

STABILITY RELATIONS OF IRON AND MANGANESE
MINERALS: PHASE EQUILIBRIA AT LIQUIDUS TEM-
PERATURES IN THE SYSTEM IRON OXIDE-
MANGANESE OXIDE-SILICA IN AIR*

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ABSTRACT

The quenching technique has been used to study phase relations in the liquidus temperature region of the system iron oxide-manganese oxide-silica in air, which represents the 0.21 atm. O₂ isobaric section through the quaternary system Fe-Mn-Si-O. The following crystalline phases exist in equilibrium with liquids in the system: Silica (cristobalite or tridymite, depending on temperature), rhodonite (MnO·SiO₂), tephroite (2MnO·SiO₂), spinel solid solution (approximately Fe₃O₄-Mn₃O₄). Dominant among the primary phase areas are those of silica and spinel, whereas the stability fields of rhodonite and tephroite are restricted to minor areas adjacent to the manganese oxide-silica join. An area comprising mixtures giving rise to two coexisting immiscible liquids occupies a large part of the diagram. Liquidus temperatures in general decrease from the iron oxide-silica join to the manganese oxide-silica join. The lowest liquidus temperature in the system in air is 1205° C. Paths of crystallization of representative mixtures are discussed, with special emphasis on the complications arising because of the presence of a temperature minimum on the liquidus curve of the bounding system iron oxide-manganese oxide.

INTRODUCTION

Stability relations among iron silicates have been the subject of many investigations over the last three decades. There has also been considerable interest in manganese silicates during the recent years. In natural occurrences as well as in technologically important systems the oxides and silicates of iron and manganese are commonly closely associated with each other. Hence a knowledge of phase relations existing among the components iron oxide, manganese oxide and silica is important to petrology, to ore genesis and to research on steelmaking processes.

The present work represents the first step in our attempt to investigate such equilibria. For practical reasons we have chosen to study the system in air. In so doing we are traversing the quaternary system Fe-Mn-Si-O along the 0.21 atm. O₂ isobar at a total pressure of 1 atm. For purpose of simplified illustration this irregularly curved surface may be projected onto a chosen plane, and the resulting diagram has the appearance of a ternary system. Methods of projecting and interpreting such diagrams have been discussed in several previous papers from our

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laboratories (Muan and Osborn, 1956; Muan, 1957*a, b*, 1958; Phillips and Muan, 1959), and their application to the present system will be dealt with in some detail in later sections of this paper.

PREVIOUS WORK

The three bounding "binary"* systems have been studied in considerable detail, but no systematic study of the "ternary" system has been reported in the literature. The system iron oxide-silica in air was studied by Darken (1948) and by Muan (1955) as part of more extensive investigations of the system $\text{FeO-Fe}_2\text{O}_3\text{-SiO}_2$. The diagram shown in

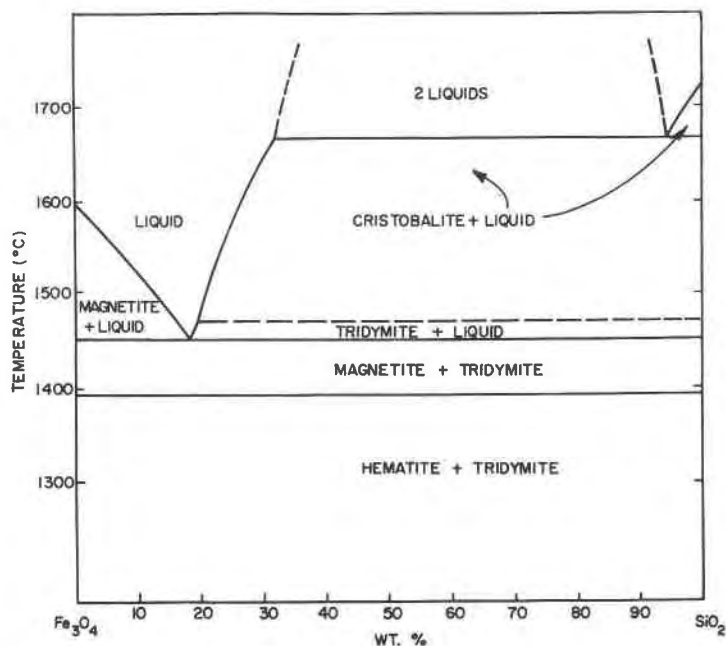


FIG. 1. Diagram showing phase relations in the system iron oxide- SiO_2 in air, after Muan (1955, 1957*a*). The system is not binary, but rather an oxygen isobaric section through the system Fe-Si-O , as explained in the original papers.

Fig. 1 is reproduced from Muan (1957*a*). Phase relations in the system manganese oxide-silica in air were determined recently by Muan (1959), and the diagram is reproduced in Fig. 2. The phase diagram for the system iron oxide-manganese oxide in air is shown in Fig. 3, based on the recent studies by Muan and Sōmiya (in press). Particular attention is

* These systems are not truly binary, but will be referred to as such for sake of simplicity. The term ternary is used with the same limitation throughout this paper.

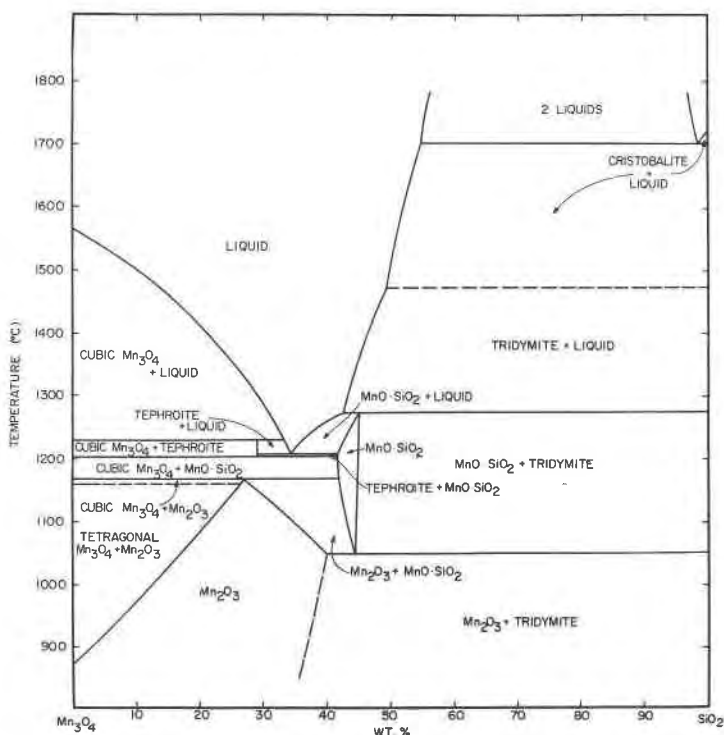


FIG. 2. Diagram illustrating phase relations in the system manganese oxide-SiO₂ in air after Muan (1959). The system is not binary, but rather an oxygen isobaric section through the system Mn-Si-O, as explained in the original paper.

called to the temperature minimum on the liquidus curve and the stabilization of the spinel structure of magnetite relative to the hexagonal structure of hematite as manganese oxide is added to iron oxide.

EXPERIMENTAL METHOD

General Procedure

The quenching technique was used in this investigation. Starting materials made up from pure oxides were held in platinum containers at selected temperatures in air until equilibrium was established among gas and condensed phases. The samples were then quenched rapidly to room temperature and the phases present determined by microscopic and x-ray examination.

Starting Materials

Reagent grade chemicals served as starting materials. The source of silica was "Baker Analyzed" silicic acid, which was dehydrated by ignition at 1200° C. for 24 hours. The iron oxide used was "Baker Analyzed"

Fe_2O_3 which was dried by heating at 400°C . for 12 hours, and the manganese oxide used was "Baker Analyzed" Mn_2O_3 .

After grinding and mixing these materials in required proportions, each mixture was preheated at suitable temperatures to slowly decompose the starting oxides to those stable at high temperatures. This process had to be carried out with utmost caution because the higher oxides of manganese (notably MnO_2 , also Mn_2O_3) give off oxygen violently with the result that material may be lost by splashing of the melts. The temperature of the final heating step was in most cases above the liquidus, and the melt thus obtained, after cooling to room temperature, consisted of glass or a heterogeneous product with small quench crystals scattered over the entire mass.

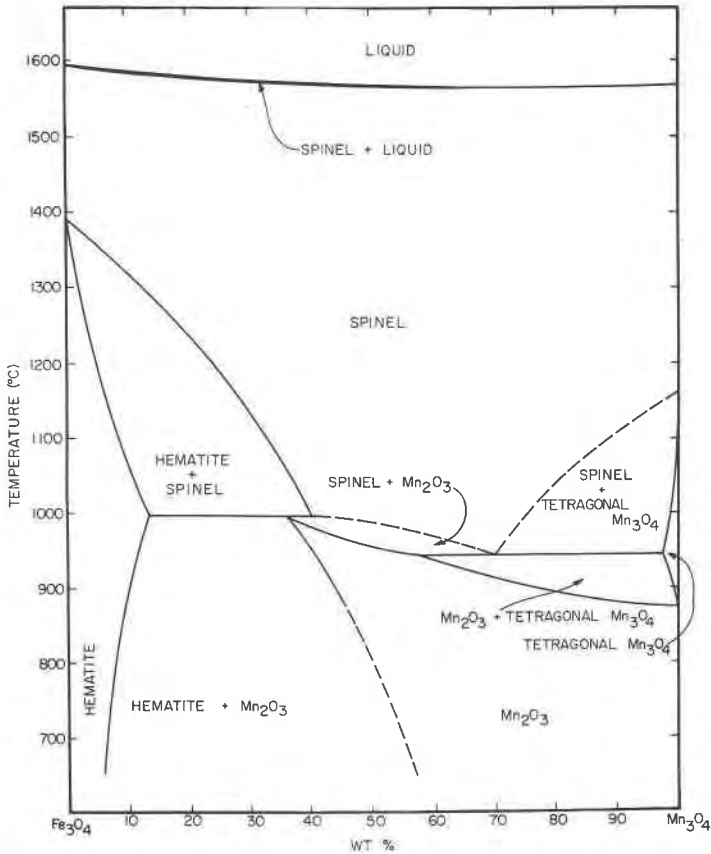


FIG. 3. Diagram showing phase relations in the system iron oxide-manganese oxide, after Muan and Sōmiya (in press). The system is not binary, but rather an oxygen isobaric section through the system Fe-Mn-O, as explained in the original paper.

Furnaces and Temperature Control

Most of the quench runs were carried out in vertical tube furnaces with resistance windings of platinum or an 80% platinum—20% rhodium alloy. Constancy of temperature in these furnaces was maintained by commercial electronic equipment activated through a thermocouple (platinum—90% platinum 10% rhodium) inserted close to the hot spot of the furnace. Actual temperatures were read with a platinum—90% platinum 10% rhodium thermocouple calibrated against known melting points defined as follows: Gold (Au), 1063° C.; diopside ($\text{CaMgSi}_2\text{O}_6$), 1391.5° C.; pseudowollastonite (CaSiO_3), 1544° C. Quench runs at temperatures above 1515° C. were carried out in a gas-air-oxygen combustion furnace in which air atmosphere was maintained around the sample by means of a zirconia protection tube separating the sample from the combustion chamber. Temperatures in this furnace were measured with an optical pyrometer calibrated at the following fixed points: Melting point of pseudowollastonite, 1544° C.; lower limit of formation of two liquids in a 90% SiO_2 —10% CaO mixture, 1707° C.; melting point of platinum, 1769° C.

Temperatures reported in the present paper are according to the Geophysical Laboratory Scale up to 1550° C., and according to the 1948 International Scale at higher temperatures. Correction factors for converting temperatures from one of these scales to the other are found in a paper by Sosman (1952). Below 1550° C. the two scales are almost identical.

Examination of Quenched Samples

The phases present in quenched samples were determined mainly by microscopic examination. Both transmitted as well as reflected light techniques were used. The former technique was useful for identification of SiO_2 (tridymite or cristobalite) and manganese silicates, whereas the latter was far superior for identification of the spinel phase. Also, the reflected light examination of polished sections was found to be much more reliable for distinguishing primary crystals grown in equilibrium with liquids at high temperatures from those formed during quenching of the liquids. The former crystals not only are larger, but in addition they show sharp outlines as distinguished from the irregular dendritic shapes of the quench crystals.

The identity of crystalline phases was further confirmed by *x*-ray investigation, using either a Norelco or a GE-XRD-3 spectrometer unit with iron radiation. The *x*-ray technique was also used to determine compositions of the spinel solid solution crystals appearing in equilibrium with liquids. The GE-XRD-3 unit was used for this purpose. The

machine was run at a scanning rate of $1/5^\circ 2\theta$ per minute, and NaCl was used as an internal standard.

RESULTS

Results of significant quench runs are illustrated graphically in Fig. 4.* The diagram presented in this figure is a simplified representation of phase relations along the 0.21 atm. O_2 isobar through the quaternary system Fe-Mn-Si-O. A quaternary system is usually represented by a

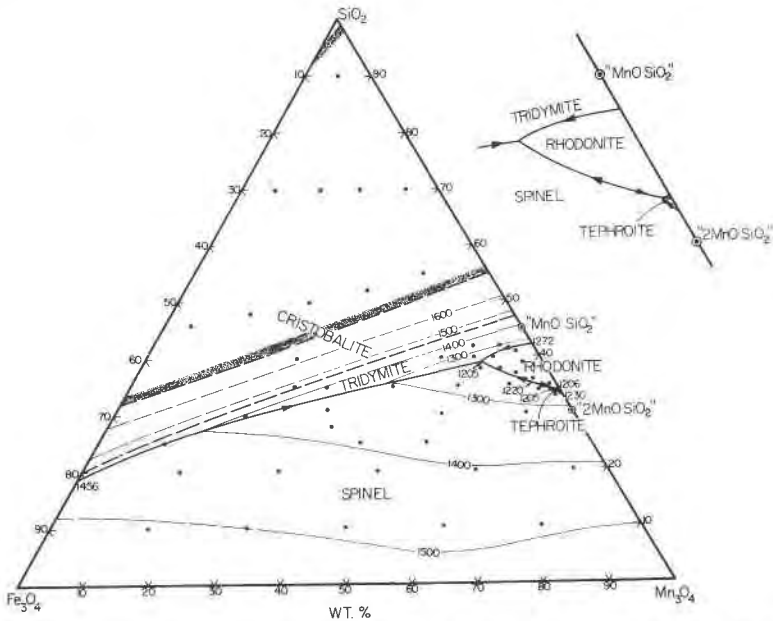


FIG. 4. Diagram illustrating phase relations at liquidus temperatures in the system iron oxide-manganese oxide-silica in air, based on data obtained in the present investigation. Heavy lines are boundary curves, with arrows pointing in directions of decreasing temperatures, lines with stippling on one side indicate limits of two-liquid region, and light lines are liquidus isotherms. Dash lines are used in regions of the diagram where data are sporadic or lacking. Dots represent compositions of mixtures studied.

regular tetrahedron, and the isobaric situation referred to above corresponds geometrically to an irregularly curved surface traversing the tetrahedron. The diagram presented in Fig. 4 is obtained by projecting points from the irregularly curved surface onto the plane Fe_3O_4 - Mn_2O_3 -

* The detailed results of the significant quench runs are available from the American Documentation Institute, Auxiliary Publications Project, c/o Library of Congress, Washington 25, D. C.; Document No. 6627; Price \$1.25 for photoprints or 35 mm. microfilm. Advance payment is required, made out to Chief, Photoduplication Service, Library of Congress.

SiO₂. The triangular diagram thus obtained has the appearance of a ternary system, and can also be treated like a ternary system as far as path of crystallization is concerned. However, it is important to keep in mind that isobaric invariant points in the triangular diagram in reality are intersections between the O₂ isobaric surface (P_{O₂}=0.21 atm.) and quaternary univariant lines. (Compare a previous paper from our laboratories, Muan 1958).

The most significant features of the phase relations are as follows: The crystalline phases occurring in equilibrium with liquids in the system are silica (tridymite or cristobalite, depending on temperature), rhodonite, tephroite and spinel solid solution. The first and the last of these phases (silica and spinel) together occupy approximately 99% of the composition area, whereas the fields of rhodonite and tephroite are restricted to minor areas adjacent to the manganese oxide-silica join. The field of tephroite in particular is very small, as only traces of iron oxide make the orthosilicate phase unstable in air. Liquidus temperatures decrease rapidly from the high temperature plateau (~1700° C.) characterizing the part of the system where two immiscible liquids coexist in equilibrium, to the 1200–1450° C. range along the tridymite-spinel boundary curve. Temperatures along the latter decrease in the direction from the iron oxide-silica join toward the manganese oxide-silica join. The lowest liquidus temperature is 1205° C. The liquidus curve in the system iron oxide-manganese oxide in air has a temperature minimum which gives rise to a trough extending part way into the "ternary" system as SiO₂ is added. This trough "dies out" before reaching any of the boundary curves in the "ternary" system, and hence no temperature minima are present along these curves.

There are two isobaric invariant situations in the system, characterized by the following phase assemblages: At 1205° C. and an O₂ pressure of the gas phase of 0.21 atm. tridymite, rhodonite, spinel and liquid of composition 9 wt.% Fe₃O₄, 52 wt.% Mn₃O₄, 39 wt.% SiO₂* coexist in equilibrium. Also at 1205° C. and the same O₂ partial pressure rhodonite, tephroite, spinel and liquid of composition <0.5 wt.% Fe₃O₄, ~45.5 wt.% Mn₃O₄ and ~54 wt.% SiO₂ are present together in stable equilibrium.

Of the crystalline phases occurring in the system, silica (tridymite or cristobalite) is a pure phase corresponding to the chemical formula SiO₂. Rhodonite has a slight variation in MnO/SiO₂ ratio (compare Fig. 2) and probably takes some iron oxide (ferrosillite) into solid solution. Tephroite probably also contains some iron oxide (fayalite) in solid solu-

* Total iron oxide expressed as Fe₃O₄ and total manganese oxide expressed as Mn₃O₄.

tion. These two phases are represented in a simplified manner by the composition points $\text{MnO} \cdot \text{SiO}_2$ and $2\text{MnO} \cdot \text{SiO}_2$, respectively, in the diagrams. Magnetite (Fe_3O_4) and the cubic form of hausmannite (Mn_3O_4) form a continuous solid solution series (spinel) at high temperatures (compare Fig. 3).

In order to illustrate relation of compositions of spinel and liquid phases coexisting in equilibrium, a diagram of fractionation curves is shown in Fig. 5. Fractionation curves are constructed from conjugation lines in such a way that the latter are tangent to the former. (A conjugation line is a straight line connecting points representing compositions of two coexisting phases.) The diagram in Fig. 5 is a simplified drawing inasmuch as it illustrates projections onto the plane Fe_3O_4 - Mn_3O_4 - SiO_2 of fractionation curves traversing the tetrahedron representing the system Fe-Mn-Si-O.

DISCUSSION

We will focus our attention in the following on the courses of crystallization of mixtures where spinel is one of the phases present. These

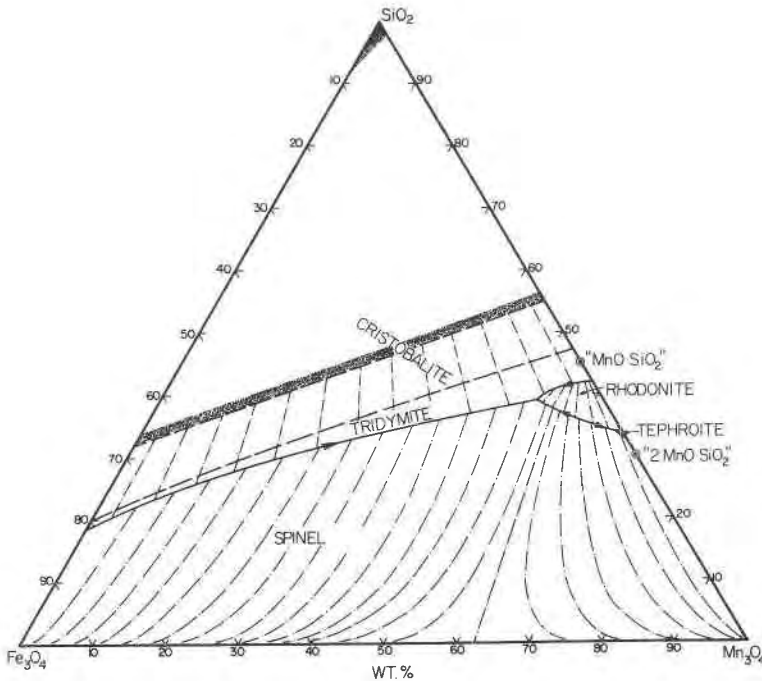


FIG. 5. Diagram illustrating as medium dash-dot lines fractionation curves in the system iron oxide-manganese oxide-silica in air. Other line symbols used have the same meanings as explained in legend to Fig. 4.

relations will be discussed by choosing specific compositions as examples to show the principles involved.

Two limiting types of crystallization are generally recognized, fractional crystallization and equilibrium crystallization. The former term refers to a crystallization taking place under conditions such that no reaction takes place between the crystals formed at any instant during crystallization and the liquid with which they are in contact. In this case the crystallization path follows the fractionation curves until a boundary curve is reached. From there on the liquid composition usually changes along the boundary curve, and the last trace of liquid disappears only after an invariant point has been reached. Hence, in the present system liquid under this type of crystallization will disappear at the temperature of one of the isobaric invariant situations at 1205° C. (see Fig. 4) or at the maximum (1220° C.) on the rhodonite-spinel boundary curve.

Somewhat more complicated is the derivation of paths of crystallization under equilibrium conditions, that is when the liquid during the crystallization process reacts with the crystals to make the composition of all crystals uniform at any instant. This equilibrium path can be derived by methods described particularly well in several contributions by members of the Staff of the Geophysical Laboratory of the Carnegie Institution of Washington. (See for instance papers by Bowen and Schairer, 1935, and by Osborn and Schairer, 1941.) The application of these principles to systems in which changes in oxidation states take place, such as in the present case, has been discussed in papers from our laboratories. (See for instance a paper in 1958 by Muan.)

Examples of paths of equilibrium crystallization are given in Figs. 6-8. Consider first mixture *A* in Fig. 6. Spinel crystals start separating out at approximately 1530° C., the first crystals having the composition *a'*. Upon further cooling, more crystals of spinel with composition changing from *a'* to *a''* separate out, and the liquid composition changes along the curved path (heavy solid line) from *A* to *a*₂. At the latter point the liquid has become saturated with SiO₂, and tridymite and spinel crystallize together as the liquid composition changes along the boundary curve from *a*₂ to *a*₃ and the spinel composition changes from *a''* to *a'''*. The last trace of liquid disappears at the temperature corresponding to point *a*₃, approximately 1340° C., leaving as end product a mixture of tridymite and spinel, the former of composition SiO₂, the latter of uniform composition *a'''*.

Mixtures *B*, *C* and *D* behave similarly, the final product of crystallization in all cases being the same as in mixture *A*. However, the early stages of crystallization differ, depending on the composition of the

original mixture. Mixture *B* consists of one homogeneous liquid above 1600° C. At the latter temperature silica starts separating out, and the liquid composition changes along the extension of the straight line from the SiO₂ corner through point *B*. As the liquid composition reaches point *b*₁, spinel crystals of composition *b'* start separating out, and as more heat is withdrawn from the system, silica and spinel of continuously changing composition (*b'-a'''*) crystallize out together. The behavior of mixture *C*

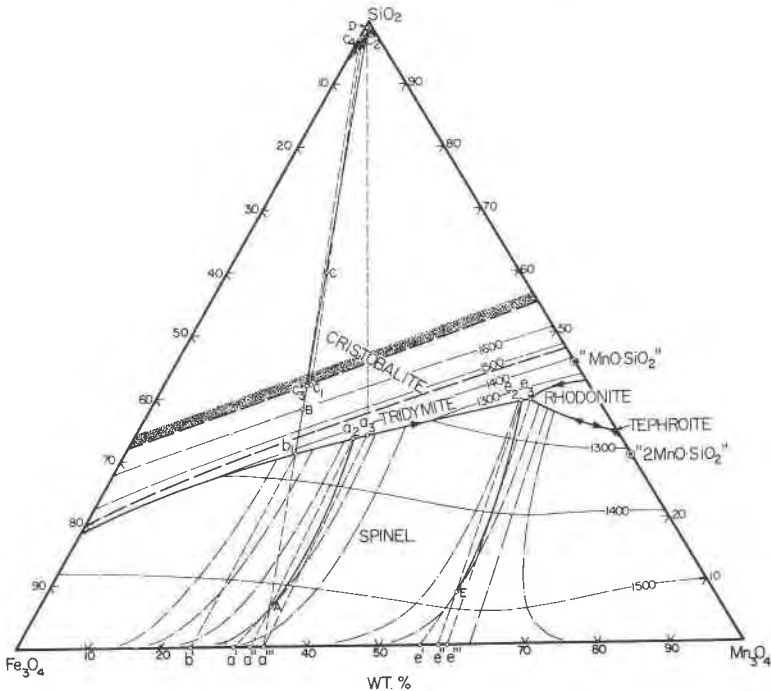


FIG. 6. Diagram showing paths of equilibrium crystallization of selected mixtures in the system iron oxide-manganese oxide-silica in air. In addition to boundary curves and liquidus isotherms shown in Fig. 4, the following line symbols are used in the present diagram: Medium dash-dot lines are fractionation curves, heavy solid lines paths of equilibrium crystallization, light lines liquidus isotherms, and lines with stippling on one side are limits of two-liquid region. Open circles with accompanying letters refer to mixtures and compositions of phases as discussed in the text. Light straight dash lines are conjugation lines connecting points representing compositions of phases coexisting in equilibrium.

is slightly different in that two immiscible liquid phases (*c*₁ and *c*₂) co-exist in equilibrium slightly above liquidus temperature. The first crystalline phase to appear is silica (cristobalite), and as this crystallizes out the composition of liquid *c*₁ changes toward *c*₃ and that of *c*₂ toward *c*₄, and the relative amount of the latter decreases toward zero. As more

heat is withdrawn from the system, silica continues to crystallize from a homogeneous liquid, and the further path of crystallization is analogous to that of mixture *B*. Mixture *D* behaves almost identically to *C* except that first a homogeneous liquid phase is present above liquidus temperature, this is followed by a temperature range of stable existence of cristobalite and one liquid phase, then a temperature range of coexistence of cristobalite and two liquids. From the latter point on, the crystallization path is identical to that of *C*.

The following sequence of phase changes is observed in mixture *E* during equilibrium crystallization: Spinel crystals of composition changing from e' to e'' separate out between approximately 1480 and 1215° C., with liquid composition changing along the curved path (heavy solid line) from *E* to e_2 . With silica (tridymite) and spinel crystallizing together, the liquid composition changes along the boundary curve from e_2 to e_3 until at the temperature of the latter (approximately 1205° C.) rhodonite separates out together with the other crystalline phases and the liquid disappears completely.

It will be noticed that in all mixtures chosen as examples so far the iron oxide/manganese oxide ratio of the spinel phase decreases as the equilibrium crystallization process proceeds with decreasing temperature. This is not the case with all mixtures in the system iron oxide-manganese oxide-silica in air, as is demonstrated in Fig. 7, showing the composition area adjacent to the manganese oxide apex of the triangle representing the system. There are three straight lines which are particularly important for purposes of classifying crystallization phenomena in this area. The first of these is the conjugation line joining the composition of the liquid at the isobaric invariant point e_3 with point e''' (compare Fig. 6) representing composition of the spinel phase in equilibrium with that liquid. The second is the straight fractionation curve g_2-g'' (compare Fig. 5) separating those with a convex curvature to the right from those with a convex curvature to the left. The third is the extension (k_2-k'') of the line joining the $\text{MnO}\cdot\text{SiO}_2$ composition point with the maximum on the rhodonite-spinel boundary curve. This maximum is determined as the point on the boundary curve for which the liquid-spinel conjugation line (the tangent to the fractionation curve) points toward the $\text{MnO}\cdot\text{SiO}_2$ composition point. Mixtures *F*, *G*, *H*, *K*, *M* in Fig. 6 are located to the left of line g_2-g'' , on line g_2-g'' , between lines g_2-g'' and k_2-k'' , on line k_2-k'' , and to the right of line k_2-k'' , respectively, in that order. During equilibrium crystallization of these mixtures the liquid compositions follow paths which can be derived from fractionation curves by methods analogous to those used in connection with Fig. 6. For the present discussion we are mainly concerned with the di-

rection of change of iron oxide/manganese oxide ratios of the spinel phase as temperature decreases and crystallization progresses. In mixture F this ratio first decreases from f' to f'' as the liquid composition changes along the curved path (heavy solid curve) from F to f_2 , and then increases from f'' to f''' as the liquid composition changes along the rhodonite-spinel boundary curve from f_2 to f_3 . The same type of reversal of change of iron oxide/manganese oxide ratio of the spinel phase is encountered in all mixtures in the spinel primary field between lines e_3-e''' and g_2-g'' .

Mixture G is located on line g_2-g'' . In this case the straight line g_2-g'' not only is the fractionation curve but also the first part of the path of crystallization. As the liquid composition changes along this line the iron oxide/manganese oxide ratio of the spinel phase remains constant (g''), and only as the liquid composition later changes along the rhodonite-spinel boundary curve from g_2 to g_3 does the iron oxide/manganese oxide ratio of the spinel phase change (from g'' to g''').

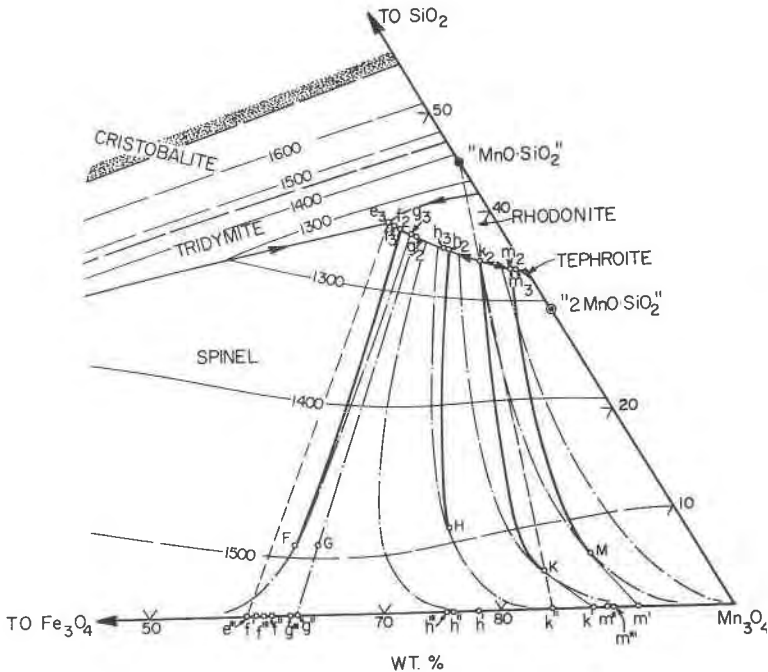


FIG. 7. Diagram illustrating paths of equilibrium crystallization of selected mixtures located in the spinel field in manganese oxide rich part of the system iron oxide-manganese oxide-silica in air. Line symbols used have the same meanings as explained in legend to Fig. 6.

In mixture *H*, located between lines g_2-g'' and k_2-k'' , the iron oxide/manganese oxide ratio of the spinel phase increases continuously during the crystallization process, first from h' to h'' as the liquid composition changes along the heavy solid line from *H* to h_2 , and subsequently from h'' to h''' as the liquid composition changes along the rhodonite-spinel boundary curve from h_2 to h_3 .

Mixture *K* is located on line k_2-k'' . As crystallization proceeds under equilibrium conditions in this mixture the iron oxide/manganese oxide ratio of the spinel phase increases from k' to k'' as the liquid composition changes along the curved path (heavy solid line) from *K* to k_2 . As the latter point is reached, the liquid phase disappears, and iron oxide/manganese oxide ratio of the spinel remains constant.

Mixture *M* is located on the right side of line k_2-k'' , and a reversal in the direction of change of composition of the spinel phase takes place during the crystallization. The iron oxide/manganese oxide ratio first increases from m' to m'' as the liquid composition changes from *M* to m_2 , and then decreases from m'' to m''' as the liquid composition changes from m_2 to m_3 .

A couple of examples of paths of crystallization involving liquids in the field of rhodonite will be discussed, because of the complications arising from the incongruent melting of this compound. The relations are illustrated in Fig. 8.

The behavior of mixture *N* is very simple. Tridymite starts separating out at approximately 1400° C., and the liquid composition changes along the straight line $N-n_2$. At the latter point rhodonite starts separating out, and tridymite and rhodonite coexist in equilibrium with a liquid changing composition along the boundary curve from n_2 to n_3 . At the temperature of the latter, approximately 1205° C., the liquid phase disappears, leaving as end product a mixture of tridymite, rhodonite and spinel.

The sequence of phase changes taking place during equilibrium crystallization of mixture *P* is more complicated. As tridymite starts to crystallize out at approximately 1300° C. the liquid composition changes along the straight line from *P* to p_2 . At p_2 rhodonite starts to crystallize and tridymite to dissolve, and the liquid composition changes along the tridymite-rhodonite boundary curve from p_2 to p_3 . At the latter point the last trace of tridymite has disappeared, and with rhodonite as the only crystalline phase present the liquid composition changes along the straight line from p_3 to p_4 . Spinel (composition p'''') starts to separate out together with rhodonite at the temperature corresponding to p_4 , and the liquid composition now changes along the rhodonite-spinel boundary curve from p_4 to n_3 . At the temperature of the latter point,

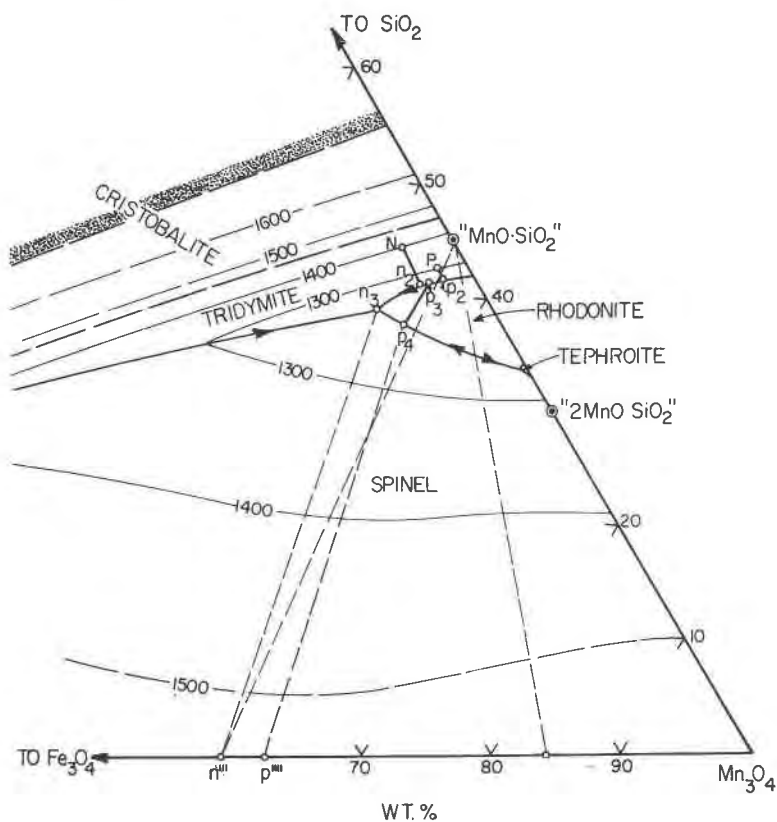


FIG. 8. Diagram illustrating paths of crystallization of selected mixtures in vicinity of rhodonite field in the system iron oxide-manganese oxide-silica in air. Line symbols used have the same meanings as explained in legend to Fig. 6.

approximately 1205° C., tridymite again makes its appearance in the phase assemblage as the liquid disappears, and the end product is a mixture of tridymite, rhodonite and spinel.

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