.700						1.296	1
1.113	3	424	5.720						1.286	1
1.101	4	415	5.719						1.167	1
1.089	3	512	5.724						1.157	1
1.071	5	503	5.728						1.147	1
1.057	3								1.096	2
1.050	2	521	5.693						1.086	2
									1.078	1
									1.055	1
		$a_0=5.709$								
		$c_0=9.037$								
		$c=0.823$								

ratio $a:c=1:1.1280$, given by Palache, refers to the doubled, face-centered structural cell, and becomes 1:1.5952 in the body-centered unit here taken.

HYDROHETAEROLITE

A small fragment from the type specimen of the fibrous hydrohetaerolite from Leadville described by Ford and Bradley was available for

study. Unfortunately, the identity of the specimen of hydrohetaerolite from Sterling Hill analyzed by Schaller appears to be lost. Several specimens of botryoidal hydrohetaerolite from Sterling Hill stated by Professor Palache to be representative of this mineral were, however, available for study.

An x-ray powder photograph of the Leadville mineral was indexed with the exception of 5 out of 31 lines in terms of a body-centered tetragonal cell with $a_0=5.71$ and $c_0=9.04$. Fe radiation was employed. The spacing data are given in Table 3. The pattern is very similar to that of hetaerolite, but relative differences in spacings and in the intensity of some lines are apparent. Further, distinct new lines appear on the hydrohetaerolite pattern. Several of these lines were indexed in terms of the cited cell, but efforts to index the others in terms of any tetragonal cell were unsuccessful. The extra lines may be due to admixture (although the sample appeared homogeneous under the microscope), or to a departure from true tetragonal symmetry. X-ray patterns also were made of specimens of so-called hydrohetaerolite from Sterling Hill. These specimens proved to be gross mixtures of chalcophanite with another mineral which could not definitely be shown to be hetaerolite or hydrohetaerolite because the critical lines were obscured by overlapping chalcophanite lines and by general fogging. The impression was gained, however, that hydrohetaerolite was present.

X-ray rotation and 0-layer and 1-layer Weissenberg photographs were taken about the fiber axis of a minute ($0.1\times0.05\times0.4$ mm.) fiber of the Leadville mineral. The films were of poor quality due to sub-parallel aggregation and a slight twisting in the fiber. The fiber-period was 8.0 ± 0.1 Å. Both the 0- and 1-layer Weissenberg films had the plane symmetry C_{2i}, with a two-fold axis of symmetry and planes of symmetry at 90°. The poor quality of the films, however, renders their true symmetry content uncertain. The (apparent) symmetry content of the films restricts the symmetry and orientation of the fibers to five possibilities:

(1) Orthorhombic, with the centrosymmetry V_h, and the rotation axis either [100], [010] or [001].

(2) Tetragonal, with the centrosymmetry D_{4h}, and the rotation axis either [100], [010] or [110].

(3) Hexagonal, with the centrosymmetry D_{6h}, and the rotation axis either [10$\bar{1}$0], [01$\bar{1}$0] or [$\bar{1}$100].

(4) Isometric, with the centrosymmetry T_h, and the rotation axis either [100], [010] or [001].

(5) Isometric, with the centrosymmetry O_h, and the rotation axis either [110], [101] or [011].

The isometric possibilities are excluded by optical characters, but the other three possibilities can not be distinguished by the evidence at hand.

The tetragonal interpretation, however, is in accordance with the symmetry and cell dimensions obtained by the powder method. The fiber-period 8.0 ± 0.1Å, is close to the calculated period (8.07 Å) of the [110] direction of the powder cell, and the periods of the simplest cell defined by the 0-layer Weissenberg film, 8.99 and 8.07 Å, correspond to periods ($c_0 = 9.04$, $d_{111} = 8.07$) of the powder cell. Both [110] and [001] would appear on the 0-layer film if the rotation axis was [110]. The systematic omissions on the Weissenberg films lead to the partial space group $I4/a\ d$, if tetragonal symmetry and a [110] orientation are assumed.

Optically, the Leadville mineral appears to be uniaxial negative. Larsen (1921) gives the indices as $\omega = 2.26 \pm 0.02$, $\epsilon = 2.10 \pm 0.02$. Larsen (1921) records the indices of hetaerolite from Franklin as $\omega = 2.34 \pm 0.02$, $\epsilon = 2.14 \pm 0.02$; Berman (cited in Palache (1928)) gives the indices of hetaerolite from Sterling Hill as $\omega = 2.35 \pm 0.02$, $\epsilon = 2.10 \pm 0.02$. Larsen states that the elongation of the fibers is positive, and the writers have found this to be true in most instances, but not for all of the fibers. On the reflecting goniometer almost all of the fibers exhibit up to six or eight cleavage surfaces at what appear (for the most part) to be random angles. The random arrangement doubtlessly is due to an intergrowth. One set of parallel faces occurs on many fibers. Most fibers, if not markedly composite, give a more or less perfect uniaxial optic axis figure. The optical data indicate that the mineral has at least one good cleavage in the elongation, and that the elongation must be perpendicular to [001] of a tetragonal mineral. The fiber used in the Weissenberg x-ray study exhibited one good cleavage along the fiber length. This cleavage was identified by the instrumental correlation between the x-ray and reflecting goniometers as {001} in the (apparent) tetragonal cell, and the direction of elongation, as already noted, appears to be [110]. The optical and x-ray data thus are consistent.

The hydrohetaerolite from Leadville and true hetaerolite are now seen to be very similar. The partial space group $I4/a\ d$ (?) and cleavage of hydrohetaerolite is consistent with the space group ($I4/amd$) and cleavage of hetaerolite. The color, luster, and hardness of the two minerals are practically identical. The specific gravity of hydrohetaerolite is relatively low, but the reported value, 4.65, is questionable because of the fibrous nature of the material. The writers failed to get values above 4.65 on the microbalance. Hydrohetaerolite differs from hetaerolite principally in its somewhat lower indices of refraction, in its smaller cell dimensions, and in the presence of a few per cent each of H_2O and SiO_2.

The atomic contents of the (apparent) tetragonal unit cell are given for the three existing analyses in Table 1. A specific gravity of 5.51 was

assumed for the purposes of the calculation; irrational cell contents are obtained if the observed specific gravities are used. The cell contents of the material from Sterling Hill analyzed by Schaller (column 2) are almost exactly $Zn_4(Mn, Si)_8O_{16} \cdot 2H_2O$, with Si:Mn = 0.148:3.852. The two analyses of the material from Leadville (columns 2, 3) show a small excess of Zn, about equal to the Si, when calculated on this basis. The cell contents of the Leadville mineral possibly may be $Zn_4(Mn, Zn, Si)_8O_{16} \cdot 2H_2O$. If the Si is deducted as hemimorphite, the cell contents are close to $Zn_4Mn_8O_{16} \cdot 2H_2O$ and the simplest formula is $ZnMn_2O_4 \cdot H_2O$, as argued by Ford and Bradley. In any case, it is difficult to accept the high value 5.51 for the specific gravity required for rational cell contents, especially in view of the fact that the calculated specific gravity of anhydrous $ZnMn_2O_4$ is only 5.23. The crystallographic and chemical characters of hydrohetaerolite are uncertain, as is its relation to hetaerolite, and the mineral can at present be classed only as a doubtful species.

Coronadite and Hollandite

Coronadite was originally described by Lindgren and Hillebrand in 1905 from the Coronado vein, Clifton-Morenci district, Arizona. The status of the mineral was brought into doubt by Fairbanks (1923), who examined a specimen in polished section and stated that it was a mixture of hollandite and an unidentified lead mineral. Later, in 1933, Lindgren drew attention to a description by Orcel (1932) of a mineral from Bou Tazoult, Morocco, apparently identical in physical and chemical properties with the original coronadite, and on this ground maintained the validity of the species. At both occurrences the mineral forms dense fibrous masses and crystallographic data are lacking.

A piece of the type-analyzed specimen of the coronadite from Morocco* and the specimen of the coronadite from Arizona, examined by Fairbanks, were available to the writers. The latter specimen is not part of the type material of Lindgren and Hillebrand, but it was examined by Lindgren in 1933 and was accepted as authentic. *X*-ray powder photographs taken in Fe radiation of the two specimens were identical, confirming the opinion of Lindgren as to the identity of the two minerals. The coronadite patterns differed entirely from the patterns of cesarolite, quenselite, manganite, psilomelane (17% BaO) and pyrolusite. The patterns were identical, however, with the pattern of hollandite from Kajlidongri, India. The specimens of hollandite consisted of large, coarse crystals embedded in quartz and were unquestionably authentic. The powder diffraction data for the two minerals are given in Table 2. Fermor,

* This specimen was presented by Orcel to Lindgren and is now preserved in the mineral collection of the Massachusetts Institute of Technology.

in 1909, considered hollandite to be pseudotetragonal and possibly triclinic or orthorhombic. However, in 1917 he measured rough and striated crystals of the mineral and considered them to be tetragonal dipyramidal, with $a:c=1:0.2039$.

Efforts to completely index the powder patterns of coronadite and hollandite in terms of a tetragonal cell were unsuccessful. The patterns, however, were indexed with the exception of a few lines in terms of a body-centered (pseudo-) tetragonal cell with $a_0=6.94$, $c_0=5.71$ for hollandite, and $a_0=6.95$, $c_0=5.72$ for coronadite. The ratio of the cell sides, $a_0:c_0=1:0.823$, is almost four times the axial ratio of Fermor for hollandite. The analyses and atomic contents of the pseudo-cells are itemized in columns 5 and 6 of Table 1. The close approach to a simple ratio of the atomic cell contents of coronadite suggests that the volume of the pseudo-cell bears a simple relation to that of the true cell. The formula of coronadite clearly is $MnPbMn_6O_{14}$ or $MnPbMn_6O_{14}\cdot H_2O$. Water is lacking in the analysis of the isostructural mineral hollandite, and this fact, together with the probable presence of hydrous impurities and capillary water in the analyzed samples of coronadite, make it likely that the mineral actually is anhydrous. The formulae $2MnO_2\cdot PbO$ and $3MnO_2\cdot RO$ were given by Orcel and by Hillebrand, respectively. The value for the specific gravity used in the calculations was 5.44. This value was the highest of eight new determinations on material from Morocco, made on the microbalance, and is preferred to the value 5.505 of Orcel and the value 5.246 of Lindgren and Hillebrand.

The isostructural relation of hollandite and coronadite indicates that the two minerals should have the same general formula. The analysis of hollandite (column 7, Table 1) immediately suggests that the mineral is the barium analogue of coronadite. The calculated atomic ratio of hollandite, however, deviates from the ratio of coronadite in an irrational excess of trivalent metals and a deficiency of divalent manganese. The analysis is stated to have been made in a rough jungle laboratory and its accuracy may be questioned. Possibly some or all of the Fe^3 actually is present as Fe^2 in substitution for Mn^2. If this is the case, the formula may be $(Mn, Fe)BaMn_6O_{14}$. A new analysis on material of demonstrated homogeneity is needed.

Fermor's belief that hollandite is the coarsely crystalline equivalent of psilomelane, and is either identical with or closely allied to romanechite, proves to be without foundation. The powder patterns of hollandite and psilomelane (17% BaO) are entirely unlike, and while both minerals are essentially oxides of Ba, Mn^2 and Mn^4, their atomic ratios appear to be different. An *x*-ray study by Vaux (1937) and unpublished *x*-ray work by one of the writers (C.F.) has shown that romanechite is

identical with psilomelane. According to Vaux, psilomelane is orthorhombic, with $a_0 = 9.1$, $b_0 = 13.7$, $c_0 = 2.86$, and has the general formula $H_4R_2Mn_8O_{20}$, where R = Mn^2, Ba, Mg, Ca, Co, Cu, and Ni. In the reported analyses of known psilomelane, Mn^2 and Ba are in the approximate ratio 1:1, with Ba corresponding to *ca.* 17 per cent BaO, and the other divalent constituents are ordinarily present in amounts of one per cent or less of RO.

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