THE AMERICAN MINERALOGIST, VOL. 49, JULY–AUGUST, 1964

PHASE EQUILIBRIA IN THE SYSTEM $FeO-Fe_2O_3-TiO_2$ AT 1300° C.[1]

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ABSTRACT

Phase relations in the system $FeO-Fe_2O_3-TiO_2$ at 1300° C. have been deduced from the relation between oxygen pressure and composition. This relation was determined by heating samples, made up from Fe_2O_3 and TiO_2, in flowing mixtures of CO_2 and H_2, and measuring the weight loss of each sample for each gas composition with a thermobalance. This relation is shown by lines of constant oxygen pressure (gas composition) plotted on the composition triangle $FeO-Fe_2O_3-TiO_2$. Phase relations were deduced from the nature of these lines. Essential features of the system at 1300° C. are complete solid solutions between magnetite and ulvöspinel ($2FeO \cdot TiO_2$), between hematite and ilmenite ($FeO \cdot 2TiO_2$), as well as between the compositions $Fe_2O_3 \cdot TiO_2$ and $FeO \cdot 2TiO_2$. Precise compositions of coexisting solid solutions are given by end points of lines of constant oxygen pressure (tie lines) which connect solid solutions. The maximum amount of vacancies in the place of cations in the spinel solid solution at 1300° C. is about 2 per cent, regardless of the titanium content.

INTRODUCTION

Most of what we know about oxide systems we have learned through a century of investigations on the Fe-O system. An understanding of the Fe-O system is absolutely necessary before the Fe-Ti-O system can be understood. Experiments beginning perhaps with Sante-Claire Deville (1870) and summarized by Darken and Gurry (1945, 1946) form the base for this and other recent studies of the Fe-Ti-O system.

The composition, crystal chemistry and magnetic properties of the Fe-Ti-Oxides are reviewed in *Advances in Physics*, Volume 4, Number 14, April 1955, and in Volume 6, Number 23, July 1957 of the same journal. Investigations since the time of these reviews can be divided into two groups. In one group are investigations stimulated by an interest in mineralogy and rock magnetism. These have been done for the most part on minerals separated from rocks, and the prime emphasis has been on the distribution of Fe and Ti between the spinel and rhombohedral structures as a function of temperature, oxygen pressure and composition. In this group are the investigations by Vincent *et al.* (1957), Akimoto *et al.* (1957), Akimoto and Katsura (1959), Wright (1959) and Basta (1960).

The other group of investigations are directed more toward a systematic understanding of phase equilibria in the system Fe-Ti-O, with an eye

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[1] Contribution No. 64-2 from the College of Mineral Industries, The Pennsylvania State University, University Park, Pennsylvania. Based on a thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, Department of Geophysics and Geochemistry, 1962.

to extractive metallurgy. Compositions in the system in equilibrium with air were determined by MacChesney and Muan (1959). The same authors (1960) determined compositions in the system in equilibrium with metallic iron. Schmahl and Meyer (1959) investigated that part of the system where the oxygen pressure is high enough to be measured directly. Schmahl *et al.* (1960) investigated the system FeO-Fe_2O_3-TiO_2 at 1100° C. using gas mixtures to control the oxygen pressure, as did Webster and Bright (1961) at 1200° C. Approximate liquidus temperatures in the system FeO-Fe_2O_3-TiO_2 have been published by the author (1963).

Verhoogen (1962) has reviewed most of this experimental work as well as thermodynamic data on Fe-Ti oxides and the mineralogy of these oxides in rocks. From these he deduces the many changes in composition and phase these comparatively simple ternary oxides may undergo as they are subject to the environment of cooling igneous rocks.

In the present work phase relations in the system FeO-Fe_2O_3-TiO_2 are investigated at 1300° C. by a technique which made it possible to measure the maximum compositional range of the various solid solutions without cooling the samples, as explained in the next section.

EXPERIMENTAL METHOD

Experimental principles. Figure 1 represents a 1300° C. isothermal section through the system FeO-Fe_2O_3-TiO_2. A–A' is a line along which the atomic ratio of iron to titanium is constant. It is one of an important family of straight lines which originate at the oxygen apex of the system Fe-Ti-O of which the system FeO-Fe_2O_3-TiO_2 is a small part. Because only a gain or loss of oxygen is involved in a change in composition along one of these lines, they have been called oxygen-reaction lines.

A sample composed of a mixture of Fe_2O_3 and TiO_2, having the aggregate composition indicated by point A in Fig. 1, loses oxygen when heated in a reactive flowing gas of low oxygen pressure (in this case CO_2). In losing oxygen the sample changes composition along the oxygen-reaction line from point A toward point A' as far as point B. The amount of oxygen lost by the sample during this reduction is measured by the weight lost by the sample, and is proportional to the distance A–B.

In addition to the aggregate composition of a reduced sample it is also necessary to determine which phases make up the sample and the precise composition of each of these phases. When this is attempted after a sample has been cooled to room temperature there is always the possibility that individual phases in the sample have changed in composition as the sample was cooled, even though the aggregate composition of the sample remained unchanged. This is a possible source of error in the work by Webster and Bright (1961). How can we determine the composition of phases in a sample without cooling it?

Recall that a sample initially having the aggregate composition indicated by point *A* in Fig. 1 is reduced by flowing CO_2 to an aggregate composition indicated by point *B* when heated to 1300° C. When other samples made up of Fe_2O_3 and TiO_2 are heated in CO_2, they are also reduced. Results of the reduction of a series of samples at 1300° C. by CO_2 are shown by the circles in Fig. 1. The line connecting these circles represents the line of constant oxygen pressure of $10^{-3.47}$ atm. (CO_2 at 1300° C.). All samples at 1300° C. in equilibrium with CO_2 have aggregate compositions along this line. All condensed phases which comprise these reduced samples must also have compositions on this line for they are also in equilibrium with CO_2.

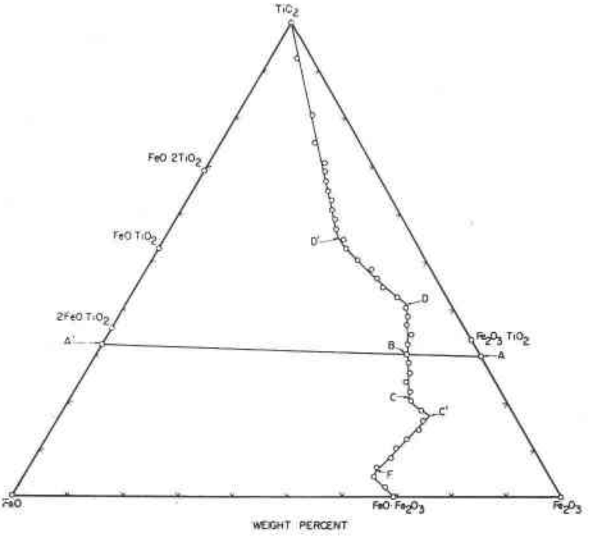

FIG. 1. Principles of the experimental method illustrated by the line which connects all compositions in the iron-titanium-oxygen system which are in equilibrium with CO_2 at 1300° C. (an oxygen pressure of $10^{-3.43}$ atm.). A mixture of Fe_2O_3 and TiO_2 having, for example, the aggregate composition represented by point *A* is reduced (loses oxygen) until it has a new aggregate composition represented by point *B*, when heated at 1300° C. in flowing CO_2. Phase boundaries are indicated by the abrupt change in the direction of this line, as explained in the text.

In order to determine how many condensed phases make up an aggregate composition, for example *B*, consider the geometry of a three-component phase diagram at a fixed temperature. Aggregate compositions made up of two condensed phases lie on the straight line connecting the points representing the compositions of these two phases. Aggregate compositions made up of three condensed phases lie within a triangle the corners of which represent the compositions of the three phases.

The aggregate composition represented by point *B* does lie on a straight segment of an oxygen isobar. This segment is a tie line connecting the points *C* and *D* which represent the compositions of the two condensed phases which make up the composition of mixture *B*. Every other sample in equilibrium with CO_2 at this temperature which has an aggregate composition between the compositions represented by points *C* and *D* is also make up of these same two condensed phases having these same two compositions.

The other straight segments of this isobaric line, *F* to C' and D' toward TiO_2 are also tie lines.

It is not always possible to tell whether such lines of constant oxygen pressure are straight or curved, that is whether samples with aggregate compositions along them are made up of one of two condensed phases. However, this may be determined by quenching a sample to room temperature and then examining it under reflected light or by *x*-ray diffraction. At first it probably appears that having to resort to quenching in such cases destroys the principal advantage of this experimental method. It should be pointed out that the composition of the sample to be quenched is chosen more or less in the middle of the segment of the isobar to be characterized, greatly reducing the chance for phase changes during quenching. The position of phase boundaries are fixed by changes in the direction of isobaric lines and thus do not depend upon examination of quenched samples.

Experimental details. Fisher's "analyzed grade" Fe_2O_3 and TiO_2 were ground together to make mixtures weighing 25 grams. Each mixture was then poured gently (without packing) into a platinum crucible and heated at 1300° C. in air for two hours, reground and reheated for another hour. The weight lost by each mixture during this heating was ascribed to two causes: loss of water and other volatile substances which would have been lost by the oxides if they had been heated separately, and loss of oxygen by reaction between the oxides because they were heated together. To distribute the observed loss of weight between these two causes, the amount of weight lost by Fe_2O_3 as well as TiO_2 when they were heated separately was measured, and all this weight loss was assumed to be volatile substances, other than oxygen. In other words TiO_2 and Fe_2O_3 were assumed to have the exact compositions their formulas indicate when heated at 1300° in air.

This assumption is difficult to prove. It has been found to be approximately true by measuring the increase in weight of "pure" metallic Fe and Ti when they are heated in air at 1300° C. In such measurements the unknown amount of oxygen dissolved in these "pure" metals at the start, particularly in metallic Ti, is probably the principal error. Nevertheless both titanium oxide and iron oxide have a fixed composition at a fixed temperature and at a fixed oxygen pressure (an invariant state in binary oxide systems). This makes a convenient reference state. If the absolute compositions these binary oxides assume when heated in air at 1300° C. are determined, the following results can be corrected accordingly.

It was easier to show that the composition of iron oxide and titanium oxide in equilibrium with air are independent of temperature in the range 800 to 1300° C. About 10 grams of "TiO_2" heated from 800° C. to 1300° C. changed weight less than 0.002 gram. When "Fe_2O_3" was heated over the same temperature interval in air and from 800 to 1430°C in oxygen, the weight loss, as measured by a thermobalance, was less than that which would have been caused if the solubility of FeO in Fe_2O_3 changed by 0.1 weight per cent. (This does not meant that the maximum solubility of FeO in Fe_3O_2 is less than 0.1 weight per cent.)

Heating mixtures of Fe_2O_3 and TiO_2 without packing them produced porous sintered cakes which were ideal samples because they reacted rapidly with gases. These cakes were broken into chunks about half an inch in diameter. Several small holes were drilled through each chunk with a dental sand-blasting machine. Finally 4 or 5 of these chunks, weighting together 8 to 15 grams, were strung like beads on a platinum wire by which they were attached to the end of an alumina rod. The rod and the attached sample were lowered into a platinum-wound resistance furnace. The cool upper end of the alumina rod was attached to one pan of an analytical balance by a long platinum wire.

When the furnace (through which air was passing at about 8 cc per second) was heated to 1300° C. the sample hanging in it continued to lose weight for about an hour. This represented the amount of oxidation taking place when the sample had previously been cooled to room temperature in air. The composition of the sample in equilibrium with air at 1300° C. was then computed from the weight (oxygen) the sample lost both during this equilibration in the thermobalance and the initial 3 hours of sintering. A correction to the weight lost by the sample in the thermobalance during heating was applied because air at 1300° C. is not as dense as air at room temperature.

This entire procedure was repeated on about 40 mixtures of Fe_2O_3 and TiO_2 to locate the air isobar as shown in Fig. 2. The accurate location of this line was very important, for all subsequent weight changes were made by reference to it.

Once a sample was equilibrated in air at 1300° C., the oxygen pressure in the gas was changed by passing CO_2, O_2, or mixtures of H_2 and CO_2 upward through the furnace tube past the sample at a rate of about 8 cc per second. The technique of mixing gases accurately and computing oxygen pressure for mixtures has been described by Darken and Gurry (1945) as well as by Muan (1958). The standard free energies of formation of H_2O, CO_2, and CO from their constituent elements, as tabulated by Coughlin (1954), were used to compute the effective oxygen partial pressures. The results of this computation for the temperature 1300° C. are shown in Table I.

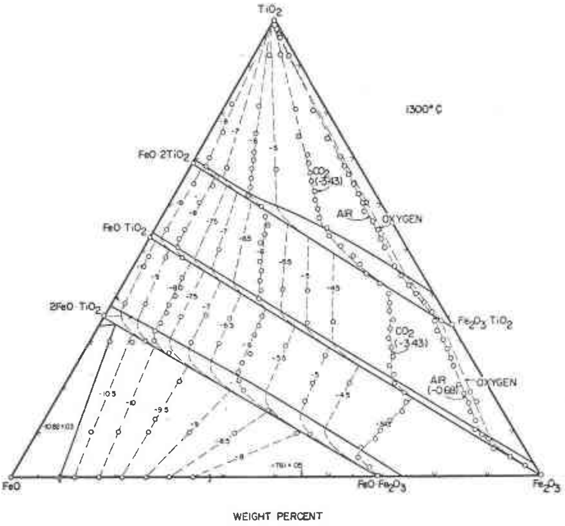

FIG. 2. Experimental points, shown by circles, representing the observed compositions of samples when heated in various atmospheres, as listed in Table II. Dashed lines connect points which represent compositions of samples heated in a gas of a certain fixed composition (fixed oxygen pressure). The composition of the gas is related to oxygen pressure by data given in Table 1, and the value of the oxygen pressure is given on each isobaric line as the log of the oxygen pressure in atmospheres. Phase boundaries, deduced from abrupt changes in the direction of isobaric lines, are drawn as heavy solid lines.

In response to a change in oxygen pressure, samples changed weight. The rate of change in weight was very rapid for the first hour, during which about 90 per cent of the total weight change took place, then the rate decreased. The more hydrogen in the gas mixture, the faster was equilibration. In order to approach constant weight, samples were kept in each gas mixture for about 16 hours. The bottom of the furnace was then opened to air and in five minutes the sample regained almost all the oxygen it originally contained when heated in air at 1300° C. In less than two hours the samples ceased gaining weight. The difference between weight loss and gain for a single sample treated in this way was as much as ±0.5 weight per cent FeO. This error was found to be time dependent when samples were strongly reduced. This was because of the vaporization of iron, particularly rapid at oxygen pressures lower than about 10^{-8} atmosphere. When the composition of a reduced sample was determined by the amount of oxygen it gained during oxidation rather than the amount of both oxygen and iron it lost during reduction, the composition was found to be independent of time and reproducible to 0.1 weight per cent FeO. Table II lists oxygen pressure (log atm.) and the corresponding weight per cent FeO for 44 different starting mixtures.

TABLE I. DATA RELATING OXYGEN PRESSURE TO GAS COMPOSITION FOR MIXTURES OF CO_2 AND H_2 AT 1300° C

The following table lists pressures (log pO_2, Atm.) for experimentally measured volume ratios of CO_2 to H_2 (log CO_2/H_2). This table was calculated from data in Coughlin (1954) as explained in Darken and Gurry (1945) and Muan (1958).

log pO_2	log CO_2/H_2
− 4.00	2.822
− 5.00	2.324
− 6.00	1.827
− 7.00	1.339
− 8.00	0.883
− 9.00	0.445
−10.00	0.058
−11.00	−0.320

RESULTS

Figure 2 represents the system $FeO-Fe_2O_3-TiO_2$ at 1300° C. drawn in weight per cent from data listed in Table II. Each circle on Fig. 2, except the one at TiO_2, corresponds to an entry in Table II and represents an experimental determination of the composition of a sample at some particular fixed oxygen pressure. Rutile, at 1300° C., is reduced only by 0.05 weight per cent oxygen when the atmosphere is changed from air to an oxygen pressure of $10^{-11.3}$ atm. Compositions of samples equilibrated in a gas of the same composition are connected by dashed lines. These dashed lines are oxygen isobars. The value of the oxygen pressure is given

TABLE II. EXPERIMENTAL DATA

Experimental data from which the subsolidus equilibria presented in Figs. 2 and 3 were deduced are tabulated below.

The first column lists sample numbers which are taken from the original laboratory notebooks. The second column gives the composition of each of these samples before heating. Because the samples were initially made up only of Fe_2O_3 and TiO_2, just the weight per cent TiO_2 is listed, the remainder being Fe_2O_3.

The rest of the table is made up of entries which relate the composition of these samples to oxygen pressure at 1300° C. Each entry is made up of two numbers. The upper number is the oxygen pressure (log pO_2), and the lower number is the weight per cent FeO in the sample at that particular oxygen pressure.

Sample	Weight % TiO_2	Oxygen Pressure (log pO_2) Weight Per Cent FeO				
673	0	−0.68 0.0	−3.43 30.8	−7.00 31.0	−7.70 63.3	−8.54 70.6
673	0	−9.49 79.2	−10.18 85.2	−10.58 88.9		
623	2	−0.68 1.9	−3.43 31.2			
624	4	−0.68 3.8	−3.43 32.3			
625	6	−0.68 5.9	−3.43 30.6			
626	8	−0.68 7.5	−3.43 27.2			
490	9	−0.68 6.8	−5.00 37.8	−5.00 39.1	−8.00 41.3	−8.50 53.0
490	9	−9.50 69.2	−10.00 75.0	−10.50 89.8		
627	10	−0.68 7.4	−3.43 25.2			
628	12	−0.68 6.3	−3.43 22.1	−9.53 66.4		
629	14	−0.68 6.3	−3.43 19.2	−6.18 43.3	−8.50 44.2	
630	16	−0.00 4.1	−0.68 5.5	−3.43 17.0	−5.00 36.1	
631	18	−0.00 4.4	−0.68 5.6	−3.43 16.6	−6.03 46.8	
632	20	−0.68 5.4	−3.43 16.9	−5.00 32.5	−6.00 46.6	−9.50 57.6

TABLE II—(*Continued*)

Sample	Weight % TiO_2	$\frac{\text{Oxygen Pressure } (\log pO_2)}{\text{Weight Per Cent FeO}}$				
633	22	$\frac{-3.43}{16.6}$	$\frac{-6.03}{45.7}$			
634	24	$\frac{-0.68}{4.2}$	$\frac{-3.43}{16.6}$	$\frac{-6.03}{44.0}$		
635	26	$\frac{-0.68}{3.9}$	$\frac{-3.43}{14.8}$	$\frac{-5.00}{27.4}$	$\frac{-6.00}{41.2}$	$\frac{-8.06}{56.2}$
636	28	$\frac{-0.68}{3.43}$	$\frac{-3.43}{13.9}$	$\frac{-5.50}{33.8}$	$\frac{-6.50}{45.6}$	$\frac{-7.00}{51.1}$
636	28	$\frac{-8.00}{58.0}$	$\frac{-8.50}{58.9}$	$\frac{-9.80}{59.8}$	$\frac{-10.5}{62.0}$	$\frac{-10.81}{66.6}$
637	30	$\frac{-0.68}{3.5}$	$\frac{-3.43}{13.6}$	$\frac{-6.00}{38.7}$	$\frac{-8.00}{56.9}$	
638	32	$\frac{-0.68}{3.45}$	$\frac{-3.43}{12.1}$	$\frac{-6.03}{36.9}$	$\frac{-8.00}{54.7}$	
639	34	$\frac{-0.68}{2.6}$	$\frac{-3.43}{10.3}$	$\frac{-6.10}{35.2}$	$\frac{-6.50}{50.3}$	$\frac{-7.00}{55.1}$
639	34	$\frac{-7.50}{49.5}$	$\frac{-8.00}{52.6}$			
640	36	$\frac{-0.68}{2.1}$	$\frac{-3.43}{9.2}$	$\frac{-6.03}{33.2}$	$\frac{-8.00}{51.1}$	$\frac{-9.00}{55.5}$
640	36	$\frac{-10.00}{59.1}$	$\frac{-11.00}{62.1}$			
641	38	$\frac{-0.68}{2.7}$	$\frac{-3.43}{9.4}$	$\frac{-6.08}{33.2}$	$\frac{-8.00}{49.0}$	
642	40	$\frac{-0.68}{2.8}$	$\frac{-3.43}{8.5}$	$\frac{-5.00}{23.6}$	$\frac{-5.50}{27.9}$	$\frac{-6.08}{31.9}$
642	40	$\frac{-7.20}{37.2}$				
643	42	$\frac{-0.68}{3.9}$	$\frac{-3.43}{9.1}$	$\frac{-6.11}{31.1}$	$\frac{-8.00}{45.8}$	
644	44	$\frac{-0.68}{3.9}$	$\frac{-3.43}{10.5}$	$\frac{-6.11}{29.2}$		
645	46	$\frac{-0.68}{4.3}$	$\frac{-3.43}{11.1}$	$\frac{-6.12}{29.3}$	$\frac{-8.00}{43.6}$	$\frac{-9.00}{45.6}$
645	46	$\frac{-10.00}{49.7}$	$\frac{-11.00}{52.5}$			
646	48	$\frac{-0.68}{5.4}$	$\frac{-3.43}{10.8}$	$\frac{-6.10}{27.8}$	$\frac{-8.00}{43.2}$	

TABLE II—(*Continued*)

Sample	Weight % TiO_2	Oxygen Pressure (log pO_2) Weight Per Cent FeO				
647	50	$\frac{-0.68}{4.3}$	$\frac{-3.43}{12.1}$	$\frac{-6.06}{27.0}$	$\frac{-8.00}{41.9}$	
648	52	$\frac{-0.68}{3.8}$	$\frac{-3.43}{12.6}$	$\frac{-6.14}{25.1}$	$\frac{-8.00}{39.8}$	$\frac{-9.00}{43.4}$
649	54	$\frac{-0.68}{3.9}$	$\frac{-3.43}{12.6}$	$\frac{-6.14}{23.8}$		
650	56	$\frac{-0.68}{4.3}$	$\frac{-3.43}{13.1}$	$\frac{-6.12}{23.0}$		
651	58	$\frac{-0.68}{4.0}$	$\frac{-3.43}{12.4}$	$\frac{-6.06}{22.9}$	$\frac{-8.00}{34.2}$	
652	60	$\frac{-0.68}{3.3}$	$\frac{-3.43}{12.0}$	$\frac{-6.03}{24.2}$		
653	62	$\frac{-0.68}{3.1}$	$\frac{-3.43}{11.2}$	$\frac{-6.04}{22.9}$	$\frac{-8.00}{27.9}$	$\frac{-9.00}{33.3}$
654	64	$\frac{-0.68}{3.1}$	$\frac{-3.43}{10.7}$	$\frac{-6.05}{21.9}$	$\frac{-8.00}{27.9}$	
655	66	$\frac{-0.68}{2.9}$	$\frac{-3.43}{10.2}$	$\frac{-5.00}{16.4}$	$\frac{-6.09}{20.7}$	$\frac{-8.00}{28.8}$
656	68	$\frac{-0.68}{2.7}$	$\frac{-3.43}{9.4}$	$\frac{-6.06}{19.3}$	$\frac{-8.00}{27.5}$	$\frac{-9.00}{30.3}$
657	70	$\frac{-0.68}{2.5}$	$\frac{-3.43}{8.6}$	$\frac{-6.00}{18.2}$		
659	74	$\frac{-0.68}{3.0}$	$\frac{-3.43}{8.3}$	$\frac{-6.04}{16.0}$	$\frac{-8.00}{22.0}$	
662	80	$\frac{-0.68}{2.4}$	$\frac{-3.43}{5.8}$	$\frac{-6.05}{11.9}$	$\frac{-8.00}{17.2}$	
668	92	$\frac{-0.68}{1.2}$	$\frac{-3.43}{2.9}$	$\frac{-6.06}{5.0}$	$\frac{-7.90}{6.36}$	
670	96	$\frac{-0.68}{0.9}$				
671	98	$\frac{-0.68}{0.6}$				

on each isobar as the logarithm of the oxygen pressure in atmospheres. Heavy solid lines, indicating phase boundaries, are drawn through the points where the oxygen isobaric lines abruptly change direction. These phase boundaries are redrawn in Fig. 3 without lines of constant oxygen pressure so that there is room to label the various compositional areas.

Starting at the top of Fig. 3 there is a small area which represents the extent of the solubility of Fe_2O_3 and FeO in the phase with the rutile structure at 1300° C. Rutile saturated with iron oxide is in equilibrium with pseudobrookite saturated with titanium oxide. These are the two condensed phases which make up all compositions in the area between rutile and pseudobrookite. The compositional range of the phase with the pseudobrookite structure is indicated between compositions $Fe_2O_3 \cdot TiO_2$ and $FeO \cdot 2TiO_2$. The compositions of most minerals which have been called pseudobrookite are not well known, but they are thought to be near $Fe_2O_3 \cdot TiO_2$. The author, in an unpublished investigation, has found that $FeO \cdot 2TiO_2$ is not stable relative to ilmenite and rutile at temperatures below about 1000° C. Composition of the pseudobrookite solution near $FeO \cdot 2TiO$ have not been found as minerals.

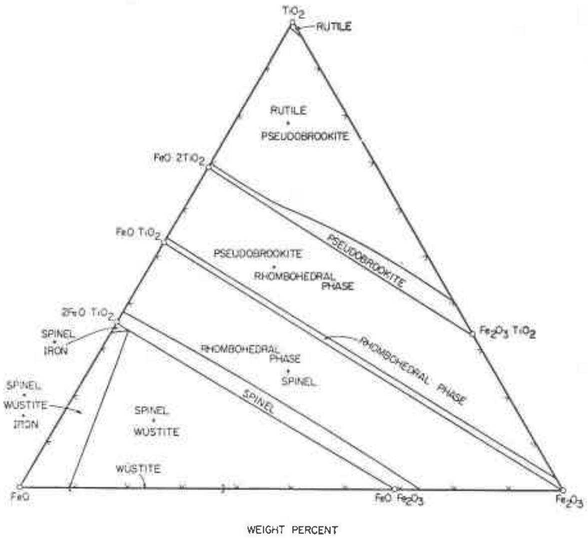

FIG. 3. Phase areas in the system FeO-Fe_2O_3-TiO_2 at 1300° C. deduced from Fig. 2. In all cases the extent of solid solution is no more than indicated. The range in composition of wüstite at 1300° C. is indicated by the brackets on the line between FeO and Fe_2O_3. Tie lines are omitted from this figure, but they can be seen on Fig. 2 as oxygen isobars.

When the rhombohedral phase becomes saturated with iron oxide, a spinel phase appears. Between the area in which the rhombohedral phase is stable and the area in which the spinel phase is stable lies a large area in which all aggregate compositions are made up of both a spinel and a rhombohedral phase. Here, as in the case of every area in which two condensed phases exist together, the compositions of the two phases can be determined for any specific composition by the location of the tie line (oxygen isobar) through the composition.

On the other side of the spinel phase is a nearly triangular area within which all compositions are made up of spinel in equilibrium with wüstite. The composition of wüsite at 1300° C. varies between the two brackets on the line FeO-Fe_2O_3 (a solubility of TiO_2 in wüstite was not detected). On the left is a small area within which all compositions are made up of three condensed phases, the compositions of which are uniquely fixed at 1300° C. These three phases are nearly pure metallic iron, wüstite, and one particular composition of spinel near the composition $2FeO \cdot TiO_2$ (ulvöspinel). Near and just below the composition $2FeO \cdot TiO_2$ is a small compositional triangle within which compositions are made up of spinel and metallic iron (strickly speaking an iron-titanium alloy, but the amount of titanium is less than 1 weight per cent).

DISCUSSION

Cubic Fe-Ti-O minerals in volcanic rocks often have compositions well within the compositional area $FeO \cdot Fe_2O_3$-$2FeO \cdot TiO_2$-$FeO \cdot TiO_2$-Fe_2O_3. From experimental work one would expect the compositions to be on the spinel join ($FeO \cdot Fe_2O_3$-$2FeO \cdot TiO_2$). These minerals have been called titanomaghemites or γ-phases by analogy to maghemite (cubic (γ) Fe_2O_3). They seem to be homogeneous, made up of a single phase.

Certainly these minerals did not form at temperatures higher than 1300° C., in fact they are most common in somewhat weathered rocks suggesting a low temperature of formation. Cubic Fe_2O_3, for example, is prepared by the low temperature oxidation of magnetite in the presence of steam. Akomoto, Katsura, and Yoshida (1957) were able to synthesize a very cation deficient cubic phase by the oxidization of various members of the $FeO \cdot Fe_2O_3$-$2FeO \cdot TiO_2$ solid solution, if the oxidation was carried out below about 500° C. The spineloid phase they produced sometimes had compositions near the Fe_2O_3-$FeO \cdot TiO_3$ join. This means that more than 11 per cent of the cation sites were vacant relative to an unoxidized spinel. In some cases this oxidation resulted in the formation of a rhombohedral phase in addition to the cubic phase.

It seems these cation-deficient phases are metastable relative to the more stoichiometric oxides to which they change upon heating. Additional evidence of the metastable nature of some γ-phases in rocks has recently been found by Akimoto and Katsura (1959). They separated a cubic Fe-Ti oxide phase from a volcanic rock by means of a magnet, and then subdivided this mineral into several fractions on the basis of Curie temperature. Each of these fractions was found to have the same Fe/Ti ratio, but a different oxygen content. Such a compositional variation within a single phase cannot occur at equilibrium (at constant temperature etc.). These minerals were probably caught in the process of either an oxidation or reduction under nonequilibrium conditions.

One may ask about the common "exsolution" textures of magnetite and ilmenite, where fine lamellae of magnetite and ilmenite alternate within a single grain of oxide, in almost any ratio. Isn't this compelling evidence for complete solid solution between magnetite and ilmenite? No, spinel-rhombohedral phase intergrowths made by the isothermal oxidation of a single spinel phase often show similar fine parallel lath-like textures which might well be mistaken as the result of cooling and unmixing of a homogeneous phase.

A high-temperature cubic form of $FeO \cdot TiO_2$, hypothesized to make a magnetite-$FeO \cdot TiO_2$ solid solution seem reasonable, was not found in this study, nor by MacChesney and Muan (1960). Judging from the complete solid solution from $FeO \cdot TiO_2$ to hematite, the limited solubility of both magnetite and ulvöspinel in $FeO \cdot TiO_2$, one must conclude, in the absence of high temperature x-ray studies, that $FeO \cdot TiO_2$ has the ilmenite structure at 1300° C.

A cubic form of $FeO \cdot TiO_2$ may exist at low temperatures, but it has been pointed out that such phases are prepared by the low temperature oxidation of stable cubic structures. There is no spinel having the same Fe/Ti ratio as $FeO \cdot TiO_2$ (unpublished investigation of the system Fe-FeO-TiO_2 by the author) from which cubic $FeO \cdot TiO_2$ could form by oxidation.

There is also some disagreement between the composition of hematite-ilmenite minerals separated from igneous rocks and the compositions which would be expected on the basis of the present study. Katsura finds that minerals of this rhombohedral solution contain more TiO_2 than compositions on the Fe_2O_3-$FeO \cdot TiO_2$ join. The excess TiO_2 appears to be proportional to the amount of ilmenite. On the other hand, the rhombohedral solution synthesized in the present work had compositions precisely on the Fe_2O_3-$FeO \cdot TiO_2$ join. As in the case of the cubic mineral, this discrepancy may indicate some oxidization of these minerals.

In conclusion let us review the history of an Fe-Ti spinel as it cools in the environment of an igneous rock. The exchange of Fe and Ti with the silicates, as discussed by Verhoogen (1962), is not considered. It probably is not significant after the rock solidifies.

At temperatures above about 900° C. the oxidation of a magnetite-ulvöspinel solid solution results in the immediate formation (precipitation) of a hematite-ilmenite solution with only a small increase in the number of cation vacancies in the spinel (a maximum of 2 per cent of the total cation sites at 1300° C., see Fig. 2). If this oxidation is continued isothermally as one might expect in an "open system," where heat may be continually brought to the rock, both the rhombohedral and spinel phase increase in Fe_2O_3 content, and the rhombohedral phase increases in amount. Constant temperature is not unlikely, for one source of heat is the oxidation itself. (A rock containing 5 per cent magnetite could be heated as much as 40° C. by the oxidation of this magnetite to hematite.)

Another sort of exchange reaction takes place if oxidation stops and cooling continues. In this case the composition of the spinel changes toward magnetite while at the same time the coexisting rhombohedral phase must change in composition toward ilmenite in such a way that the aggregate composition remains constant (Vincent 1957).

Remember that during the interplay of these two processes, as the temperature falls, immiscibility begins to develop first in the rhombohedral phase, and, when the temperature falls below about 600° C., in the spinel solution as well.

Recall also that up to now we have assumed equilibrium among all phases. But at some unknown, and probably widely variable temperature, depending perhaps upon the oxidizing media, the spinel solid solution may oxidize and yet remain a single spineloid phase, even though it contains many more cation vacancies than it can at much higher temperatures. Why the spinel oxidizes precipitating the hematite-ilmenite solid solution in one case, and to a cation deficient cubic phase in another, is unknown. One is tempted to consider this metastable oxidation a phenomenon which results because of the difficulty of forming a new phase in the solid state at low temperatures. This is not the case, for Katsura and Kushiro (1961) report the occurrence of titanomaghemite on grains of stoichiometric spinel even when there are abutting grains of the rhombohedral phase which it would seem could have acted as seeds. Perhaps the explanation of this "meta stable" oxidation will be found through study of the Fe-O-H system.

ACKNOWLEDGMENT

The author wishes to express appreciation for the support given this work by the American Iron and Steel Institute through the College of Mineral Industries.

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Manuscript received, December 26, 1963; accepted for publication, February 12, 1964.