ELEMENT DISTRIBUTION AMONG COEXISTING PHASES IN THE SYSTEM $MgO-FeO-Fe_2O_3-SiO_2$ AS A FUNCTION OF TEMPERATURE AND OXYGEN FUGACITY[1]

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Abstract

Compositions of coexisting phases in the system $MgO-FeO-Fe_2O_3-SiO_2$ have been determined as a function of temperature and oxygen fugacity (f_{O_2}) under equilibrium conditions at a total pressure of one atmosphere. At subsolidus temperatures if f_{O_2} remains constant or increases as temperature decreases, the Mg:Fe ratio increases in all three magnesium-iron solid solution phases: olivine, pyroxene, magnesioferrite. If the decrease of f_{O_2} with temperature is like that in pure water, the Mg:Fe ratio in magnesioferrite remains essentially constant, while this ratio increases in pyroxene and in olivine, more so in olivine than in pyroxene. If the decrease of f_{O_2} with temperature is larger, approximating that of the hematite-magnetite buffer, the Mg:Fe ratio of magnesioferrite decreases, that of pyroxene remains essentially constant, and that of olivine increases. Magnesioferrite at solidus temperatures contains generally less than 2 weight per cent MgO at 10^{-6} atm f_{O_2}, and smaller amounts at lower oxygen fugacities.

Introduction

The system $MgO-FeO-Fe_2O_3-SiO_2$ has been described by Muan and Osborn (1956) and discussed further relative to fractional crystallization in basalt systems by Osborn (1959). In these papers the important effect of oxygen partial pressure[2] on phase relations in iron oxide containing systems is emphasized. In view of the importance of iron oxides in magma systems, further experimental work on the system $MgO-FeO-Fe_2O_3-SiO_2$ was done to obtain more data on the compositions of coexisting phases. Composition data have been obtained for the first time for the magnesioferrite phase and additional data were obtained for coexisting pyroxene and olivine phases, as a function of temperature and oxygen fugacity.

Figure 1 shows a tetrahedron representing the system $MgO-FeO-Fe_2O_3-SiO_2$. The front face is the system $MgO-FeO-Fe_2O_3$, the rear apex is SiO_2, and the system $MgO-FeO-SiO_2$ forms the base. A few lines are drawn to

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[2] Subsequently in this paper we will use the term oxygen fugacity, f_{O_2} rather than oxygen partial pressure, p_{O_2}.
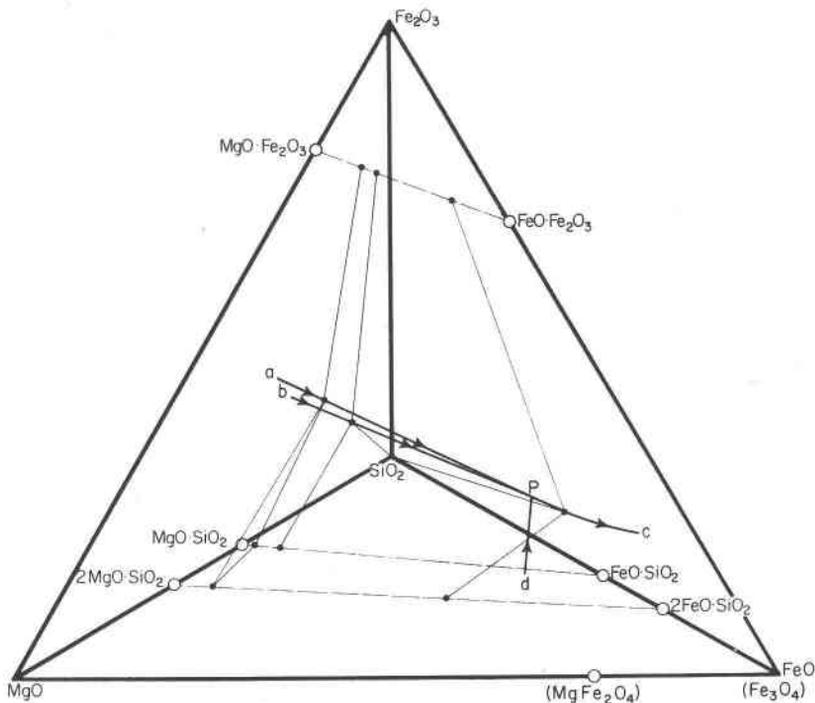
Fig. 1. Tetrahedron sketched to illustrate certain phase equilibrium relations in the system MgO-FeO-Fe_2O_3-SiO_2. The base of the tetrahedron represents the system MgO-FeO-SiO_2 on which are shown by dashed lines the pyroxene ($MgO \cdot SiO_2$-$FeO \cdot SiO_2$) and olivine ($2MgO \cdot SiO_2$-$2FeO \cdot SiO_2$) joins. On the front face representing the system MgO-FeO-Fe_2O_3 is shown the magnesioferrite join ($MgO \cdot Fe_2O_3$-$FeO \cdot Fe_2O_3$). Univariant curves of special interest within the tetrahedron are shown as heavy lines with arrows. These curves, after Muan and Osborn (1956), represent compositions of liquids in equilibrium with three crystalline phases and a gas phase. Arrows indicate directions of decreasing temperature. The fugacity of oxygen decreases from a to P, from b to P, and from P to c. Three sets of conjugation lines have been sketched to illustrate compositions of three crystalline phases in equilibrium with a liquid along each of the three univariant curves a-P, b-P, and P-c (after Muan and Osborn, 1956). Points representing $MgFe_2O_4$ and Fe_3O_4 where all iron oxide is calculated as FeO are shown by ($MgFe_2O_4$) and (Fe_3O_4) on the join FeO-MgO.

illustrate certain relations which are particularly pertinent to this discussion. Along three joins, shown as light dashed lines, complete or extensive solid solution exists: $MgO \cdot Fe_2O_3$-$FeO \cdot Fe_2O_3$ (magnesioferrite);$MgO \cdot SiO_2$-$FeO \cdot SiO_2$ (pyroxene); $2MgO \cdot SiO_2$-$2FeO \cdot SiO_2$ (olivine). Although $FeSiO_3$ as well as the pyroxene solid solutions approaching this composition are stable only at pressures greater than one atmosphere (Akimoto, Fujisawa, and Katsura, 1964; Lindsley, Davis, and MacGregor, 1964),

FeSiO₃ is shown to represent the end-member of the solid solution series. The heavy lines with arrows are quaternary liquidus univariant lines experimentally determined at a total gas pressure of one atmosphere. They represent the compositions of liquids in equilibrium with gas and three crystalline phases, after Muan and Osborn (1956). The liquids represented by the line *a-P* are in equilibrium with crystals of olivine, pyroxene, and magnesioferrite; the liquids of the line *b-P* are in equilibrium with pyroxene, tridymite, and magnesioferrite; and the liquids represented by the line *P-c* are in equilibrium with olivine, tridymite, and magnesioferrite. The temperature and the oxygen fugacity for phase assemblages along the lines *a-P*, *b-P*, and *P-c* decrease from left to right. Determination of the compositions of these crystalline phases in each of the above crystalline assemblages with changing conditions of temperature, oxygen fugacity and bulk composition was the object of this study.

Experimental Procedure

The conventional quenching technique was utilized under conditions of controlled oxygen fugacity at a total gas pressure of one atmosphere, as described by Darken and Gurry (1945), and Muan and Osborn (1956). Mechanically mixed and sintered oxides of a composition known from previous work (Muan and Osborn, 1956) to give the desired assemblages were held at constant temperature under the chosen atmospheric conditions for 10 to 21 days. Each sample was ground and replaced in the furnace two to three times to facilitate attainment of equilibrium. Samples run in air were contained in platinum foil envelopes open to the atmosphere. Because appreciable iron may be lost to platinum at lower oxygen fugacities (Taylor and Muan, 1963), Ag-Pd alloy envelopes were used as containers for runs in atmospheres other than air at temperatures of 1200°C and lower. The effective upper limit for this use of these alloys is about 1200°C (Muan, 1963). At higher temperatures in atmospheres other than air, pressed pellets were supported in thin (0.004″) Pt wire slings. The mass of the sample was so much greater than the mass of the Pt wire in contact with the sample that the Fe-loss to the wire was negligible.

The samples were quenched to room temperature and examined under the petrographic microscope and by X-ray diffraction techniques. Quantitative determinations of the compositions of the crystalline phases were performed with an electron microprobe analyzer. Details of the analytical technique and assignment of uncertainty are described elsewhere (Speidel, 1965).

The beam current of the microprobe analyzer was adjusted to read a constant value on the specimen, in this case, 0.05 μA at 20kV. The beam current capacitors were charged to capacity and the relative charge of the elements on the X-ray channel capacitors was recorded on a strip chart. A series of (Mg, Fe)Fe₂O₄ solid solutions was prepared by heat treatment in air at 1300°–1400°C using the data of Phillips, Sōmiya and Muan (1961). These solid solutions were used as standards to determine the Mg:Fe ratios of the magnesioferrite phase. Two natural olivines,[1] one natural amphibole,[1] and one synthetic olivine[2] were

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[1] The samples and an analysis of their chemical composition were furnished by E. W. White, Mineral Constitution Laboratory, The Pennsylvania State University. They have the following designations: R 1839ol; R 2449 am; R 2468ol.

[2] This analyzed sample, supplied by Ralph Nafziger, has the following composition in weight percent: 58.3 Mg₂SiO₄, 41.7 Fe₂SiO₄.

used as standards for the determination of the Mg/Fe ratio of the silicate phases. By representing the compositions of solid solution series by points along the appropriate linear joins Mg_2SiO_4-Fe_2SiO_4, $MgSiO_3$-$FeSiO_3$ and $MgFe_2O_4$-Fe_3O_4, knowledge of the amount of FeO will allow quick calculation of the amount of MgO and SiO_2 in a phase. The magnesioferrite phase, $MgFe_2O_4$-Fe_3O_4, cannot be represented as a linear join under all condtiions. It can contain several weight percent excess Fe_2O_3. Reference to Figure 1 will show that all of the tie lines considered approach the join from the Fe_2O_3-poor side. Recent work in this laboratory (Speidel, 1966) has indicated that the magnesioferrite on the Fe_2O_3-poor side always has a cation to anion ratio of 0.750. Therefore, the magnesioferrite phase can be represented on the join $MgFe_2O_4$-Fe_3O_4 and the determination of the ratio Fe_2O_3/FeO for the phase, knowing MgO and total iron oxide content is a simple calculation.

The uncertainty in FeO-content of the olivine and pyroxene phases is approximately 5 to 7 percent of the amount of FeO present. The uncertainty in FeO-content of the magnesioferrite varies between 0.3 and 3 percent of the amount of iron oxide present, the uncertainty increasing as the amount of MgO increases.

TABLE 1. COMPOSITION (WT.%) OF COEXISTING CRYSTALLINE AND LIQUID PHASES AT FIXED OXYGEN FUGACITIES IN THE SYSTEM MgO-FeO-Fe_2O_3-SiO_2[1]

Temp (°C)	$\log f_{O_2}$	CO_2:H_2	FeO in Olivine	FeO in Pyroxene	FeO in Magnetite	FeO in Liquid	MgO in Liquid	Tridymite
1375	−0.7	—	8.5	4.5	85.5	40.0	19.0	—
1365	−0.7	—	—	5.0	86.0	38.0	16.5	p
1285	−5.6	132	35.0	20.0	98.0	52.0	12.5	—
1277	−5.8	132	—	22.0	97.5	50.5	10.0	p
1255	−7.1	40	40.0	27.5	98.5	56.5	6.5	p
1160	−8.8	24	48.0	—	99.0	64.5	1.5	p
1144[2]	−9.2	19	70.7	—	100.0	65.5	0.0	p

[1] The compositions of the magnetite phase were determined in the present study. All other values are from Muan and Osborn (1956). All iron oxide is calculated as FeO. p =tridymite present. The f_{O_2} value for a given temperature and CO_2:H_2 ratio is taken from Porter, 1966.

[2] Phase relations at 1144°C are for the assemblage fayalite-silica-magnetite-liquid-gas in the limiting ternary system FeO-Fe_2O_3-SiO_2 (Muan, 1955).

EXPERIMENTAL RESULTS

The compositions of coexisting crystalline and liquid phases at a series of oxygen fugacities are listed in Table 1 and shown by points in Figure 2. Temperatures for the existence of the various assemblages, and compositions of pyroxene, olivine, and liquid are taken from the work of Muan and Osborn (1956). Composition of the magnesioferrite phase in these assemblages was determined in the present study using mixtures equilibrated in the appropriate atmosphere at a temperature just below the solidus. By using these completely crystalline mixtures, the presence of abundant magnesioferrite for analysis was assured. The change in composition of the magnesioferrite occurring in the few degrees interval between the temperature of coexistence of three crystalline phases with liquid and the temperature used for these runs is very small (see mag-

nessofesrite curves in Figs. 5, 6, and 7). Total iron oxide in all phases is recalculated and plotted as FeO in Figure 2, after the manner of Presnall (1964, 1966). For the situation of triangle (a), f_{O_2} is fixed at $10^{-0.7}$ atm., and for cases (b) and (d) the $CO_2 : H_2$ mixing ratio is experimentally fixed at 132 and 24 respectively. Hence three crystalline phases are the maximum number which can coexist with liquid and gas phases in (a), (b), and (d). Triangle (c) on the other hand represents an invariant situation in the four component system. The liquid is point P of Figure 1. Here four crystalline phases (olivine, tridymite, pyroxene and magnesioferrite) are in equilibrium with liquid P and vapor. The f_{O_2} is $10^{-7.1}$ atm. and the temperature is 1255°C. The ratio $CO_2 : H_2$ is approximately 40. If the progression shown by the series of diagrams in Figure 2 is continued for another step with the liquid composition corresponding to point c of Figure 1, fayalite, magnetite (Fe_3O_4), and silica coexist with liquid and a gas of $CO_2 : H_2$ ratio of 19 ($f_{O_2} = 10^{-9.2}$ atm.) at a temperature of 1144°C (Muan, 1955).

Compositions of the liquids coexisting in equilibrium with the indicated crystalline phases are illustrated by the numbered points and by P in the triangles of Figure 2. Point 1 in (a) and (b) represents in each case a point on the line a-P of Figure 1, $i.e.$, a liquid in equilibrium with olivine, pyroxene, magnesioferrite and gas. Point 2 in (a) and (b) represents in each case a point along the line b-P of Figure 1, $i.e.$, a liquid in equilibrium with pyroxene, tridymite, magnesioferrite and gas. Point 3 in (d) represents a point along the line P-c of Figure 1, $i.e.$, a liquid in equilibrium with olivine, tridymite, magnesioferrite and gas. Because the Fe_2O_3/FeO ratio for the composition of liquid and magnesioferrite is not shown in Figure 2 the composition of these phases is not completely given by a point in these triangles. Location of the composition point within the MgO-FeO-Fe_2O_3-SiO_2 tetrahedron (Fig. 1) would be necessary to show its complete composition. The temperatures and oxygen fugacities for the various assemblages are also shown in Figure 2.

By representing compositions of crystalline phases along the appropriate linear joins, $MgFe_2O_4$-Fe_3O_4, $MgSiO_3FeSiO_3$, Mg_2SiO_4-Fe_2SiO_4, knowledge of the total iron oxide calculated as FeO will allow quick graphical estimation of phase composition. The curves of Figure 3 show the changes in composition of phases coexisting in univariant equilibrium, as a function of temperature and oxygen fugacity. They are drawn from the data of Table 1 as was Figure 2.

Referring to Figures 2 and 3, the following points are of special note in connection with these assemblages of three crystalline phases, a liquid phase and a vapor phase: (1) The condensed phases all decrease in Mg: Fe ratio as temperature and oxygen fugacity decrease concomitantly.
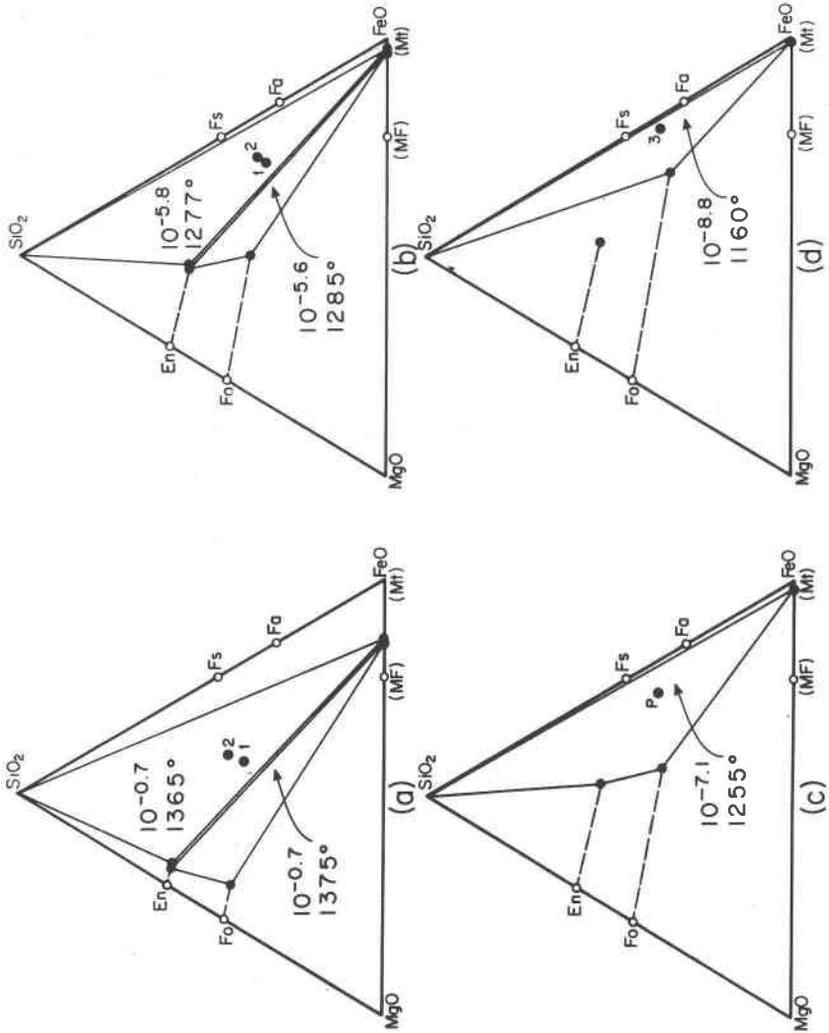
FIG. 2. Triangular diagrams representing phase relations for the system MgO-FeO-Fe$_2$O$_3$-SiO$_2$. All iron oxide is calculated as FeO, making possible representation of points on a plane, as if points in the tetrahedron of Figure 1 were projected onto the base, MgO-FeO-SiO$_2$, from the oxygen apex of a tetrahedron for the system MgO-FeO-SiO$_2$-O. Solid lines within triangles are conjugation lines joining compositions of coexisting crystalline phases. Dots labeled 1, 2, 3, and P represent compositions of liquids as determined by Muan and Osborn (1956), coexisting with the crystalline phases shown.

Diagram (a) represents invariant phase relations at the fixed f_{O_2} of air ($f_{O_2} = 10^{-0.7}$ atm). Two inner triangles represent two different phase assemblages. Olivine, pyroxene, and magnesioferrite coexist with liquid 1 at 1375°C. Pyroxene, tridymite, and magnesioferrite

(2) Olivine in equilibrium with pyroxene, magnetite and liquid is always more Fe-rich than the coexisting pyroxene. This same trend was found by Bowen and Schairer (1935) under conditions such that metallic iron rather than magnetite is in equilibrium with the silicates and a liquid. (3) Olivine shows the widest variation in Fe-content of all the crystalline phases. (4) At low temperatures the Fe-content of olivine increases very rapidly with decreasing temperature when it is in equilibrium with tridymite, magnesioferrite, liquid and vapor. In the temperature interval, 1165° to 1144°C, the FeO content of olivine increases by more than 25 weight percent. The corresponding change in f_{O_2} is less than $10^{0.5}$ atm.

The lines of Figure 4 represent univariant equilibrium relations for five assemblages in an f_{O_2}-$1/T$ plot. Straight line relations have been assumed. Lines b-P, a-P, and P-c correspond to the conditions represented by the composition of liquids along the univariant lines of Figure 1. The line P-p represents conditions for the univariant subsolidus assemblage olivine, tridymite, pyroxene, magnesioferrite and vapor.[1]

Determinations of the compositions of coexisting crystalline phases in equilibrium with vapor at subsolidus temperatures are listed in Table 2. From these data in conjunction with those for the phases in equilibrium with liquid and vapor (Table 1 and Fig. 3) projections can be made of phase composition changes as a function of temperature and oxygen fugacity change below the solidus. For example, in Figure 5 lines have been constructed to illustrate the inferred manner of change of f_{O_2} with decreasing temperature for a given constant iron oxide content of

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[1] The f_{O_2}-T values of Assemblage 5 (olivine, tridymite, pyroxene, liquid, and vapor) are estimated from values given by Muan and Osborn (1956). Liquid compositions lie along the line P-d, Figure 1. This is discussed fully in a forthcoming publication (Speidel and Nafziger, 1966). The sixth univariant curve, vapor absent, is not represented.

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coexist with liquid 2 at 1365°C. Compositions of crystaline phases are shown by apices of the triangles.

Diagram (b) represents invariant phase relations at a fixed gas mixing ratio of CO_2:H_2 = 132. Olivine-pyroxene-magnesioferrite-liquid 1 coexist at a temperature of 1285°C and f_{O_2} of $10^{-5.6}$ atm. Pyroxene-tridymite-magnesioferrite-liquid 2 coexist at a temperature of 1277°C and f_{O_2} of $10^{-5.8}$ atm.

Diagram (c) represents an invariant situation in the system. Six phases are present. The CO_2:H_2 ratio is approximately 40. Olivine, tridymite, pyroxene, and magnesioferrite coexist with liquid P at 1255°C at $f_{O_2} = 10^{-7.1}$ atm.

Diagram (d) represents invariant phase relations at a CO_2:H_2 ratio of 24. Olivine, tridymite, and magnesioferrite coexist with liquid 3 at 1160°C at $f_{O_2} = 10^{-8.8}$ atm.

En = $MgSiO_3$, Fs = $FeSiO_3$, Fo = Mg_2SiO_4, Fa = Fe_2SiO_4, MF and Mt = $MgFe_2O_4$ and Fe_3O_4, respectively, with all iron oxide calculated at FeO.
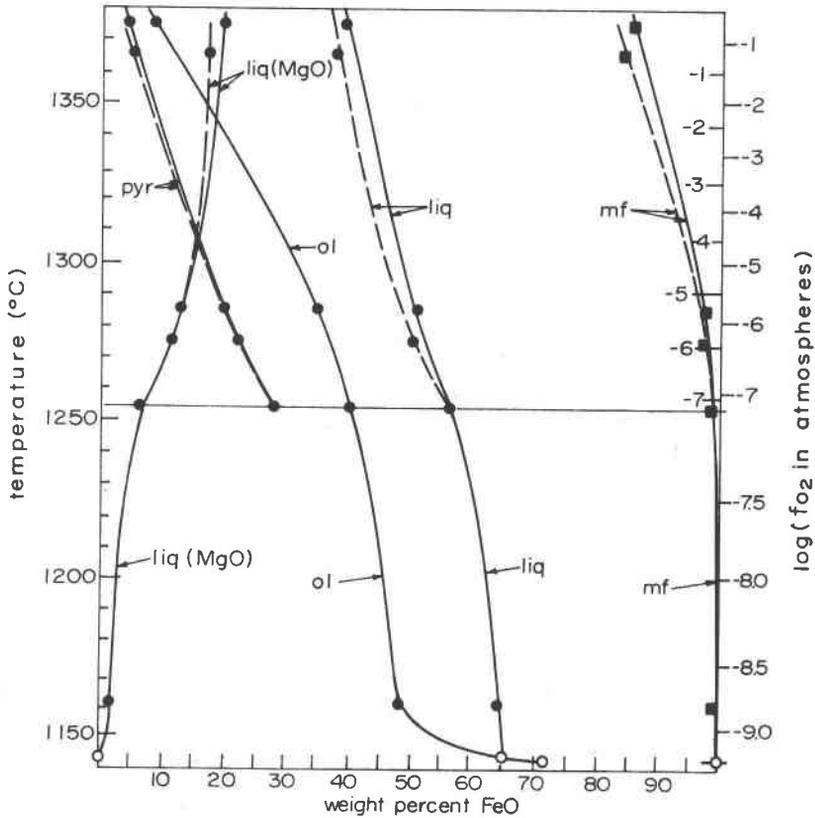
FIG. 3. Curves to show change in total iron oxide content (plotted as FeO) of condensed phases in the system MgO-FeO-Fe₂O₃-SiO₂ coexisting in univariant equilibrium, replotted from Figure 2. For the liquid phase, MgO as well as iron oxide is shown. In the upper part of the diagram solid curves represent change in composition of condensed phases in the assemblage: olivine-pyroxene-magnesioferrite-liquid-gas, and the exterior oxygen fugacity scale applies. Dashed curves represent change in composition of pyroxene, magnesioferrite, and liquid in equilibrium with tridymite and gas, and the interior oxygen fugacity scale applies. Curves in the lower part of the diagram show change in composition of olivine, magnesioferrite, and liquid in equilibrium with tridymite and gas at oxygen fugacities as indicated along the right verticle line. The horizontal line shows the temperature and f_{O_2} conditions for the invariant assemblage: olivine-pyroxene-tridymite-magnesioferrite-liquid-gas. The conditions apply to point P of Figures 1 and 2. Compositions determined by Muan and Osborn (1956) are given by dots. Compositions determined by the present work are given by squares. Compositions at point c, Figure 1, in the ternary system FeO-Fe₂O₃-SiO₂ are given by the bottom termination of the curves, open circles, after Muan (1955). mf=magnesioferrite, ol=olivine, pyr=pyroxene, liq=liquid.
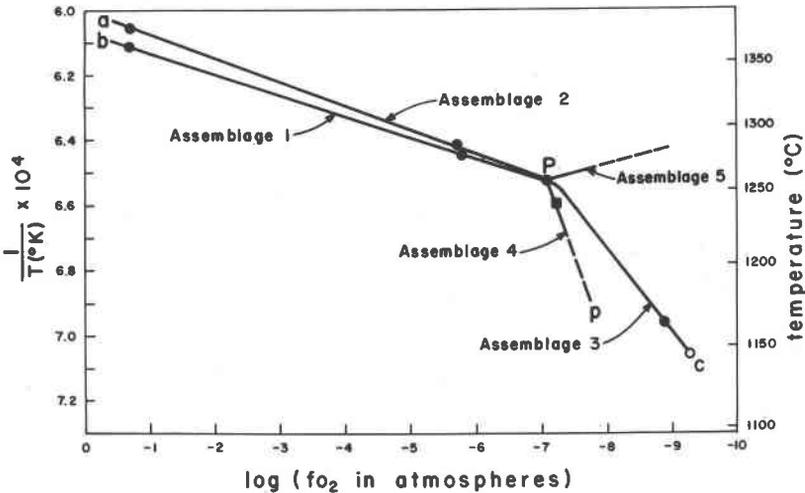
FIG. 4. Plot to show relation of temperature to oxygen fugacity along univariant curves in the system $MgO-FeO-Fe_2O_3-SiO_2$. Assemblage 1 = pyroxene-tridymite-magnesioferrite-liquid-gas; assemblage 2 = olivine-pyroxene-magnesioferrite-liquid-gas; assemblage 3 = olivine-tridymite-magnesioferrite-liquid-gas; assemblage 4 = olivine tridymite-pyroxene-magnesioferrite-gas; assemblage 5 = olivine-tridymite-pyroxene-liquid-gas. The curves for assemblages 1, 2, and 3 are after Muan and Osborn (1956), solid circles, and Muan (1955), open circle, and were checked by the present work. The curve for assemblage 4 is inferred from the present work, solid square. The curve for assemblage 5 is inferred from the work of Muan and Osborn (1956).

TABLE 2. IRON OXIDE CONTENT OF COEXISTING CRYSTALLINE PHASES IN THE SYSTEM $MgO-FeO-Fe_2O_3-SiO_2$[1] AS DETERMINED IN THE PRESENT INVESTIGATION

Mixture Composition (wt. %)			Temp (°C)	$\log f_{O_2}$	$CO_2:H_2$	FeO in Olivine	FeO in Pyroxene	FeO in Magnetite	Tridymite
M_gO	F_eO	SiO_2							
26.7	55.5	17.8	1350	−0.7	—	9.0 (2)	4.5 (18)	85.5 (16)	—
			1126	−0.7		10.0 (9)	4.0 (2)	85.7 (10)	—
18.4	46.0	35.6	1350	−0.7			5.5 (8)	86.0 (16)	p
14.9	60.1	25.0	1240	−6.3	132	32.0 (11)	20.0 (14)	97.5 (14)	—
8.0	61.0	31.0	1240	−6.3	132	32.0 (11)	21.0 (2)	98.0 (2)	p
			1240	−7.3	40	39.0 (2)	27.0 (2)	98.5 (2)	p
			1165	−8.3	40	33.5 (10)	—	98.7 (12)	p
			1125	−9.3	24	47.0 (10)	—	99.0 (2)	p
			1080	−10.0	24	45.5 (10)	—	99.0 (2)	p
7.1	82.0	10.9	1240	−7.3	40	39.0 (14)	27.0 (2)	98.5 (10)	p

[1] Numbers in parentheses indicate the number of electron microprobe determinations used to calculate the composition. All iron oxide is calculated as weight percent FeO. p = tridymite present. The f_0 value for a given temperature and $CO_2:H_2$ ratio is taken from unpublished curves by V. Porter.
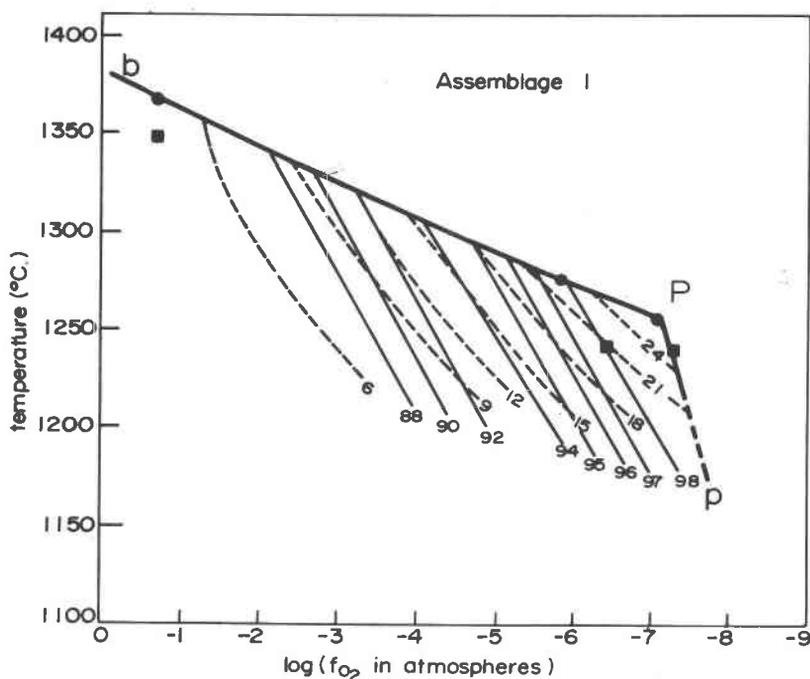
Fig. 5. Curves sketched to show iron oxide content (calculated as FeO and indicated by the numbers on the curves) of pyroxene (dashed) and magnesioferrite (solid)in equilibrium with tridymite and gas in the system MgO-FeO-Fe₂O₃-SiO₂. The curve b-P is one of the univariant curves of Figures 1 and 4 and P-p is the subsolidus univariant curve of the assemblage olivine-tridymite-pyroxene-magnesioferrite-gas (Fig. 4). Dots correspond to data listed in Table 1, after Muan and Osborn (1956); squares correspond to data listed in Table 2.

pyroxene (dashed lines) or of magnesioferrite (solid lines) in the assemblage: pyroxene-tridymite-magnesioferrite-vapor.

The curves of Figure 6 apply to the assemblage, olivine-pyroxene-magnesioferrite-vapor. The magnesioferrite curves (solid lines) have the steepest slopes, approximating the slope for the curve P-p of Figures 5, 6, and 7 and these slopes are also similar to the temperature-oxygen fugacity curve for water.[1] The less steep pyroxene curves (short-dashed lines) have a slope similar to that of the fayalite-tridymite-magnetite buffer, curve c-f of Figure 7 (Eugster and Wones, 1962). The olivine curves have the lowest slope. The type of change of f_{O_2} on cooling will therefore determine composition changes of phases in this pyroxene-olivine-magnesioferrite-vapor assemblage under equilibrium conditions.

[1] Curves for water at 1 bar and 1000 bars are plotted in Figure 9 of Osborn (1963), taken from data compiled by Kennedy (1948).
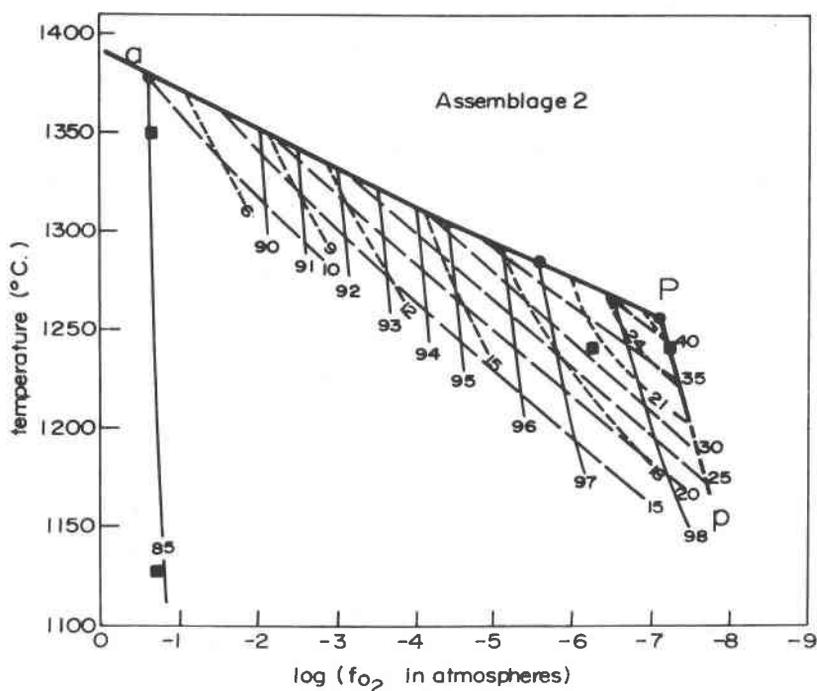
Fig. 6. Curves sketched to show iron oxide content (calculated as FeO and indicated by the numbers on the curves) of pyroxene (short dashes), olivine (longer dashes) and magnesioferrite (solid lines) coexisting in equilibrium with gas in the system MgO-FeO-Fe₂O₃-SiO₂. The line *a-P* is one of the univariant curves of Figures 1 and 4 and *P-p* is the subsolidus univariant curve of the assemblage olivine-tridymite-pyroxene-magnesioferrite-gas (Fig. 4). Dots correspond to data listed in Table 1, after Muan and Osborn (1956); squares correspond to data listed in Table 2.

If the decrease of f_{O_2} with temperature is similar to that for water or for the *P-p* assemblage, the magnesioferrite composition remains essentially constant, while the Mg:Fe ratios of pyroxene and olivine increase, olivine more than pyroxene. If the decrease of f_{O_2} with temperature is somewhat greater, like the slope of the fayalite-tridymite-magnetite buffer or of the magnetite-hematite buffer (Eugster and Wones, 1962), then pyroxene will remain approximately constant in composition while the Mg:Fe ratio in magnesioferrite decreases and that in olivine increases.

In Figure 7 are curves applicable to the equilibrium of coexisting olivine-tridymite-magnesioferrite-vapor. The curve *P-c* is a univariant curve shown in Figures 1 and 4, and *c-f* represents T-f_{O_2} relations for the univariant equilibrium of coexisting fayalite-tridymite-magnetite-vapor in the ternary system FeO-Fe₂O₃-SiO₂ (Eugster and Wones, 1962).
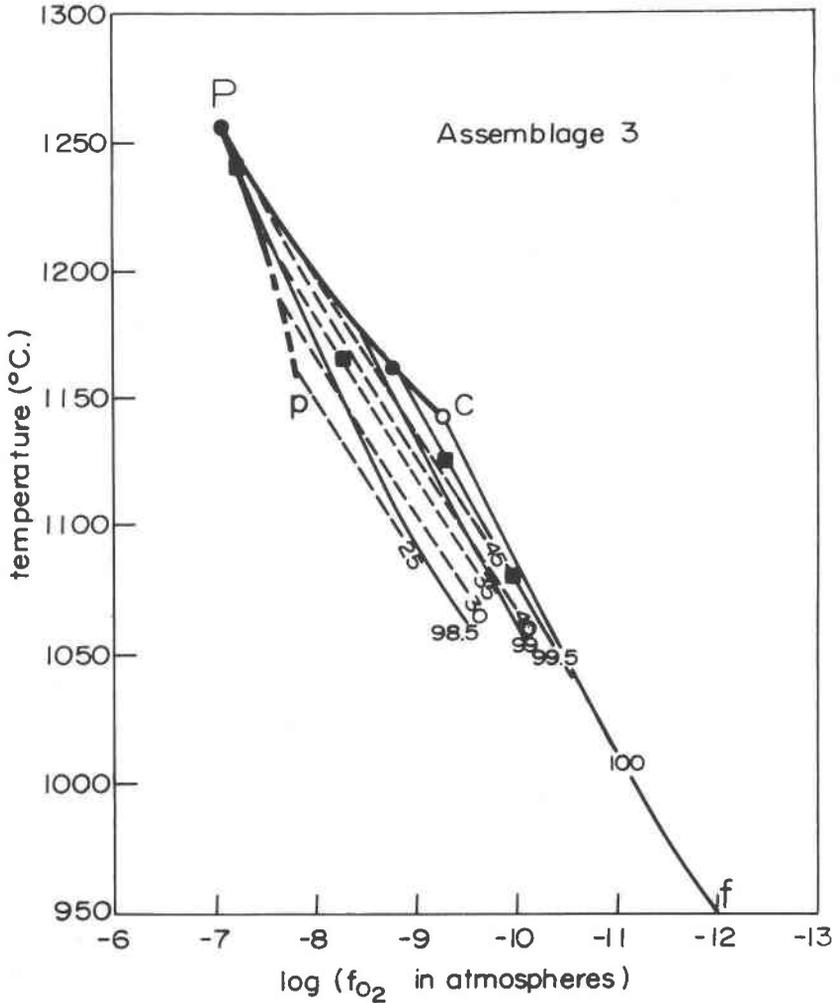
FIG. 7. Curves sketched to show iron oxide content (calcuated as FeO and indicated by the numbers on the curves) of olivine (dashed) and magnesioferrite (solid lines) in equilibrium with tridymite and gas in the system MgO-FeO-Fe₂O₃-SiO₂. P-c is a univariant curve shown in Figures 1 and 4 and P-p is the subsolidus univariant curve of the assemblage olivine-tridymite-pyroxene-magnesioferrite-gas (Fig. 4). The curve c-f represents temperature-f_{O_2} relations for the univariant equilibrium of coexisting fayalite (70.7 wt. % FeO), magnetite (100 wt. % iron oxide), and gas at one bar total pressure, after Eugster and Wones (1962). Dots correspond to data listed in Table 1, after Muan and Osborn (1956); squares correspond to data listed in Table 2.

Conclusions

The composition of olivine, pyroxene, and magnesioferrite in the system MgO-FeO-Fe_2O_3-SiO_2 in equilibrium with vapor at sub-solidus temperatures changes as a function of temperature and oxygen fugacity. If on equilibrium cooling of a three-crystalline phase assemblage the change in f_{O_2} is such that the Mg:Fe ratio in one of the three crystalline phases remains constant, this ratio in another phase in equilibrium with it must change. There is no way that the assemblage olivine-pyroxene-magnesioferrite can be cooled under equilibrium conditions without two or all three of these phases changing in composition, or for the assemblages pyroxene-tridymite-magnesioferrite or olivine-tridymite-magnesioferrite without one or both of the iron-containing phases changing in composition. If f_{O_2} is held constant during equilibrium cooling or decreases at the moderate rate of the pure water buffer, the increase in the Mg:Fe ratio is olivine greater than pyroxene greater than magnesioferrite.

Applying these composition trends to basic and ultrabasic rocks, one conclusion is that the Mg:Fe ratio in olivine, orthopyroxene, and magnetite may be significantly different at lower temperatures than at original crystallization temperatures. Olivine and to a lesser extent orthopyroxene may have increased in Mg:Fe ratio on cooling, while at the same time magnetite may have decreased in Mg-content.

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