

EQUILIBRIUM PHASE COMPOSITIONS AND THERMODYNAMIC PROPERTIES OF OLIVINES AND PYROXENES IN THE SYSTEM MgO-"FeO"-SiO₂¹

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ABSTRACT

Compositions of coexisting solid-solution phases in the system MgO-"FeO"-SiO₂ at low oxygen partial pressures have been determined at solidus and subsolidus temperatures. The data have been used to derive activity-composition relations for the silicate solid solutions within the system, and stability data for end-member compounds. The olivine solid solution has a moderate positive deviation from ideality, whereas the pyroxene solid solution is practically ideal in its activity-composition relation.

The data obtained provide means of checking and refining some of the assumptions which have been made by previous authors in dealing with problems of the distribution of Fe²⁺ and Mg²⁺ among rock-forming minerals. Comparison of the data obtained in the present investigation with those available for meteorites and terrestrial rocks may also be used as a valuable guide to judge whether equilibrium among selected phases has been approached in some of these natural bodies.

INTRODUCTION

One of the most important systems which can be conveniently studied experimentally and whose phase assemblages occur in many important natural and technological systems is MgO-iron oxide-SiO₂. Experimental data on this system can be applied to problems of basic igneous rocks and meteorites, and in materials sciences. Of special interest in the geochemical application of this system has been the question of element distribution among coexisting silicate phases at high temperatures under reducing atmospheric conditions.

The main objective of the present work is to provide a thermodynamic basis for predicting and understanding these distributions. Toward this end, high-temperature equilibrium measurements are made which permit calculation of the parameters of primary importance. These are the free-energies of formation of the silicate end members, and the activity-composition relations in the solid-solution phases.

PREVIOUS WORK

Experimental investigations of parts of the system MgO-"FeO"-SiO₂² were initiated some fifty years ago by Bowen and Andersen (1914), and

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² The lowest oxide of iron ("FeO") is not of stoichiometric O/Fe ratio, but is represented by this simple chemical formula for sake of convenience. Similarly, systems containing iron oxide and one or two other oxide components are referred to as "binary" and "ternary", respectively, although these are approximations only.

were followed by additional investigations by other members of the staff of the Geophysical Laboratory (Greig, 1927; Bowen and Schairer, 1932, 1935). It was the work of Bowen and Schairer in 1935 which established a comprehensive knowledge and understanding of phase relations in the system MgO -“ FeO ”- SiO_2 . The latter authors showed that there is a complete solid-solution series extending from $MgSiO_3$ part-way toward $FeSiO_3$, the maximum content of the latter component being approxi-

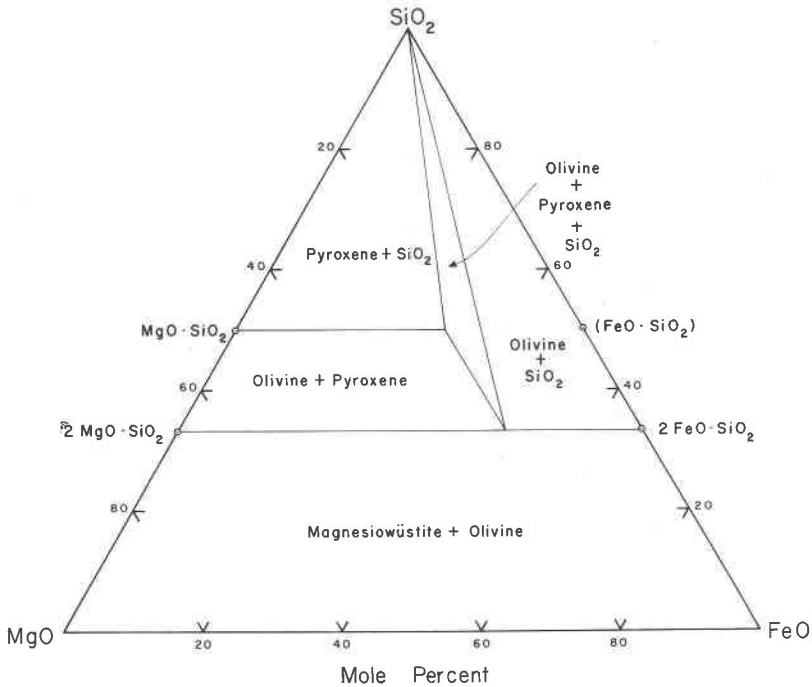


FIG. 1. Subsidiary isothermal section through the system MgO -“ FeO ”- SiO_2 in contact with metallic iron, showing the various phase assemblages present (based on data of Bowen and Schairer, 1935).

mately 56 mole percent at solidus temperatures (see Fig. 1). Muan and Osborn (1956) have studied phase relations in the system MgO - FeO - Fe_2O_3 - SiO_2 at liquidus temperatures and over a large range of oxygen partial pressures.

No satisfactory determinations of activity-composition relations of the olivine and pyroxene solid solutions at high temperatures in the system under investigation have been reported in the literature, as far as is known. Previous authors (Mueller, 1961; Bartholomé, 1962; Bradley, 1962; Craig, 1964; Mueller, 1964) have inferred thermodynamic relations

in the olivine and pyroxene series in order to explain and predict distributions of cations among coexisting mineral phases. Usually, their inferences were based on structural considerations together with heat-of-solution data (Sahama and Torgeson, 1949). In general, it has been assumed that both the olivine and the pyroxene solid solutions are ideal in their activity-composition behavior at high temperatures.

Activity-composition data obtained at high temperatures are available for the magnesiowüstite solid solution, "(Mg, Fe)O", which constitutes one of the bounding "binary" systems of MgO-"FeO"-SiO₂. Hahn and Muan (1962) have shown that magnesiowüstite solid solutions exhibit a pronounced positive deviation from Raoult's law at 1100°C and 1300°C. Their observations have been confirmed by Engell (1962), although there are some differences between the two sets of data as far as the degree of positive deviation is concerned.

Free-energies of formation of anhydrous silicates are listed in several compilations of thermodynamic data (Kelley, 1962; Elliott, *et al.*, 1963). Usually, the values in these compilations have been calculated from calorimetric data obtained at room temperature, and entropy and specific heat data. There are considerable uncertainties in extrapolating these data to higher temperatures, however, and some of the data listed in such compilations are not very reliable for use in equilibrium problems at high temperatures.

EXPERIMENTAL METHODS

General. The thermodynamic properties of the phases occurring in the system MgO-"FeO"-SiO₂ were derived from experimentally determined compositions of solid-solution phases coexisting in equilibrium under controlled atmospheric conditions. Three different techniques were used for these measurements.

One involved the equilibration of a selected series of MgO-iron oxide-SiO₂ mixtures at chosen temperature and oxygen pressure. The latter was chosen to be slightly above that required to precipitate metallic iron from pure iron oxide at the temperature in question. After attainment of equilibrium, the samples were quenched to room temperature, and the compositions of the phases were determined by X-ray diffraction lattice parameter measurements and comparisons with solid solutions of known compositions. The lattice parameters for the oxide and olivine phases in the system MgO-iron oxide-SiO₂ varied sufficiently with composition to allow precise measurements, whereas determination of pyroxene compositions by X-ray methods was found to be too imprecise, and was not used. Pyroxene compositions for mixtures in the olivine-pyroxene stability field were determined by extrapolation of straight lines connect-

ing the experimentally determined olivine composition point and the point representing the bulk composition for each mixture.

In the second experimental technique, two or three series of mixtures within a two-phase area (see Fig. 5) were first heated as above at an oxygen pressure sufficiently high to prevent formation of metallic iron. The oxygen pressure at which the oxide phases are in equilibrium with metallic iron was then determined, first by decreasing the oxygen pressure in small increments until a trace of Fe appeared, and then by increasing the oxygen pressure until the metallic phase disappeared. Approaching this condition from both directions served to define the point more precisely, and to ensure that equilibrium has been attained. Conjugation lines for coexisting solid-solution phases were then constructed by connecting points of equal oxygen pressures for precipitation of metallic iron from mixtures in each series.

The third technique involved the determination of solidus temperatures for mixtures located within areas where two solid-solution phases coexist in equilibrium. The oxygen pressures in these runs were kept just above those at which metallic iron precipitates, at each temperature. Profiles of solidus temperatures along mixture joins can then be drawn, and solidus isotherms constructed. The solidus isotherms represent one side of a three-phase triangle wherein two solid phases coexist in equilibrium with a minute amount of liquid phase (see paper by Bowen, *et al.*, 1933, for instructive use of such relations).

Experimental Details. Reagent-grade oxides served as starting materials for all mixtures used in the present investigation. The MgO was heated at 1300–1400°C for 24 hours, silicic acid at 400°C for 3 hours, at 900°C for 3 hours, and at 1400°C for 36 hours, and Fe₂O₃ at 850°C for 24 hours. Ten-gram mixtures were prepared by weighing the heat-treated oxides in the desired proportions, followed by grinding under acetone in an agate mortar and in a Spex ball mill, utilizing tungsten carbide balls. Most mixtures were then placed in iron-saturated platinum crucibles and fired either in a “globar” furnace at temperatures of 1180°C to 1500°C for 24 to 48 hours or in a gas-air or gas-oxygen furnace at temperatures between 1630°C and 1670°C for at least one hour. The mixtures were then reground under acetone, ball-milled, and refired. This procedure was repeated up to four times to ensure homogeneity. Mixtures having olivine + SiO₂ as the stable phase assemblage were fired in silica crucibles for 12 hours at approximately the expected liquidus temperatures (1205°–1340°C), in a reducing atmosphere corresponding to an oxygen pressure above that at which metallic iron precipitates. After firing, all mixtures were pressed into small pellets of ~6 mm diameter, 2.5 mm thick, and weighing ~0.5 gram. Mold pressures of ~100 to ~200 atm. were used. A couple of drops of water were added to effect firmer pellets. A 0.1 mm diameter Pt wire was pressed into most of the pellets for suspension in the furnace. Some pellets did not have the Pt wire pressed into them, but were held in the equilibration furnace by a basket of Pt wire (0.1 mm diameter) which touched the pellets at only four points.

All equilibration runs were made in vertical quench furnaces with 80%Pt20%Rh or “Kanthal A-1” resistance windings. Temperature constancy to $\pm 3^\circ\text{C}$ was obtained with

commercial regulators activated through a Pt *versus* 90%Pt10%Rh thermocouple. Actual temperatures were measured with a second Pt *versus* 90%Pt10%Rh thermocouple which was calibrated against the melting points of gold (1063°C) and diopside (1391.5°C). The temperatures reported are believed to be accurate to $\pm 5^\circ\text{C}$ or better.

The desired oxygen pressures were obtained by mixing carbon dioxide and hydrogen in controlled proportions, using a gas mixer similar to that described by Darken and Gurry (1945). The capillaries used were calibrated with a commercial wet test meter for the higher flowrates and with a bubble tower for lower flow rates. Data tabulated by Coughlin (1954) were used to calculate the oxygen partial pressures from the gas mixtures used.

The equilibration procedures were as follows: The pellets were held at the desired temperature for one to 14 days at an oxygen partial pressure just above that estimated for the precipitation of metallic iron. The pellets were drop-quenched in the furnace atmosphere, reground under acetone, re-pelletized, and reheated in the same atmosphere. This procedure was repeated up to three times to allow the various oxide and silicate phases to reach equilibrium before the metallic phase was precipitated. For the X-ray lattice parameter measurements, the run procedure was stopped before the metallic phase was precipitated. For runs involving appearance of metallic iron as a phase, the pre-reacted pellets were placed in the furnace for an additional one to four days at selected, lower oxygen pressures, and then drop-quenched.

Pellets from the latter runs were examined under reflected light for the presence or absence of a metallic phase after having been cut in various directions and properly ground and polished. Transmitted light microscopy was used in conjunction with reflected light to ascertain the presence or absence of liquid in the solidus runs, and to check crystal form and size.

X-ray lattice parameter measurements were made on a General Electric XRD-5 diffractometer with Mn-filtered iron radiation. Scanning speeds of $0.2^\circ 2\theta/\text{min}$ and/or $1^\circ 2\theta/\text{min}$ were used. The $d(200)$ peaks for the oxide solid solutions and the $d(131)$ or $d(112)$ peaks for the olivine solid solutions were used. Spinel (MgAl_2O_4) supplied by the United States Bureau of Mines served as an internal standard. Qualitative phase identification was performed on a Norelco low-angle X-ray diffractometer using the same filtered radiation at a scanning speed of $1^\circ 2\theta/\text{min}$.

THERMODYNAMIC EQUATIONS

The derivations of the appropriate equations for determining thermodynamic properties from directions of conjugations lines have been presented elsewhere [Wagner, 1952; Rudy 1963; Muan, 1965; Schwerdtfeger and Muan (with Darken), 1966; Muan 1967]. Only a brief presentation is made in the following of the expressions applicable to the various phase assemblages occurring in the present investigation.

(a) *The phase assemblage pyroxene* + SiO_2 (see Fig. 1)

For the reaction



we may write

$$\log a_{\text{FeSiO}_3} = \frac{\Delta G^\circ(1)}{2.303RT} + \frac{1}{2} \log p_{\text{O}_2} \quad (1^a)$$

where a_{FeSiO_3} is the activity of FeSiO_3 in the pyroxene solid solution, $\Delta G^{\circ}_{(1)}$ is the change in standard free energy for the reaction, and p_{O_2} is the oxygen pressure of a gas phase in equilibrium with the metasilicate solid solution, silica, and metallic iron. It is advantageous (Muan, *et al.*, 1964) to introduce the function α defined by the equation

$$\log \gamma_{\text{FeSiO}_3} = \alpha(1 - N_{\text{FeSiO}_3})^2 \quad (2)$$

where γ_{FeSiO_3} and N_{FeSiO_3} are the activity coefficients and mole fractions, respectively, of FeSiO_3 in the pyroxene solid solution. Equation (1a) may then be re-written in the form

$$\log N_{\text{FeSiO}_3} - \frac{1}{2} \log p_{\text{O}_2} = -\alpha(1 - N_{\text{FeSiO}_3})^2 + \frac{\Delta G^{\circ}_{(1)}}{2.303RT} \quad (3)$$

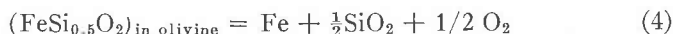
A plot of $(\log N_{\text{FeSiO}_3} - \frac{1}{2} \log p_{\text{O}_2})$ versus $(1 - N_{\text{FeSiO}_3})^2$ gives the value of

$$\frac{\Delta G^{\circ}_{(1)}}{2.303RT}$$

as the intercept with the vertical axis by extrapolation of the curve to $(1 - N_{\text{FeSiO}_3})^2 = 0$, and $-\alpha$ as the slope of the curve.

(b) *The phase assemblage olivine + SiO₂ (see Fig. 1)*

For the reaction



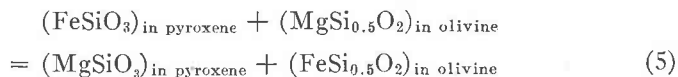
we may write

$$\log a_{\text{FeSi}_{0.5}\text{O}_2} = \frac{\Delta G^{\circ}_{(4)}}{2.303 RT} + \frac{1}{2} \log p_{\text{O}_2} \quad (4^a)$$

where p_{O_2} is the oxygen pressure of the gas phase in equilibrium with the three condensed phases olivine solid solution, silica and metallic iron, and the other symbols with appropriate subscripts have the same meanings as explained above (a). The value of p_{O_2} can be determined experimentally, and $\Delta G^{\circ}_{(4)}$ is known from previous literature data.

(c) *The phase assemblage pyroxene + olivine (see Fig. 1)*

For the reaction



the change in standard free energy is

$$\Delta G^{\circ}_{(5)} = \frac{1}{2}G^{\circ}_{\text{Fe}_2\text{SiO}_4} + G^{\circ}_{\text{MgSiO}_3} - \frac{1}{2}G^{\circ}_{\text{Mg}_2\text{SiO}_4} - G^{\circ}_{\text{FeSiO}_3} \quad (5^a)$$

where the G° -values with appropriate subscripts are the free-energies of formation of the various end-member compounds from their oxide components.

Activity coefficients of the end-member components of the olivine solid solution are calculated from the expressions

$$\log \gamma_{\text{FeSi}_{0.5}\text{O}_2} = -N_{\text{MgSi}_{0.4}\text{O}_2} \log C + \int_0^N \text{MgSi}_{0.5}\text{O}_2 \log C \, dN_{\text{MgSi}_{0.5}\text{O}_2} \quad (6)$$

and

$$\log \gamma_{\text{MgSi}_{0.5}\text{O}_2} = (1 - N_{\text{MgSi}_{0.5}\text{O}_2}) \log C + \int_1^N \text{MgSi}_{0.5}\text{O}_2 \log C \, dN_{\text{MgSi}_{0.5}\text{O}_2} \quad (7)$$

where C is the quotient

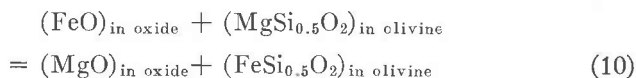
$$\frac{a_{\text{MgSiO}_3} \cdot N_{\text{FeSi}_{0.5}\text{O}_2}}{a_{\text{FeSiO}_3} \cdot N_{\text{MgSi}_{0.5}\text{O}_2}} \quad (8)$$

The values of a_{MgSiO_3} and a_{FeSiO_3} are taken from equilibrium (a), and $N_{\text{FeSi}_{0.5}\text{O}_2}$ and $N_{\text{MgSi}_{0.5}\text{O}_2}$ are determined experimentally in equilibrium (c). The value of $\Delta G^\circ_{(5)}$ is then calculated from the equation

$$-\frac{\Delta G^\circ_{(5)}}{2.303 RT} = \log C + \log \gamma_{\text{FeSi}_{0.5}\text{O}_2} - \log \gamma_{\text{MgSi}_{0.5}\text{O}_2} \quad (9)$$

(d) *The phase assemblage olivine + oxide (see Fig. 1)*

A study of the equilibrium between olivine and oxide (= magnesio-wüstite) solid solutions provides a check of the olivine data obtained from formulas presented above under (c), because activity-composition relations in magnesio-wüstites are known [see previous references to papers by Hahn and Muan (1962), and by Engell, (1962)]. The following equations apply to this assemblage: For the reaction



we may write

$$\Delta G^\circ_{(10)} = \frac{1}{2}G^\circ_{\text{Fe}_2\text{SiO}_4} - \frac{1}{2}G^\circ_{\text{Mg}_2\text{SiO}_4} \quad (10^a)$$

Activity coefficients of the orthosilicate solid solution are calculated from the expressions

$$\log \gamma_{\text{FeSi}_{0.5}\text{O}_2} = - N_{\text{MgSi}_{0.5}\text{O}_2} \log C' + \int_0^{N_{\text{MgSi}_{0.5}\text{O}_2}} \log C' d N_{\text{MgSi}_{0.5}\text{O}_2} \quad (11)$$

$$\log \gamma_{\text{MgSi}_{0.5}\text{O}_2} = (1 - N_{\text{MgSi}_{0.5}\text{O}_2}) \log C' + \int_1^{N_{\text{MgSi}_{0.5}\text{O}_2}} \log C' d N_{\text{MgSi}_{0.5}\text{O}_2} \quad (12)$$

where C' is the quotient

$$\frac{a_{\text{MgO}} \cdot N_{\text{FeSi}_{0.5}\text{O}_2}}{a_{\text{FeO}} \cdot N_{\text{MgSi}_{0.5}\text{O}_2}} \quad (13)$$

The value of $\Delta G^\circ_{(10)}$ is then calculated from the equation

$$-\frac{\Delta G^\circ_{(10)}}{2.303 RT} = \log C' + \log \gamma_{\text{FeSi}_{0.5}\text{O}_2} - \log \gamma_{\text{MgSi}_{0.5}\text{O}_2} \quad (14)$$

RESULTS

The phase assemblage pyroxene + SiO₂ Results obtained from equilibrations involving pyroxene solid solutions, SiO₂, metallic iron and a gas phase of known oxygen pressures are listed in Table 1. Values of $(\log N_{\text{FeSiO}_3} - \frac{1}{2} \log p_{\text{O}_2})$ calculated from these data are shown in the last column of the table, and a plot of this function versus $(1 - N_{\text{FeSiO}_3})^2$ is presented in Figure 2. The straight line having the best fit to the observed points is practically horizontal; the value of α is 0.07 ± 0.12 . Hence the

TABLE 1. RESULTS OF EQUILIBRATION RUNS FOR THE PHASE ASSEMBLAGE PYROXENE + SILICA + METALLIC IRON IN THE SYSTEM MgO-“FeO”-SiO₂ AT 1250 °C

Bulk Composition ^a			N_{FeSiO_3}	$(1 - N_{\text{FeSiO}_3})^2$	$\log p_{\text{O}_2}$	$\log N_{\text{FeSiO}_3} - 1/2 \log p_{\text{O}_2}$
N_{FeO}	N_{MgO}	N_{SiO_2}				
0.035	0.409	0.556	0.079	0.848	-13.76	5.78+0.08
0.052	0.391	0.557	0.117	0.780	-13.32	5.73+0.04
0.076	0.371	0.558	0.161	0.704	-13.13	5.78±0.04
0.108	0.332	0.559	0.245	0.570	-12.74	5.76±0.05
0.148	0.291	0.561	0.337	0.440	-12.50	5.78±0.06
0.189	0.249	0.562	0.432	0.323	-12.30	5.79±0.06
0.233	0.204	0.564	0.533	0.218	-12.16	5.81±0.08
1.000*	—	—	—	—	-11.38	—

^a Total iron oxide calculated as FeO.

pyroxene solid solution is practically ideal in its activity-composition relation. Extrapolation of the curve in Figure 2 to $(1 - N_{\text{FeSiO}_3})^2 = 0$ gives $\Delta G^\circ_{(1)} = +40.6$ Kcal, and combination of this with the $\Delta G^\circ_{(16)}$ value for the reaction



gives for the reaction

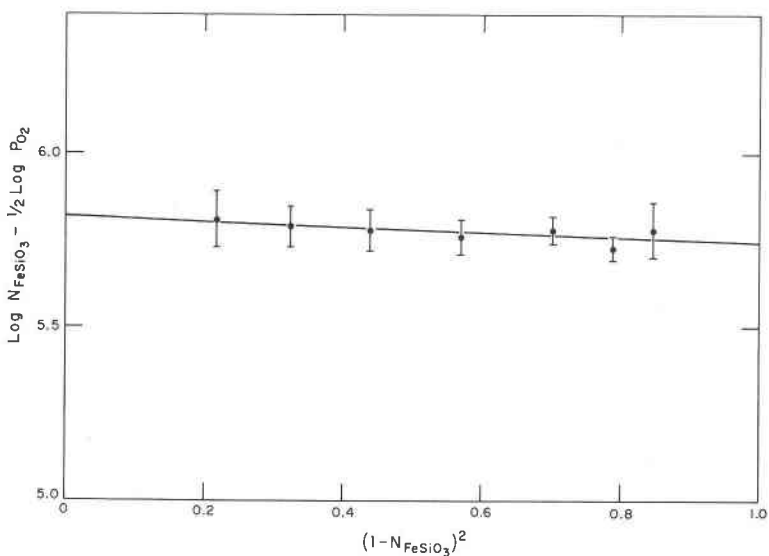


FIG. 2. Plot of $(\log N_{\text{FeSiO}_3} - \frac{1}{2} \log p_{\text{O}_2})$ versus $(1 - N_{\text{FeSiO}_3})^2$ for the pyroxene-SiO₂ equilibrium in the system MgO-"FeO"-SiO₂ at 1250°C. The solid curve represents the best fit through the experimentally determined points. Estimated errors are indicated by vertical lines through the respective points.

a $\Delta G^\circ_{(16)} = -0.9 \pm 0.5$ Kcal. This is in excellent agreement with the value of -1 Kcal estimated by Muan, *et al.*, (1964) and with the value of -1.3 ± 0.3 Kcal determined by Schwerdtfeger and Muan (1966) from equilibrium measurements in the system MnO-"FeO"-SiO₂. In comparing the data obtained from the system MgO-"FeO"-SiO₂ with those from the system MnO-"FeO"-SiO₂, it should be kept in mind, however, that there is a slight difference in structure of the metasilicate phase in the two systems. Hence, the $\Delta G^\circ_{(16)}$ -values obtained for FeSiO₃ from the two systems should not be strictly identical, although it is expected that they would not differ much.

TABLE 2. RESULTS OF EQUILIBRATION RUNS FOR THE PHASE ASSEMBLAGE OLIVINE + SILICA + METALLIC IRON IN THE SYSTEM MgO-“FeO”-SiO₂ AT 1150, 1176, AND 1200° C

Bulk Composition ¹			Temperature °C	log p_{O_2}	$d(131)\text{Å}^2$	$N_{FeSi_{0.5}O_2}$	$a_{FeS_{0.5}O_2}$
N_{FeO}	N_{MgO}	N_{SiO_2}					
0.443	0.123	0.433	1150	-12.89±0.03	2.5527	0.79	0.74±0.09
0.467	0.100	0.433	1150	-12.83±0.03	2.5534	0.80	0.79±0.10
0.492	0.075	0.433	1150	-12.71±0.03	2.5552	0.83	0.89±0.11
0.513	0.053	0.433	1150	-12.70±0.04	2.5596	0.91	0.89±0.11
0.667	—	0.333	1150	-12.58±0.05			
1.000	—	—	1150	-12.11±0.05			
0.417	0.150	0.433	1200	-12.55±0.02	2.5507	0.76	0.72±0.12
0.443	0.123	0.433	1200	-12.48±0.02	2.5530	0.80	0.79±0.12
0.467	0.100	0.433	1200	-12.44±0.03	2.5534	0.80	0.81±0.15
0.492	0.075	0.433	1200	-12.37±0.02	2.5574	0.87	0.87±0.12
0.667	—	0.333	1176	-12.35±0.02			
1.000	—	—	1200	-11.84±0.05			

¹ Total iron oxide calculated as FeO.

² The X-ray lattice parameter measurements were made on samples equilibrated at $P_{O_2}=10^{-12.5}$ at 1150°C or $10^{-11.8}$ at 1200°C and subsequently quenched to room temperature.

The phase assemblage olivine+SiO₂ Results of equilibrations involving olivine, SiO₂, metallic iron and a gas phase of known oxygen pressures are listed in Table 2. The runs were made at three different temperatures, because fayalite+SiO₂ and one of the selected olivine+SiO₂ mixtures contain liquid at 1200°C. The compositions of the olivine phase were checked by X-ray lattice parameter measurements, and comparison with data for olivines of known compositions as listed in Table 3. Within limits of error, the relationship is linear, in accordance with Vegard's rule. The calculated activities of FeSi_{0.5}O₂ in the olivine solid solution

 TABLE 3. $d(131)$ AND $d(112)$ AS FUNCTIONS OF OLIVINE COMPOSITION IN THE SYSTEM MgO-“FeO”-SiO₂

$N_{FeSi_{0.5}O_2}$	$d(131)\text{Å}$	$d(112)\text{Å}$
1.00	2.5644	2.4991
0.67	2.5454	2.4842
0.33	2.5265	2.4694
0.07	2.5123	2.4592
0.00	2.5087	2.4568

Measurements made on samples equilibrated at 1200°C and $p_{O_2}=10^{-11.8}$ atm. for 120 hours and subsequently quenched to room temperature.

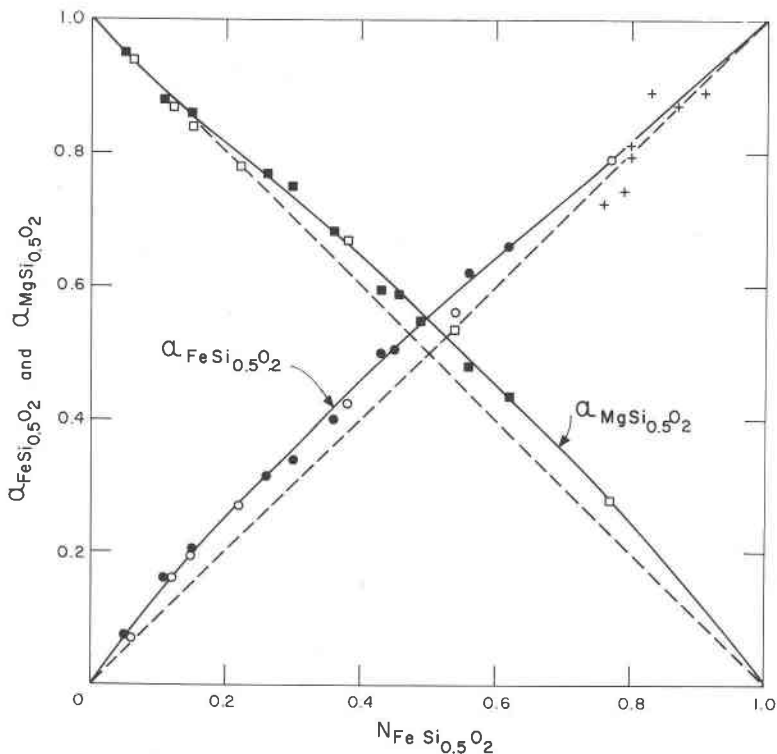


Fig. 3. Activity-composition relations along the olivine join of the system $\text{MgO}-\text{FeO}-\text{SiO}_2$. Crosses represent $a_{\text{FeSi}_{0.5}\text{O}_2}$ -values obtained from the olivine+ SiO_2 phase assemblage at 1150°C and 1200°C, solid circles and solid squares represent $a_{\text{FeSi}_{0.5}\text{O}_2}$ - and $a_{\text{MgSi}_{0.5}\text{O}_2}$ -values, respectively, obtained from the olivine+pyroxene phase assemblage at 1200°C. Open circles and open squares represent $a_{\text{FeSi}_{0.5}\text{O}_2}$ - and $a_{\text{MgSi}_{0.5}\text{O}_2}$ -values, respectively, obtained from the olivine+magnesiowüstite phase assemblage at 1200°C (see later section of text).

are listed in the last column of Table 2 and shown graphically as part of Figure 3 (crosses).

The phase assemblage olivine+pyroxene: Compositions of olivine solid solutions coexisting in equilibrium with pyroxenes as determined by X-ray spacing measurements are shown in Table 4. Also listed in the same table are compositions of a gas phase coexisting in equilibrium with olivine, pyroxene and metallic iron. A plot of $\log \text{CO}_2/\text{H}_2$ versus $N_{\text{FeO}}/N_{\text{FeO}}+N_{\text{MgO}}$ is shown in Figure 4 for two series of mixtures in the composition area of the above phase assemblage, one series near the olivine join and one near the pyroxene join. Compositions of coexisting phases

TABLE 4. EQUILIBRIA OF SOLID SOLUTIONS AND GAS PHASE AT 1200°C.

(a) Compositions of olivine solid solutions in equilibrium with pyroxene solid solutions in the system MgO-⁶⁶FeO⁷⁷-SiO₂ at 1200°C¹

Bulk Composition			<i>d</i> (112)Å	<i>N</i> _{FeSi_{0.5}O₂}
<i>N</i> _{FeO}	<i>N</i> _{MgO}	<i>N</i> _{SiO₂}		
0.034	0.612	0.354	2.4583	0.05
0.058	0.461	0.481	2.4608	0.11
0.212	0.308	0.480	2.4745	0.43
0.277	0.247	0.478	2.4801	0.56
0.297	0.220	0.483	2.4826	0.62

(b) Compositions of gas phase in equilibrium with olivine, pyroxene and metallic iron in the system MgO-⁶⁶FeO⁷⁷-SiO₂ at 1200°C.

Bulk Composition			$\frac{N_{FeO}}{N_{FeO} + N_{MgO}}$	log CO ₂ /H ₂
<i>N</i> _{FeO}	<i>N</i> _{MgO}	<i>N</i> _{SiO₂}		
0.058	0.461	0.481	0.11	-1.167 ± 0.030
0.098	0.550	0.352	0.15	-1.018 ± 0.030
0.168	0.478	0.355	0.26	-0.833 ± 0.020
0.128	0.388	0.485	0.25	-0.801 ± 0.015
0.228	0.419	0.354	0.35	-0.736 ± 0.030
0.212	0.308	0.480	0.41	-0.649 ± 0.017
0.319	0.327	0.353	0.49	-0.610 ± 0.015

¹ Determined by X-ray lattice parameter measurements of samples equilibrated at *p*_{O₂} = 10^{-11.8} atm. and subsequently quenched to room temperature.

derived on the basis of this graph are listed in Table 5, and the resulting conjugation lines as well as those obtained from the X-ray measurements are shown as part of Figure 5.

Data from solidus determinations in the olivine+pyroxene field are summarized in Table 6 and illustrated graphically in Figure 6.

Activity-composition data for the olivine solid solution as determined from the olivine+pyroxene equilibrium are listed in Table 7 and shown graphically as part of Figure 3 (solid circles and solid squares). The curves drawn to fit the points are consistent with a binary Gibbs-Duhem integration along the olivine join. It is seen that the olivine solid solution displays a moderate positive deviation from ideality.

The phase assemblage olivine+oxide. Activity-composition relations in the oxide solid solution in contact with metallic iron is an important basis for evaluation of equilibria in the olivine+oxide phase assemblage.

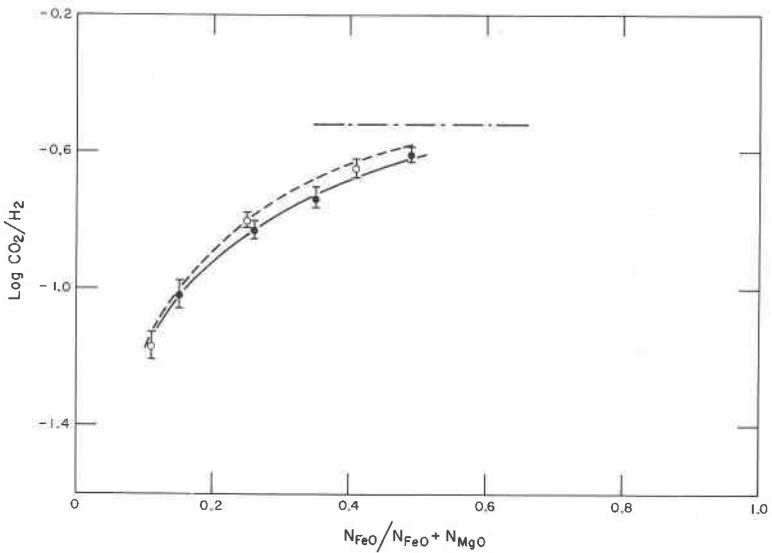


FIG. 4. $\text{Log CO}_2/\text{H}_2$ versus $N_{\text{FeO}}/N_{\text{FeO}}+N_{\text{MgO}}$ at 1200°C for the phase assemblage olivine+pyroxene+metallic iron in the system $\text{MgO}-\text{FeO}-\text{SiO}_2$. The solid curve represents the best fit of the experimental data (solid dots) for mixtures near the olivine composition join and the dashed line represents the data (open circles) for mixtures near the pyroxene composition join. Estimated errors are indicated by vertical lines through the respective points. The dot-dashed line represents the $\text{log CO}_2/\text{H}_2$ value for the phase assemblage olivine+pyroxene+silica+metallic iron at 1200°C .

TABLE 5. COMPOSITIONS OF COEXISTING OLIVINES AND PYROXENES IN EQUILIBRIUM AT 1200°C IN THE SYSTEM $\text{MgO}-\text{FeO}-\text{SiO}_2$

$N_{\text{FeSi}_{0.5}\text{O}_2}$	N_{FeSiO_3}	Method
0.05	0.05	X ray
0.11	0.11	X ray
0.11	0.11	Gas Composition
0.15	0.14	Gas Composition
0.26	0.22	Gas Composition
0.30	0.24	Gas Composition
0.36	0.29	Gas Composition
0.43	0.40	X ray
0.45	0.40	Gas Composition
0.49	0.45	Gas Composition
0.56	0.52	X ray
0.62	0.56	X ray

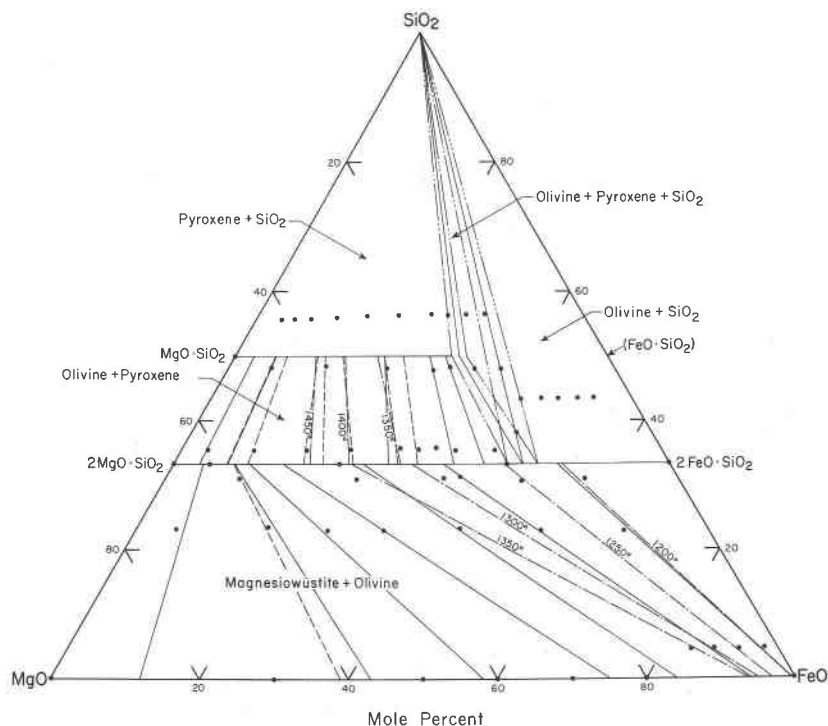


FIG. 5. Conjugation lines and solidus isotherms in the system $\text{MgO}-\text{FeO}-\text{SiO}_2$ as determined in the present investigation. Solid dots represent bulk compositions of the mixtures studied, solid lines represent equilibrium compositions of coexisting phases as determined by room-temperature X-ray measurements on samples equilibrated at 1200°C , dashed lines represent the same parameter as determined by the iron precipitation method at 1200°C , and single-dot dashed lines are solidus isotherms with temperatures indicated in $^\circ\text{C}$. Double-dot dashed lines outline the three-phase triangle olivine+pyroxene+ SiO_2 at 1250°C , and triple-dot dashed lines outline the same area at 1150°C .

Curves showing these relations for the temperature range $1100\text{--}1300^\circ\text{C}$ are presented in Figure 7, based on data determined by Hahn and Muan (1962). Their data were confirmed in the present investigation. The curve for a_{MgO} was calculated from the a_{FeO} -values by a Gibbs-Duhem integration of the equation

$$d \log a_{\text{MgO}} = - \frac{1}{2} \left(\frac{N_{\text{O}} - N_{\text{Mg}}}{N_{\text{Mg}}} \right) d \log p_{\text{O}_2} \quad (17)$$

where N_{O} and N_{Mg} are the atomic fractions of oxygen and magnesium of the ternary magnesiowüstite solid solutions in equilibrium with me-

TABLE 6. SOLIDUS TEMPERATURES FOR MIXTURES IN THE OLIVINE+PYROXENE FIELD OF THE SYSTEM MgO - FeO - SiO_2

Bulk Composition			$\frac{N_{FeO}}{N_{FeO} + N_{MgO}}$	Solidus Temperature °C
N_{FeO}	N_{MgO}	N_{SiO_2}		
0.369	0.278	0.353	0.570	1301
0.277	0.247	0.478	0.529	1308
0.340	0.303	0.358	0.529	1319
0.319	0.327	0.353	0.494	1325
0.212	0.308	0.480	0.408	1341
0.291	0.351	0.358	0.453	1344
0.228	0.419	0.354	0.352	1395
0.128	0.388	0.485	0.248	1443
0.168	0.478	0.355	0.260	1450

tallic iron. These values were taken from the data published recently by Katsura and Kimura (1965).

Data on spacings in the oxide solid solution as a function of composition are listed in Table 8 and shown graphically in Figure 8.

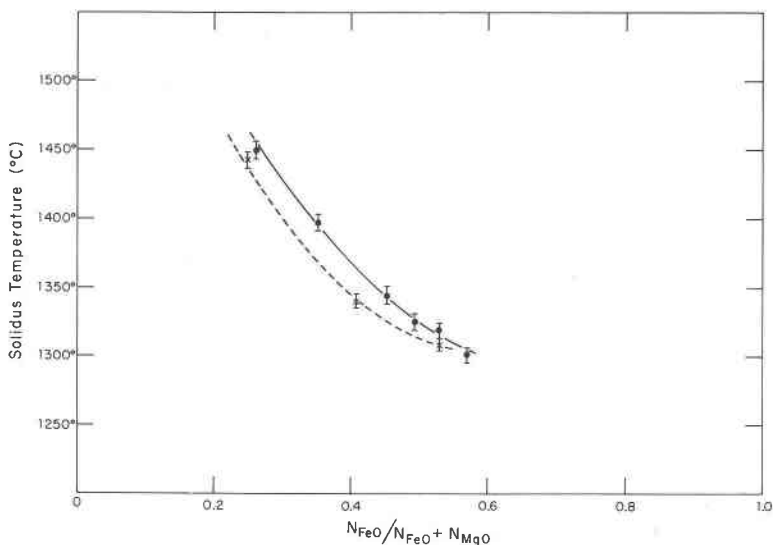


FIG. 6. Solidus temperatures as a function of composition for mixtures in which olivines are in equilibrium with pyroxenes in the system MgO - FeO - SiO_2 . The two curves represent solidus temperature profiles at constant SiO_2 contents (solid curve for mixtures near the olivine join, dashed curve for those near the pyroxene join). Vertical lines through the respective points represent estimated errors.

TABLE 7. ACTIVITIES IN OLIVINE SOLID SOLUTIONS IN THE SYSTEM MgO-“FeO”-SiO₂ AT 1200°C AS DETERMINED FROM THE OLIVINE+PYROXENE EQUILIBRIUM

$N_{\text{FeSi}_{0.5}\text{O}_2}$	$N_{\text{MgSi}_{0.5}\text{O}_2}$	log C	$a_{\text{FeSi}_{0.5}\text{O}_2}$	$a_{\text{MgSi}_{0.5}\text{O}_2}$
0.05	0.95	-0.08±0.05	0.08	0.95
0.11	0.89	-0.08±0.06	0.16	0.88
0.15	0.85	-0.03±0.07	0.21	0.86
0.26	0.74	+0.05±0.10	0.32	0.77
0.30	0.70	+0.11±0.09	0.34	0.75
0.36	0.64	+0.11±0.08	0.40	0.69
0.43	0.57	+0.04±0.08	0.50	0.60
0.45	0.55	+0.07±0.08	0.51	0.59
0.49	0.51	+0.07±0.06	0.55	0.55
0.56	0.44	+0.07±0.07	0.62	0.48
0.62	0.38	+0.12±0.07	0.66	0.44

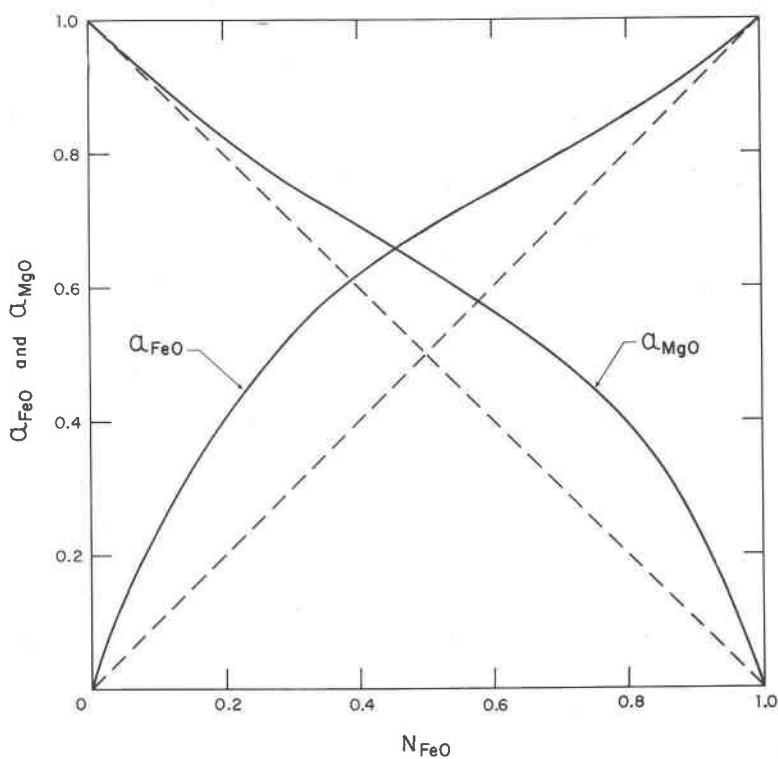


FIG. 7. Activities of FeO and MgO *versus* composition in the system MgO-“FeO”, based on data of Hahn and Muan (1962). Light dash lines represent the linear dependence in accordance with Raoult's law.

TABLE 8. $d(200)$ AS A FUNCTION OF COMPOSITION IN MAGNESIOWÜSTITE SOLID SOLUTION

N_{FeO}	N_{MgO}	$d(200)\text{Å}$
1.00	0.00	2.1543
0.80	0.20	2.1494
0.70	0.30	2.1457
0.60	0.40	2.1405
0.50	0.50	2.1358
0.30	0.70	2.1234
0.00	1.00	2.1052

Measurements made at room temperature on samples equilibrated at 1200°C and at $p_{\text{O}_2} = 10^{-11.8}$ atm.

Compositions of coexisting magnesiowüstite and olivine phases at 1200°C are listed in Table 9 and shown graphically as part of Figure 5. Most of the data of this table were derived from X-ray spacing measurements. In these equilibration runs, the conjugation lines connecting the independently determined composition points for the magnesiowüstite and olivine phases pass approximately through the point representing

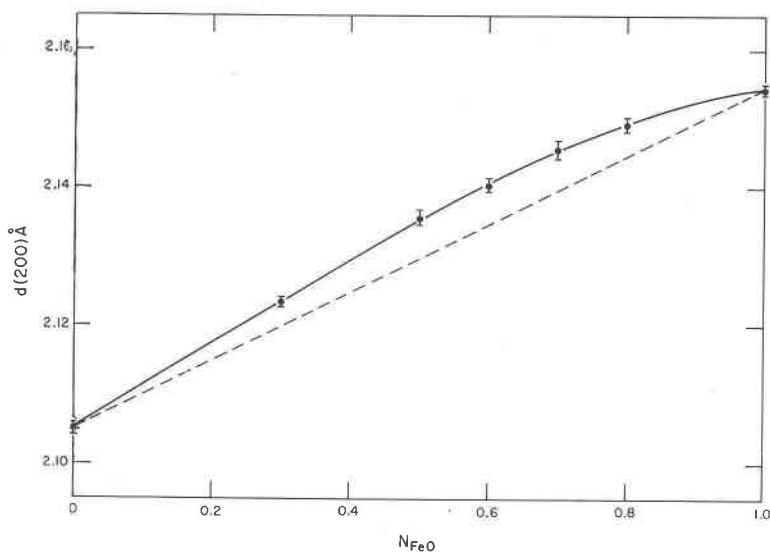


FIG. 8. $d(200)$ versus composition for magnesiowüstite solid solutions measured at room temperature after equilibration at 1200°C and an oxygen pressure of $10^{-11.8}$ atm. The solid curve is the best fit for the experimental data, the dashed curve represents the linear relationship according to Vegard's rule, and vertical lines through each point indicate estimated errors.

TABLE 9. COMPOSITIONS OF COEXISTING MAGNESIOWÜSTITES AND Mg-Fe OLIVINES AT 1200°C

Bulk Composition			Magnesiowüstite Solid Solution				Olivine Solid Solution		
N_{FeO}	N_{MgO}	N_{SiO_2}	$d(200)\text{Å}$	N_{FeO}	a_{FeO}	a_{MgO}	$d(131)\text{Å}$	$N_{FeSi_{0.5}O_2}$	$N_{MgSi_{0.5}O_2}$
0.052	0.715	0.232	2.1126	0.12	0.27	0.89	2.5116	0.06	0.94
0.100 ¹	0.590	0.310	—	0.39	0.61	0.70	—	0.12	0.88
0.176	0.589	0.235	2.1314	0.43	0.64	0.67	2.5148	0.12	0.88
0.258	0.512	0.229	2.1398	0.58	0.73	0.58	2.5169	0.15	0.85
0.331	0.439	0.230	2.1474	0.75	0.83	0.45	2.5206	0.22	0.78
0.432	0.334	0.234	2.1505	0.84	0.88	0.35	2.5296	0.38	0.62
0.543	0.230	0.227	2.1530	0.94	0.95	0.16	2.5381	0.54	0.46
0.657	0.114	0.229	2.1545	1.00	1.00	0.00	2.5516	0.77	0.23

¹ Data for this mixture were determined by the iron precipitation method, whereas the rest of the data were determined by X-ray spacing measurements.

bulk compositions of the mixtures in all cases. The small deviation of the position of the conjugation line from the bulk composition is believed to be caused mainly by the experimental uncertainties in the X-ray lattice parameter measurements.

Results of solidus temperature determinations in the magnesiowüstite-olivine field are listed in Table 10 and shown graphically in Figure 9. Conjugation lines determined from the latter diagram are included in Figure 5. Activity-composition data for the olivine solid solutions as

TABLE 10. SOLIDUS TEMPERATURES FOR MIXTURES IN WHICH MAGNETIOWÜSTITES ARE IN EQUILIBRIUM WITH Mg-Fe OLIVINES

Bulk Composition			$\frac{N_{FeO}}{N_{FeO} + N_{MgO}}$	Solidus Temperature °C
N_{FeO}	N_{MgO}	N_{SiO_2}		
0.563	0.127	0.310	0.815	1199
0.480	0.214	0.307	0.692	1250
0.394	0.292	0.314	0.574	1285
0.373	0.318	0.310	0.540	1295
0.258	0.433	0.309	0.373	1360
0.432	0.334	0.234	0.564	1354
0.543	0.230	0.227	0.702	1288
0.657	0.114	0.229	0.852	1206
0.838	0.117	0.045	0.877	1354
0.869	0.085	0.046	0.912	1288
0.902	0.052	0.046	0.946	1241
0.935	0.018	0.047	0.982	1200

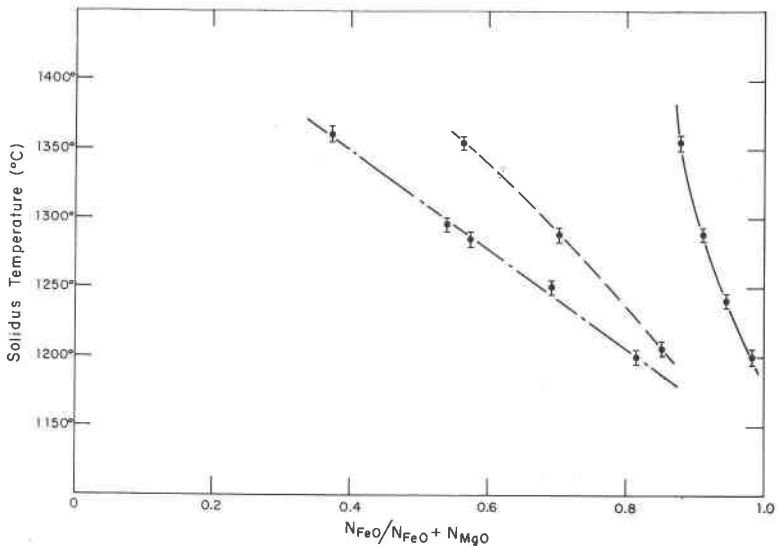


FIG. 9. Solidus temperatures as a function of composition for mixtures in which Mg-Fe olivines are in equilibrium with magnesiowüstites. The three curves represent solidus temperature profiles at constant SiO_2 content as follows: solid line, $N_{\text{SiO}_2} \cong 0.05$; dashed line, $N_{\text{SiO}_2} \cong 0.23$; and single-dot dashed line, $N_{\text{SiO}_2} \cong 0.31$. Vertical lines through the experimental points represent estimated errors.

determined from the olivine+oxide equilibrium are listed in Table 11 and shown graphically as part of Figure 3 (open circles and open squares). The data are in excellent agreement with those obtained from the pyroxene+olivine equilibrium (solid circles and solid squares in Fig. 3). This demonstrates the internal consistency of the data of the present investigation, and their excellent agreement with the previous activity-composition data on magnesiowüstites.

TABLE 11. ACTIVITIES IN OLIVINE SOLID SOLUTIONS IN THE SYSTEM MgO -“ FeO ”- SiO_2 AT 1200°C AS DETERMINED FROM THE OLIVINE+OXIDE EQUILIBRIUM

$N_{\text{FeSi}_{0.5}\text{O}_2}$	$N_{\text{MgSi}_{0.5}\text{O}_2}$	$\log C'$	$a_{\text{FeSi}_{0.5}\text{O}_2}$	$a_{\text{MgSi}_{0.5}\text{O}_2}$
0.06	0.94	-0.72 ± 0.08	0.07	0.94
0.12	0.88	-0.81 ± 0.05	0.16	0.87
0.12	0.88	-0.86 ± 0.04	0.17	0.87
0.15	0.85	-0.85 ± 0.07	0.20	0.84
0.22	0.78	-0.81 ± 0.10	0.27	0.78
0.38	0.62	-0.62 ± 0.15	0.43	0.67
0.54	0.46	-0.69 ± 0.10	0.56	0.54
0.77	0.23	-0.84 ± 0.25	0.79	0.28

The value of $2\Delta G^\circ_{(10)}$ (see equations 10 and 14) calculated from the olivine-oxide equilibrium data is +9.6 Kcal. The free energy of formation of fayalite (Fe_2SiO_4) from the oxide components "FeO" and SiO_2 at 1200°C is -3.5 Kcal (Schwerdtfeger and Muan, 1966). Combining this value with $2\Delta G^\circ_{(10)}$ gives for Mg_2SiO_4 a free-energy of formation from the oxide components of -13.1 ± 1.9 Kcal. This compares with the value of -14.9 Kcal listed in commonly used tables of thermodynamic data (Kelley, 1962, Elliott; Gleiser and Ramakrishna, 1963).

GEOCHEMICAL SIGNIFICANCE OF THE DATA

The equilibrium distribution of cations among coexisting solid solution phases depends primarily on two thermodynamic parameters: The relative stabilities of the various end-member compounds, and the activity-composition relations of the components of the solid solutions. These parameters in turn are related to other parameters (for instance ionic size and polarizability) commonly used as main criteria for deriving rules governing distribution of elements in minerals and rocks (see for instance Goldschmidt, 1926). The data obtained in the present investigation permit a quantitative evaluation of such distributions for phases in the system MgO -"FeO"- SiO_2 .

The data on the equilibrium between olivine, pyroxene and metallic iron, as determined in the present investigation, have their most direct application in the study of meteorites. Nearly all meteorites contain a greater or lesser amount of a metallic phase, in large part metallic iron, associated with other, nonmetallic phases. The most common of the latter are the Mg-Fe olivines and the Mg-Fe pyroxenes (Mason, 1962). Since meteorites exhibit a close genetic relationship with the earth, and the chondrites especially have been termed as the best chemical model of the earth (MacDonald, 1959), the delineation of the origin and environment of meteorites is of major importance to earth scientists.

Consider the distribution of cations between coexisting olivine and pyroxene phases according to equation (5) for which the equilibrium constant (K) may be written

$$K = \frac{N_{\text{FeSi}_{0.5}\text{O}_2} \cdot \gamma_{\text{FeSi}_{0.5}\text{O}_2} \cdot N_{\text{MgSiO}_3} \cdot \gamma_{\text{MgSiO}_3}}{N_{\text{MgSi}_{0.5}\text{O}_2} \cdot \gamma_{\text{MgSi}_{0.5}\text{O}_2} \cdot N_{\text{FeSiO}_3} \cdot \gamma_{\text{FeSiO}_3}} \quad (18)$$

In the equilibrium study of the present investigation, the value of K in the temperature range 1200–1250°C was found to be 1.07 ± 0.16 .

Ringwood (1961) determined the composition of olivines and pyroxenes in 34 analyzed chondrites. Using the results from 19 of these in which data for both olivines and pyroxenes are given, the activity coefficients determined in the present study, and equation (18), a K -value

of 1.33 ± 0.18 is obtained. This value is of the same order of magnitude as that observed in the present equilibrium study and suggests that the cation distribution between olivine and pyroxene phases in chondrites is reasonably close to the equilibrium obtained at 1200°C . No precise statement of the degree of equilibrium attained among the olivine and pyroxene phases in meteorites can be made at present, because the effects of temperature, total pressure, and changes in crystalline modifications of the pyroxene phase on the above equilibrium are unknown. However, it is thought that the latter parameters will have only a relatively small effect. Attempts have been made in previous literature to derive the temperature coefficient of K from available data (see for instance Craig, 1965). It is our opinion that the basis for such derivations is too uncertain at present to warrant any confidence in the conclusions made therefrom.

Although the present data regarding distribution of Mg^{2+} and Fe^{2+} between coexisting olivine and pyroxene phases in the system MgO -iron oxide- SiO_2 were determined at or near equilibrium with metallic iron, they are also valid at higher oxygen pressures within the stability region of these phases, because practically no Fe^{3+} has been found to be present in these phases. Hence, the data are also applicable to problems of $\text{Mg}^{2+}/\text{Fe}^{2+}$ distributions between olivines and pyroxenes in terrestrial rocks. The reasoning involved is similar to that used in connection with meteorites.

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REFERENCES

- BARTHOLOMÉ, P., (1962) Iron-magnesium ratio in associated pyroxenes and olivines. *In Petrologic Studies: A Volume to Honor A. F. Buddington*, Geol. Soc. Amer., New York, p. 1-20.
- BOWEN, N. L. AND O. ANDERSEN (1914) The binary system MgO - SiO_2 . *Amer. J. Sci.*, **187**, 487-500.
- AND J. F. SCHAIRER (1932) The system FeO - SiO_2 . *Amer. J. Sci.*, **224**, 173-213.
- AND ——— (1935) The system MgO - FeO - SiO_2 . *Amer. J. Sci.*, **229**, 151-217.
- , ——— AND E. POSNJAK (1933) The system CaO - FeO - SiO_2 , *Amer. J. Sci.*, **226**, 193-284.
- BRADLEY, R. S. (1962) Thermodynamic calculations on phase equilibria involving fused salts; part II: solid solutions and applications to the olivines. *Amer. J. Sci.*, **260**, 550-554.
- COUGHLIN, J. P. (1954) Contributions to the data on theoretical metallurgy XII. Heats and free energies of formation of inorganic oxides. *U. S. Bur. Mines Bull.* **542**.
- CRAIG, H. (1964) Petrological and Compositional Relationships in Meteorites. *In* H.

- Craig, S. L. Miller, and G. J. Wasserburg, (ed.), *Isotopic and Cosmic Chemistry*. North-Holland Publishing Co., Amsterdam, p. 401-451.
- DARKEN, L. S., AND R. W. GURRY, (1945) The system iron-oxygen I. The wüstite field and related equilibria. *J. Amer. Chem. Soc.*, **67**, 1398-1412.
- ELLIOTT, J. F., M. GLEISER AND V. RAMAKRISHNA (1963) *Thermochemistry for Steelmaking, Vol. 2. Thermodynamics and Transport Properties*. Addison-Wesley Publishing Co., Reading, Mass.
- ENGELL, H. J. (1962) Gleichgewichtsmessungen an Oxyd-Mischkristallen. *Z. Physik. Chem.* **35**, 192-195.
- GOLDSCHMIDT, V. M. (1926) Geochemische Verteilungsgesetze der Elemente. *Skr. Norske Vid.-Akad. Oslo I. Mat-Naturvid. Kl.*, No. 7-8.
- GREIG, J. W., 1927. Immiscibility in silicate melts, *Amer. J. Sci.*, **213**, 1-44; 133-154.
- HAHN, W. C., JR., AND A. MUAN (1962) Activity measurements in oxide solid solutions: the system "FeO-MgO in the temperature range 1100° to 1300°C. *Trans. AIME*, **224**, 416-420.
- KATSURA, T., AND S. KIMURA (1965) Equilibria in the system FeO-Fe₂O₃-MgO at 1160°C. *Bull. Chem. Soc. Japan*, **38**, 1664-1670.
- KELLEY, K. K. (1962) Heats and free energies of formation of anhydrous silicates. *U. S. Bur. Mines Rep. Invest.* **5901**.
- MACDONALD, G. J. F., 1959. Chondrites and the chemical composition of the earth. In P. H. Abelson (ed.) *Researches in Geochemistry*. John Wiley and Sons, New York, p. 476-494.
- MASON, B. (1962) *Meteorites*. John Wiley and Sons, New York.
- MUAN, A. (1965) Equilibria among cobalt oxides containing phases with NaCl-type, spinel-type, and olivine-type structures. In G.-M. Schwab (ed.), *Reactivity of Solids* Elsevier Publishing Company, Amsterdam, p. 596-605.
- (1967) Determination of thermodynamic properties of silicates from locations of conjugation lines in ternary system, *Amer. Mineral.* **52**, 797-804.
- R. H. NAFZIGER AND P. L. ROEDER (1964) A method for determining the instability of ferrosilite. *Nature*, **202**, 688-689.
- AND E. F. OSBORN (1956) Phase equilibria at liquidus temperatures in the system MgO-FeO-Fe₂O₃-SiO₂. *J. Amer. Ceram. Soc.*, **39**, 121-140.
- MUELLER, R. F. (1961) Analysis of relations among Mg, Fe, and Mn in certain metamorphic minerals. *Geochim. Cosmochim. Acta*, **25**, 267-296.
- (1964) Phase equilibria and the crystallization of chondritic meteorites. *Geochim. Cosmochim. Acta*, **28**, 189-207.
- RINGWOOD, A. E. (1961) Chemical and genetic relationships among meteorites. *Geochim. Cosmochim. Acta*, **24**, 159-197.
- RUDY, E. (1963) Zur Thermodynamik der Phasenumsetzungen in Ternären Systemen. *Z. Metallk.*, **54**, 112-122; 213-233.
- SAHAMA, TH. G., AND D. R. TORGESON (1949) Thermochemical study of the olivines and orthopyroxenes. *U. S. Bur. Mines Rep. Invest.* **4408**.
- SCHWERTFEGER, K., AND A. MUAN (1966) Activities in olivine and pyroxenoid solid Solutions of the system Fe-Mn-Si-O at 1150°C, with appendices by L. S. Darken and K. Schwertfeger, *Trans. AIME*, **236**, 201-211.
- WAGNER, C., 1952. *Thermodynamics of Alloys*, Addison-Wesley Publishing Co., Reading, Mass.