

BIRNESSITE FROM MEXICO

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Birnessite has been found to be a major constituent of a multi-ton shipment of manganese ore received from Mexico. The exact origin of the ore is not known, but the supplier has traced the shipment to one of six mines located north and east of the city of Zacatecas. The mines are: Montaña de Manganeso and Prieta in San Luis Potosi; Manganita, Cerrito and Mezquite in Zacatecas; and the Virgen (location unknown). Wilson and Rocha (1956) have described the Montaña de Manganeso mine, and the others, except the Virgen mine, are described or listed by Trask and Cabo (1948).

Jones and Milne (1956) described and named birnessite, approximately $(\text{Na}, \text{Ca})\text{Mn}_7\text{O}_{14} \cdot 2.8\text{H}_2\text{O}$, on the basis of study of a Recent fluvio-glacial deposit at Birness, Scotland. They noted that a mineral the same as birnessite had previously been reported from Canada, but it was not named or described in any detail. Jones and Milne (1956) showed that synthetic materials known as "manganous manganite" and delta- MnO_2 are identical with, or related to, naturally occurring birnessite. Frondel *et al.* (1960) found birnessite at Cummington, Massachusetts, as an oxidation product of rhodonite, rhodochrosite and other manganese minerals, and at Sterling Hill, New Jersey, as a weathering product of franklinite-willemitite ore. Glemser *et al.* (1961) have discussed the preparation, properties, thermal conversions, etc., of synthetic delta- MnO_2 and give references to several additional natural occurrences of birnessite which have been reported in the literature. These additional occurrences are (1) as a constituent of manganese nodules from the Atlantic and Pacific Oceans, (2) from the Tachaki Mine, Japan, and (3) from a manganese bog in Norway. From the descriptions of the occurrences it can be concluded that birnessite has been found only as a supergene or secondary mineral formed under conditions of low temperature. Whether or not the Mexican material is of supergene origin is difficult to say. It is possible that it may be hypogene, having formed from very low-temperature rising solutions. Previous to finding birnessite in ton quantities in the Mexican ore, the mineral apparently had been found in very minor amounts at most, if not at all, of the eight reported occurrences.

The ore from Mexico consisted mostly of dense black lumps with only a small amount of soft or sooty material. X-ray diffraction patterns were obtained on about a dozen randomly selected samples from which

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TABLE 1. PARTIAL ANALYSIS OF BIRNESSITE
(WITH ADMIXED PYROLUSITE) FROM MEXICO

$K_2O = 1.3\%$
$Na_2O = 0.4\%$
$CaO = 0.8\%$
$BaO = 0.4\%$
$Fe_2O_3 = 2.3\%$
$Al_2O_3 = 1-5\%$ estimate
$TiO_2 = 1-2\%$ estimate
Zn, Ni, Cu, V, Cr = traces
G = 3.1

birnessite was determined to be a major constituent of one-half of the specimens. Pyrolusite was the most abundant mineral in the ore, but birnessite comprised about 25 per cent of the shipment. Other minerals identified include calcite, tridymite and materials referred to as beta- MnO_2 , gamma- MnO_2 and rho- MnO_2 . Although usually found in association with pyrolusite, birnessite was identified on x-ray films with all of the above manganese oxides. The birnessite was identified by its characteristic x-ray diffraction pattern which consists of four lines: 7.2 Å (10), 3.60 Å (5), 2.40 Å (6), and 1.42 Å (1); the numbers in parentheses are relative intensities.

A partial chemical analysis (Table 1) was carried out on the purest specimen found, but x-ray patterns of the analyzed material indicated perhaps 25 per cent impurities, chiefly pyrolusite (but no cryptomelane). Frondel *et al.* (1960) pointed out that the role of Ca and the alkalis in their material was speculative, and these elements may not be essential. They suggested that Ca, Mg and the alkalis may occupy vacant lattice sites. If the values reported in Table 1 are taken at face value, the Mexican birnessite contains more potassium than any of the elements under discussion, whereas the Cummington material (Frondel *et al.*, 1960) is high in calcium and the Birness material (Jones and Milne, 1956) is predominantly a sodium type.

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