

STABILITY AND INTERCONVERTIBILITY OF PHASES
IN THE SYSTEM Mn-O-OH*CYRUS KLINGSBERG† AND RUSTUM ROY, *The Pennsylvania State University, University Park, Pennsylvania*

ABSTRACT

Equilibrium and non-equilibrium reactions in the system Mn-O-OH have been studied under high water pressures and with varying oxygen pressures. Reproducible syntheses of well crystallized pyrochroite ($\text{Mn}(\text{OH})_2$) and manganite ($\text{MnO}(\text{OH})$) are described. The univariant p-t curves for the reactions $\text{Mn}(\text{OH})_2 \rightleftharpoons \text{MnO} + \text{H}_2\text{O}$ and $2\text{MnOOH} = \text{Mn}_2\text{O}_3 + \text{H}_2\text{O}$ have been determined. At 15,000 psi they pass through points at 392° C. and 272° C. respectively and are very steep in the range 3000 to 25,000 psi H_2O pressure. The isomorphous minerals, groutite and ramsdellite, have been shown to be interconvertible by low temperature oxidation or reduction. A phase intermediate in composition between these two and presumably of the same structure has been synthesized. Hydrohausmannite is shown to be unstable above 100° C. No evidence was obtained for partial entry of protons into either pyrolusite or ramsdellite to give solid solutions towards the MnOOH composition.

INTRODUCTION

Much descriptive work on the oxides and hydrous oxides of manganese may be found in the literature. However, fewer equilibrium data exist for these oxides, hydroxides, and oxyhydroxides than for many less common minerals. The main reason for this is the fact that in many of the important dehydration reactions, the manganese minerals would not only lose water but would also lose or gain oxygen.

Thus, to study a pure dehydration reaction it is necessary to be able to control the partial pressure of oxygen so that the manganese does not change valence during the reaction. To be able to do this, however, one has to be able to maintain a wide range of pressures of oxygen, hydrogen, and water vapor at high temperatures. Since it has recently become possible to do this an attempt was made to study such reactions. There are four main hydrated oxides of manganese: pyrochroite $\text{Mn}(\text{OH})_2$, manganite and groutite MnOOH , and hydrohausmannite $\text{Mn}_3\text{O}_4 \cdot \text{H}_2\text{O}$. In addition, there is the possibility that the poorly formed manganese dioxides of considerable importance in the battery industry may contain essential hydroxyl in a solid solution of the type $\text{Mn}_{(1-n)}^{4+}\text{Mn}_n^{3+}\text{O}_{2-n}(\text{OH})_n$.

As a preliminary study for this work it was necessary to know the equilibrium $p\text{O}_2$ -T curves for the interconversions of the anhydrous oxides of manganese. The literature data for the equilibrium reactions of the

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lower valence oxides is thought to be good but the data for the $\text{MnO}_2 = \text{Mn}_2\text{O}_3 + \frac{1}{2}\text{O}_2$ and $\text{Mn}_2\text{O}_3 = \text{Mn}_3\text{O}_4 + \frac{1}{2}\text{O}_2$ curves left much to be desired. These reactions have been re-studied and our results on the anhydrous system are reported elsewhere (Klingsberg and Roy, 1959).

It is not possible to review the literature on the manganese oxides adequately in a short space. Hence for definitions of terms, methods of preparation etc. the reader is referred to excellent reviews by Cole, Wadsley and Walkley (1947), Wadsley and Walkley (1951), and McMurdie and Golovato (1948).

APPARATUS

Familiar hydrothermal techniques were used throughout this investigation. Morey bombs were used only when large amounts of material (i.e., about 5–10 grams) had to be synthesized. For example, MnO and $\text{Mn}(\text{OH})_2$ for use as starting materials were prepared in this way. The primary high pressure vessel, however, was the test tube bomb of eight inches in length, one inch outside diameter, one-fourth inch inside diameter, with an internal volume of about seven milliliters. Gold or platinum foil was folded into tiny envelopes to serve as sample holders. "De-ionized" water was supplied to these bombs through stainless steel tubing by means of an air-operated pump.

Temperatures were maintained in base metal resistance wound furnaces by various commercial electronic controllers and were measured by chromel-alumel thermocouples placed in wells in the bombs.

What is believed to be an innovation in hydrothermal research is the introduction of oxygen under controlled pressures to a bomb for the purpose of influencing the oxidation state of the cation under examination. For this purpose, commercially purchased tank oxygen was delivered to the vessels by a separate line and kept separate from the water line by means of appropriate valves.

Calibrated gauges, designed to operate between 0–80 psi, 0–500 psi, 0–3000 psi, 0–30,000 psi, and 0–80,000 psi of total pressure, were used interchangeably so that whatever the pressure in a particular run might be, a gauge could be used that would operate at optimum accuracy for that pressure.

STARTING MATERIALS

In the course of this investigation 15 different starting materials were used. Before its use, each was ground to a fine powder. Some were naturally occurring crystalline minerals but most were synthetically prepared compounds, crystalline or sub-crystalline. The purity of the synthetic starting materials was examined by *x*-ray fluorescence analysis. All had much less than 0.1% iron.

Naturally occurring minerals:

- | | |
|---------------------|--|
| 1. Hydrohausmannite | Langban, Sweden (kindly supplied by Professor C. Fron-
del of Harvard University) |
| 2. Manganite | Ilfeld, Harz, Germany (No. 258 Genth Collection of the
Pennsylvania State University) |
| 3. Groutite | 1. Sagamore Mine, Minnesota (kindly supplied by Pro-
fessor J. W. Gruner of the University of Minnesota)
2.* Marquette, Mich. (Genth Collection, Pennsylvania
State University) |
| 4. Ramsdellite | Chisholm, Minnesota (obtained from Dr. R. I. Harker) |

Synthetic crystalline compounds:

- | | |
|-----------------------------------|--|
| 1. Manganese metal | Fisher Scientific Co. analyzed for Fe content 0.1% |
| 2. MnO | Prepared hydrothermally in a silver lined Morey bomb
from manganese metal (480° C. and 15,000 psi water
pressure for two days) |
| 3. Mn(OH) ₂ | Prepared hydrothermally in a silver lined Morey bomb
(350° C. and 15,000 psi water pressure for two days) |
| 4. Mn ₂ O ₃ | Mn(HO ₃) ₂ · 6H ₂ O heated in air for eight hours at 700° C. |
| 5. β-MnO ₂ | Baker Chemical Co. |

Synthetic sub-crystalline com-
pounds:

- | | |
|---------------------------|---|
| 1. MnO ₂ | Will Corporation |
| 2. Delta-MnO ₂ | Reduction of boiling KMnO ₄ solution with HCl (Mc-
Murdie, 1944) |
| 3. Gamma-MnO ₂ | Kindly supplied by Dr. S. B. Levin of the U. S. Army
Signal Corps Engineering Laboratories |
| 4. Rho-MnO ₂ | Same as above |
| 5. MnOOH | Precipitated from a solution of MnSO ₄ and NaOH (Part-
ington, 1949) |

Identification of the Phases

Phases were identified almost entirely by use of a Phillips Norelco Hi-Angle diffractometer employing CuK α radiation with a nickel filter. Most phases could be positively identified from their x-ray patterns in the region 17° to 44° 2 θ .

Use of the petrographic microscope was restricted to the less common occasions when crystal size of the specimen was sufficient to permit identification of the phase. Another limitation of the microscope is the fact that manganese in its higher oxidation states forms opaque compounds.

EXPERIMENTAL PROCEDURE

A. General Statement

By now a general familiarity with the techniques of hydrothermal synthesis is probably widespread, but some description of the slightly more complicated technique of adding

* This sample was labelled manganite and represents an addition to the relatively few localities recorded for groutite.

oxygen gas to water vapor, as a means of further controlling the environment of a sample seems to be in order. When water or oxygen is used individually, it is pumped into a bomb through suitable valves before a run begins. Sealing the bomb is effected by closing these same valves. The bomb is then placed in a furnace and when after about thirty minutes it reaches its desired temperature an adjustment is usually necessary to raise or lower the pressure to its proper value. For this operation the valve need be opened only momentarily.

B. Runs Using One Gas

Certain data were obtained by the introduction of water alone. For example, the reaction manganosite-pyrochroite was studied as a function of water pressure and temperature.

Other data were obtained by the use of oxygen alone as the gaseous phase. The reaction pyrolusite-bixbyite was thus studied as a function of oxygen pressure and temperature. The data determined through the heating of various materials in air are similarly examples of runs using just one gas.

C. Runs Using Two Gases

In this case both water vapor and oxygen are used. Either may be present as a trace or in an appreciable amount as long as the gas of lower pressure is introduced to the bomb first. Where oxygen was admitted first, there was no experimental difficulty. Introducing a trace of water vapor was not possible since it was "liquid" water that was pumped through the tubing connected to the bomb. For those runs described as having a trace of water present, the procedure involved putting three drops of water in a bomb just after the samples were put in (if this order is reversed, the sample envelopes may stick to the wet walls of the bomb at varying heights). The bomb was then sealed to the system and oxygen admitted. This amount of water was experimentally found to influence the total pressure in a run by only a fraction of an atmosphere after the bomb had been raised above 100° C.

D. An Important Experimental Difficulty: Failure of Gases to Mix

In the early part of this work it was hoped that it would be possible to study the reactions of interest under any chosen condition of the partial p_{O_2} and total pressure. Thus, one could hope to study the influence of *total* pressures on a particular p_{O_2} -T point on a curve. It was gradually realized that some factor was complicating the work with two gases present.

Early work in this laboratory indicated strongly that under moderate pressure and even at temperatures of 500°–1000° C., two gases such as O_2 and H_2O or CO_2 and N_2 , do not mix effectively in the test tube bombs which have been described. Harker (1958) has recently established this observation with detailed work.

For very low pressures (*i.e.*, those that are described as containing a "trace" of water), the chance for mixing is much greater, whereas when both gases are at pressures of even a few hundred atmospheres, the mean free path of the molecules is so reduced that mixing by diffusion is a very slow process. This result, which was intuitively quite unexpected, had far reaching results:

1. It made it impossible to work quantitatively with two gases. This does not detract from the work done, *e.g.*, on the manganite-bixbyite univariant curve in which, by trial and error, a proper ratio of oxygen pressure and water pressure was found to hold all solid phases in the desired oxidation state.

2. It made it necessary to be quite circumspect with regard to the types of starting materials run together in a bomb. Thus the combined use of hydrous and anhydrous starting materials might result in the liberation of water vapor in the immediate area. Even in a run of high p_{O_2} , if the liberated water vapor stays exclusively at the bottom of

the bomb, the actual pO_2 around the samples would be quite different from the gauge reading.

E. The Importance of Heating and Quenching Procedures

A run is said to begin when the bomb, and therefore the sample within it, reaches the desired pressure and temperature for that run. It takes as long as 30 minutes in some cases to reach this point and during this time some or all of the starting materials may convert to another form. If this happens, the sample under study when the run "begins" is not the same as the sample that was originally put into the bomb. A change of this sort, if undetected by the investigator can lead to serious errors in interpretation of the run. Thus, A is put into a bomb. While the bomb is heating to its terminal temperature, A converts to B. The run lasts two days at a given pressure and temperature during which time B converts to C. An unwary investigator will report that for the given pressure and temperature, $A \rightarrow C$. Or, if B persists for two days, the result might be given as $A \rightarrow B$ whereas this reaction may have taken place at a lower pressure and at hundreds of degrees lower temperature, with subsequent persistence of B.

For much of hydrothermal work (or dry synthesis, for that matter), the heating and quenching paths used are of little consequence. However, this is not always the case, and it was found during the course of this work that caution on this account was needed particularly in two cases:

First, it was found that in attempting to study one equilibrium curve it was sometimes necessary to cross another curve that was not under study. In such cases, a starting material might change before the run actually "began." This problem was examined by taking several starting materials up to the P-T condition of a run by different paths and immediately quenching the samples. In most cases, the starting materials had begun to alter before the run "began."

Second, there is the possibility of altering a product during the quenching of a run. This can only be a problem if the product can react with great speed. Considerations of this nature were important during the development of the equilibrium curve for the reaction: $Mn(OH)_2 = MnO + H_2O$. The speed of this reaction in either direction (at elevated pressures and temperatures) is such that the results of a run are completely unintelligible unless the quenching procedure employed is known for that run.

F. The Control of the Oxidation State of Manganese

Oxygen was admitted to a bomb under known and reproducible pressures for one of two reasons:

1. For reactions such as $4MnOOH + O_2 = 4MnO_2 + 2H_2O$, oxygen was used to make it possible to study the reaction as a function of oxygen pressure and temperature.
2. For the reaction $Mn_2O_3 \cdot H_2O = Mn_2O_3 + H_2O$, there is no change of oxidation number for the manganese, and a necessary pressure of oxygen was admitted to the bomb to maintain the trivalent state during the course of the run.

Manganese metal was used as a starting material to create reducing conditions by reacting with the water in a bomb. For the pyrochroite-manganosite curve, starting materials as well as products would have oxidized to Mn_3O_4 but for the presence of the hydrogen released from the reduction of water by the manganese metal. Also, there is the advantage that the use of manganese metal introduces no cation foreign to the Mn-O-OH system.

G. Accuracy of the Data

Temperatures were measured to an accuracy of $\pm 1^\circ C$. but since the furnaces were controlled only to $\pm 5^\circ C$. over long periods this figure more properly reflects the accuracy

of the data. However, in determining an equilibrium curve, the accuracy may be increased somewhat by the multiplicity of points measured along the curve.

Uncalibrated chromel-alumel thermocouples were used throughout this investigation but they were replaced frequently. Due to frequent changing of gauges, pressures are taken as accurate to $\pm 5\%$ of the gauge reading, although the gauges are in general more accurate than this.

In a future section it will be seen that the tables of data list pressures of oxygen and pressures of water vapor. Unfortunately, for simplicity, accuracy is sacrificed in that these pressures refer to different measurements. No problem arises if only one gas is present in a run, or when water is present only in trace amount. In a run involving the use of two gases, oxygen is admitted to a bomb first since it is always of lower pressure than the water. The oxygen pressure that is recorded is the pressure of the admitted gas at room temperature. This pressure increases during the course of the run as the bomb rises in temperature, but this higher oxygen pressure can no longer be measured accurately since it is now part of the total pressure of which the water vapor has the far greater share. This increase in oxygen pressure has been examined experimentally, and it is a very small fraction of the introduced pressure due to the fact that only a portion of the gas in the system is heated. The gas in the gauge and tubing remains at room temperature during the course of a run, and it is only that portion of oxygen that is in the bomb that is heated.

H. Interpretation of the Data

Equilibrium is time-independent but the criteria by which it is determined are very much dependent upon the rates of the reactions being studied. The following classification will illustrate this point for the reaction, $X \rightleftharpoons Y$:

1. Both the forward and the reverse rates are such as to permit study of the reaction in each direction. This provides the most rigorous data and is used whenever possible. The manganosite-pyrochroite reaction was studied in this way.

2. At a given pressure and temperature the X structure persists for long periods of time, and at the same pressure but at a few degrees higher temperature, X rapidly inverts to Y, and it is everywhere impossible to make Y go to X. A curve determined according to this principle may or may not reflect stable equilibrium. More than likely it will indicate a series of temperatures that are higher than the equilibrium temperatures by an amount sufficient to overcome any activation energy barrier that may exist for the given reaction. The Manganite-bixbyite reaction was examined partly according to this rule and partly according to the next one.

3. Neither the forward nor the reverse reaction proceed with sufficient speed to be studied in the laboratory. A third compound, Z, must be found which because of its more active state, amorphous structure, hydrous nature, etc., will rapidly form either X or Y. While a reaction of this nature was not encountered in this work, amorphous MnOOH played a comparable role in readily forming either manganite or bixbyite when it was found impossible to hydrate bixbyite.

I. THE SYNTHESIS AND PROPERTIES OF PHASES*

During the course of this work it became possible for the first time, to synthesize reproducibly certain phases. Other naturally occurring

* Since it is reasoned that the diagrams summarize the authors' interpretation of the data and since most journals find it increasingly difficult to publish long tables of data, the data on the runs are omitted. A complete record of the runs may be obtained in the original dissertation by C. Klingsberg (Ph.D. Geochemistry, 1958) from the Library of the Penna. State University or from University Microfilms, Ann Arbor, Mich.

Mn-O-OH minerals still elude synthesis. For some of the hydrous minerals the hydrothermal method offers not only an alternative method of preparation, but a far better way of preparing compounds of unmatched purity and crystallinity. This is particularly true for pyrochroite and manganite.

A. Pyrochroite

A simple, effective preparation was found. This material can be synthesized hydrothermally, for example, from powdered manganese metal at 360° C. and 2000 psi. of water pressure. In quenching, the temperature must be lowered while the pressure is maintained. The hydrogen generated keeps all the manganese divalent.

The compound prepared in this way appears as a white powder consisting of microscopic hexagonal euhedral crystals and gives a very sharp *x*-ray pattern. Upon standing in air for a few days it turns dark brown but shows no change in *x*-ray pattern. This change in color is supposedly due to the partial oxidation of divalent to trivalent manganese with a concomitant substitution of oxygen ions for hydroxyls to preserve electrical neutrality. The *x*-ray pattern for this material is given in Table 1.

The air oxidation of Mn(OH)₂ is a reaction well known to chemists. In contact with aqueous solution it is a reaction that is difficult to prevent (Partington, 1949). If special precautions are observed it is possible to keep (Mn(OH)₂) reduced and white indefinitely. One of the samples of Mn(OH)₂ that resulted from the examination of the pyrochroite-manganosite reaction was washed with a copious amount of alcohol and dried rapidly. This prevented it from turning brown on standing. The sample was divided into two parts, one of which was left in air, while the other was placed in a desiccator. The sample exposed to air was dark brown in two weeks. The portion in the desiccator is still white after a year.

B. Manganite

While there are reports in the literature about the synthesis of manganite (Feitknecht and Marti, 1945, Moore et al. 1950), they all involve some measure of doubt as to the identification of the actual product. Hydrothermally, manganite is easily and reproducibly synthesized, for example, from Mn(OH)₂ or MnOOH at 225° C. under 10 psi. O₂ and 15,000 psi H₂O pressures.

C. Attempted Synthesis of Groutite and Ramsdellite

The attempted syntheses of groutite has been unsuccessful. This

TABLE 1, X-RAY DIFFRACTION DATA

Pyrochroite (synthetic)		Hausmannite (synthetic)	
<i>d</i>	I/I.	<i>d</i>	I/I.
4.726	100	3.087	45
		2.879	19
2.870	18	2.768	73
2.453	40	2.486	100
2.361	6	2.366	27
1.825	26	2.037	38
1.658	6	1.797	19
1.567	4	1.706	12
1.381	8	1.575	38
		1.544	38
1.346	3	1.441	24
1.180	3		
"Groutellite" (Synthetic—this work)			
<i>d</i>	I/I.	<i>hkl</i>	
4.219	100	110	
2.633	60	130	
2.380	40	040	

means that groutite and ramsdellite are the only phases in the Mn-O-OH system for which no synthesis has been reported.

Since groutite is not common in nature, the ability to synthesize it would provide mineralogists with an abundant supply so that its characterization might be more easily pursued. Also, if it could be synthesized hydrothermally, some indication of natural origin might result. This is equally true for ramsdellite, and since the reversibility of the groutite-ramsdellite reaction has been demonstrated, the synthesis of either mineral would in effect involve the synthesis of both.

Unfortunately, the above mentioned advantages were not realized, despite repeated efforts to determine the necessary conditions of synthesis. It is likely that these phases are everywhere metastable in which case a systematic attempt at synthesis might fail where an "accidental" preparation might succeed.

Since γ -MnO₂ has been described as a poorly crystalline ramsdellite it was a likely starting material for the synthesis of ramsdellite (many other compounds were used as well). However, under a wide variety of temperature and pressures of water and oxygen, γ -MnO₂ either remained unchanged or converted to pyrolusite.

D. Ramsdellite-Groutellite-Groutite

The reduction of ramsdellite to groutite involves no change in structure types since these minerals both have the diaspore structure. What is involved is merely the addition of a proton to an O^- and an electron to a Mn^{4+} . It has been pointed out (H. Kedesdy, personal communication) that what is required structurally is merely a slight angular twist between the oxygen octahedra. The absence of solid solution between these phases is demonstrated by the absence of variations in *d* interplanar spacings. This means that there is no gradual rotation but rather a "displacive" change of a fixed amount in the oxygen positions when the protons are added. However, the change does not take place in one step. An intermediate compound was found to form (tentatively named groutellite*) whose unit cell is undoubtedly related to those of ramsdellite and groutite:

	<i>a</i>	<i>b</i>	<i>c</i>
Ramsdellite	4.52 Å	9.27 Å	2.87 Å
Groutellite	4.71	9.52	—
Groutite	4.56	10.00	3.03

It is very likely that groutellite represents an ordered structure as the hydroxyls only partly replace oxygen ions in some statistical manner during the reduction of ramsdellite to groutite. Its powder pattern is given in Table 1. Groutellite was not observed to form during the reverse reaction, *i.e.*, oxidation of groutite to ramsdellite.

E. Table of X-Ray Data

Since *x*-ray diffraction was used as the primary tool for identification it was essential to have accurate powder data for all the phases in the system. A complete list of powder data for these phases is in the original publication (Klingsberg, 1958). In most cases† the diffractometer data for the minerals agree with one or another of the many sources of such data. However, revised data are necessary for the following synthetic phases: pyrochroite, hausmannite, and two new phases. These data are given in Table 1.

* While this phase is strictly not a mineral, there seems to be no advantage in representing it by a chemical formula which would not indicate its genetic relationship to groutite, rather than a name.

† Pyrochroite natural, manganosite synthetic, bixbyite synthetic and natural, manganite synthetic and natural, groutite natural, pyrolusite synthetic and natural, ramsdellite natural.

The following compounds were either not examined at all or not in sufficient detail to report on:

Manganosite natural, hausmannite natural, pyrochroite natural, α - $MnOOH$, β - $MnOOH$, manganous manganite, cryptomelane, δ - MnO_2 , γ - MnO_2 , ρ - MnO_2 .

II. EQUILIBRIUM REACTIONS

A. The Pyrochroite-Manganosite Reaction

It was discovered in the course of studying the reaction, $\text{Mn}(\text{OH})_2 = \text{MnO} + \text{H}_2\text{O}$, that either phase is so readily convertible to the other that a partial conversion will take place if the equilibrium curve is crossed during the quenching of a run. A point on the $\text{Mn}(\text{OH})_2$ side of the curve can best be determined by a P-T heat (pressure is applied before heating) and a T-P quench (*i.e.*, temperature is quenched first and then the pressure is released). In this way the starting materials never enter the field of MnO and should therefore show no trace of manganosite after the run. Figure 1 is drawn from these data.

On the MnO side of the curve a point is best determined by P-T quench (pressure is reduced to 1 atm. after which the temperature is quickly quenched). The heating curve was not important in this case since the equilibrium curve had to be crossed to get to the MnO field, and it did not matter when or how it was crossed. These runs should show no trace of pyrochroite.

Before the runs can be interpreted in this way, it must first be determined how much time is required for the starting materials to react completely, *i.e.*, to achieve equilibrium at the given pressure and temperature of the point under study.

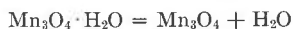
B. The Manganite-Bixbyite Reaction

For the reaction, $2\text{MnOOH} = \text{Mn}_2\text{O}_3 + \text{H}_2\text{O}$, no oxidation or reduction is desired during the course of a run. Therefore just enough oxygen was admitted to each run (about 15 psi) to keep the manganese in the trivalent state. Frequently there were inadvertent changes in oxidation state.

It was found that manganite could be dehydrated but that bixbyite could not be hydrated. Their structures are completely different, and the reaction involves a major crystalline rearrangement rather than the removal of a loosely held water molecule. Some care had to be exercised that manganite was not dehydrated during the quenching of a run. The starting material of greatest use was amorphous MnOOH which crystallized either as manganite or bixbyite with great ease. Figure 2 is drawn on the basis of the data obtained and tabulated in the original publication.

C. The Hydrohausmannite-Hausmannite Reaction

An attempt to study the reaction,



under equilibrium conditions was unsuccessful due to the fact that only the dehydration reaction could be made to take place. Repeated attempts to synthesize hydrohausmannite hydrothermally were not successful. This

result was not expected in light of the fact that its synthesis has already been reported by wet-chemical techniques at room temperature (Feitknecht, and Marti, 1945).

Since this is known to be a low temperature mineral, only temperatures up to 400° C. were tried under varying conditions of low and high water pressures and low and high oxygen pressures. The starting materials used

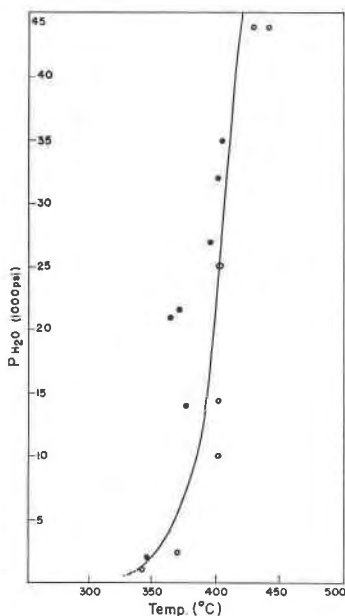


FIG. 1. The pyrochroite-manganosite reaction.

Mn(OH)_2 ●; MnO ○

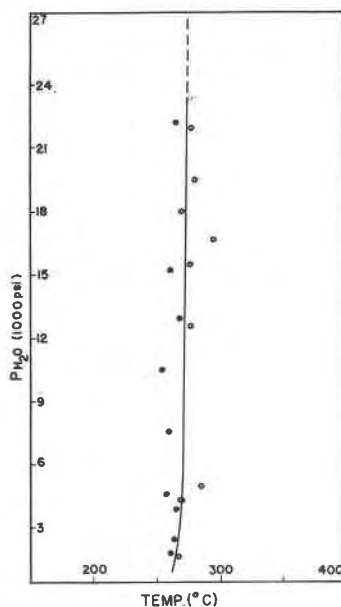


FIG. 2. The manganite-bixbyite reaction.

$\text{Mn}_2\text{O}_3 \cdot \text{H}_2\text{O}$ ●; Mn_2O_3 ○

were MnO , Mn(OH)_2 , and MnOOH . Hausmannite, manganite, and pyrolusite were produced depending upon the conditions of the run.

Apparently the hydrohausmannite structure is not stable even at the lowest hydrothermal temperatures, and its maximum stability would appear to be near the boiling point of water. Under 3000 psi of water pressure it will persist at least one day at 78° C. but will convert to hausmannite (and manganite) at 132° C.

III. NON-EQUILIBRIUM REACTIONS

A. Manganite-Pyrolusite Interconvertibility

The manganite-pyrolusite reaction was not studied under conditions of equilibrium. However, interconvertibility between these two minerals was realized.

The existence of at least partial solid solution between these compounds was considered a distinct possibility, since pyrolusite often occurs in nature as a pseudomorph after manganite. Samples of manganite partly oxidized to pyrolusite, as well as partly reduced pyrolusite, were examined by x -radiation for a shift in d spacing for either the manganite or the pyrolusite. No evidence of a shift was found, and on this basis the "complete" absence of solid solution is reported. Unlike groutite-ramsdellite, there is no intermediate compound between manganite and pyrolusite.

In air, manganite converts to pyrolusite at about 130° C. The following abbreviated table shows the redox conditions under which the manganite-pyrolusite interconvertibility can be observed.

TABLE 2. DATA ON MANGANITE-PYROLUSITE INTERCONVERTIBILITY

Temp. (° C.)	Press. (psi)H ₂ O	Press. (psi)O ₂	Time (days)	Initial Condition	Result
252	2,300	30	1	Manganite MnOOH Mn(OH) ₂	Mang. and β -MnO ₂ Mang. and tr. β -MnO ₂ Mang. and tr. β -MnO ₂
172	14,000	0	2	β -MnO ₂ Mn metal	Mang. and β -MnO ₂ Mn(OH) ₂

B. Groutite-Ramsdellite Interconvertibility

The isostructural relationship between groutite (Mn-OHO) and ramsdellite (orthorhombic MnO₂) was known in 1949 when Collin and Lipscomb (7) and Bystrom (5) determined their structures and showed them to be members of the diaspore-goethite family.

The relationship is perhaps best seen by a comparison of unit cell parameters:

		<i>a</i>	<i>b</i>	<i>c</i>
groutite	Mn O OH	4.56	10.70	2.85
ramsdellite	Mn O O	4.52	9.27	2.87
diaspore	Al O OH	4.40	9.39	2.84
goethite	Fe O OH	4.64	10.00	3.03
montroseite	(V, Fe)O(OH)	4.54	9.97	3.03
paramontroseite	V O O	4.89	9.39	2.93

Hydrothermal reductions were controlled by changes in the duration of runs and by variations in the amount of manganese metal used as a

starting material. The first two following runs differ in that a slightly greater amount of manganese metal was used in the second run:

TABLE 3. DATA ON GROUTITE-RAMSDELLITE INTERCONVERTIBILITY

Temp. (° C.)	Press. (psi)H ₂ O	Added O ₂ (psi)O	Time (days)	Initial Condition	Result
173	13,500	0	2	Ramsdellite Mn Metal	Ramsdellite and Groutellite Mn(OH) ₂
172	15,000	0	2	Ramsdellite Mn metal	Groutellite + Groutite Mn(OH) ₂
235	0	1,650	2	Groutite	Ramsdellite

In air, groutite was found to persist indefinitely below 130° C. At about 130° C, it oxidizes partly to ramsdellite in fourteen days; at 300° C. it oxidizes in a few hours. Above 300° C. it goes directly to pyrolusite.

C. Reactions in Air

Maximum temperatures of stability for a variety of manganese compounds heated in air are given in this section. They do not represent equilibrium temperatures, for in no case can the reverse reaction take place at the same temperature. The results obtained are summarized in Fig. 3.

Since these temperatures do not represent points of reversibility, the time parameter becomes significant. In this sense these are the lowest temperatures at which a reaction takes place at such a rate as to be easily observed in the laboratory. No doubt many of these reactions could be made to take place in air at even lower temperature if a substantially longer period of time were allowed to elapse.

These data, even though they do not reflect equilibrium conditions, can still serve to define limits for the reactions involved. For example, the following statement has been observed in a number of chemistry texts, "Mn₂O₃ can be prepared by heating pyrolusite at 600° C." As recently as 1956 (Kissinger et al., 1956), 550° C. was reported as the temperature of conversion as determined by differential thermal analysis.

While these statements are both valid, it is still useful to report that this same reaction was made to take place at a temperature as low as about 510° C. although the reaction is considerably slower at this temperature.

The temperature, 510° C., must provide enough energy not only to reach the equilibrium dissociation temperature at 0.21 atmospheres of

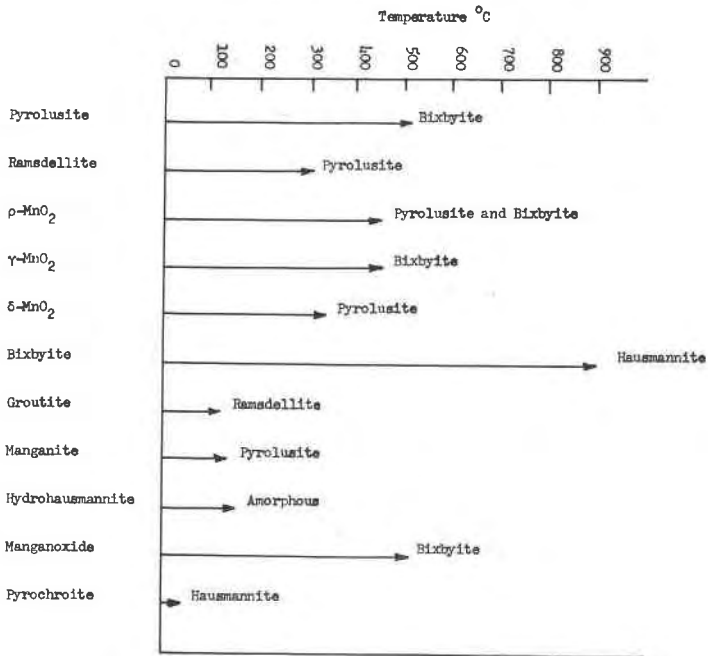


FIG. 3. Reactions in air.

O_2 , but also enough to overcome the considerable activation energy required, and must therefore be substantially higher than the equilibrium value.

TEMPERATURES OF REACTIONS AS VIEWED FROM CRYSTAL CHEMISTRY

Before considering the crystal chemical generalizations which derive from the present data, there are summarized below many of the pertinent data on the oxides and hydroxides of related systems. The first table (Table 4) summarizes the structural relations among some of the variable valence elements in relation to the size of the cation. The second table (Table 5) of trivalent hydroxide and oxide structures relationship shows the temperatures at which corresponding reactions take place.

A. Dehydration of the Brucite-type Lattice

It is one of the goals of crystal chemistry to predict thermochemical reactions. It cannot be claimed that this state of development has been achieved for this relatively new field, but the continued accumulation of thermal data of solid-solid and solid-vapor reactions should hasten the development of a more quantitative treatment of this field.

TABLE 4. STRUCTURAL RELATIONS AMONG SOME OXIDES OF VARIABLE VALENCE ELEMENTS

Element	Structure Type of Oxide			
	MO ₂	M ₂ O ₃	M ₃ O ₄	MO
Increasing Cation Size†	Fe (Rutile*)	Corundum	Spinel	Halite ($a_0=4.29$)
	V Rutile	Corundum	None	Halite ($a_0=4.08$)
	Diaspore (Paramontroseite)			
	Ti Rutile	Corundum	None	Halite ($a_0=4.24$)
	Mn Rutile (Pyrolusite)	C-Type Rare Earth	Distorted Spinel	Halite ($a_0=4.44$)
	Diaspore (Ramsdellite)			
U	Fluorite	None	None	Halite ($a_0=4.92$)

* Compounds of tetravalent iron, such as BaFeO₃, are analogous to TiO₂.

† This order is not correct for all oxidation states and is given here for the trivalent ions.

Generally, the deformation of an anion is described as being related to the polarizing power of a cation. The polarizing power of a cation, in turn, is a function of its field strength (ratio of charge to size) and its electron configuration (noble-gas ions are less polarizing than non-noble-

TABLE 5. EQUILIBRIUM DECOMPOSITION TEMPERATURES OF MOOH TO M₂O₃

Element	Diaspore Structure	Decomposition Temperature*	Boehmite Structure	Oxide Structure	
Increasing Cation Size	Al	390° C.	Boehmite	Corundum	
	Ga	300° C.	—	Corundum	
	Fe	150° C.	Lepidocrocite	Corundum	
	V	—	—	Corundum	
	Mn	Groutite	270° C.	(Manganite)†	C-Type Rare Earth
	Sc	Sc-diaspore	410° C.	—	C-Type Rare Earth

* At 15,000 psi of water pressure.

† Not rigorously true. Manganite is more like lepidocrocite chemically than structurally.

TABLE 6. DATA ON REACTIONS IN AIR

Temp. (° C.)	Pressure (atmos- phere) <i>air</i>	Time (days)	Initial Condition	Result
507	1	8	β -MnO ₂	amorphous
515	1	4	MnO ₂	β -MnO ₂ and Mn ₂ O ₃
316	1	4	Ramsdellite	Ramsdellite
313	1	14	Ramsdellite	Ramsdellite and tr. β -MnO ₂
465	1	4	γ -MnO ₂	β -MnO ₂ and Mn ₂ O ₃
430	1	5	γ -MnO ₂	amorphous
452	1	1	γ -MnO ₂	amorphous
465	1	4	γ -MnO ₂	Mn ₂ O ₃
343	1	4	γ -MnO ₂	β -MnO ₂
885	1	1	MnOOH	Mn ₂ O ₃
892	1	1	MnOOH	Mn ₃ O ₄
110	1	14	Groutite	Groutite
131	1	14	Groutite	Groutite and ramsdellite
117	1	3	Manganite	Manganite
132	1	6	Manganite	Manganite and β -MnO ₂
145	1	8	Hydrohausmannite	Hydrohausmannite (very poor)
32	1	2	Mn(OH) ₂	Mn ₃ O ₄

gas ions). Anions exert a similar, but in most cases, a weaker influence upon the cation.

It is frequently difficult to find a case which permits direct comparison of the influence of these various qualitative concepts. (This point will be illustrated in the next section.) However, in the case of the equilibrium dehydration of the brucite-type lattice there now exists an opportunity to examine a problem in crystal chemistry for which the data are good.

Consider the following equilibrium temperatures of dehydration at 15,000 psi of water pressure:

Ni(OH)₂:300° C. (unpublished, this laboratory)

Mg(OH)₂:650° C. (Roy and Roy, 1957)

Mn(OH)₂:380° C. (Figure 2)

Ca(OH)₂:740° C. (Majumdar and Roy, 1956)

Comparisons of these hydroxides fall into the following categories:

1. Where both cations are noble-gas ions (Ca⁺⁺ and Mg⁺⁺), the O-H bond strength is apparently greater for the larger cation, as evidenced by the fact that Ca(OH)₂ is slightly more stable (90° C. higher dissociation). This is to be expected from the weakening of the metal-oxygen bond with increasing size and the resulting increased ionic nature of the compound. The pair Mn(OH)₂ and Ni(OH)₂ appear to bear this out.

2. With cationic sizes held constant, the "fit" in a crystal of Ni(OH)₂

TABLE 7. DATA ON REACTION, MANGANITE \rightleftharpoons BIXBYITE AND WATER

Temp. (° C.)	Press. (psi)H ₂ O	Press. (psi)O ₂	Time (days)	Initial Condition		Result
268	21,500	0	2	Mang. MnOOH Mn(OH) ₂	Mang. Mn ₃ O ₄ Mn ₃ O ₄	
271	17,300	50	2	Mang. MnOOH Mn(OH) ₂ MnO	β -MnO ₂ Mang. and β -MnO ₂ β -MnO ₂ β -MnO ₂ and Manox.	
259	14,500	0	3	Mn ₂ O ₃ Mang.	Mn ₂ O ₃ Mang.	
254	10,000	10	2	Mang. MnOOH Mn(OH) ₂	Mang. Mn ₃ O ₄ Mn ₃ O ₄	
256	7,000	20	5	Mang. MnOOH Mn(OH) ₂	Mang. and β -MnO ₂ Mang. and tr. β -MnO ₂ β -MnO ₂ and Manox.	
271	12,500	10	2	Mang. MnOOH Mn(OH) ₂	Mang. Mn ₃ O ₄ Mn ₃ O ₄	
265	4,000	20	2	Mang. MnOOH Mn(OH) ₂	Mang. and β -MnO ₂ Mang. and β -MnO ₂ β -MnO ₂	
257	4,000	25	1	Mang. MnOOH Mn(OH) ₂	Mang. and tr. β -MnO ₂ Mang. and tr. β -MnO ₂ Mang. and tr. β -MnO ₂ and Manox.	
265	2,100	30	1	Mang. MnOOH Mn(OH) ₂	Mang. and tr. β -MnO ₂ Mang. Mang. and tr. β -MnO ₂ and Manox.	
257	1,250	20	1	Mang. MnOOH Mn(OH) ₂	Mang. and β -MnO ₂ Mang. Mang.	
274	21,500	10	5	Mang. MnOOH Mn(OH) ₂	Mn ₂ O ₃ and β -MnO ₂ β -MnO ₂ and Mn ₂ O ₃ and tr. Mn(OH) ₂ Mn(OH) ₂	

Abbreviations: Manox. = manganoxide, a new synthetic phase, Mang. = manganite, Mn₂O₃ = bixbyite, Mn₃O₄ = hausmannite, MnOOH = amorphous, β -MnO₂ = pyrolusite.

TABLE 7—(Continued)

Temp. (° C.)	Press. (psi)H ₂ O	Press. (psi)O ₂	Time (days)	Initial Condition	Result
282	19,000	0	2	Mang. MnOOH Mn(OH) ₂	Mn ₂ O ₃ Mn ₃ O ₄ Mn ₃ O ₄
275	12,300	15	2	Mang. MnOOH Mn(OH) ₂	β-MnO ₂ β-MnO ₂ and Mn ₂ O ₃ β-MnO ₂
279	9,000	10	3	Mang. MnOOH Mn(OH) ₂	Mang. and Mn ₂ O ₃ Mang., Mn ₃ O ₄ , tr. Mn ₂ O ₃ Mang., Mn ₃ O ₄ , Mn ₂ O ₃
260	4,600	300	2	Mang. MnOOH Mn(OH) ₂	Mang. and Mn ₂ O ₃ Mn ₃ O ₄ Mn ₃ O ₄
267	3,800	20	2	Mang. MnOOH Mn(OH) ₂	Mn ₂ O ₃ and β-MnO ₂ β-MnO ₂ and Mn ₂ O ₃ β-MnO ₂ and Manox.
265	1,100	20	2	Mang. MnOOH Mn(OH) ₂	Mn ₂ O ₃ and β-MnO ₂ β-MnO ₂ and Mn ₂ O ₃ β-MnO ₂ and Manox.

must be the same as that of Mg(OH)₂. However, Ni⁺⁺ is not a noble-gas ion, and as a result is expected to have a greater polarizing power than the Mg⁺⁺ ion. With an increase in covalency in the metal-oxygen bond, the thermal stability of Ni(OH)₂ is markedly reduced (by 350° C.) below that of Mg(OH)₂, likewise Mn(OH)₂ and Ca(OH)₂.

B. Dehydration of the Diaspore-type Lattice

In the last section it was indicated that it frequently is difficult to find examples within the framework of crystal chemistry that permit clear comparisons to be made that reflect the influence of only one characteristic of bond type. Unfortunately, the dehydration of groutite is an example of this, and therefore, can not be treated in the same manner as the dehydration of pyrochroite.

Groutite has a diaspore-like structure, and the desire is strong to compare its thermal stability with that of the Al, Ga, Sc or Fe diaspore structures. However, while the above diaspore structures convert to a corundum structure, groutite converts to a C-type rare earth structure.

TABLE 8. DATA ON REACTION: $\text{Mn}(\text{OH})_2 \rightleftharpoons \text{MnO} + \text{H}_2\text{O}$

Temp. (° C.)	Press. (psi)H ₂ O	Press. (psi)O ₂	Time (days)	Initial Condition	Result
344	1,950	0	1	Mn(OH) ₂ MnO Mn	Mn(OH) ₂ Mn(OH) ₂ and tr. MnO β-MnO ₂
375	14,000	0	2	Mn MnOOH	Mn(OH) ₂ Mn ₃ O ₄ (very poor)
369	21,600	0	2	Mn MnO Mn(OH) ₂	Mn(OH) ₂ Mn(OH) ₂ Mn(OH) ₂
363	21,000	0	1	Mn Mn(OH) ₂	Mn(OH) ₂ Mn(OH) ₂ and tr. Mn ₃ O ₄
395	27,000	0	1	Mn MnO Mn(OH) ₂	Mn(OH) ₂ MnO and Mn(OH) ₂ Mn ₃ O ₄
404	32,000	0	2	Mn MnO (Mn(OH))	Mn(OH) ₂ Mn(OH) ₂ and tr. MnO Mn ₂ O ₃
405	35,000	0	1	Mn Mn(OH) ₂ MnO	Mn(OH) ₂ Mn(OH) ₂ Mn ₃ O ₄
417	51,000	0	$\frac{1}{5}$	Mn MnO Mn(OH) ₂	Mn(OH) ₂ Mn(OH) ₂ Mn(OH) ₂ and Mn ₃ O ₄
428	44,000	0	1	Mn MnO Mn(OH) ₂	MnO MnO and tr. Mn(OH) ₂ MnO and tr. Mn(OH) ₂
438	44,000	0	1	Mn MnO Mn(OH) ₂	MnO MnO and tr. Mn(OH) ₂ MnO and tr. Mn(OH) ₂
400	25,000	0	1	Mn MnO Mn(OH) ₂	MnO MnO and Mn(OH) ₂ Mn ₂ O ₃
400	14,500	0	2	Mn	MnO
400	10,000	0	2	Mn MnO	MnO MnO
368	2,600	0	1	Mn MnO Mn(OH) ₂	MnO MnO and Mn(OH) ₂ Mn ₃ O ₄
338	1,200	0	2	Mn MnO Mn(OH) ₂	MnO and Mn ₃ O ₄ MnO and Mn(OH) ₂ Mn ₃ O ₄

Abbreviation: β-MnO₂=pyrolusite.

The dissimilarity of structural products could undoubtedly account for a greater difference in the energetics involved in such a transformation than could be attributed to differences in cation size or type.

However, where the breakdown involves largely the formation of water from $(\text{OH})^-$ groups the comparison may still show useful results. Thus, the Al-diaspore to corundum transformation is again at a much higher temperature than the corresponding iron one, and above the Ga one, reflecting the influence of polarizability. The stronger the metal-oxygen bond, the weaker the O-H bond and lower the decomposition temperature. The Sc^{3+} and Mn^{3+} phases should have somewhat higher decomposition temperatures than the Ga^{3+} and Fe^{3+} analogues reflecting the weakening of the metal-oxygen bond due to increased size of the cation. This is borne out experimentally.

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