

The synthesis of birnessite, cryptomelane, and some other oxides and hydroxides of manganese

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SUMMARY. Detailed methods are described for the laboratory preparation of the manganese minerals manganosite, hausmannite, manganite, partridgeite, birnessite, cryptomelane, pyrolusite, and todorokite. New data are presented on the conversion of birnessite to cryptomelane, and on the exchange properties of potassium in these two minerals. It was found that the upper limit of potassium in cryptomelane is about 7% K, while the lower limit lies between 0.25% and 2.2% K.

DURING the course of an investigation into the adsorption of metal ions by manganese oxides, it became necessary to prepare a number of pure synthetic oxides of various types. A large number of methods have been described in the literature, but attempts to reproduce these were not always successful. Many of the earlier descriptions of methods suffered from uncertainties in the identification of the products, and lack of uniformity in the nomenclature of the many oxides and hydroxides of manganese. A number of the published methods were described only briefly, and duplication of these is difficult because of the lack of detail given, since seemingly minor variations in conditions or starting materials can influence the results.

Considerable experience has been gained during the course of this work, and it is the purpose of this paper to place this on record, with sufficient detail to allow the methods to be reproduced without difficulty. It is not intended to review the literature, and only those mineral forms of interest in the present investigations have been included. Some of the more recently published methods are quoted to illustrate the difficulties encountered, and to serve as an introduction to the methods finally adopted. Reviews of the literature on methods of preparation of a number of the oxides and hydroxides of manganese have been given by Bricker (1965) and by Moore, Ellis, and Selwood (1950).

In the methods described below, the use of double distilled water is essential, as the oxides of manganese adsorb cations very strongly. All samples, unless otherwise stated, were dried in an air oven at 35°C. Identification of the minerals was made by X-ray diffraction, using a 5.73 cm diameter powder diffraction camera and Fe- $K\alpha$ radiation. Surface areas were determined by the adsorption of nitrogen gas at the temperature of liquid nitrogen in a continuous-flow apparatus, after outgassing for 15 hours at 95°C in a stream of dry oxygen-free nitrogen.

Manganosite was prepared by Moore, Ellis, and Selwood (1950) starting with recrystallized manganous nitrate. The carbonate was precipitated with ammonium

carbonate, and washed in a Buchner funnel, while maintaining a layer of CO_2 in the funnel to prevent oxidation. After washing with alcohol and ether, the carbonate was dried by evacuation over P_2O_5 , and converted to manganosite by heating under vacuum at 500°C for 48 hours. They state that the stability of the oxide so prepared depends on the time and temperature of heating, the more active samples being pyrophoric. This method was found to be satisfactory provided certain precautions were taken, and the details of the method used are as follows.

The carbonate was prepared from reagent grade manganous sulphate as described by Moore *et al.* and placed in an 8" by 1" Pyrex test-tube, to the open end of which was sealed a length of glass tubing long enough to protrude several inches through the furnace door. A plug of glass wool was placed at the neck of the test-tube, and a two-stage rotary vacuum pump was connected directly to the glass tubing. Use of a ground-glass joint was found to be unsatisfactory, as sufficient air was admitted to cause oxidation. The tube was evacuated cautiously to a pressure of about 0.01 mm, and slowly inserted into a muffle furnace at 400°C . This process was carried out over a period of two hours, as rapid evacuation or heating caused a sudden evolution of gas that carried the sample out of the tube. The temperature of the furnace was then raised to 600°C , and maintained at this temperature for 48 hours. Samples prepared at 550°C ignited and oxidized immediately the tube was opened, and even at 600°C material at the ends of the tube, where the temperature was somewhat lower, oxidized when the tube was opened.

Hausmannite was prepared by Moore, Ellis, and Selwood (1950) by thermal decomposition of manganous sulphate in air at 1000°C , and in fact this preparation can be carried out by ignition of any of the oxides or hydroxides of manganese. Rapid cooling in vacuum prevents reoxidation during cooling. This method, although reliable, gives an unreactive product, thought to be due to the annealing and healing of crystal imperfections during heating (Wadsley and Walkley, 1951). A number of wet methods of preparation have been described, although some of these give mixed products, or variable oxygen contents. Moore *et al.* (1950) and Bricker (1965) described the oxidation of manganous hydroxide to a material with an oxygen content corresponding to $\text{MnO}_{1.5}$. This oxide is known as $\gamma\text{-Mn}_2\text{O}_3$, but the X-ray pattern is practically identical to that of hausmannite. The following wet method was found to be reliable.

A solution of 0.2 moles $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ in one litre of water was precipitated with 0.5 moles of NaOH , and the hydroxide was washed by repeated decantation, keeping the flask completely filled and stoppered while settling to prevent oxidation. When the sodium content of the washings fell to less than 1 p.p.m. the hydroxide was suspended in one litre of water and oxidized by bubbling oxygen for 5 hours at room temperature (20°C). The product was pure hausmannite, containing 0.004% Na, and had a surface area of $41 \text{ m}^2/\text{g}$.

Manganite ($\alpha\text{-MnOOH}$) was prepared by Feitknecht and Marti (1945) by precipitation of a manganous salt with ammonia in the presence of hydrogen peroxide. They found that with an excess of ammonia the product was a mixture of hausmannite, $\alpha\text{-MnOOH}$, $\beta\text{-MnOOH}$, and manganous manganite, but with a deficiency of ammonia they always obtained manganite. Moore, Ellis, and Selwood (1950) prepared manganite by a similar method, using less hydrogen peroxide and a slight excess of ammonia. Bricker (1965) oxidized a suspension of manganous hydroxide with hydrogen peroxide.

A number of attempts to reproduce these three methods during the present work gave hausmannite by the first method, a mixture of β -MnOOH, hausmannite, and manganite by the second, and a mixture of hausmannite and manganite by the third. The following method for the preparation of manganite was finally adopted.

A solution of 0.35 moles $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ in two litres of water was precipitated with 0.75 moles NaOH. The hydroxide was washed by decantation, keeping the flask filled and stoppered while settling, and then oxidized by adding slowly 90 ml of 30 % hydrogen peroxide. This gave a mixture of hausmannite and manganite, which was slowly converted to pure manganite by bubbling air through the boiling suspension, while stirring with a magnetic stirrer. A reflux condenser was used to prevent loss of water from the mixture. The proportion of manganite to hausmannite slowly increased until, after 21 days, only manganite was detected by X-ray diffraction. The treatment was continued for a further 14 days to ensure complete conversion.

Partridgeite (α - Mn_2O_3). Moore, Ellis, and Selwood (1950) prepared pyrolusite by ignition of the nitrate, and converted this to partridgeite by ignition in air at 600 °C to constant weight. They found that some oxygen was lost at temperatures above 600 °C. No difficulties were experienced with this method, which gave a product with a surface area of 3 m²/g. A finer-grained product was also prepared by igniting the fine-grained pyrolusite obtained from the hydrolysis of MnCl_4 , described in the section on pyrolusite. This had a surface area of 13 m²/g.

Birnessite (manganous-manganite, or δ - MnO_2) is a naturally occurring, poorly crystalline oxide of tetravalent manganese. It is one of the most common forms of mineralized manganese in soils (Taylor, McKenzie, and Norrish, 1964), and is readily synthesized by a variety of methods. Natural birnessite generally contains foreign ions such as sodium, calcium, and potassium, but these are non-essential, and synthetic birnessite can be prepared free from foreign ions. Both the natural and synthetic forms always contain less than the stoichiometric proportion of oxygen. Buser, Graf, and Feitknecht (1954) referred to their preparations as manganous-manganite or δMnO_2 , depending on whether the oxygen : manganese ratio was less than or greater than 1.9. The two forms could be distinguished by the presence or absence of basal reflections in the X-ray diffraction patterns. Bricker (1965), however, considered that the presence or absence of the basal reflections is a function of particle size. He recommended that the name 'manganous-manganite' be dropped, and that these materials be called ' δ - MnO_2 '. Jones and Milne (1956) proposed the name *birnessite* for the naturally occurring mineral, and this name will be used here.

The most common methods for the synthesis of birnessite are by the oxidation of manganous hydroxide or the reduction of potassium permanganate, using a variety of oxidizing or reducing agents. Birnessites with low potassium contents are readily converted to γ - MnO_2 or cryptomelane by boiling, and, since many of the preparations are carried out at the boiling point, those methods that maintain a large excess of potassium ions throughout, and so give high potassium contents, are the most reliable.

Cole, Wadsley, and Walkley (1947) prepared birnessite by the dropwise addition of concentrated hydrochloric acid to a boiling solution of potassium permanganate.

Wadsley (1950), and Buser *et al.* (1954) bubbled air or oxygen through a mixture of manganous hydroxide and sodium hydroxide. This gave intermediate products of uncertain identity, which were converted to birnessite on prolonged oxidation. Buser *et al.* (1954) also prepared birnessite by combining a solution of manganous chloride in 2*N* acetic acid with an aqueous solution of potassium permanganate. The two solutions were heated to 60°C and poured together into a beaker. The product was a series of birnessites containing 0.08–0.25 % K. The first of these three methods was adopted without change for the work reported here, and the second was modified by the substitution of potassium hydroxide for sodium hydroxide, which led to a more rapid oxidation to birnessite without the formation of intermediate products. A slightly modified version of the third method, discussed later, gave cryptomelane. The details of the methods used were:

1. Two moles of concentrated hydrochloric acid was added dropwise to a boiling solution of one mole of potassium permanganate in 2.5 litres of water, with vigorous stirring. After boiling for a further ten minutes, the precipitate was filtered and washed. This gave a brown birnessite with a potassium content of 9.5 % K, and a surface area of 32 m²/g.

2. A mixture of 0.4 moles of manganous sulphate and 5.5 moles of potassium hydroxide in two litres of water was cooled to 5°C and oxidized by bubbling oxygen for 5 hours. This produced a black birnessite containing 9.0 % K, with a surface area of 75 m²/g. A more dilute suspension at room temperature gave a product with lower potassium content.

Cryptomelane (α -MnO₂) is a naturally occurring manganese dioxide, containing potassium as an essential constituent. The potassium content is variable, but never exceeds the amount required to fill approximately 50 % of the potassium sites in the lattice. Laboratory preparations are often called α -MnO₂, a name that is extended to include the isostructural minerals hollandite and coronadite.

Most of the methods of synthesis involve the preparation of birnessite and conversion to cryptomelane by heat or hydrothermal treatment. Neither of the two birnessites prepared during the present work could be converted to cryptomelane by boiling, but that prepared from HCl and KMnO₄ was converted to a well-crystallized cryptomelane by ignition as described below. The pH of a 1:200 suspension of the latter material increased sharply after ignition, and some of the potassium could then be removed by washing with water. Prior to ignition, only negligible amounts of potassium could be removed with water, but it could be completely removed by prolonged treatment with a solution of manganous sulphate or dilute acid.

The series of birnessites with low potassium contents prepared by Buser *et al.* (1954) as previously described were converted to γ -MnO₂ on boiling. The same authors prepared another series of birnessites containing 3.8–6.2 % K from HCl and KMnO₄ and these were converted to cryptomelane on boiling. However, if most of the potassium was replaced by manganese, by leaching with a manganous salt solution, the birnessites were then converted to γ -MnO₂. During the present work the action of manganous sulphate in acetic acid on potassium permanganate, as described below, gave a direct preparation of cryptomelane. The two methods used for the preparation of cryptomelane are:

1. A birnessite was prepared by the dropwise addition of HCl to KMnO_4 as previously described. This was washed, dried, and ignited at 400°C for 60 hours, and again washed with water. This gave a cryptomelane containing 7.2 % K, with a surface area of $58\text{ m}^2/\text{g}$.

2. A solution of 0.35 moles of KMnO_4 in 800 ml of water was heated to 60°C and poured into a solution of 0.5 moles of MnSO_4 in one litre of 2*N* acetic acid. The mixture was heated to 80°C and stirred for five minutes. The result was a fine-grained cryptomelane containing 2.2 % K, with a surface area of $222\text{ m}^2/\text{g}$.

A further study of this recrystallization was carried out on two samples of birnessite prepared by different methods. Sample A was prepared by the addition of concentrated hydrochloric acid to a boiling solution of potassium permanganate, and contained 9.4 % K. This sample was unchanged by boiling for 24 hours, but was converted to cryptomelane by ignition at 400°C for 60 hours. Washing the ignited cryptomelane with water reduced the potassium content to 7.0 %. When the potassium content of the original birnessite was reduced to 5.1 % by washing with dilute hydrochloric acid, it was converted to cryptomelane on boiling. Sample B, prepared by bubbling oxygen through a suspension of manganous hydroxide in a solution of potassium hydroxide, gave similar results, except that in this case a pure cryptomelane was not obtained, showing that this preparation was more difficult to convert to cryptomelane. Ignition gave cryptomelane (major) + birnessite, and acid washing to a potassium content of 4.5 % followed by boiling gave birnessite (major) + cryptomelane.

The results of Buser *et al.* (1954), as previously discussed, show the influence of low potassium contents on the recrystallization of birnessite, and the present experiments show that there is also an *upper* limit to the potassium content at which cryptomelane is obtained by boiling. At 9.4 % K, this conversion is only accomplished by ignition, and the excess potassium is expelled as KOH, which may then be removed by washing with water. When some of the potassium is removed from the original material, the conversion is readily accomplished by boiling. These results are in accordance with the discussion of the structure given by Byström and Byström (1950), who state that the presence of some large cations is necessary to prevent the structure from collapsing. They give the general formula as $\text{K}_{2-y}\text{Mn}_{8-z}\text{O}_{16}$, in which O may be replaced by OH, and Mn by lower-valence ions. y is always approximately unity, so that the two K positions per unit cell are only half filled. The short K–K distance of 2.8 \AA would make the structure unstable, due to repulsive forces between the cations, if all of the K sites were filled. Taking $y = 1$, and neglecting z , which is always small, the above formula gives a potassium content of 5.3 % K. The results of the present work, and those of Buser *et al.* (1954) show that the upper limit for potassium in cryptomelane is about 7 % K, while the lower limit lies between 0.25 % and 2.2 % K.

The difference in the ease with which the two birnessites may be converted to cryptomelane is probably due to the difference in crystal form, as shown by the electron micrographs in fig. 1. The untreated sample A consists of clumps of fine needles which on acid washing and boiling recrystallize to larger needles of cryptomelane. The untreated sample B consists of platy crystals of irregular shape, which are only partly converted to cryptomelane by acid washing and boiling. The difference in crystal form of the birnessites is not shown by the sharpness or number of lines in the X-ray

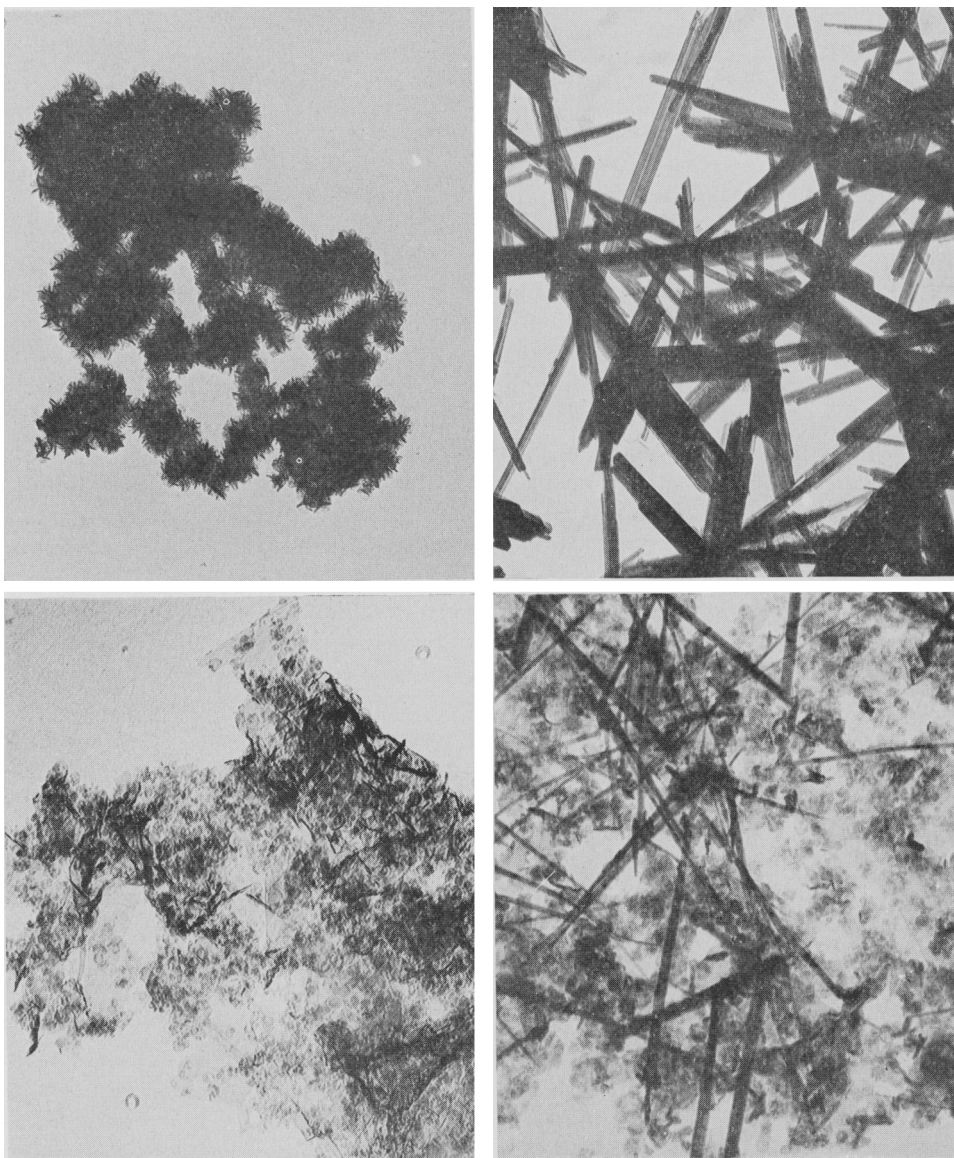


FIG. 1. Conversion of birnessite to cryptomelane. *a*, top left: sample A untreated—birnessite. *b*, top right: sample A after acid washing and boiling—cryptomelane. *c*, bottom left: sample B untreated—birnessite. *d*, bottom right: sample B after acid washing and boiling—birnessite + cryptomelane. All $\times 37\ 500$.

diffraction patterns, which are identical. A possible reason for the difference in crystal form is that, whereas sample A was precipitated from solution, sample B was prepared by oxidation of $\text{Mn}(\text{OH})_2$, which has a layer structure. Oxidation of this structure could lead to a product in a crystal form pseudomorphous with the original material. This type of pseudomorphism is common among the manganese minerals.

The exchange properties of potassium in the birnessites and cryptomelanes are also of interest. These were investigated by shaking 0.1 g samples of the oxides with 20 ml of 0.1 molar CuCl_2 solution for varying periods, and measuring the amounts of copper taken up by the mineral and potassium released into solution (McKenzie, 1970). In a sample of birnessite similar to B, the potassium content was reduced from 8.7% to 0.5% K by exchange with copper, and in a sample similar to A, the potassium content was reduced from 9.5% to 0.5% K. However, when the latter sample was converted to cryptomelane by ignition, the potassium content was only reduced to 4.4% K by exchange with copper. The cryptomelane prepared by the action of potassium permanganate on manganous sulphate in acetic acid contained 2.2% K. After shaking in CuCl_2 solution for 12 weeks, measurement of the amount of potassium showed that the mineral still contained 2.15% K. However, in this case there was a rapid release of potassium on the first day, much of which was then slowly reabsorbed (McKenzie, 1970). This is interpreted as a rapid release of potassium from the exchange sites, and its slow absorption into vacant potassium sites in the crystal lattice. From this it may be concluded that during the conversion of birnessite to cryptomelane there is a migration of some of the potassium from exchange sites to crystal lattice sites, where it is no longer exchangeable. In addition, there is a loss of some potassium where the original content of the birnessite was greater than about 7%. Where the potassium content of the cryptomelane is low, as in the sample discussed above, there is a strong tendency to take up potassium from solution.

Pure *pyrolusite* ($\beta\text{-MnO}_2$) is readily prepared by gentle ignition of manganous nitrate. Moore, Ellis, and Selwood (1950) described a number of methods, differing slightly in detail, all of which produced pyrolusite. The method used in the present work was essentially the same as those described.

A solution of manganous nitrate was evaporated nearly to dryness and heated in a muffle furnace at 180°C for 48 hours. The product was ground, washed with water, and heated for a further 24 hours. This produced a pyrolusite containing the stoichiometric proportion of oxygen, with a surface area of 3 m²/g.

Cole, Wadsley, and Walkley (1947) produced manganese dioxides by hydrolysis of MnCl_4 . They found that when the MnCl_4 was prepared from a mixture of $\gamma\text{-MnO}_2$ and cryptomelane, the hydrolysis product was $\gamma\text{-MnO}_2$, but when the starting material was pure artificial pyrolusite, the product was pyrolusite. This method was reproduced satisfactorily in the following manner.

50 g of MnO_2 was added a little at a time to 800 ml of concentrated hydrochloric acid at 8°C, with vigorous stirring. The mixture was allowed to stand for 15 minutes with occasional stirring, and then filtered through a sintered glass filter into 5 litres of water. The resulting precipitate was filtered, washed, and dried. This method gave a fine-grained pyrolusite when

the starting material was a pure artificial pyrolusite. However, when the preparation was repeated using as starting material a laboratory reagent MnO_2 , which was a birnessite containing 9% K, the product was identified as $\rho\text{-MnO}_2$ (A.S.T.M. card No. 12-714). The product contained 0.1% K, and had a surface area of 178 m^2/g .

$\rho\text{-MnO}_2$ is a synthetic oxide identical with one of the varieties of nsutite (Zwicker *et al.* 1962) and thus belongs to the $\gamma\text{-MnO}_2$ group of oxides. Cole *et al.* did not comment on the different products obtained from different starting materials, but it is evident, from their work and that reported here, that the product depends on the potassium content of the starting material. Pyrolusite is produced when potassium is absent, and $\gamma\text{-MnO}_2$ when potassium is present.

Todorokite. Wadsley (1950) prepared an oxide of approximate formula $(\text{Na, Mn})\text{Mn}_3\text{O}_7 \cdot n\text{H}_2\text{O}$ by passing oxygen through a mixture of one mole of manganous nitrate and 14 moles of sodium hydroxide in 4.5 litres of water. The product contained 3.9% Na, which was completely exchangeable by a number of other ions. Attempts to reproduce this procedure at room temperature (20 °C) during the present work gave only hausmannite, but at 10 °C a product containing 6.0% Na was formed, and at 5 °C the sodium content of the product was 9.1% Na. A product similar to the latter could also be prepared at room temperature if the reaction mixture was diluted threefold. The X-ray diffraction patterns of these three products were similar, but differed from that obtained by Wadsley. This material was the starting-point for the preparation of todorokite, for which no previous synthesis has been reported.

A mixture of one mole of manganous sulphate and 14 moles of sodium hydroxide in 4.5 litres of water was cooled to 5 °C and oxidized by bubbling oxygen for 5 hours. The product was washed with water and shaken for 24 hours with a 10% solution of copper, cobalt, or nickel chloride. The sodium was completely replaced, and the products had X-ray diffraction patterns identical to that of todorokite.

X-ray data for the sodium manganese oxide is shown in table I, and analyses of the four products in table II. The copper, cobalt, and nickel contents of these

TABLE I. X-ray data for the sodium manganese oxide used for the preparation of todorokite

<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>
7.12 Å	vvs	2.42 Å	s	1.81 Å	m	1.47 Å	m
4.61	m	2.32	vw	1.63	w	1.44	m
3.56	vs	2.21	w-m	1.55	vw	1.42	w-m
2.70	w	2.14	m-s	1.52	vw	1.39	w-m
2.52	m-s	1.86	w-m				

samples are far greater than those in any of the todorokites previously described, and these elements are not essential constituents of the naturally occurring mineral. The samples prepared here should therefore be regarded as analogues of todorokite.

TABLE II. Analysis of sodium manganese oxide and the todorokites prepared from it. Analyses on oven-dried (105 °C) material

	1	2	3	4
MnO ₂	67.4	62.4	62.8	62.2
MnO	12.7	7.0	7.4	12.4
Na ₂ O	12.2	0.018	0.018	0.022
CuO	—	19.3	—	—
CoO	—	—	18.3	—
NiO	—	—	—	11.3
H ₂ O (> 105 °C)	7.5	10.8	10.9	13.6
Total	99.8	99.5	99.4	99.5

1. Na-Mn oxide. 2, 3, and 4. Cu, Co, and Ni analogues of todorokite.

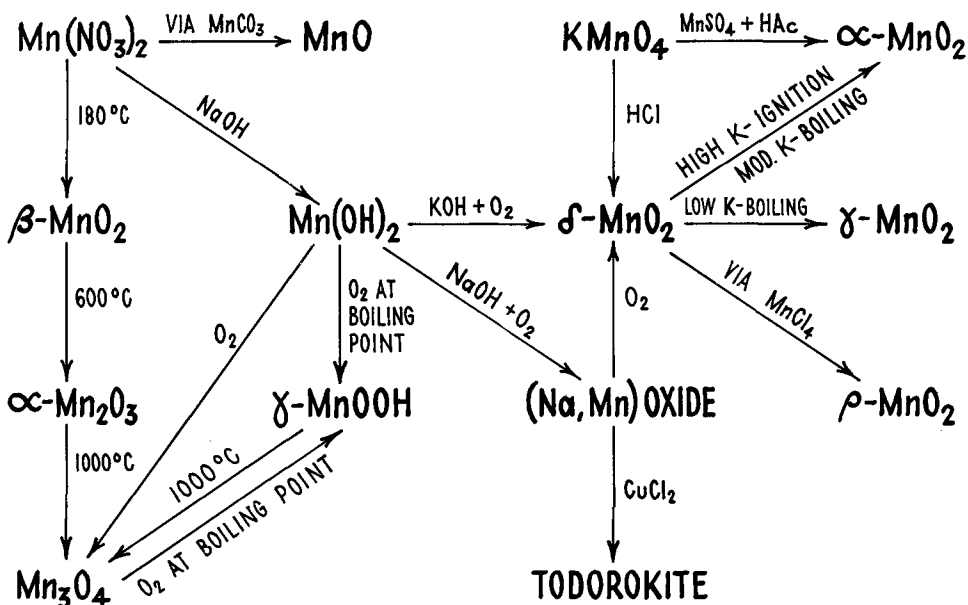


FIG. 2. Relationships between the various synthetic oxides of manganese.

Conclusions

The methods of preparation of the various oxides, and the discussion of the published methods, show the importance of such factors as temperature, pH, purity of the reagents used, the presence of other ions, and the order in which reagents are added, as well as the more obvious factors such as type of oxidizing or reducing agents. Bricker (1965) has also discussed the influence of rate of oxidation of Mn(OH)₂.

The relationships between the various synthetic oxides, and methods for their preparation are summarized in fig. 2. This diagram is somewhat idealized in that

the conversion of ignited hausmannite to manganite, although theoretically possible, would be extremely slow, and the conversion to cryptomelane of a birnessite prepared using NaOH would be possible only if the sodium in the birnessite were replaced by potassium.

In the scheme shown for the synthetic oxides, the pathway from the lower to the higher oxides is by the oxidation of $\text{Mn}(\text{OH})_2$ under strongly alkaline conditions. These conditions rarely occur in nature, yet the lower oxides have not been found in soils. It is probable that under natural conditions the oxidation is by bacterial action, or by the disproportionation of hausmannite and manganite. The fact that birnessite is common in soils, but cryptomelane (or its barium analogue, hollandite) and $\gamma\text{-MnO}_2$ are rare (Taylor, McKenzie, and Norrish, 1964), is explained by the high concentration of foreign ions in the birnessites in soils. The same explanation would account for the absence of pyrolusite in soils, as this is apparently only formed from fairly pure oxides.

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