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High-Temperature Activity-Composition Relations of Equilibrium Spinels, Olivines, and Pyroxenes in the System Mg-Fe-O-SiO_2

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Abstract

Sufficient high-temperature data delineating the equilibrium compositions of coexisting phases in the Mg-Fe-O-SiO_2 system have become available to permit calculation of activity-composition relations of the important spinels, olivines, and pyroxenes. Three methods of calculation involving (1) the thermodynamic properties of equilibrium magnesiowüstites, (2) spinel-hematite equilibria, and (3) magnesiowüstite defect data are employed. Within estimated uncertainties, the spinels generally exhibit negative deviations from ideality at 850°C and 1300°C, whereas the activity-composition relations at 1160°C are less well defined due to greater uncertainties in phase composition data. Spinel data calculated by methods 1 and 3, and 2 and 3, agree within the uncertainties inherent in the calculations at 1300°C. These uncertainties in the calculated data preclude meaningful correlations with temperature. At 1160°C, olivines and pyroxenes in equilibrium with spinels exhibit positive deviations from ideality, with olivines showing a more significantly pronounced deviation and pyroxenes showing near-ideality. This is similar to previous determinations at 1200–1250°C at lower oxygen fugacities where the silicate phases are in equilibrium with metallic iron. At 1300°C, olivines and pyroxenes in equilibrium with spinels show nearly ideal or slightly negative deviations from ideality in their activity-composition relations. Internal consistency of the data calculated from different equilibrium phase assemblages is demonstrated for the olivines.

Introduction

The spinel phase in the system Mg-Fe-O is recognized as an important constituent in many basic igneous rock-forming systems (see, for example, Muan and Osborn, 1956; Osborn, 1959, 1962). It is also the major stable phase in the Fe-O system at oxygen fugacities associated with such rocks (Nafziger, 1970). Osborn (1956) has pointed out the effect of this phase in the steel industry with respect to refractory brick. In addition, ferrites are finding increased applications in electronics, computer technology, and communication systems. However, little attention has been directed toward the thermodynamic properties to aid in understanding the behavior of this important phase. On the basis of thermal balance experiments in a controlled atmosphere, Schmahl *et al* (1961) concluded that the spinel phase is nearly ideal at 800–1000°C. Using emf methods, Gordeev and Tretyakov (1963) observed small positive deviations from ideality for the spinel solid solution at 900–1200°C. However, no activity values were presented. Additional experimental equilibrium phase composition data have become available in the past few years to permit calculations of component activities in the spinel phase at high temperatures in the Mg-Fe-O system.

Methods for Calculation of Spinel Activities

Inasmuch as there is a considerable area of spinel solid solution in the system Mg-Fe-O at temperatures above approximately 850°C (see, for example, Katsura and Kimura, 1965; Speidel, 1967), and because wüstite exhibits a cation-deficient structure (Darken and Gurry, 1945), relatively simple thermodynamic calculations cannot be applied. Figure 1 shows a schematic subsolidus isothermal section of a portion of this system derived from data presented by the aforementioned authors. At temperatures in the range 850°–1300°C, complete solid solution exists along the spinel join (Phillips and Muan, 1962; Alcock and Iyengar, 1967; Katsura and Kimura, 1965; Speidel, 1967). Three different methods were used to calculate activity-composition relations of these spinels.

Calculation from magnesiowüstite thermodynamic properties (method 1)

High-temperature activity-composition relations of magnesiowüstites in equilibrium with metallic iron (line FG in Figure 1) have been determined by several authors (Hahn and Muan, 1962; Alcock and Iyengar, 1967). The magnesiowüstites exhibit complete solid solubility at temperatures of interest. The data of Hahn and Muan (1962) formed the basis for calculations in the present study. These authors equilibrated two samples simultaneously in each of their runs. One sample with FeO content above the equilibrium value and the other with metallic iron and oxide of FeO content below the equilibrium value served as starting materials. Equilibrium was demonstrated as a function of time when the phase assemblages were identical after the runs. No significant differences in activity-composition relations for magnesiowüstites in equilibrium with metallic iron were found between 1100° and 1300°C. Uncertainties in bulk compositions ranged from ±0.015 to ±0.03. These activity-composition data can be used together with oxygen fugacity values of the equilibrium gas phase in the magnesiowüstite stability region (area DEFG, Figure 1) to calculate activity-composition relations of the magnesiowüstites in equilibrium with spinels (along line DE, Figure 1) by a ternary integration of the Gibbs-Duhem equation (Schuhmann, 1955). Isothermal oxygen fugacity data in the spinel-magnesiowüstite field (area ACED) are then used to obtain activities of MgO and FeO in spinels along the spinel + spinel-magnesiowüstite boundary (curve AC in Figure 1). The derived data are used with equilibrium constant data in the Fe-O and Mg-O systems to obtain activity-composition relations in the spinel solid solution. The spinel-magnesiowüstite equilibrium may be represented by

$$\mathrm{FeO} + 1/6\ \mathrm{O_2} = 1/3\ \mathrm{Fe_3O_4} \qquad (1)$$

where it is understood that FeO is not stoichiometric, but is represented for sake of convenience by this simple chemical formula. It is also understood that simple written oxides in this equation, and appropriate silicates and oxides in equations (10), (13), (14), and (16) are actually components in the respective solid solutions.

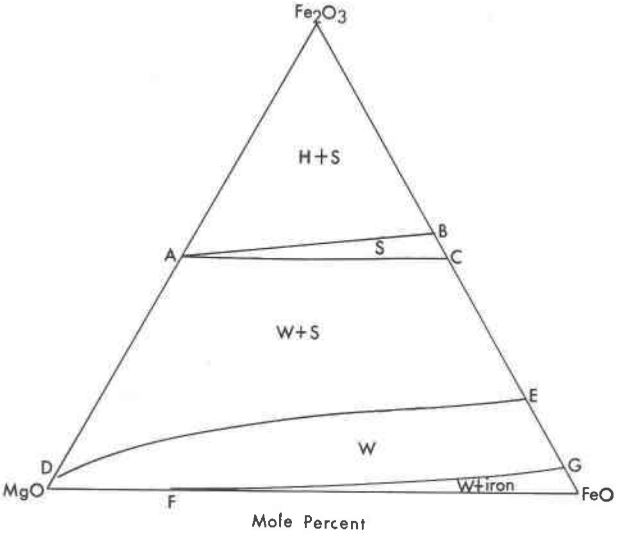

FIG. 1. Schematic subsolidus isothermal diagram of the system MgO-FeO-Fe_2O_3 showing phase fields. Abbreviations are: H = hematite, W = magnesiowüstite, and S = spinel. Points A and C correspond to $MgFe_2O_4$ and Fe_3O_4, respectively.

From equation (1) we can calculate the equilibrium constant [$K_{(1)}$] as

$$K_{(1)} = \frac{a^{1/3}{}_{\mathrm{Fe_3O_4}}}{f^{1/6}{}_{\mathrm{O_2}} \cdot a_{\mathrm{FeO}}} = \frac{a_{\mathrm{FeO_{4/3}}}}{f^{1/6}{}_{\mathrm{O_2}} \cdot a_{\mathrm{FeO}}} \qquad (2)$$

Thus

$$a_{\mathrm{FeO_{4/3}}} = K_{(1)} \cdot f^{1/6}{}_{\mathrm{O_2}} \cdot a_{\mathrm{FeO}} \qquad (3)$$

Here a and f denote activity and fugacity, respectively. Values of $K_{(1)}$ are given in Table 1. In this case

$$\left[\log a_{\mathrm{FeO}} = \log a^*{}_{\mathrm{FeO}} + \tfrac{1}{2}(\log f_{\mathrm{O_2}} - \log f^*{}_{\mathrm{O_2}}) - \frac{1}{2}\int_{\log f^*{}_{\mathrm{O_2}}}^{\log f_{\mathrm{O_2}}} \left(\frac{\partial n_{\mathrm{O}}}{\partial n_{\mathrm{Fe}}}\right)_{n_{\mathrm{Mg}},\ \log f_{\mathrm{O_2}}} d \log f_{\mathrm{O_2}}\right]_{n_{Fe}/n_{\mathrm{Mg}}} \qquad (4)$$

where the * notation represents the magnesiowüstite-metallic iron equilibria, and n denotes mole fraction. The terms n_{Fe} and n_{O} refer to mole fractions of total iron and oxygen, respectively. The derivation of equation (4) follows the reasoning of Schuhmann (1955) or Benner and Kenworthy (1966), together with appropriate substitution into Schuhmann's equation (11) of activity and equilibrium constant values for the iron-wüstite equation. Therefore

$$\mathrm{Fe}_{(1-x)}\mathrm{O} = (1 - x)\ \mathrm{Fe} + \tfrac{1}{2}\ \mathrm{O_2} \qquad (5)$$

The activities of the hypothetical component $(a_{\mathrm{MgO_{4/3}}})^1$ in the spinel solid solution were obtained in an analogous manner. This method is outlined in greater detail by Schwerdtfeger and Muan (1967).

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[1] Although this "molecule" does not exist in reality, its use simplifies the calculations for this method by involving only one cation, thereby facilitating the appropriate formulation of the law of mass action.

Calculation from spinel-hematite equilibria (method 2)

A second method for calculating spinel activity-composition relations in the Mg-Fe-O system involves the determination of the activity of Fe_3O_4 in spinels in equilibrium with hematite (AB in Figure 1) and the subsequent calculation of spinels in equilibrium with magnesiowüstites (AC in Figure 1) using equilibrium oxygen fugacity data. The activity of Fe_2O_3 in the spinel field (area ABC in Figure 1) is calculated first by a ternary integration of the Gibbs-Duhem equation and using

$$\log a_{Fe_2O_3} = \left(\int_{\log f_{O^+_2}}^{\log f_{O_2}} \frac{1}{3+2(n_{Fe_2O_3}/n_{Fe_3O_4})} \, d \log f_{O_2} \right)_{(n_{Fe_2O_3}/n_{MgO})}$$

where log $f_{O_2}{}^{+}$ is the oxygen fugacity in equilibrium with spinel and hematite along the phase boundary AB in Figure 1, and $n_{Fe_2O_3}$ refers to one of the components of the ternary system (Figure 1). The paths of integration therefore emanate from the Fe_3O_4-$MgFe_2O_4$ composition line (AC in Figure 1) and intersect curve AB at known oxygen fugacity isobars. The activity of Fe_3O_4 is calculated from the equation

$$3\,Fe_2O_3 = 2\,Fe_3O_4 + \tfrac{1}{2}\,O_2 \qquad (7)$$

where

$$a_{Fe_3O_4} = \left[\frac{K_{(7)} \cdot a^3_{Fe_2O_3}}{f^{1/2}_{O_2}} \right]^{1/2}. \qquad (8)$$

Equation (6) is derived from Schuhmann (1955), equation (11), with appropriate substitution of the three components of equation (7). Table 1 gives the values of $K_{(7)}$. In practice, the actual integration is most easily accomplished graphically. The activity of $MgFe_2O_4$ in the spinel phase can be calculated along either curves AB or AC by a binary integration of the Gibbs-Duhem equation. Benner and Kenworthy (1966) have illustrated this method as it applies to the ZnO-Fe_3O_4-Fe_2O_3 system. This method provides a check for internal consistency of the data and calculations with the first method outlined above, provided enough reliable data points are available.

TABLE 1. Calculated Values for Constants Used in Calculating Activity-Composition Relations of Spinels and Silicates in the System Mg-Fe-O-SiO₂*

	850°C		1160°C		1300°C	
	This Paper	Williams**	This Paper	Williams**	This Paper	Williams**
$K_{(1)}$	647.3	368.0	62.5	56.3	29.4	29.3
$\Delta G^o_{(1)}$	-14.4	-13.2	-11.8	-11.4	-10.4	-10.6
$K_{(7)}$	1.3×10^{-4}	--	0.03	--	0.18	--
$\Delta G^o_{(7)}$	20.0	--	9.9	--	5.3	--
$\Delta G^o_{(10)}$	--	--	-31.6	-29.5	-29.2	-26.3
$\Delta G^o_{(14)}$	--	--	-9.9	-9.8	-9.3	-8.8
$\Delta G^o_{(16)}$	--	--	-9.3	-9.6	-8.9	-8.9

*ΔG^o values are given in kcal.

$\Delta G^o_{(1)}$ values were calculated from data presented by Stull, et al. (1971) for the reactions forming FeO and Fe_3O_4 from Fe and O_2.

K values were calculated from the relation $\log K = \frac{\Delta G^o}{-2.303\ RT}$, where R is 1.987 cal. deg^{-1} $mole^{-1}$ and T is the temperature in °K.

$\Delta G^o_{(7)}$ values were calculated in a similar manner to those of $\Delta G^o_{(1)}$, using standard free energies of formation of Fe_3O_4 and Fe_2O_3 from Fe and O_2.

$\Delta G^o_{(10)}$ and $\Delta G^o_{(14)}$ values were calculated as indicated in the text.

$\Delta G^o_{(16)}$ values were calculated using appropriate combinations of $\Delta G^o_{(10)}$ and $\Delta G^o_{(14)}$.

** These data were calculated as described in the text from the values of K presented by Williams (1971).

Calculation from magnesiowüstite defect data (method 3)

The activity of Fe_3O_4 in the spinel phase in equilibrium with magnesiowüstites may also be computed from the equation

$$\log a_{Fe_3O_4} = \frac{1}{2} \int_{\log f_{O_2{}^a}}^{\log f_{O_2}} (1 - 3x) \, d \log f_{O_2} \qquad (9)$$

where log $f_{O_2}{}^{a}$ is the equilibrium oxygen fugacity over the Fe_3O_4-FeO equilibrium in the binary Fe-O system, and x represents the degree of nonstoichiometry in the magnesiowüstites [the same x which appears in equation (5)]. The derivation of equation (9) is given in a paper by Oleinikov *et al.* (1968). This equation is evaluated from experimental phase equilibrium and composition-log f_{O_2} data in the Mg-Fe-O system (Katsura and Kimura, 1965; Alcock and Iyengar, 1967; Speidel, 1967), using the Gibbs–Duhem–Margules equations.

Activity-Composition Relations for Spinels

In Figure 2 values for oxygen fugacities of the gas phase [log f_{O_2} and log $f_{O_2}{}^*$ in equation (4)] in equilibrium with condensed phases at 850°, 1160°, and 1300°C are plotted as a function of bulk composition (Katsura and Kimura, 1965; Alcock and Iyengar, 1967; Speidel, 1967). The corresponding values for a_{FeO}, $a_{FeO}{}^*$, a_{MgO}, and $a_{MgO}{}^*$ versus composition for the phases shown in Figure 1 are presented in Figure 3. The activity-composition relations for the spinels along line AC (Figure 1) calculated by the first method described in this paper are shown in Figure 4 at 850°, 1160°, and 1300°C. The required

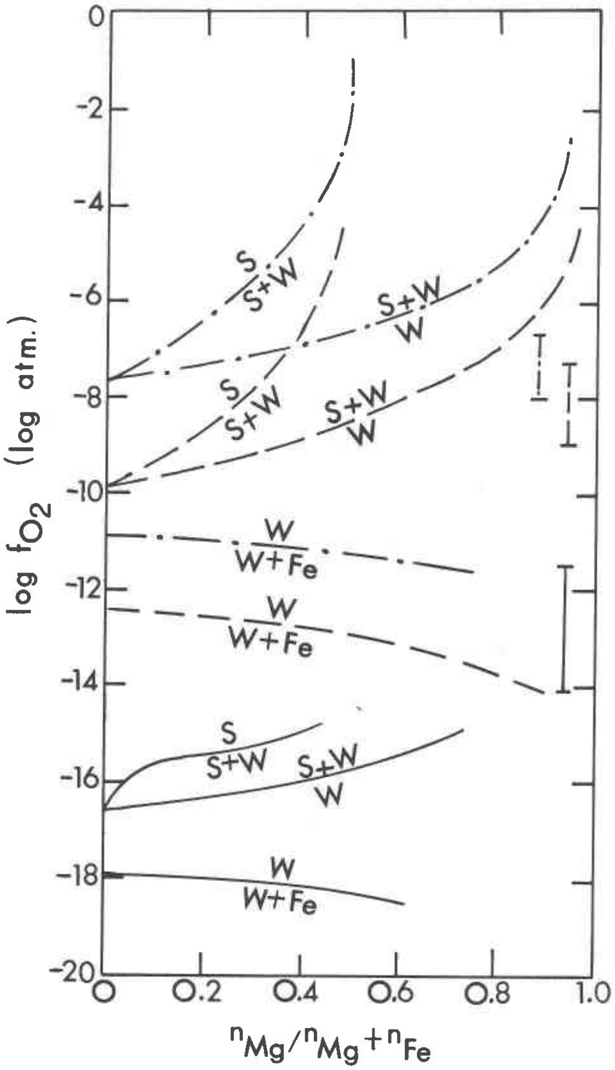


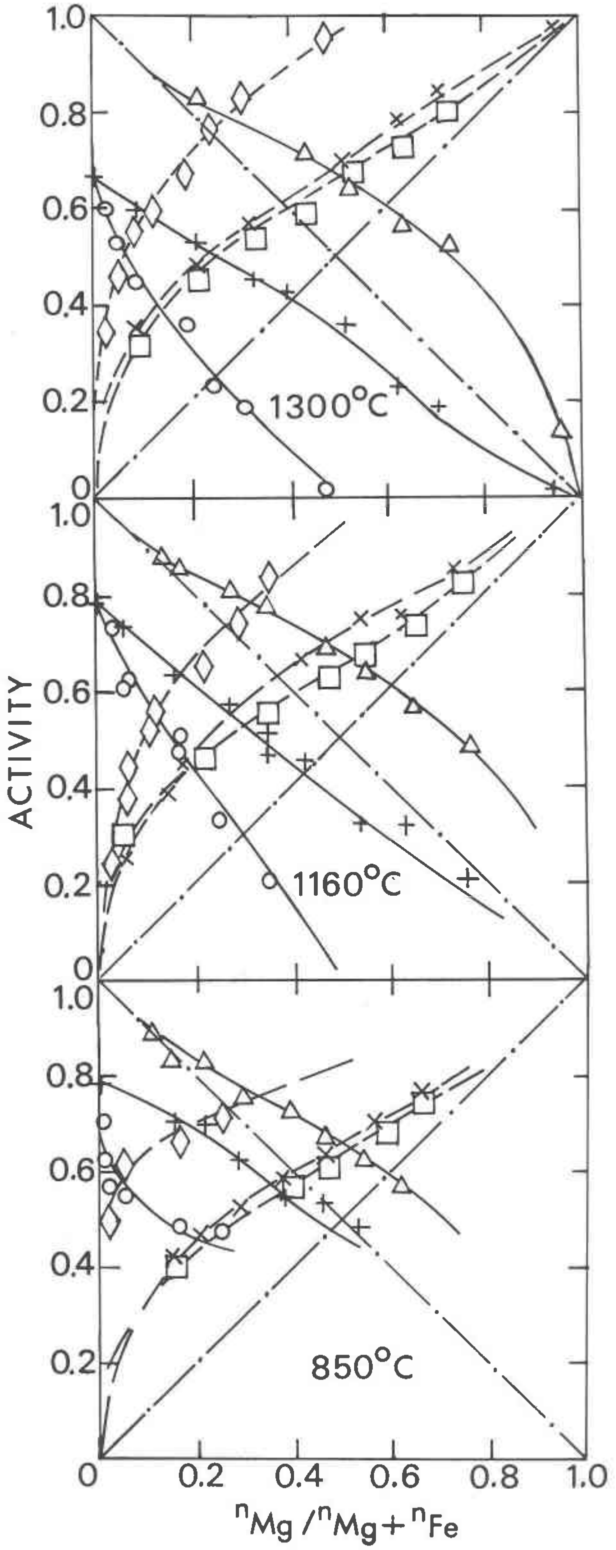
FIG. 2. Oxygen fugacity of the equilibrium gas phase as a function of bulk composition for boundary curves AC, DE, and FG (Figure 1) at 850°C (solid lines), 1160°C (dashed lines), and 1300°C (dot-dashed lines). The vertical lines at the right represent f_{O_2} ranges of olivine basalts and hypersthene-augite andesites at the respective temperatures (Nafziger, 1970). Abbreviations have the same meanings as in Figure 1, and Fe = iron. In this and subsequent figures, n_{Fe} refers to total iron.

oxygen fugacity-composition data were taken from Alcock and Iyengar (1967), Katsura and Kimura (1965), and Speidel (1967), at the respective temperatures. Williams (1971) has combined his experimental data, which involve phases in equilibrium with metallic iron, with those of the quartz-fayalite-magnetite buffer of Wones and Gilbert (1969) to obtain a set of derived reactions, some of which are applicable to the present study. Values of $K_{(1)}$ and $\Delta G^{\circ}_{(1)}$ used in this paper are compared in Table 1 with those calculated from Williams' data. If the data of Williams for $K_{(1)}$ are substituted for those used in this paper, the resulting values of $a_{FeO_{4/3}}$, for example, fall well within the estimated uncertainties (see Figure 4). There is a discrepancy at 850°C, but the $K_{(1)}$ data used in the present study are preferred, since Williams' data yield $a_{FeO_{4/3}} = 0.5$ at $n_{Mg}/n_{Mg} + n_{Fe} = 0$.

The most reliable oxygen fugacity versus composition data are considered to be those of Katsura and Kimura, and of Speidel. Katsura and Kimura used starting mixtures in which the Mg/Fe ratios were equal but whose initial degrees of oxidation were different. Thermogravimetric runs were conducted in which the samples were heated in air to constant weight. The oxygen fugacity was then altered and the samples were again equilibrated to constant weight for at least an hour. Samples were also analyzed after each run. A constant composition for the same starting material under identical conditions and the constancy of Fe^{2+} both inside and outside the sample pellet after the run ensured that equilibrium was attained. Speidel estimated uncertainties of ±0.15 wt percent for equilibrium compositional data. Equilibrium at 850°C is difficult to attain and data at this temperature are considered less reliable. However, Alcock and Iyengar determined that 48–72 hours were sufficient to attain equilibrium in quenched samples as evidenced by constant Fe^{3+}/Fe^{2+} analytical data throughout each sample.

In Figure 4, a possible slight negative deviation from Raoult's Law for $FeO_{4/3}$ in the spinel solid solution is indicated at 850° and 1300°C, whereas a positive deviation results from calculations using the aforementioned data at 1160°C. At 1300°C, the activity of $MgO_{4/3}$ shows a negative deviation from ideality. At lower temperatures, near-ideality is indicated except for lower total iron concentrations at 850°C. The estimated uncertainties in the activity data are ±0.1 at 1300° and at 1160°C, and ±0.15 at 850°C. These uncertainties are compounded throughout all calculations and are derived from (1) composition-oxygen fugacity data, (2) activity-composition data of the magnesiowüstite-metallic-iron equilibria, and (3) the defect structure in both phases, which becomes more pronounced with increasing iron oxide content. The uncertainties preclude any precise correlation of activity data with temperature.

These data have been recalculated in terms of $a_{Fe_3O_4}$ and are plotted together with the same pa-



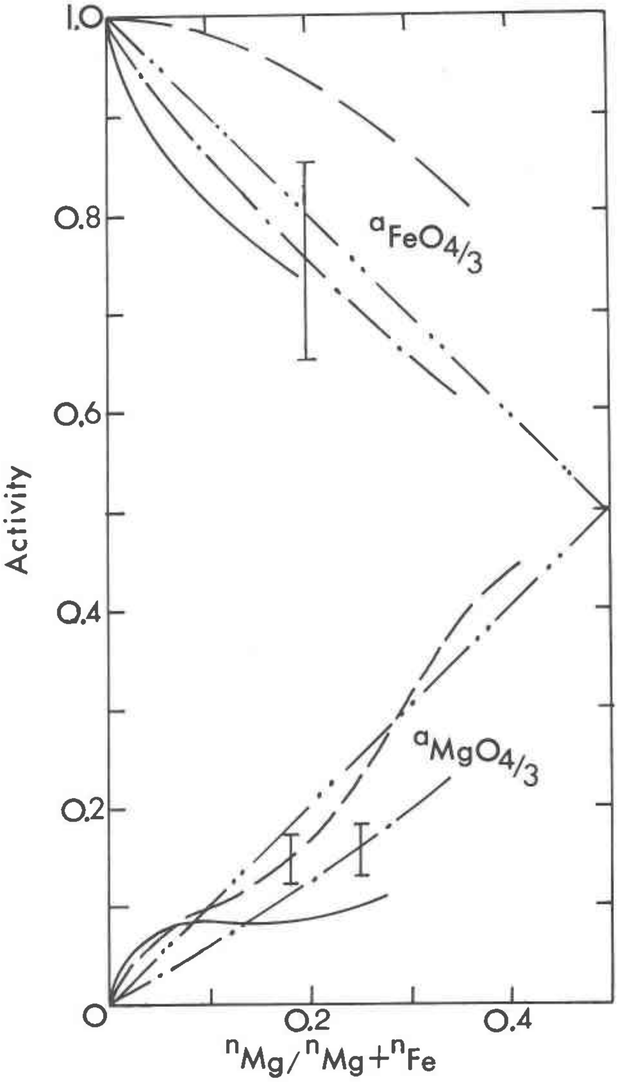


FIG. 4. Activity-composition relations for high-iron spinels along line AC (Figure 1) in the Mg-Fe-O system calculated from method 1 (see text) at 850°C (solid lines), 1160°C (dashed lines), and 1300°C (dot-dashed lines). The length of the vertical lines indicates estimated uncertainties in the calculations. Double dot-dashed lines indicate ideal behavior.

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FIG. 3. Activity-composition relations for FeO and MgO in coexisting magnesiowüstites and spinels in the Mg-Fe-O system at 850°, 1160°, and 1300°C. The solid lines represent the activities of FeO, and the dashed lines represent MgO activities. The dot-dashed lines indicate ideal activity-composition relations. Abbreviations are: △ and □, boundary curve FG (Figure 1) data points for FeO and MgO, respectively; + and ×, boundary curve DE (Figure 1) data points for FeO and MgO, respectively; ○ and ◇, boundary curve AC (Figure 1) data points for FeO and MgO, respectively.

rameter (*i.e.*, $a_{Fe_3O_4}$) as calculated by means of the second and third methods outlined in this paper. These activity-composition data at 1160° and 1300°C (Fig. 5) illustrate general agreement within the stated uncertainties between methods 1 and 3, and 2 and 3, at 1300°C. In Figure 5, $n_{Fe_3O_4}$ represents compositions projected onto the spinel join (AC in Figure 1). The indicated discrepancies between data calculated from methods 1 and 2 at 1300°C are probably due to the more uncertain and less numerous experimental data available for area ABC in Figure 1. This would affect the values calculated from method 2. Both Katsura and Kimura (1965) and Speidel (1967) concentrated their detailed equilibrium measurements in the spinel-magnesiowüstite equilibrium areas (ACDFG in Figure 1). However, an accurate evaluation of the integral in equation (6) depends on numerous data points. Therefore, activity values calculated from methods 1 and 3 are considered more reliable than those calculated from method 2 at 1300°C. At 1160°C, the discrepancy between activity-composition relations calculated from methods 1 and 3 is believed due to (1) the large number of computing steps and of additional data (with their inherent uncertainties) that are required for method 1, and (2) uncertainties in the tangent intercepts required for evaluating the integral in method 1. For these reasons, data calculated from the more simple method 3 at 1160°C are considered more reliable.

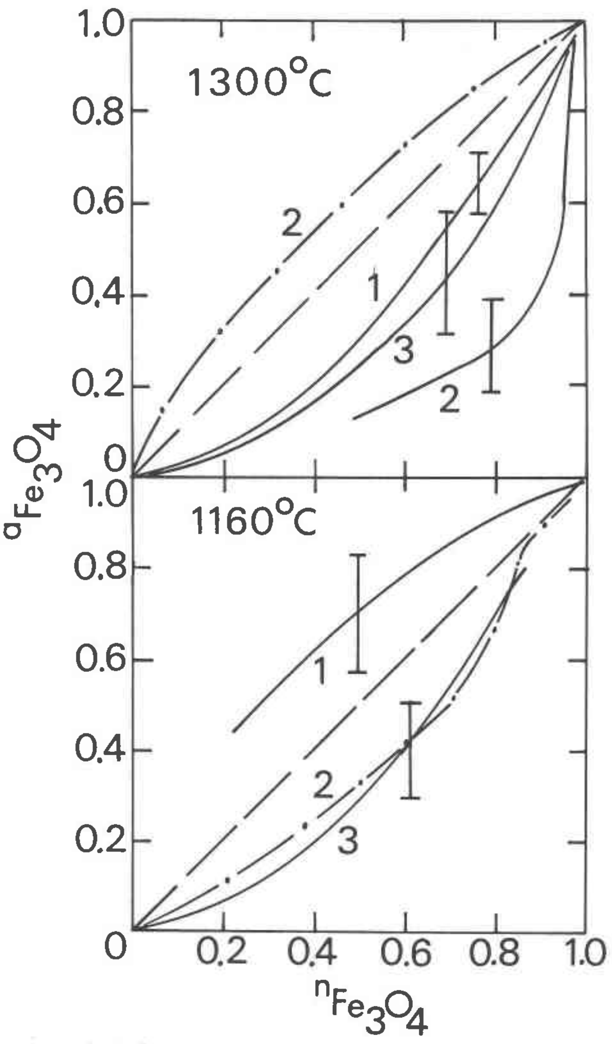

FIG. 5. Solid curves denote activity-composition relations of Fe_3O_4 in spinels along line AC (Figure 1) in the Mg-Fe-O system at 1160° and 1300°C, calculated from methods 1, 2, and 3 (see text), as indicated. Insufficient experimental data were available at 1160°C to calculate activities by method 2, and hence no solid curve is shown for method 2 at 1160°C. The dot-dashed lines represent spinels in equilibrium with hematite (line AB in Figure 1). The dashed lines represent ideality, and the vertical lines indicate estimated uncertainties.

Also shown in Figure 5 are the activity-composition relations of Fe_3O_4 in the spinels in equilibrium with hematite in the Mg-Fe-O system. A moderate positive deviation from ideality for spinels in equilibrium with hematite is noted at 1300°C, whereas a corresponding negative deviation is noted at 1160°C. Deviations from ideality for spinels in equilibrium with magnesiowüstites are negative at 1300°C and 1160°C as calculated from method 3. The negative deviation from ideality, or a tendency for one type of atom to group with the other, for the spinel solid solution in equilibrium with magnesiowüstites is expected in view of the formation of the inverse spinel compounds in the join $MgO_{4/3}$-$FeO_{4/3}$.

Derived Activity Data for Silicate Phases

The present thermodynamic data in combination with interpolations of phase composition versus oxygen fugacity given by Speidel and Osborn (1967) for olivine-silica-spinel, pyroxene-silica-spinel, and olivine-pyroxene-spinel equilibria in the system Mg-Fe-O-SiO_2 permit an estimation of the activity-composition relations of these olivines and pyroxenes at higher oxygen fugacities than relations previously given by Nafziger and Muan (1967). These higher fugacities are more applicable to terrestrial igneous rocks. Speidel and Osborn (1967) have demonstrated that equilibrium was attained in their work. Samples were ground and replaced two to three times during run lengths of 10–21 days. In addition, phase compositions as determined by electron microprobe work showed that in runs of three days, equilibrium was not attained. However, equilibrium was demonstrated statistically in runs of six days duration. Compositional uncertainties of FeO in olivines and pyroxenes were stated as 5–7 percent of the amount present. Uncertainties of FeO in spinels ranged from 0.3 percent at high FeO contents, to 3 percent in high MgO compositions.

In the following discussion, the assumption is made that the spinel compositions in equilibrium with the silicate phases are approximately equal to those in equilibrium with the magnesiowüstites, within the limits of error involved.

Activity-composition relations of pyroxenes from pyroxene-silica-spinel equilibrium data

In the pyroxene-silica-spinel equilibrium region, the reactions of interest are

$$\tfrac{1}{2}\,O_2 + 3\,FeSiO_3 = Fe_3O_4 + 3\,SiO_2 \qquad (10)$$

and

$$\Delta G^0_{(10)} = -2.303RT \log \frac{a^3_{SiO_2} \cdot a_{Fe_3O_4}}{f^{1/2}_{O_2} \cdot a^3_{FeSiO_3}} \qquad (11)$$

where ΔG° represents the free energy change for the reaction R is the gas constant, and T the absolute temperature (K). Since the components of the other phases are essentially insoluble in SiO₂, $a_{SiO_2} = 1$. Hence,

$$\log a_{FeSiO_3} = \frac{\Delta G^0_{(10)}/2.303RT + \log a_{Fe_3O_4} - \tfrac{1}{2} f_{O_2}}{3}. \qquad (12)$$

The values for $a_{Fe_3O_4}$ may be obtained from Figure 5. If $a_{FeO_{4/3}}$ is used, (calculation method 1 as outlined previously), equation (10) becomes

$$1/6\,O_2 + FeSiO_3 = FeO_{4/3} + SiO_2 \qquad (13)$$

and a_{FeSiO_3} is calculated therefrom. The pyroxenes are probably monoclinic because the work of Speidel and Osborn (1967) involved quenched samples. Larimer (1968) obtained mostly clinopyroxenes in his quenched samples in work on the Fe-MgO-SiO₂-O₂ system. The oxygen fugacity values were determined from the literature (*e.g.*, Alcock and Iyengar, 1967; Katsura and Kimura, 1965; Speidel, 1967). The value for ΔG°₍₁₀₎ (see Table 1) was calculated by appropriate combinations of the free energies of formation for Fe₃O₄ (or FeO₄/₃) and FeO (Stull *et al*, 1971), and FeSiO₃ from its constituent oxides (FeO and SiO₂). Values of ΔG°₍₁₀₎ calculated from the aforementioned data and used in this paper are compared in Table 1 with those calculated from the

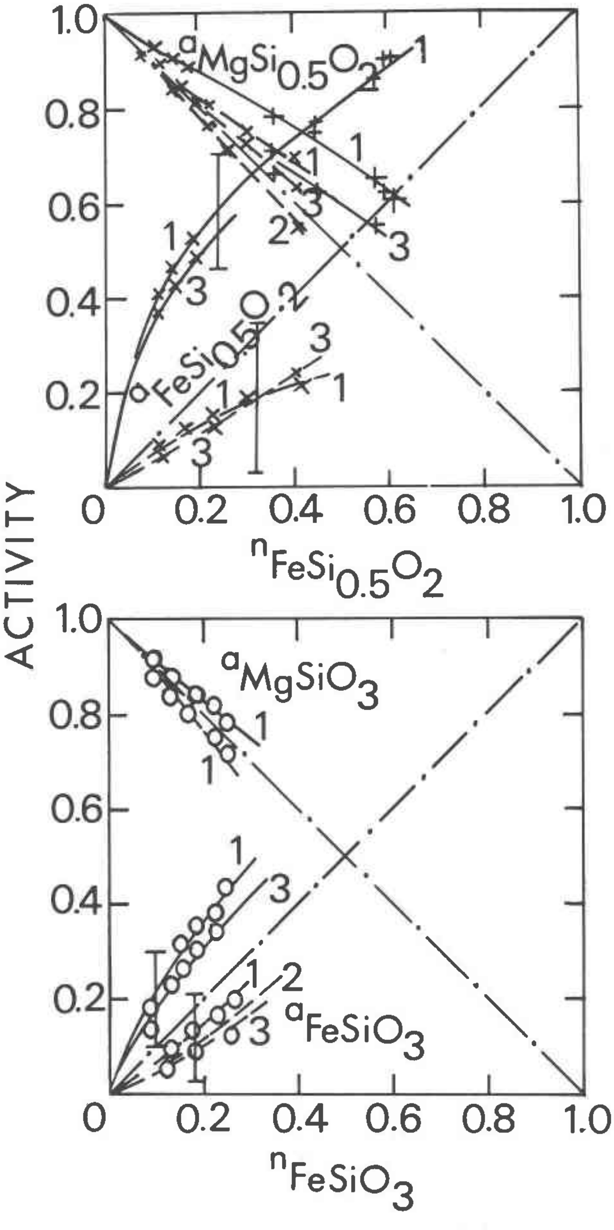

FIG. 6. Activity-composition relations of olivines (upper) and pyroxenes (lower) in equilibrium with spinels at 1160°C (solid lines) and 1300°C (dashed lines) in the system Mg-Fe-O-SiO₂. The dot-dashed line represents ideal conditions and the vertical lines indicate estimated uncertainties. Abbreviations are: × = calculated from olivine-pyroxene-spinel data, + = calculated from olivine-spinel-silica data, and ○ = calculated from pyroxene-silica-spinel data. Calculations from spinel activity data derived by methods 1, 2, and 3 (see text) are so indicated.

data presented by Williams (1971). The free energies of formation for $FeSiO_3$ used in the present study were interpolated and extrapolated from data presented by Schwerdtfeger and Muan (1966) and Nafziger and Muan (1967). These values were −1.26 kcal at 1160°C and −0.7 kcal at 1300°C. Compositions of the coexisting pyroxene and spinel phases were obtained from Speidel and Osborn (1967). Calculated activity values for $FeSiO_3$ and $MgSiO_3$ in pyroxenes at 1160° and 1300°C are shown in Figure 6. At 1160°C, a slight positive deviation from ideality is indicated, whereas at 1300°C, a slight negative deviation is shown. However, the uncertainties derived from the data and calculations, as represented in the figure, show that the activity-composition relations for the $FeSiO_3$-$MgSiO_3$ pyroxenes in equilibrium with spinels may be considered nearly ideal. This is essentially the same result obtained by Nafziger and Muan (1967) at 1200–1250°C for pyroxenes in equilibrium with metallic iron at lower oxygen fugacities.

Olivine activity-composition relations from olivine-silica-spinel equilibrium data

For the olivine-silica-spinel equilibria in the Mg-Fe-O-SiO_2 system, the reaction

$$1/6\ O_2 + FeSi_{0.5}O_2 = FeO_{4/3} + \tfrac{1}{2}\ SiO_2 \qquad (14)$$

applies. Hence,

$$\log a_{FeSi_{0.5}O_2} = \frac{\Delta G^\circ_{(14)}}{2.303RT} + \log a_{FeO_{4/3}} - 1/6 \log f_{O_2} \qquad (15)$$

Spinel activity, oxygen fugacity, and condensed phase equilibrium compositional data were obtained from previously cited sources. The value for $\Delta G^\circ_{(14)}$ (see Table 1) were derived from calculations using data presented by Stull *et al.* (1971) for the free energies of formation of $FeO_{4/3}$ and $FeSi_{0.5}O_2$. Data for the latter compound were also obtained from the work of Schwerdtfeger and Muan (1966), and interpolated from Kelley (1962). Comparisons of resulting $\Delta G^\circ_{(14)}$ values with those calculated from Williams' (1971) data are shown in Table 1. The calculated olivine activity-composition relations are shown in Figure 6 for 1160°C and 1300°C. The relations with respect to the two temperatures are similar to those obtained for the pyroxenes, although greater deviations from ideality at 1160°C are indicated. This also conforms with the results obtained for lower oxygen fugacities at 1200°C (Nafziger and Muan, 1967). Uncertainties preclude precise comparisons between olivines and pyroxenes, however. Correlations of activity data with temperature are also not possible, although a closer approach to ideality with increasing temperature seems plausible.

Activity-composition calculations from olivine-pyroxene-spinel equilibrium data

As a check for internal consistency with the previous calculations, additional literature data for the olivine-pyroxene-spinel equilibrium in the Mg-Fe-O-SiO_2 system may be used (Speidel and Osborn, 1967). In this region, the reaction

$$2FeSi_{0.5}O_2 + 1/6\ O_2 = FeO_{4/3} + FeSiO_3 \qquad (16)$$

is of interest. Either pyroxene or olivine activities may in principle be calculated using previously cited data and the activity-composition relations shown in Figure 6 of the equilibrium olivines or pyroxenes, respectively, together with olivine-pyroxene-spinel equilibrium composition data. Olivine results are plotted in Figure 6 and agree well with values derived from the olivine-silica-spinel calculations. However, not enough data are available to permit this type of calculation for the pyroxenes.

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References

ALCOCK, C. B., AND G. N. K. IYENGAR (1967) A study of the oxidation-reduction equilibria of dilute magnesiowüstites. *Proc. Brit. Ceram. Soc.* **8**, 219–229.

BENNER, R. L., AND H. KENWORTHY (1966) The thermodynamic properties of the ZnO-Fe_2O_3-Fe_3O_4 system at elevated temperatures. 1. The thermodynamic properties as related to the spinel structure. *U.S. Bur. Mines Rep. Invest.* **6754**, 44 pp.

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.

GORDEEV, I. V., AND YU. D. TRETYAKOV (1963) Thermodynamics of solid solutions of magnesium ferrite with magnetite. *Zh. Neorgan. Khim.* **8**, 1814–1819 [*Russ. J. Inorg. Chem.* **8**, 943–947].

HAHN, W. C., JR., AND A. MUAN (1962) Activity measurements in oxide solid solutions: The system "FeO"-MgO in the temperature interval 1100° to 1300°C. *Trans. AIME,* **224**, 416–420.

KATSURA, T., AND S. KIMURA (1965) Equilibria in the system FeO-Fe$_2$O$_3$-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,** 32 pp.

LARIMER, J. W. (1968) Experimental studies on the system Fe-MgO-SiO$_2$-O$_2$ and their bearing on the petrology of chondritic meteorites. *Geochim. Cosmochim. Acta*, **32,** 1187–1209.

MUAN, A., AND E. F. OSBORN (1956) Phase equilibria at liquidus temperatures in the system MgO-FeO-Fe$_2$O$_3$-SiO$_2$. *J. Amer. Ceram. Soc.* **39,** 121–140.

NAFZIGER, R. H. (1970) The join diopside-iron oxide-silica and its relation to the join diopside-forsterite-iron oxide-silica. *Amer. Mineral.* **55,** 2042–2052.

———, AND A. MUAN (1967) Equilibrium phase compositions and thermodynamic properties of olivines and pyroxenes in the system MgO-"FeO"-SiO$_2$. *Amer. Mineral.* **52,** 1364–1385.

OLEINIKOV, N. N., R. YU. DOBROVINSKII, V. F. BALAKIREV, A. N. MEN', YU. D. TRETYAKOV, AND G. I. CHUFAGOV (1968) Determination of component activities in a Fe$_3$O$_4$-FeCr$_2$O$_4$ solid solution. *Izv. Akad. Nauk SSSR, Neorg. Mater.* **4,** 1362–1384. [*Inorg. Mater.* **4,** 1216–1218].

OSBORN, E. F. (1956) Importance of the spinel phase in the steel industry. *Regional Tech. Pap., Amer. Iron Steel Inst.*, 1–16.

——— (1959) Role of oxygen pressure in the crystallization and differentiation of basaltic magma. *Amer. J. Sci.* **257,** 609–647.

——— (1962) Reaction series for subalkaline igneous rocks based on different oxygen pressure conditions. *Amer. Mineral.* **47,** 211–226.

PHILLIPS, B., AND A. MUAN (1962) Phase equilibria in the system MgO-FeO-Fe$_2$O$_3$ in temperature range 1400° to 1800°C. *J. Amer. Ceram. Soc.* **45,** 588–591.

SCHUHMANN, R., JR. (1955) Application of Gibbs-Duhem equations to ternary systems. *Acta Met.* **3,** 219–226.

SCHMAHL, N. G., B. FRISCH, AND G. STOCK (1961) Gleichgewichtsuntersuchungen an magnesiowüstiten und magnesioferriten. *Arch. Eisenhüttenw.* **32,** 297–302.

SCHWERDTFEGER, 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. Schwerdtfeger. *Trans. AIME,* **236,** 201–211.

———, AND ——— (1967) Phase equilibria in the system Fe-Mn-O involving "(Fe,Mn)O" and (Fe,Mn)$_3$O$_4$ solid solutions. *Trans. AIME,* **239,** 1114–1119.

SPEIDEL, D. H. (1967) Phase equilibria in the system MgO-FeO-Fe$_2$O$_3$: The 1300°C isothermal section and extrapolations to other temperatures. *J. Amer. Ceram. Soc.* **50,** 243–248.

———, AND E. F. OSBORN (1967) Element distribution among coexisting phases in the system MgO-FeO-Fe$_2$O$_3$-SiO$_2$ as a function of temperature and oxygen fugacity. *Amer. Mineral.* **52,** 1139–1152.

STULL, D. R., *et al.* (1971) *JANAF thermochemical tables,* Second Ed. The Thermal Research Laboratory, Dow Chemical Co., Midland, Michigan. **NSRDS-NBS-37.**

WILLIAMS, R. J. (1971) Reaction constants in the system Fe-MgO-SiO$_2$-O$_2$ at 1 atm between 900° and 1300°C: Experimental results. *Amer. J. Sci.* **270,** 334–360.

WONES, D. R., AND M. C. GILBERT (1969) The fayalite-magnetite-quartz assemblage between 600°C and 800°C. *Amer. J. Sci.* **267-A,** 480–488.

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