

## BIRNESSITE ON COLEMANITE AT BORON, CALIFORNIA

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### ABSTRACT

Birnessite occurring in minute clusters implanted on colemanite has been studied by X-ray diffraction and by scanning electron microscope. Analysis by electron microprobe tends to confirm the composition originally proposed for this mineral.

### INTRODUCTION

Birnessite was named by Jones and Milne (1956) who found it in a "manganese pan . . . in a fluvio-glacial deposit" as black grains in a soft black cement coating fragments of gravel and filling interstices. Since then the mineral has been reported from many places (Fron del, Marvin, and Ito, 1960; Hariya 1961; Nambu and Tanida 1961; Levinson 1962; Sorem and Gunn 1967), always associated with other manganese minerals as an alteration or weathering product. Though it is commonly identified by means of X-ray diffraction it has not been assigned a lattice. Chemical analyses have been incomplete or made on contaminated material and the formula assigned to it had not been confirmed prior to this study.

### OCCURRENCE AND ASSOCIATIONS

Colemanite clusters flecked with small pepper-like blackish to brown colored specks (birnessite) were collected along the western edge of the open pit (approximate mine coordinates 4800N-19300E of the United States Borax and Chemical Corporation, Barnard and Kistler, 1966) at Boron, Kern County, California. This area contained several north-westerly trending small fractures and faults, probably a subsystem of the Portal fault which is the major east-west structural feature forming the southern boundary of most of the sodium borate deposit constituting the main ore body. The area is west of the Suckow fault system and slightly east of the western extremity of the borax beds.

The main sodium borate ore body (borax and kernite), some 200 feet thick with intercalated lean or barren zones, lies about 300 feet below the original surface. It is immediately overlain by claystone with ulexite, ulexite and tuff referred to as the "ulexite facies" by Barnard and Kistler (1966, fig. 3 and fig. 4, (also Morgan and Erd, 1969, fig. 1 and Smith, 1968, fig. 2)) over which there is claystone with colemanite, the "colemanite facies." In the development of the open pit mine overburden was stripped. Except for occasional blasting of the two massive ulexite-colemanite beds occurring in this area of the open pit, stripping in the barren colemanite and ulexite facies was generally a uniform layer by layer removal and mineralized zones of special interest were gradually exposed, greatly facilitating collecting.

In certain areas the ulexite beds were replaced by, or graded into, colemanite. Cavities

in the colemanite were usually lined with clear, sharp-bladed colemanite crystals up to about an inch in length. Specimens of birnessite associated with clear colemanite crystals were collected from the upper colemanite-ulexite bed of the ulexite facies, which at this location consisted essentially of highly fractured (cellular) or recrystallized colemanite; ulexite was absent. Claystone beds of the colemanite facies formed the hanging wall. Open cavities and vugs were lined with colemanite crystals still wet from contact with ground water or original mother liquor. Peppering of colemanite crystals with flecks of birnessite was most noticeable (see Figure 1) and drew attention to the colemanite which was otherwise not unusual except for its highly fractured nature. The rocks in this area were entirely removed by the stripping operations in 1959 and later. So far as known to us no other occurrences of birnessite have been uncovered by later operations and the mineral cannot now be collected in place at Boron.

In most occurrences birnessite is associated with other manganese minerals. At Boron no other manganese minerals have been found with the colemanite on which the birnessite is implanted. Morgan and Erd (1969, p. 166) record that "A single occurrence of rhodochrosite has recently been found in the bluish-green shales of the colemanite facies . . ."

The colemanite, on which the birnessite is implanted, is in large groups of sharp bladed crystals generally less than one cm long and remarkably simple and constant in habit.

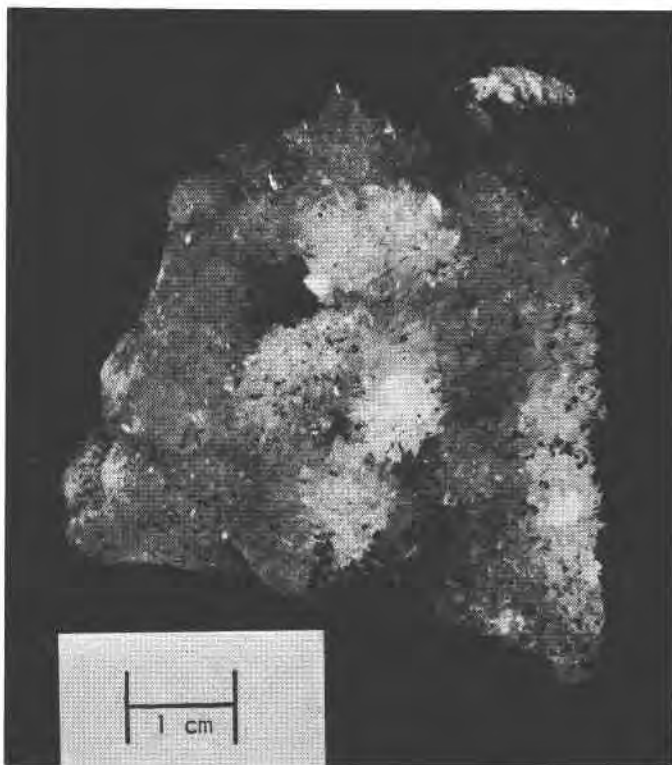


FIG. 1. Group of colemanite crystals with flecks (black) of birnessite. "Ulexite facies," Kramer beds, Boron, California (1959).

Five crystals were measured by 2-circle goniometer. Mostly they are bounded by the forms  $\{110\}$  and  $\{301\}$ . The prism faces are perfectly mirror-like, those of  $\{301\}$  are often rounded or wavy, grading into other  $\{h01\}$  forms.  $\{601\}$  was identified in one case. This corresponds exactly to Eakle's (1902, plate 2, fig. 6) description of his "Habit 4," a habit first described and pictured by H. S. Washington (Whitfield, 1887) on crystals from Death Valley. The "sharp and pointed 'razor' habit" pictured by Morgan and Erd (1969, p. 147) is probably the same. Many small spear points protrude from the groups of crystals of this habit. These are bounded by just three faces, (110), (1 $\bar{1}$ 0) and (301), coming to a sharp point. The angle between the terminal edges of the (110) faces is  $42^\circ 18'$  and between the terminal edges of the (301) faces is  $65^\circ 50'$ .

#### MEGASCOPIC DESCRIPTION

The birnessite is but lightly attached to the colemanite crystals and the small arborescent clusters of birnessite can easily be brushed or shaken off entirely free of any contamination. The clusters may reach two mm or more in dimensions but many are smaller. They are extremely fragile and tend to fall apart even with gentle handling. The birnessite clusters are very irregularly distributed over the colemanite crystals. On some specimens they lie close together but elsewhere individual clusters lie several centimeters apart from others on clean, bladed colemanite.

#### X-RAY IDENTIFICATION

Five, apparently clean, dark clusters were mounted at the tips of glass fibers in 114.59 mm diameter powder cameras so that only the clusters were in the X-ray beam. They yielded similar powder patterns showing the material to be ultrafine grained but differing in the amount of diffuse background, with some stray spots and fragmentary lines, some attributable to bits or dust of colemanite and others possibly arising from varying minor amounts of other manganese oxides or unknown phases. In Table 1 are recorded only those lines that are common to all of the patterns. These are the characteristic lines constituting the whole of the confirmed powder pattern of birnessite as reported by various observers. Hariya (1961) has included five additional lines in a pattern stated to represent birnessite, and Bricker (1965) published a pattern from synthetic material which includes three of the four characteristic birnessite lines plus four others. This is included as pattern 18-1802 in XRDF and marked "(birnessite)". Frondel *et al.*, (1960, p. 871) stated that the four birnessite lines "probably are orders of (001)". If so, they might be the 1st, 2nd, 3rd, and 5th orders, but the agreement is rather rough and our observations do not lend support to this suggestion.

#### PHYSICAL PROPERTIES

Jones and Milne (1956) determined the specific gravity of slightly contaminated material to be 2.9 by micro-pycnometer and estimated the

TABLE 1. CHARACTERISTIC X-RAY POWDER LINES FOR BIRNESSITE FROM VARIOUS SOURCES

Scotland (Jones & Milne, 1956)		Massachusetts (Frondel <i>et al.</i> , 1960)		Mexico (Levinson, 1962)		Washington (Sorem & Gunn, 1967, table 4)		California (This study) <sup>a</sup>	
<i>I</i>	<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>	<i>d</i>
s	7.27	10	7.31	10	7.2	100	7.2	s	7.24 ± 0.07
w	3.60	5	3.60	5	3.60	50	3.6	mw, w	3.55 ± 0.07
m	2.44	7	2.44	6	2.40	10	2.45	m	2.46 ± 0.01
m	1.412	8	1.418	1	1.42	10	1.42	m	1.424 ± 0.004

<sup>a</sup> *d* values for the California birnessite are averages for five samples with indication of the spread of the measured values. Width or diffuseness of the first two lines contributes to this spread. On our patterns the 2.46 line is invariably sharper than the other lines and the 3.60 line is decidedly the weakest of the characteristic lines.

specific gravity of birnessite to be 3.0. An attempt was made at determining the specific gravity of the Boron birnessite by Bloss' method (1961, p. 61), using three small clusters suspended in a diiodomethane—chloronaphthalene mixture and observing their movements under a microscope. This yielded a value of  $2.9 \pm 0.1$  in apparent agreement with Jones and Milne. However, in view of the cellular structure of birnessite it seems highly probable that the "true" density of birnessite is higher and that the agreement is fortuitous.

Jones and Milne (1956) reported that "The crystals are faintly birefringent and give an indistinct uniaxial negative interference figure. The refractive indices are approximately  $\epsilon = 1.69$  and  $\omega = 1.73$ ." Frondel *et al.*, (1960) found that earthy birnessite from Sterling Hill, New Jersey, barely transmits light and shows parallel extinction but that its refractive indices could not be measured. The birnessite from Boron is translucent and birefringent on some edges but, due to its ultrafine grain, extinction cannot be recognized. The indices are somewhat above 1.80. Higher index liquids, based on  $\text{AsBr}_3$ , attack and bleach the birnessite, vitiating further attempts at index determination.

#### BEHAVIOR ON HEATING

One of the clusters of birnessite that had been examined by X-rays was heated in air for 2 hours at 600°C. An X-ray diffraction pattern of the heated cluster was obtained in the same manner as from the unheated birnessite. This proved to be the X-ray pattern of hausmannite, plus a few faint unidentified lines that may be attributed to other phases arising from the components that do not enter into the hausmannite struc-

ture. This is in agreement with Okada (1961) who reported that birnessite on heating changes to cryptomelane and then through an amorphous state to hausmannite, and that in some specimens cryptomelane is not formed in the process. No attempt has been made to discern possible intermediate states in the present case. Birnessite has been considered to be the natural counterpart of  $\delta$ -MnO<sub>2</sub>. Klingberg and Roy (1959) reported that  $\delta$ -MnO<sub>2</sub> goes to pyrolusite at *ca.* 300+°C and then to bixbyite at *ca.* 500+°C when heated in air.

#### SCANNING ELECTRON MICROSCOPE OBSERVATIONS

Scanning electron microscope observations were made at magnifications from 20 to 20,000; 28 photographs being taken. Two of these are reproduced here as Figure 2 and 3. Figure 2 and many similar pictures, even at the highest magnifications, show that the birnessite is perched on smooth colemanite surfaces. There is no indication of overlap of the

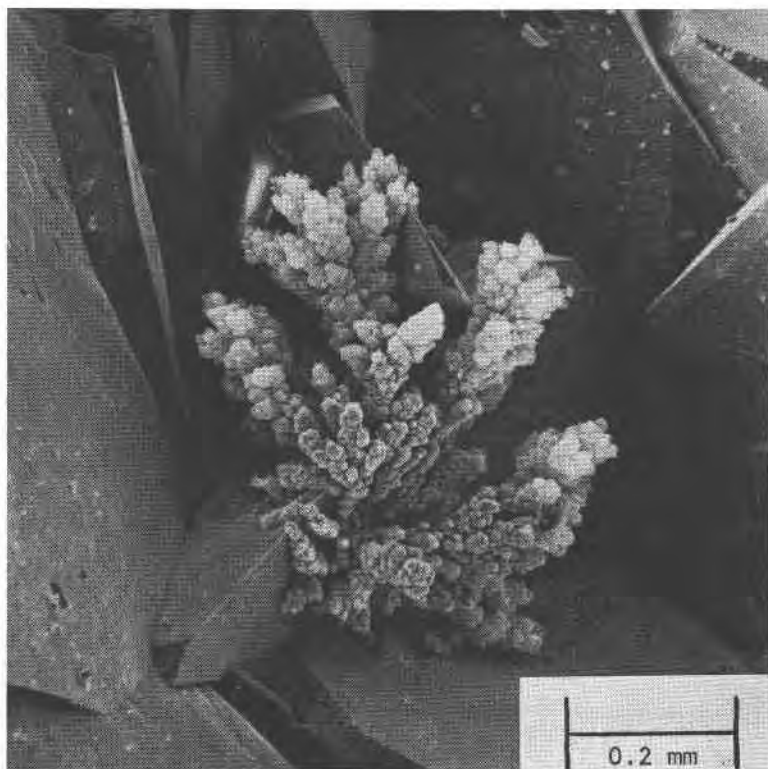


FIG. 2. Scanning electron micrograph of a single cluster of birnessite implanted on colemanite. Dr. Norman Hodgkin, Micrographics.

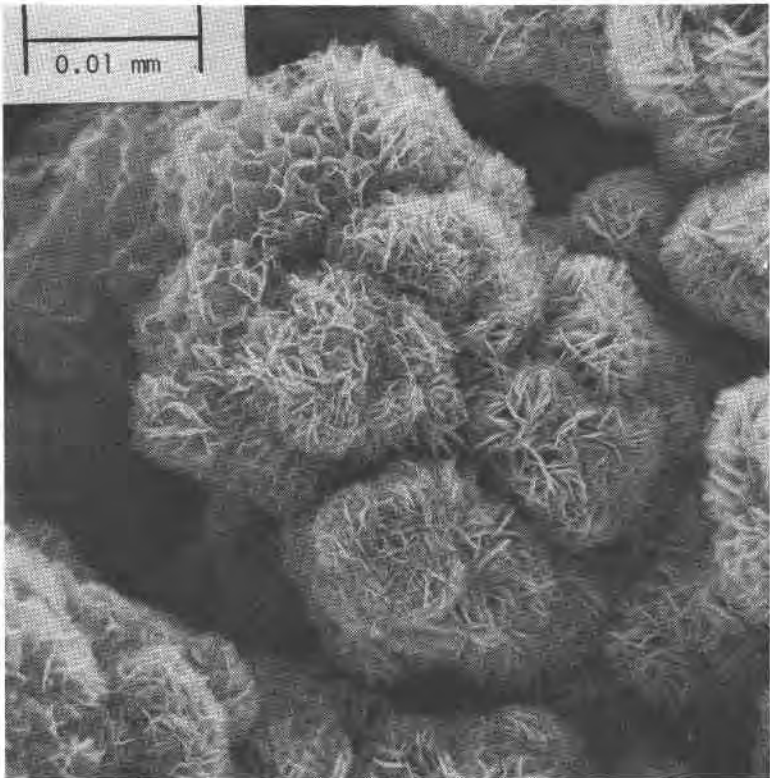


FIG. 3. Scanning electron micrograph of a small portion of a cluster of birnessite. Dr. Norman Hodgkin, Micrographics.

periods of crystallization of the two minerals. Figure 3 shows that each of the segments of a birnessite cluster has a cellular structure formed by a more or less haphazard array of thin, slightly bent, lamellae. Measurements on photographs at 20,000X show that these lamellae at their edges are about 2,000 Å thick and that the spaces between them have dimensions of the order of 10,000 Å. A few photographs at high magnification show a suggestion of etching of the colemanite surfaces adjacent to the perched birnessite.

#### MICROPROBE STUDY

Several small clusters of birnessite were removed from the colemanite crystals, mounted in epoxy-resin, and polished. Although the material was very difficult to polish, several areas ranging from 7 to 20 microns in size were well polished. These areas were analyzed with the electron

TABLE 2. ANALYSES OF BIRNESSITE

	(1)	(2)	(3)
TiO <sub>2</sub>	—	< .02	
Fe <sub>2</sub> O <sub>3</sub>	—	< .02	
MnO <sub>2</sub>	80.34	87.5	79.38
MnO	6.71	—	6.63
CaO	2.45	4.1	4.1
Na <sub>2</sub> O	3.16	2.4	2.4
H <sub>2</sub> O	7.34	—	(7.49)
	100.00		100.00

(1) Analysis calculated from formula of Jones and Milne (1956).

(2) Microprobe analysis of birnessite from Boron, California. All Mn as MnO<sub>2</sub>.

(3) Microprobe analysis recalculated to conform to Mn<sup>4+</sup>/Mn<sup>2+</sup> of Jones and Milne. Water by difference.

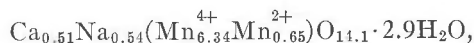
microprobe, using a small beam diameter (*ca.* 1.5 microns) and a sample current of *ca.* 0.04 microamperes. The standards used were polianite, assumed to be stoichiometric MnO<sub>2</sub>, and analyzed aenigmatite and clinopyroxene. Atomic number and background corrections were made; the background curves were constructed using spinel, hematite, and nickel oxide. The average analysis of the birnessite is given in Table 2.

The amount of calcium present was remarkably constant, however the sodium content was variable, ranging from 2.2–3.0 weight percent. The constancy of the calcium content both within single areas, and from one area to another seems to exclude the possibility that the material is contaminated with colemanite—the only other mineral known to be present in the specimen. A much greater variation in the calcium content would be expected if this were the case. Accordingly it is thought that both the calcium and sodium are essential to birnessite.

#### COMPOSITION AND FORMULA

The chemical composition of birnessite as calculated from the formula of Jones and Milne (1956) is given in column 1 of Table 2. Just how these workers derived the formula from their analysis is not clear. In column 2 of Table 2 the microprobe analysis of birnessite is given with all Mn calculated as MnO<sub>2</sub>, and column 3 gives the analysis with Mn distributed between Mn<sup>4+</sup> and Mn<sup>2+</sup> in the same ratio as that of Jones and Milne (1956). The amount of water present (given in parentheses in column 3) was calculated by difference from 100 percent.

The formula derived from the microprobe analysis is



calculated on the basis of 17 oxygens. The formula given by Jones and Milne is  $\text{Na}_{.7}\text{Ca}_{0.3}\text{Mn}_7\text{O}_{14} \cdot 2.8\text{H}_2\text{O}$ . The correspondence between the two formulas is remarkably good, the main difference being in the ratio of calcium to sodium. The sum of the calcium and sodium, however, is very nearly the same in both cases, being 1.0 or close to it.

## ACKNOWLEDGMENTS

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