THE AMERICAN MINERALOGIST, VOL. 44, SEPTEMBER-OCTOBER, 1959

STABILITY RELATIONS AMONG SOME MANGANESE MINERALS*

ARNULF MUAN
The Pennsylvania State University, University Park, Pennsylvania

ABSTRACT

Stability relations among crystalline phases in the system manganese oxide-SiO_2 have been studied in atmospheres of controlled O_2 pressures ranging from $10^{-2.5}$ to 1 atm. and at temperatures ranging from 973 to 1206° C. The crystalline phases encountered in the present study are Mn_3O_4, braunite (Mn_2O_3(SS)), tephroite ($2MnO \cdot SiO_2$), rhodonite ($MnO \cdot SiO_2$(SS)) and tridymite (SiO_2). Equations are given relating O_2 partial pressures and temperatures for 6 different univariant situations characterized by the equilibrium coexistence of gas and three crystalline phases.

INTRODUCTION

Examination of natural minerals as well as laboratory studies of "synthetic minerals" are necessary in order to arrive at intelligent inferences regarding conditions prevailing during formation and alteration of minerals and rocks in nature. Laboratory studies have been concentrated in the past mainly on phase equilibrium investigations in dry silicate systems. Such studies, pioneered by staff members of the Geophysical Laboratory of the Carnegie Institution of Washington and taken up by other groups of geochemists, ceramists and metallurgists, have improved tremendously our understanding of the behavior of liquid and crystalline silicates. Most of these phase equilibrium studies have been restricted to combinations of oxides of noble gas type ions, such as for instance SiO_2, Al_2O_3, MgO, CaO, etc. Notable exceptions are investigations of systems containing iron oxide as a component. Bowen and Schairer (1932) 25 years ago developed an experimental technique for studying such systems, making the runs in iron crucibles in a N_2 atmosphere. The N_2 gas, after purification, contains only very small traces of O_2, but usually enough to cause a very slight oxidation of the crucible. In this way, an O_2 potential in the system is automatically maintained corresponding, at any particular temperature, to the equilibrium between metallic iron and its lowest oxide, "FeO" (wüstite). If the gas is so low in O_2 that the crucible does not oxidize, the O_2 potential of the system is defined by the equilibrium

$$2\,Fe_{crucible} + Fe^{3+}_{melt} = 3\,Fe^{2+}_{melt}$$

at any temperature. In both cases the crucible serves to maintain a certain partial pressure of O_2 of the gas phase, and this pressure is low enough

---

* Contribution No. 58-36 from College of Mineral Industries, The Pennsylvania State University, University Park, Pennsylvania.

to keep essentially all iron of the oxide phase(s) in the divalent state. This technique permitted the careful study of phase relations in a large number of important rock forming systems such as for instance "FeO"-SiO_2 (Bowen and Schairer, 1932) and MgO-"FeO"-SiO_2 (Bowen and Schairer, 1935). However, the technique has the shortcoming of not permitting the variation of O_2 pressure independently of temperature. From such studies of "dry" silicate systems at atmospheric pressure, geochemists have branched out during recent years to investigations at high hydrostatic pressures and studies of the influence of water and other volatiles on silicate equilibria, the latter usually in combination with elevated pressures.

Discussions of the problem of the oxygen potential prevailing during the crystallization of magmas have appeared in the literature (Kennedy, 1948), and theoretical derivation of the distribution of elements in a gravitational field has been presented by Brewer (1951). However, very little systematic experimental work has been done on phase relations in mineral systems under controlled, varying O_2 partial pressures. Such studies may well lead to the development of reliable O_2 pressure indicators, or perhaps even a combination of a "geological O_2 barometer" and a geological thermometer.

Studies of iron oxide containing systems under conditions such that the O_2 pressure can be varied as an independent parameter have been carried out by metallurgists for more than 20 years. Particularly important among these studies is the investigation of the system Fe-O by Darken and Gurry (1945, 1946). They used CO_2-CO or CO_2-H_2 gas mixtures to define the O_2 partial pressure, while keeping the total pressure constant at 1 atm. in their experiments. Darken (1948) also studied parts of the system Fe-Si-O and obtained important data regarding subsolidus stability relations among iron oxides and fayalite ($2FeO \cdot SiO_2$). These studies seem to have received less attention than they deserve among mineralogists and geochemists. The same methods used by Darken and Gurry have been extended to the detailed study of liquidus relations in the system FeO-Fe_2O_3-SiO_2 (Muan, 1955) and the system MgO-FeO-Fe_2O_3-SiO_2 (Muan and Osborn, 1956) in connection with research on steelplant refractories systems. Paths of crystallization under chosen idealized conditions were derived for these systems, and Osborn (in press) has used these principles recently to derive a new theory for the courses of reactions to be expected in the crystallization of a magma under various conditions of O_2 partial pressures.

An experimental study by Flaschen and Osborn (1957) of equilibria in parts of the system Fe-Si-H-O established some general relations between O_2 partial pressure and stability among important dry and hydrated mineral phases in that system. However, because of the experimental difficulties involved, no accurate quantitative figures were obtained that permitted the use of these data as O_2 pressure indicators.

The present paper describes results of a study establishing quantitative relations between O_2 partial pressure and temperature for univariant situations among some manganese oxide containing minerals. It is the first in a series of investigations dealing with systems made up from combination of manganese oxides with other oxides. Silica was chosen as component in addition to manganese oxide in the present study. This work supplements previous investigations of the system manganese oxide-SiO_2 in air (Muan, in press) and under conditions of low O_2 partial pressures (Glasser, 1958). The present investigation was limited to the temperature range from 973° C. up to the liquidus, and to O_2 partial pressures in the range $10^{-2.5}$ to 1 atm. The lower temperature limit was dictated by the necessity of working under conditions where reaction rates are high enough for equilibrium to be attained within a reasonable period of time. The range of O_2 partial pressures ($10^{-2.5}$ to 1 atm.) was chosen because all equilibria of particular interest in the present investigation fall in this region for the chosen temperature interval. Whereas working with O_2 pressures above 1 atm. would require experimental techniques entirely different from those used in the present investigation, there would be no particular difficulties working at O_2 partial pressures below the lower limit ($10^{-2.5}$ atm.) used. However, extreme caution must be exercised when working in the range 10^{-3} to 10^{-5} atm. O_2 because of the small "buffering capacity" in that range of the gas mixture generally used. These problems have been discussed in detail in a previous paper (Muan, 1958).

PREVIOUS WORK

Stability relations among the various oxides of manganese have been the subject of numerous studies, but so far no equilibrium diagram for the system Mn-O has been presented. The stability fields of MnO,* Mn_3O_4 and Mn_2O_3 have been reported in a recent publication by Hahn and Muan (in press); previous data on these equilibria have also been reviewed and discussed in considerable detail in that paper. The diagram in Fig. 1 includes curves for the Mn_2O_3/Mn_3O_4 and Mn_3O_4/MnO equilibria based on their data.

The system manganese oxide-silica in the liquidus temperature region has been studied by a large number of investigators. The most recent work is that carried out by Glasser (1958) who used a CO_2-H_2 atmosphere to keep essentially all manganese in the divalent state. The reader is re-

---

* The oxygen to manganese ratio of this phase is known to vary. The simplified formula MnO is used for sake of convenience in this paper.

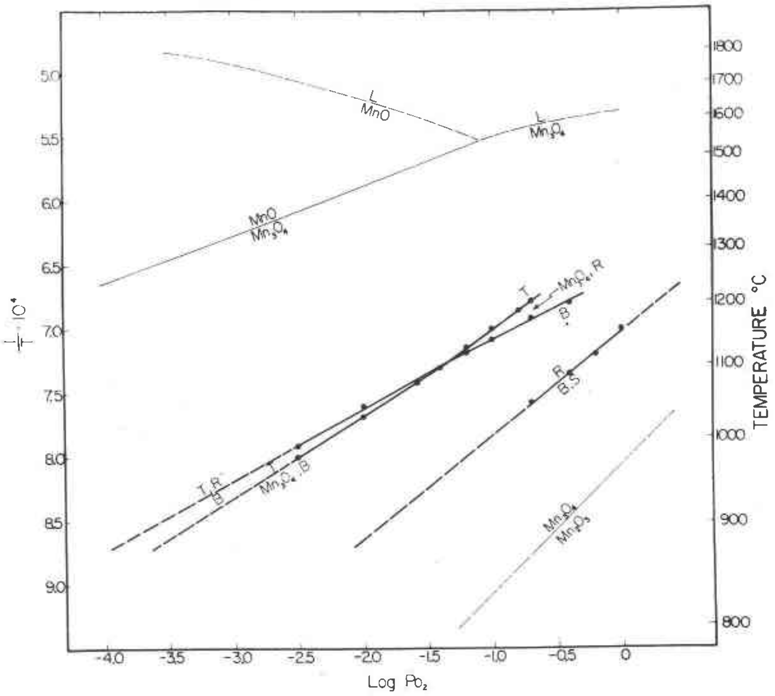

FIG. 1. Diagram illustrating relations of O_2 partial pressure and temperature for univariant equilbria in the system Mn-Si-O. Solid dots represent experimentally determined conditions for equilibrium coexistence of three crystalline phases and a gas, and the solid lines are drawn to pass through these points as closely as possible. Light lines represent conditions for coexistence of a gas and two crystalline phases in univariant equilibrium in the binary system Mn-O, based on data of Hahn and Muan (in press) and of Coughlin (1954). Dashed lines in the diagram are extrapolations into regions where no experimental data are available. Abbreviations used in the diagram have the following meanings: S = silica (tridymite); B = braunite (Mn_2O_3(SS)); R = rhodonite ($MnO \cdot SiO_2$(SS)); T = tephroite ($2MnO \cdot SiO_2$); L = liquid.

ferred to his paper also for a review of previous investigations of the system MnO-SiO_2. Phase relations in the system manganese oxide-SiO_2 in air in the liquidus region and at subsolidus temperatures were studied recently by Muan (in press). Most remarkable among the relations established in the latter study was the stable existence, in air, of a phase analogous to the natural mineral braunite (Mn_2O_3(SS)) but with SiO_2 contents varying from 0 to approximately 35 wt.%.

Chemical composition and optical properties of the various manganese minerals occurring as phases in the present investigation have been reported in numerous papers and in mineralogy texts, such as for instance Dana's System of Mineralogy (1944).

EXPERIMENTAL METHOD

General Procedure

The quenching technique was used throughout this investigation. Premelted mixtures of oxides were heated at chosen constant temperatures and chosen atmospheric conditions until equilibrium was reached among gas and crystalline phases. The samples were then quenched rapidly to room temperature and the phases present determined by microscopic and *x*-ray examination.

Starting Materials

The mixtures used in this investigation were made from reagent grade oxides. "Baker Analyzed" MnO_2 was the source of manganese oxide, and "Baker Analyzed" Silicic Acid was the source of silica. The latter was iginited at 1300° C. for 24 hrs. before use. Stock batches were prepared by weighing these materials in desired proportions, carefully grinding and mixing and slowly heating in air to temperatures above the liquidus. After crushing to minus 100 mesh these quenched liquids served as starting materials for the equilibration runs. In a number of experiments the attainment of equilibrium was checked by using as starting materials samples prepared by crystallizing these quenched liquids at controlled temperature and O_2 partial pressure. Two such samples, containing the phases present on opposite sides of a phase boundary curve, were equilibrated side by side to make sure that the reaction would proceed in both directions across the boundary.

Control of Atmosphere

The desired O_2 partial pressure of the atmosphere was attained by mixing O_2 and N_2 gases in required proportions. The O_2 was taken directly from a cylinder of high purity gas (Matheson, purity $\geq 99.6\%$), while the N_2 cylinder gas was purified by passing over copper gauze kept at approximately 600° C., and subsequently through drying towers containing commercial drying agents ("Drierite"). A gas mixer working on the same principle as that described by Darken and Gurry (1945) and later used in previous studies in our laboratories (Muan, 1955; Muan and Osborn, 1956) was used to control the gas flow to the furnace. The rate of flow of each gas was measured separately through pre-calibrated capillaries in two differential flow meters. The gases were then mixed in a large container, and the gas mixture was passed through a third manometer measuring the total flow of gas into the furnace. The rate of flow was maintained at approximately 0.15 cu. ft. per hour, corresponding to a linear rate of flow of approximately 1 cm. per sec. through the furnace tube.

Furnaces and Temperature Control

The quenching experiments were carried out in a vertical platinum-wound tube furnace. A gas tight high temperature porcelain tube was inserted inside the heating element and protruded above and below the furnace shell. The top of the porcelain tube was provided with a gas-tight watercooled brass head into which sample holder and thermocouple protection tube could be clamped in gas tight connection. The lower end of this tube was provided with a metal container in gas-tight connection with the tube. The gas was introduced into the lower end of the porcelain tube and escaped at the top, through a bottle containing a small amount of sulfuric acid. In this way a slight overpressure (3–4 mm. Hg.) over atmospheric was maintained in the furnace. The samples were contained in small envelopes made of thin platinum foil. No visible contamination of the platinum with manganese was experienced at the relatively high O_2 partial pressures ($>10^{-2.5}$ atm.) used in this investigation. (Such contamination has been observed at much lower O_2 partial pressures.*) After equilibrium was reached, the samples were quenched rapidly by letting them fall into this cup without disturbing the atmosphere in the furnace. This was accomplished by electrically melting off a thin platinum wire from which the samples were suspended.

The temperature of the furnace was controlled by a platinum-90% platinum 10% rhodium thermocouple inserted close to the hot spot of the furnace and connected to a commercial electronic control device. Actual temperatures in the furnace were measured before and after each run with a second platinum—90% platinum 10% rhodium thermocouple. This was calibrated against melting points defined as follows: Au, 1063° C.; $LiSiO_3$, 1201° C.; $CaMgSi_2O_6$, 1391.5° C.

Examination of Quenched Samples

The identity of phases present in quenched samples was determined by *x*-ray methods and by examination under a petrographic microscope. The *x*-ray work was carried out on a Norelco spectrometer unit with Fe radiation.

RESULTS

Results of quenching experiments carried out at various O_2 partial pressures are presented in Table I and shown graphically in Fig. 1. Heavy solid lines in this diagram are curves approximately passing through points (solid dots) representing experimentally determined values of O_2 partial pressures and temperatures for equilibrium coexistence of three crystalline phases and a gas phase in univariant situations in the

---

* W. C. Hahn, Jr., personal communication.

TABLE I. RESULTS OF EQUILIBRIUM STUDIES

Total Comp. of Mixture (Wt. %)		Temp. of Quench Run	Log p_{O_2} (Atm.)	Phases Present*
Mn_3O_4	SiO_2			
55.0	45.0	1,160	0	R+S (tr.)
		1,152		B+S
55.0	45.0	1,122	−0.20	R+S (tr.)
		1,113		B+S
80.0	20.0	1,204	−0.40	M+R
		1,197		M+B
55.0	45.0	1,095	−0.40	R+S (tr.)
		1,082		B+S
55.0	45.0	1,051	−0.70	R+S (tr.)
		1,045		B+S
71.0	29.0	1,206	−0.70	T
		1,202		M+R
		1,170		M+R
		1,166		B+R
71.0	29.0	1,189	−0.80	T
		1,185		M+R
71.0	29.0	1,163	−1.00	T
		1,151		H+R
		1,141		H+R
		1,136		B
71.0	29.0	1,131	−1.20	T
		1,124		H+R
		1,115		B
71.0	29.0	1,098	−1.40	T
		1,095		B
71.0	29.0	1,080	−1.58	T
		1,071		B+H
64.0	36.0	1,053	−2.00	T+R
		1,043		T+R+B
		1,040		B+R
71.0	29.0	1,034	−2.00	T
		1,022		B+H
71.0	29.0	1,005	−2.50	T
		991		T
		981		T
		973		H+B
64.0	36.0	1,005	−2.50	T+R
		991		T+R+B
		981		B+R

* Abbreviations used have the following meanings: H = crystals of hausmannite (= tetragonal Mn_3O_4); M = crystals of cubic Mn_3O_4; T = crystals of tephroite ($2MnO \cdot SiO_2$), R = crystals of rhodonite ($MnO \cdot SiO_2$(SS)); B = crystals of braunite (Mn_2O_3(SS)); S = crystals of silica (tridymite, SiO_2); tr. = trace.

ternary system Mn-Si-O. These curves have been extrapolated as straight lines (dashed) down to lower temperatures in order to indicate approximate locations of these equilibria in a region where experimental studies are difficult to carry out. Light solid lines in the same diagram illustrate for comparison relations between O_2 partial pressure and temperature for equilibria among gas and two condensed phases (2 crystalline or 1 crystalline and 1 liquid) in univariant situations in the binary system Mn-O, based on recent data of Hahn and Muan (in press) and by Coughlin (1954). It is to be noted that the curve representing the Mn_3O_4/MnO equilibrium in the binary system also will represent the conditions for equilibrium coexistence of the three condensed phases Mn_3O_4, MnO and liquid in the system Mn-Si-O if no silica gets into the structure of Mn_3O_4 or MnO.

The data contained in Table I and Fig. 1 can be summarized in the equations below, representing relations of O_2 partial pressure and temperature for the following univariant situations in the system Mn-Si-O:

Mn_2O_3, Mn_3O_4 : $\log p_{O_2} = 8.05 - 10{,}100 \cdot 1/T$
Mn_3O_4, MnO : $\log p_{O_2} = 13.31 - 26{,}000 \cdot 1/T$
MnO, Mn : $\log p_{O_2} = 7.65 - 40{,}700 \cdot 1/T$
Mn_3O_4, tephroite, braunite : $\log p_{O_2} = 10.08 - 15{,}700 \cdot 1/T$
Mn_3O_4, tephroite, rhodonite : $\log p_{O_2} = 8.25 - 13{,}200 \cdot 1/T$
Mn_3O_4, braunite, rhodonite : $\log p_{O_2} = 13.18 - 20{,}000 \cdot 1/T$
Braunite, tephroite, rhodonite : $\log p_{O_2} = 12.48 - 19{,}000 \cdot 1/T$
Braunite, rhodonite, tridymite : $\log p_{O_2} = 8.56 - 12{,}200 \cdot 1/T$

Heats of oxidation for the reactions represented by these univariant equilibria can be calculated from the slopes of the curves in Fig. 1, as follows:

$2MnO \cdot SiO_2 + O_2 = Mn_3O_4 + Mn_2O_3(SS);$ $\Delta H = 72{,}000$ cal.
$2MnO \cdot SiO_2 + O_2 = Mn_3O_4 + MnO \cdot SiO_2(SS);$ $\Delta H = 60{,}000$ cal.
$MnO \cdot SiO_2(SS) + Mn_3O_4 + O_2 = Mn_2O_3(SS);$ $\Delta H = 91{,}000$ cal.
$2MnO \cdot SiO_2 + MnO \cdot SiO_2(SS) + O_2 = Mn_2O_3(SS);$ $\Delta H = 87{,}000$ cal.
$MnO \cdot SiO_2(SS) + O_2 = Mn_2O_3(SS) + SiO_2;$ $\Delta H = 56{,}000$ cal.

These equations are not balanced because solid solution crystals of variable compositions are involved in the equilibria. The heats of oxidation given are for reactions in which 1 mol of O_2 is consumed, and are average values in the temperature interval for which the curves in Fig. 1 have been drawn.

The diagram in Fig. 1 has the shortcoming that it does not show the compositions of the three condensed phases coexisting along the univariant lines or of the two condensed phases coexisting in the areas between the univariant curves. A supplementary diagram is presented in Fig. 2 to show the phase relations as a function of total composition (manganese

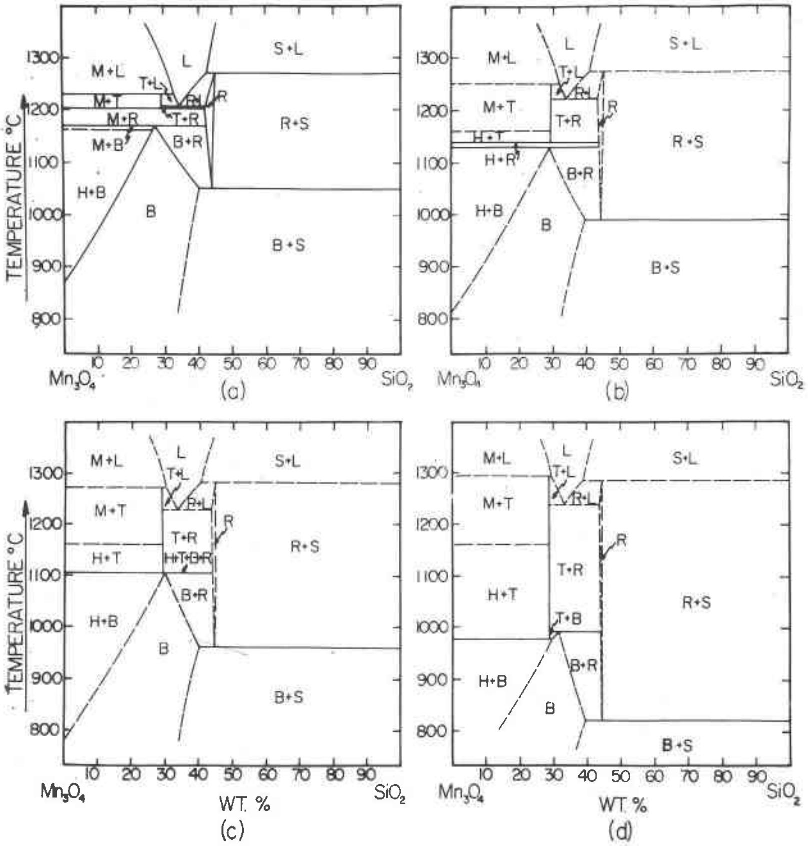

FIG. 2. Diagrams showing phase relations at various levels of O_2 partial pressure in the system Mn-Si-O. The diagrams, labeled *a* through *d* are plotted for O_2 partial pressures of $10^{-0.7}$, $10^{-1.1}$, $10^{-1.35}$ and $10^{-2.5}$ atm., in that order. They are in reality projections of ternary relations into the chosen join Mn_3O_4-SiO_2. The diagram in *c* is exceptional in that it shows phase assemblages present at the O_2 pressure ($10^{-1.35}$ atm.) corresponding to a ternary subsolidus invariant situation in the system Mn-Si-O. In addition to the abbreviations used in Fig. 1, the following have been used in this diagram: M = cubic Mn_3O_4; H = hausmannite (tetragonal Mn_3O_4).

oxide to silica ratio) of the mixtures at various levels of O_2 partial pressures. The sequence of phase changes occurring as O_2 partial pressure is lowered from that of air to $10^{-2.5}$ atm. can be followed by inspection of the sketches in Fig. 2*a* through *d*, in that order.

DISCUSSION

The data obtained in the present investigation confirm previous observations (Goldschmidt, 1954) of the high stability of Mn^{2+}-containing phases as compared to those where manganese is present only in higher valence states. Of all phases where manganese is present essentially as Mn^{2+}, the oxide itself, MnO (manganosite), is of course the least resistant to oxidation. It will be observed that MnO does not occur as a phase at the combinations of O_2 pressure and temperature used in the present investigation. In tephroite, $2MnO \cdot SiO_2$, the Mn^{2+} is considerably better screened because of the presence of SiO_2 in structure. This phase therefore appears under our experimental conditions, but only at relatively moderate O_2 pressures. In air this phase is stable only in the temperature interval from 1230° C. down to 1204° C. At the latter temperature it oxidizes to the phase assemblage Mn_3O_4 plus rhodonite ($MnO \cdot SiO_2$ (SS)). The Mn^{2+} in these phases is somewhat better screened than in tephroite, and they persist to considerably lower temperatures before oxidation takes place. For instance, rhodonite is stable down to 1048° C. (Muan, in press) and pure Mn_3O_4 is stable down to 877° C. in air (Hahn and Muan, in press). However, these phases do not exist *together* in equilibrium down to these temperatures in air. Instead an intermediate phase, here designated Mn_2O_3 (SS), is formed. This phase seems to be analogous to the natural mineral braunite, and probably contains some of its manganese in the divalent state. (For a discussion of this problem, the reader is referred to a recent paper by Muan (in press), where previous literature has been surveyed.) This Mn^{2+} is apparently well screened in the structure, and the phase probably persists stably down to low temperatures.

It is interesting to compare quantitatively the reduction-oxidation equilibria of manganese with those of iron in minerals for which reliable data are now available. An attempt to do this is illustrated in Fig. 3, which shows curves relating O_2 partial pressure and temperature for univariant subsolidus equilibria in parts of the systems Fe-Si-O and Mn-Si-O. In the case of the binary subsystems Fe-O and Mn-O these equilibrium situations are characterized by the coexistence of two condensed phases and gas, while in the ternary systems three condensed phases and gas are present together in equilibrium under conditions represented by the appropriate curves as labeled in Fig. 3. In order to orient the reader, two additional curves are included in Fig. 3, showing relations of O_2 partial pressure and temperature for pure CO_2 and pure H_2O, two of the most important species of the gas phase present in rock systems. One characteristic difference between the patterns of the Mn curves and the Fe curves is recognized immediately: the Mn curves are more "spread out." While MnO is reduced to Mn only at O_2 pressures significantly lower than those at which "FeO" is reduced to Fe, MnO persists as a phase to much higher O_2 pressures than "FeO," and likewise Mn_3O_4 resists oxidation to Mn_2O_3 much better than Fe_3O_4 (magnetite) to Fe_2O_3

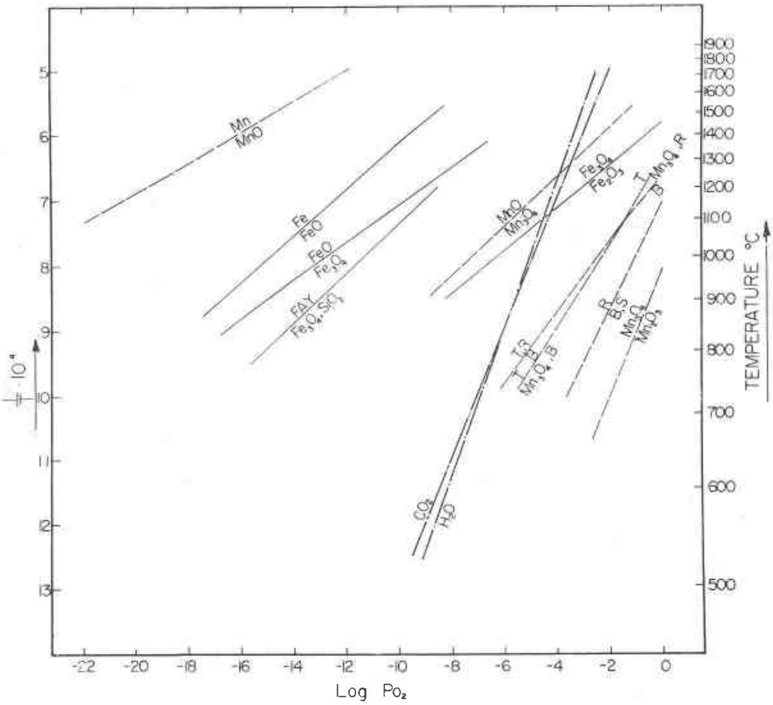

FIG. 3. Diagram presented in order to compare stability relations among various manganese and iron minerals as a function of temperature and O_2 partial pressure. Solid lines represent univariant equilbria in the systems Fe-O and Fe-Si-O, and dash lines represent those in the systems Mn-O and Mn-Si-O. In addition, two lines are drawn to show the O_2 pressure as a function of temperature for the gases H_2O (dash-dot line) and CO_2 (dash-double dot line), as discussed in the text. Abbreviation not explained in previous diagrams has the following meaning: Fay.=fayalite ($2FeO \cdot SiO_2$).

(hematite). These observations of course are equivalent to the statement that Mn^{2+} is exceptionally stable as compared to Fe^{2+}. Another characteristic difference between the behavior of Mn^{2+} and Fe^{2+} is the much greater stabilizing effect of SiO_2 in the case of the former. This is demonstrated by the relatively large distance between the MnO/Mn_3O_4 curve and the curves representing the oxidation of Mn^{2+} silicates, as compared to the situation existing between the FeO/Fe_3O_4 curve and that for oxidation of fayalite ($2FeO \cdot SiO_2$).

The use of the diagram for predicting quantitatively the resistance to oxidation of the various phases represented in Fig. 3 is of course quite simple. Take as an example the situation prevailing at a constant temperature of 1200° C. Starting with extremely reducing conditions and gradually increasing the O_2 partial pressure, Mn oxidizes to MnO at approximately 10^{-20} atm. O_2 and Fe to "FeO" at approximately 10^{-12} atm. at this temperature. As O_2 pressure is increased farther, "FeO" oxidizes to Fe_3O_4 at approximately 10^{-9} atm., and fayalite oxidizes to Fe_3O_4 and tridymite at an O_2 pressure only slightly higher, approximately $10^{-8.5}$ atm. The next phase to yield to oxidation as O_2 pressure increases is MnO, which reacts to form Mn_3O_4 at an O_2 pressure of $10^{-4.5}$ atm. At a p_{O_2} value of approximately 10^{-3} atm. Fe_3O_4 oxidizes to Fe_2O_3, and at an O_2 partial pressure of $10^{-0.7}$ atm. tephroite oxidizes to rhodonite and Mn_3O_4. These phases subsequently react at a slightly higher O_2 pressure ($10^{-0.4}$ atm.) to form braunite. Rhodonite oxidizes (to braunite plus silica) only at O_2 pressures above 1 atm. at this temperature.

It should be emphasized that the relations just discussed apply only in the case of the ternary system Mn-Si-O and Fe-Si-O taken separately. For the quaternary system Mn-Fe-Si-O the relations will undoubtedly be drastically different because of extensive solid solution formation among at least some of the phases encountered. The equilibria in such mixed systems could be calculated if we had a quantitative knowledge of the deviation from ideal behavior of the mixed crystals. More experimental data are needed to fill this gap. This work is presently being extended in that direction.

The curves in Fig. 1 representing equilibria where Mn_3O_4 is one of the phases present have a slight change in their slopes at the temperature where the phase transition from tetragonal to cubic Mn_3O_4 takes place (approximately 1160° C., Van Hook and Keith, 1958). However, the heat effect accompanying this transformation is too small to change significantly the straight line relation pictured in the diagram.

The curves shown in Fig. 1 can be extrapolated as straight lines down to lower temperatures and tentative phase diagrams sketched for O_2 partial pressures substantially lower than that prevailing in diagram *2d*($10^{-2.5}$ atm.). It is likely that the subsolidus relations will be similar to that in *2d*, except that the horizontal lines indicating the lower temperature limits of rhodonite and tephroite will be shifted downwards. From the curves in Fig. 1 it is estimated that rhodonite is stable down to approximately 500° C. at an O_2 pressure of 10^{-8} atm. and tephroite down to approximately 600° C. under the same conditions.

The intersection at 1104° C. of the two univariant curves in Fig. 1 along which the phases braunite (B), Mn_3O_4, rhodonite (R), gas, and Mn_3O_4, rhodonite, tephroite (T), gas, respectively, coexist in equilibrium is an interesting feature of the system. These phase assemblages therefore can exist under equilibrium conditions only at temperatures above 1104° C. and at O_2 pressures above that corresponding to the point of intersection, $10^{-1.35}$ atm. Below this temperature and O_2 partial pressure the phase assemblages Mn_3O_4, braunite, tephroite, gas, and braunite, rhodonite, tephroite, gas, respectively, are stable. These relations are easily recognized by an inspection of Fig. 2 together with Fig. 1.

The present data were obtained at a constant total pressure of 1 atm. In order to infer conditions prevailing during formation and alteration of naturally occurring manganese minerals, the effect of elevated hydrostatic pressures must be considered. All equilibria determined in the present study are concerned only with crystalline phases in addition to the gas phase unless extreme pressures are used, the activities of the crystalline phases remain essentially constant, and the curves plotted in Fig. 1 would still apply as a good approximation at elevated hydrostatic pressures if the vertical scale is taken to mean log fugacity values of O_2 instead of log p.

The results of this study seem to offer a promising possibility of inferring some of the conditions prevailing during the formation of manganese minerals. Best known among such deposits are those at Långban in Sweden, which have been described in several papers appearing in the literature (Magnusson, 1924; Flink, 1926; Palache, 1929). A critical analysis of these mineral deposits in view of laboratory data on stability relations established among manganese minerals will be attempted only after the influence of iron oxide and Al_2O_3 on these equilibria has been established. Such studies are presently in progress in our laboratories.

SUMMARY

Stability relations among crystalline phases in the system manganese oxide-SiO_2 have been studied in the temperature interval 973–1206°C. and at O_2 partial pressures varying from $10^{-2.5}$ to 1 atm. Equations relating O_2 partial pressure and temperature for ternary univariant situations have been determined for equilibria involving the phases Mn_3O_4, braunite (Mn_2O_3 (SS)), tephroite ($2MnO \cdot SiO_2$), rhodonite ($MnO \cdot SiO_2$ (SS)), and tridymite (SiO_2). Each of these univariant situations is characterized by the coexistence in equilibrium of a gas and three crystalline phases.

A comparison of these data with similar data for iron oxides and fayalite ($2FeO \cdot SiO_2$) demonstrates the far greater stability of Mn^{2+} than of Fe^{2+} in common mineral structures. While Mn^{2+} in oxides at high temperatures is reduced to metallic manganese only at O_2 partial pressures far below those sufficient to reduce Fe^{2+} to metallic iron, Mn^{2+} oxidizes to higher valence states only at considerably higher O_2 partial pressures than those necessary to oxidize Fe^{2+} to Fe^{3+}.

The data obtained in the present investigation may perhaps be used to estimate O_2 partial pressure or combination of O_2 partial pressure and

temperature prevailing during formation and alteration of manganese oxide containing mineral deposits. Although the present data were obtained at a constant total pressure of 1 atm., it is expected that the phase relations will remain essentially the same also at somewhat elevated hydrostatic pressures. It is worth noting that the phase assemblage Mn_3O_4, braunite, rhodonite, gas, and likewise the phase assemblage of Mn_3O_4, tephroite, rhodonite, gas can exist in stable equilibrium only at temperatures above 1104° C. and at O_2 partial pressures above $10^{-1.35}$ atm. Below this temperature and O_2 partial pressure the phase assemblages Mn_3O_4, braunite, tephroite, gas or braunite, tephroite, rhodonite, gas are stable.

ACKNOWLEDGMENTS

This work was carried out as part of a research project entitled Phase Equilibrium Studies of Steelplant Refractories Systems, sponsored by the American Iron and Steel Institute.

REFERENCES

BOWEN, N. L. AND SCHAIRER, J. F. (1932), The System FeO-SiO_2: *Am. J. Sci.*, **24,** 177–213.

——— (1935), The System MgO-FeO-SiO_2: *Am. J. Sci.*, **29,** 151–217.

BREWER, LEO (1951), The Equilibrium Distribution of the Elements in the Earth's Gravitational Field: *J. Geol.*, **59,** 490–497.

COUGHLIN, J. P. (1954), Contributions to the Data on Theoretical Metallurgy. XII—Heats and Free Energies of Formation of Inorganic Oxides: *U. S. Bureau of Mines, Bull.* 542.

DANA, J. D. AND DANA, E. S. (1944), The System of Mineralogy; rewritten by Palache, Charles, Berman, Harry and Frondel, Clifford: New York, John Wiley and Sons, Inc., 7th Edition, Volume I, 834 pp.

DARKEN, L. S. AND GURRY, R. W. (1954), The System Iron-Oxygen: I, The Wüstite Field and Related Equilibria: *J. Am. Chem. Soc.*, **67,** 1398–1412.

DARKEN, L. S. AND GURRY, R. W. (1946), The System Iron-Oxygen: II. Equilibrium and Thermodynamics of Liquid Oxide and Other Phases: *J. Am. Chem. Soc.*, **68,** 798–816.

DARKEN, L. S. (1948), Melting Points of Iron Oxides on Silica; Phase Equilibria in the System Fe-Si-O as a Function of Gas Composition and Temperature: *J. Am. Chem. Soc.*, **70,** 2046–2053.

FLASCHEN, S. S. AND OSBORN, E. F. (1957), Studies of the System Iron Oxide-Silica-Water at Low Oxygen Partial Pressures: *Econ. Geol.*, **52,** 923–943.

FLINK, GUSTAV (1926), Långban and Its Minerals: *Am. Mineral.*, **11,** 195–199.

GLASSER, F. P. (1958), The System MnO-SiO_2: *Am. J. Sci.*, **256,** 398–412.

GOLDSCHMIDT, V. M. (1954), Geochemistry: London, Oxford Univ. Press, 730 p.

HAHN, W. C. AND MUAN, ARNULF, Studies in the Sytem Mn-O: *Am. J. Sci.* (in press).

KENNEDY, GEORGE C. (1948), Equilibrium between Volatiles and Iron Oxides in Igneous Rocks: *Am. J. Sci.*, **246,** 529–549.

MAGNUSSON, NILS H. (1924), The Långban Minerals from a Geological Point of View: *Geol. Fören. Stockholm Förhandl.*, 284–300.

MUAN, ARNULF (1955), Phase Equilibria in the System FeO-Fe_2O_3-SiO_2: *J. Metals*, **7,** September 1955; *Trans. Am. Inst. Mining Met. Engrs.*, **203,** 965–976.

Muan, Arnulf and Osborn, E. F. (1956), Phase Equilibria at Liquidus Temperatures in the System MgO-FeO-Fe_2O_3-SiO_2: *J. Am. Ceram. Soc.*, **39**, 121–140.

Muan, Arnulf, Phase Equilibria in the System Manganese Oxide-SiO_2 in Air: *Am. J. Sci.* (in press).

Muan, Arnulf (1958), Phase Equilibria at High Temperatures in Oxide Systems Involving Changes in Oxidation States: *Am. J. Sci.*, **256**, 171–207.

Osborn, E. F., The Crystallization and Differentiation of Basaltic Magma: *Am. J. Sci.* (in press).

Palache, Charles (1929), A comparison of the Ore Deposits of Långban, Sweden, with those of Franklin, New Jersey: *Am. Mineral.*, **14**, 43–47.

Van Hook, H. J. and Keith, M. L. (1958), The System Fe_3O_4-Mn_3O_4: *Am. Mineral.*, **43**, 69–83.

Manuscript received November 10, 1958