

## NOTES AND NEWS

## NEW DATA ON BIRNESSITE AND HOLLANDITE\*

C. FRONDEL, U. B. MARVIN AND J. ITO, *Harvard University, Cambridge, Massachusetts.*

## BIRNESSITE

Natural delta-MnO<sub>2</sub> or "manganous manganite" was first described under the name birnessite from a manganese-rich hardpan in fluvioglacial gravel at Birness, Scotland, by Jones and Milne (1956), who summarize the work on synthetic manganese manganites identical with or related to  $\delta$ -MnO<sub>2</sub>. An occurrence of the same mineral in Canada had been reported earlier by McMurdie and Golovrato (1948). We have identified birnessite by  $x$ -ray study in specimens collected at Cummington, Massachusetts, and Sterling Hill, New Jersey.

At Cummington, small discontinuous lenses or beds containing rhodonite, rhodochrosite, tephroite, spessartite, alleghanyite, cummingtonite and a manganoan and ferroan variety of dolomite occur conformably in metamorphosed sedimentary rocks, chiefly mica schist (Mosier and Thomas, 1949). The ore oxidizes very readily and the outcrop is overlain and penetrated along cracks by hard to friable crusts of black manganese oxide. Blocks of pink primary ore thrown on the waste heap of the mine quickly weather black. Although the black oxidation product appears to the eye to be homogeneous, it is usually found on  $x$ -ray and optical examination to consist of granular rhodonite, rhodochrosite, garnet or quartz with the secondary manganese oxide present in very minor amount, often as little more than a stain along grain boundaries. When separated, the manganese oxide generally does not give a distinct  $x$ -ray pattern, although we have identified cryptomelane in some samples. On a few specimens small patches were found of a soft, fine-grained black mineral which gave a relatively sharp  $x$ -ray pattern of  $\delta$ -MnO<sub>2</sub> (Table 1). The four lines recorded in the pattern probably are orders of (00 $l$ ), from a layer-structure. This mineral is opaque under the microscope. Other samples of soft black material proved to be mixtures of birnessite and  $\gamma$  type MnO<sub>2</sub>. The patches rich in birnessite appear to have been produced by the oxidation of a particular mineral in the primary ore which we have not been able to identify. The earlier work on the  $x$ -ray powder pattern of  $\delta$ -MnO<sub>2</sub> is summarized by Jones and Milne (1956).

A chemical analysis of a bulk sample purified as far as possible by heavy liquid and sedimentation techniques, but which still contained about 10 per cent of impurities, is cited in Table 2. The  $x$ -ray pattern of

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TABLE 1. X-RAY DATA FOR BIRNESSITE AND HOLLANDITE

Fe radiation, Mn filter, in Angstroms

Patterns taken on film in 114 mm. diameter cameras

Birnessite Cummington, Mass.		Birnessite Sterling Hill, N. J.		Hollandite Langenberg, Saxony	
I	<i>d</i>	I	<i>d</i>	I	<i>d</i>
10	7.31	10	7.36	5	6.98
5	3.60	9	3.67	3	4.93
7	2.44	8	2.46	8	3.47
8	1.418			10	3.13
				1	2.68
				9	2.40
				$\frac{1}{2}$	2.24
				8	2.15
				$\frac{1}{2}$	1.98
				6	1.83
				$\frac{1}{4}$	1.74
				2	1.65
				7	1.55
				2	1.43
				2	1.363

this sample showed some faint extra lines corresponding to the darkest lines in the patterns of quartz, spessartite, rhodochrosite, and  $\gamma$ -MnO<sub>2</sub>. The chemical analysis is hardly more satisfactory than that of Jones and Milne (1956) for the purpose of deriving a formula. If the MnO<sub>2</sub> and MnO determinations are taken at face value the atomic ratio of total Mn:O is 1.78, with Mn<sup>4</sup>:Mn<sup>2</sup>=3.38:1. The material of Jones and Milne is near Mn:O=1:1.91 with Mn<sup>4</sup>:Mn<sup>2</sup>=9.51:1. Both values fall into the range of composition of synthetic manganous manganite, with Mn:O between about 1.74 and 1.96. The role of the Ca, Mg, alkalies, and H<sub>2</sub>O in our material is speculative, if indeed these cations are essential constituents. Possibly the Ca, Mg and alkalies occupy vacant lattice sites, analogous to the relation of the hollandite group of minerals to  $\alpha$ -MnO<sub>2</sub>, and the general formula can then be written (Ca, Mg, Na<sub>2</sub>, K<sub>2</sub>)<sub>x</sub>(Mn<sup>4</sup>, Mn<sup>2</sup>)(O, OH)<sub>2</sub>, where *x* may be compensated by variation in the Mn<sup>4</sup>:Mn<sup>2</sup> or O:OH ratios.

Birnessite also was identified by its x-ray pattern (Table 1) as a secondary mineral associated with chalcophanite as a weathering product of franklinite—willemite ore from the old surface workings of the Noble

TABLE 2. CHEMICAL ANALYSES OF BIRNESSITE AND HOLLANDITE

	1. Birnessite Cummington	2. Hollandite Langenberg
MnO <sub>2</sub>	66.66	70.38
MnO	16.07	8.98
MgO	0.23	0.20
CaO	1.05	0.05
BaO	—	13.32
K <sub>2</sub> O	0.09	0.98
Na <sub>2</sub> O	0.16	0.03
Fe <sub>2</sub> O <sub>3</sub>	0.86	0.11
Al <sub>2</sub> O <sub>3</sub>	0.83	0.39
SiO <sub>2</sub>	2.62	0.40
H <sub>2</sub> O	10.83	4.76
Rem.	1.47	0.74
Total	100.87	100.34

1. Birnessite. Rem. is SrO~0.01, Li<sub>2</sub>O~0.005, NiO 0.01, CuO 0.005, SO<sub>3</sub> 0.14, MoO<sub>3</sub> ~0.005, Sc<sub>2</sub>O<sub>3</sub> tr., (Zr, Nb, Ti) oxides 1.29. Al<sub>2</sub>O<sub>3</sub> contains some (Y, Yb). Analyst: J. Ito.
2. Hollandite. Rem. is SrO~0.01, Li<sub>2</sub>O~0.005, CoO~0.05, NiO~0.05, CuO 0.14, PbO 0.001, ZnO 0.01, SO<sub>3</sub> 0.17, P<sub>2</sub>O<sub>5</sub> 0.28, V<sub>2</sub>O<sub>5</sub>~0.01, ZrO<sub>2</sub> 0.01, TiO<sub>2</sub>~0.001. Analyst: J. Ito.

pit at the south end of the ore-body at Sterling Hill, New Jersey. It occurs very sparingly as black crusts varying from hard and dense to earthy in consistency. The earthy material appears under the microscope as minute laths and needles that barely transmit light; the extinction is parallel, but the indices of refraction could not be measured.

#### HOLLANDITE

A specimen labelled "wad" from Langenberg, Saxony, collected prior to 1865 and acquired by the Harvard Museum from the J. B. Pearse collection, consists of a botryoidal crust with a radial-fibrous to fern-like internal structure (Fig. 1). The mineral is dark brownish-black in color; the powder is dark brown, and tends to smear out in the mortar to a glistening film. It has the general appearance of todorokite, but it contains barium and on x-ray study and chemical analysis was identified as hollandite. The spacings are given in Table 1. The specific gravity and hardness could not be measured accurately because of the fibrous habit. The earthy manganese and iron oxide deposits at Langenberg (Beck, 1902, 1909) are secondary concentrations derived by the weathering

and erosion of veins and stockworks containing fine grained varieties of silica with barite, calcite, manganite, braunite, pyrolusite, hausmannite, hematite. Hollandite occurs as a product of metamorphism of sedimentary manganese deposits, as in India and Sweden, and is found in other types of hypogene environments, but at Langenberg it is a supergene mineral. Numerous other supergene occurrences of hollandite are mentioned by Hewett and Fleischer (1960).

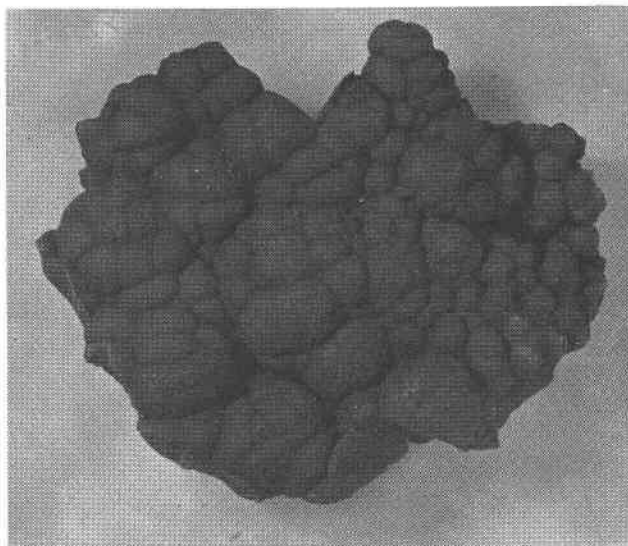


FIG. 1. Hollandite from Langenberg, Saxony. About  $\frac{1}{2}$  natural size.

#### *Chemical Composition*

The members of the hollandite group can be considered as derivatives of the  $\alpha$ - $\text{MnO}_2$  structure, for which the idealized unit cell contents can be written  $\text{V}_2\text{Mn}_8\text{O}_{16}$  (where V denotes vacant structural sites), as shown by A. and A. M. Byström (1950, 1951). Infilling of the vacancies by divalent or monovalent cations, which in the members of the hollandite group are large 8-coordinated cations Ba, Pb or K, is, in natural material, compensated electrostatically by a valence shift in the manganese ions as indicated in the formula  $(\text{V}_{2-x}\text{A}_x)_x(\text{Mn}^{4}_{8-x}\text{Mn}^{2}_x)_8\text{O}_{16}$  where A is Ba, Pb, K, and possibly also  $\text{NH}_4$  (Butler and Thirsk, 1952) or  $\text{H}_2\text{O}$ . Vacancies also can occur to a small extent in the 6-coordinated ( $\text{Mn}^{4}$ ,  $\text{Mn}^{2}$ ) positions, and OH can substitute for O. The analysis of the Langenberg mineral, cited in Table 1, indicates that A is chiefly Ba with minor K and that  $x$  is approximately 1. The approximate formula also can be

written  $(\text{Ba}, \text{K}_2, \text{Mg}, \text{Ca}, \text{Na}_2, \text{Co}, \text{Ni})\text{Mn}^2\text{Mn}^4\text{O}_{16} \cdot n\text{H}_2\text{O}$ , with  $\text{Ba}:\text{K} \sim 8:1$ . The amount of essential water, if any, is uncertain; the analysis is close to  $2\text{H}_2\text{O}$ .

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## CHEVKINITE IN VOLCANIC ASH\*

E. J. YOUNG AND H. A. POWERS, *U. S. Geological Survey, Denver, Colorado.*

Chevkinite, a titano-silicate of the cerium earths, first found as large crystals presumably from a nepheline syenite pegmatite (Rose, 1839), has been found in samples of volcanic ash of rhyolitic composition. Noteworthy are its apparent paragenesis, its trifling abundance and its wide distribution. It occurs as separate phenocrysts embedded in volcanic glass in all the samples, and as inclusions within phenocrysts of fayalite, ferroaugite, and sanidine in several samples. Its abundance is on the order of a thousandth of a per cent; only a few crystals can be concentrated from ten grams of sample. It has been separated from a tuffaceous sand in the Dubose member of the Whitsett formation of Eocene age from Texas, an early Pleistocene ash from Idaho, and from the so-called

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