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Birnessite, a new manganese oxide mineral from Aberdeenshire, Scotland.

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Summary.—A manganese pan near Birness contains grains of an optically uniaxial negative mineral near $(\text{Na}_{0.7}\text{Ca}_{0.3})\text{Mn}_7\text{O}_{14}\cdot 2\cdot 8\text{H}_2\text{O}$, giving an X-ray powder pattern similar to that of synthetic materials described as 'manganous manganite' and $\delta\text{-MnO}_2$. Material giving a similar pattern has been described from a natural occurrence in Canada, but no mineral name was assigned; the name *birnessite* is now proposed. The mineral is probably formed by air-oxidation of manganous oxides under alkaline conditions.

MANGANESE oxides are sometimes concentrated in pans or concretions (Wheeting, 1936; Winters, 1938; Drosdoff and Niki-foroff, 1940; Sherman, Tom, and Fujimoto, 1949), but there is little known of such oxides beyond their chemical composition. A manganese pan found at Birness, Aberdeenshire, has provided a source of oxide, which has been examined by chemical, optical, and X-ray methods. These indicate that the manganese oxide is a new mineral to which the name *birnessite*, after the locality, is given.

Field occurrence. The manganese pan was found in a cutting in a fluvio-glacial deposit of gravel beside the road at Birness, which is about

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20 miles north of Aberdeen. The deposit resembles a kame of the Lower Grey Boulder Clay described by Bremner (1915) and is overlaid by a fine, red clay typical of the Strathmore drift.

The pan is of irregular thickness ($\frac{1}{2}$ to $1\frac{1}{2}$ in.) and occurs at a depth of about 12 ft. below the top of the deposit. Unlike the iron oxide of an iron pan which penetrates rocks or pebbles throughout the level of a pan, the soft, black manganese oxide cementing this pan only coats the fragments of gravel and fills the interstices between fragments. The birnessite was found in this black cementing material.

Physical and chemical properties. Black grains, up to $4 \times 8 \times 3$ mm. in size, were picked out of the pan and it was noted that the smaller ones occasionally showed well-defined facets. The hardness of the grains is $1\frac{1}{2}$; their specific gravity, determined with a micro-pycnometer on ground material, is 2.9, and after correcting for the contaminating minerals (see table II) the specific gravity of the birnessite is found to be 3.0. The grains consist largely of birnessite as very fine crystals which are nearly opaque and dark brown in transmitted light. The crystals are faintly birefringent and give an indistinct, uniaxial negative interference figure. The refractive indices vary but are approximately $\epsilon = 1.69$ and $\omega = 1.73$. They are thus comparable to those of pyrochroite, $\text{Mn}(\text{OH})_2$, which are $\epsilon = 1.681$ and $\omega = 1.723$.

X-ray powder patterns were taken with a modified Unicam camera of 9 cm. diameter using unfiltered iron radiation. Small grains with well-defined facets gave the X-ray powder pattern of birnessite which consists of four lines. After the birnessite is heated in air to 110°C . the two inner lines disappear but the others remain even after heating to 300°C . The X-ray powder pattern of birnessite is given in table I together with the patterns of 'manganous manganite' given by Feitknecht and Marti (1945a), Cole, Wadsley, and Walkley (1947), and Buser, Graf, and Feitknecht (1954), and those of $\delta\text{-MnO}_2$ given by McMurdie (1944) and McMurdie and Golovato (1948). With two exceptions, these authors have given diagrams of the X-ray powder patterns from which approximate values of d have been calculated.

The grains (up to $4 \times 8 \times 3$ mm.) removed from the pan were ground to pass a 200-mesh I.M.M. sieve. Chemical analysis of the powder (table II) shows that it consists mostly of a hydrated manganese oxide together with other minerals. The amounts of these minerals were estimated by a mineral count of 1019 grains and the results, expressed as percentages by weight, are included in table II. Although the results of this mineral count may not be precise, because of some variation in

TABLE I. X-ray powder data for birnessite, 'manganous manganite', and δ -MnO₂

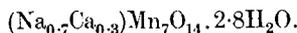
Birnessite.		'Manganous manganite.'			δ -MnO ₂ .				
Jones and Milne.		Cole <i>et al.</i>	Feitknecht and Marti.	Buser <i>et al.</i> A ₂ (2).	McMurdie	McMurdie and Golovato.			
						C11.	Canada.		
<i>d</i> , Å.	<i>I</i> .	<i>d</i> , Å.	<i>I</i> .	<i>d</i> , Å.	<i>I</i> .	<i>d</i> , Å.	<i>I</i> .		
7.27	s	7.13	ms	6.90	ms	7.4	ms	7.4	vs
3.60	w	3.53	w	3.49	w	3.71	w	3.64	vw
2.44	m	2.41	m	2.42	m	2.49	m	2.39b	
		2.14	vwb					2.41	mw
				1.69	m				
				1.50	w	1.44	m		
1.412	m	1.418	vw					1.40	b

grain size, it is possible when considering the composition of the manganese mineral to disregard silica, which is present largely as quartz and also to a small extent as clay. The small amounts of aluminium, titanium, and iron are also disregarded since they are likewise due to contamination with clay and titanium and iron oxide minerals respectively.

TABLE II. Chemical and point-counter analyses of the manganese pan containing birnessite. Spectrographic analysis showed that the following elements were present in trace amounts: As, Ba, Cr, Co, Cu, Ge, K, Li, Mg, Mo, Ni, P, Pb, Sr, and Zr.

	%.		% by weight.
SiO ₂	. . . 18.92	Quartz	. . . 20.0
Al ₂ O ₃	. . . 3.32	Clay	. . . 7.3
Fe ₂ O ₃	. . . 2.88	Limonite.	. . . 5.2
TiO ₂	. . . 0.28	Rutile	. . . 0.1
MnO ₂	. . . 54.24	Birnessite	. . . 67.4
MnO	. . . 4.66		
CaO	. . . 1.65		100.0
Na ₂ O	. . . 2.17		
H ₃ O ⁺	. . . 4.99		
H ₂ O ⁻	. . . 5.88		
	<u>98.99</u>		

The formula of the birnessite is thus close to:



After allowing for oxygen in combination with sodium and calcium, the atomic ratio of O:Mn is 1.90 which lies within the range of 1.74 to 1.96 reported for 'manganous manganite' and δ -MnO₂ by Feitknecht and Marti (1945a and 1945b) and Buser, Graf, and Feitknecht (1954).

Discussion. The X-ray powder pattern of the Aberdeenshire birnessite is similar to the patterns of various synthetic 'manganous manganites' and of $\delta\text{-MnO}_2$, as shown in table I. There was, until recently, some confusion about 'manganous manganite' and $\delta\text{-MnO}_2$. Originally $\delta\text{-MnO}_2$ was the name given by McMurdie (1944) to a synthetic manganese oxide whose X-ray powder pattern consisted of only two lines, at 2.39 Å. and 1.40 Å. Later, McMurdie and Golovato (1948) reported two additional lines, at 7.0 Å. and 3.64 Å., in the powder pattern of a synthetic $\delta\text{-MnO}_2$. The name 'manganous manganite' was given originally by Feitknecht and Marti (1945*a*) to a manganese oxide that gives a similar powder pattern and was prepared by oxidizing an alkaline manganous solution with either air or oxygen. Using this and other methods they prepared 'manganous manganite' with the atomic ratio of O:Mn ranging from 1.74 to 1.96 (Feitknecht and Marti, 1945*b*). The most oxidized forms were considered to be disordered because the two inner lines of the X-ray powder patterns disappeared. The X-ray powder pattern of a 'manganous manganite' prepared by Cole, Wadsley, and Walkley (1947) agrees with that of Feitknecht and Marti (1945*a*), and Cole *et al.* were the first to suggest that McMurdie's original $\delta\text{-MnO}_2$ is similar to 'manganous manganite'. More recently Buser, Graf, and Feitknecht (1954) have confirmed this suggestion and have clarified the relationship between 'manganous manganite' and $\delta\text{-MnO}_2$.

By oxidizing an alkaline manganous solution with oxygen Buser, Graf, and Feitknecht obtained a hydrous manganese oxide with formula $3\text{MnO}_2 \cdot \text{Mn}(\text{OH})_2 \cdot x\text{H}_2\text{O}$. The X-ray powder pattern showed that this was similar to an oxide described previously by Wadsley (1950) with a formula, computed from his analysis, of $\text{NaMn}_6\text{O}_{12} \cdot 2.5\text{H}_2\text{O}$. It was metastable and recrystallized, with further oxidation, to a 'manganous manganite' with the formula $4\text{MnO}_2 \cdot \text{Mn}(\text{OH})_2 \cdot 2\text{H}_2\text{O}$ and an equivalent ratio of O:Mn of 1.80. This 'manganous manganite' was well crystallized, as shown by the X-ray powder pattern of twenty-four lines (Buser *et al.*, table II, loc. cit.). They also prepared a series of poorly crystalline 'manganous manganites' by methods involving the decomposition of permanganate solutions with either HCl or manganous solutions. The O:Mn ratio of these oxides ranged from 1.76 to 1.95 and because the inner lines disappeared from the X-ray powder patterns of the most highly oxidized forms it was concluded that the degree of disorder increased with increasing oxidation. The X-ray powder patterns of the most highly oxidized forms were identical with those given by the original $\delta\text{-MnO}_2$ (McMurdie, 1944). Between this extreme and that

represented by the well-crystallized 'manganous manganite' there are intermediate forms giving X-ray powder patterns similar to that of birnessite. While Buser *et al.* (1954) show that 'manganous manganite' and δ -MnO₂ are the same crystal phase they suggest that both names be retained and that δ -MnO₂ be used for those oxides with O:Mn > 1.90.

Feitknecht and Marti (1945*a*) concluded that the structure of 'manganous manganite' could be derived from the layer lattice of the parent manganous hydroxide, pyrochroite, and suggested that layers of 4MnO₂ are interspersed with layers of Mn(OH)₂·2H₂O. The similarity of the optics of birnessite and pyrochroite provides some evidence for the first part of this theory. The well-crystallized 'manganous manganite' prepared by Buser *et al.* (1954) enabled them to confirm the theory of its structure and they assigned to it an hexagonal unit-cell with $a = 5.82 \text{ \AA}$. and $c = 14.62 \text{ \AA}$. In the more highly oxidized samples the interlayers of 4MnO₂ and Mn(OH)₂·2H₂O no longer exist as regular structural units. Instead, there are only individual double layers which are randomly oriented; the result is that the basal reflections of δ -MnO₂ eventually disappear. Thus 'manganous manganite' and δ -MnO₂ are shown to be variously disordered forms of a distinct crystal phase and are not disordered forms of cryptomelane (α -MnO₂) as has been suggested by McMurdie (1944) and more recently by Butler and Thirsk (1953).

The optical, chemical, and X-ray data of birnessite show that it is a naturally occurring δ -MnO₂. The only published report of such a mineral is by McMurdie and Golovato (1948) who, without other description, present an X-ray powder pattern of δ -MnO₂ from Canada. Since synthetic 'manganous manganite' and δ -MnO₂ are easily converted to cryptomelane (α -MnO₂) or to γ -MnO₂ by heat, such an oxide should occur in nature only where temperatures have been low both during and since deposition. An oxide of supergene origin has been reported as similar to 'manganous manganite' (Samson and Wadsley, 1948), but the X-ray powder pattern shows much more similarity to cryptomelane. The Canadian material and the present occurrence are thus the first evidence of 'manganous manganite' or δ -MnO₂ occurring naturally.

The clay which overlies the gravel at Birness probably provided the source of manganese for the pan. This clay was transported from the south where it was derived from Old Red Sandstone material, and it is known that soils developed from this parent material in the Laurencekirk area are high in manganese oxides, which are sometimes conspicuous as black stains (Rep. Macaulay Inst. Soil Res., 1947-1948, p. 8). The manganiferous clay at Birness was probably laid down in a shallow

lake. Under such anaerobic conditions, micro-organisms would reduce the manganese oxides thereby releasing the manganous ion; as the water table was lowered, the manganous ion would migrate into the underlying gravel where it could be oxidized in a horizon of higher alkalinity. The gravel is now well drained and the pan is some feet above the highest level of the water table; it is therefore probable that aeration and oxidation have for some time been uninterrupted. This is somewhat analogous to the oxidation in the laboratory of an alkaline manganous solution which, if prolonged, leads to the formation of 'manganous manganite' or $\delta\text{-MnO}_2$.

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