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Activity Measurements in Orthosilicate and Metasilicate Solid Solutions. I. Mg_2SiO_4-Fe_2SiO_4 and $MgSiO_3$-$FeSiO_3$ at 1204°C

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The activity-composition relations in ortho-, and metasilicate solid solutions in the FeO-MgO-SiO_2 system are determined at 1204°C on the basis of the measurement of equilibrium oxygen partial pressures. Both the olivine and the pyroxene solid solutions show significant deviations from ideality. Using the present data, the standard free energy change of formation of ferrosilite (hypothetical compound, $FeSiO_3$) is calculated to be -41.7 ± 0.2 kcal/mol on the basis of the equilibrium between metallic iron and silica, and to be -1.6 ± 0.2 kcal/mol on the wüstite (" FeO ") and silica.

Recently, much efforts are being concentrated on the thermodynamic properties of ortho-, and metasilicate equilibria found in some ternary oxide systems at high temperatures under one atmospheric pressure. Of these, the relationship between activity and composition of the olivine-components (orthosilicate) and the pyroxene-components (metasilicate) is no doubt of the fundamental problem to exactly understand the stable co-existence of these solid solutions. Schwerdtfeger and Muan¹⁾ have determined the activities of a component Fe_2SiO_4 in olivine and of a component $FeSiO_3$ in pyroxene solid solutions in the FeO-MnO-SiO_2 system at 1150°C on the basis of the CO_2/CO ratio in the gas phase in equilibrium with co-existing solid solutions, and concluded that both solid solutions behave ideally. In their Appendix, Darken and Schwerdtfeger²⁾ made clear statistically the expression of activity of the component Fe_2SiO_4 in the olivine solid solution to be written as $a_{FeSi_{0.5}O_2}$ as empirically had been accepted by many investigators. Masse, Rosen, and Muan³⁾ also published the activity-composition relations in Co_2SiO_4-Fe_2-SiO_4 solid solution at 1180°C, and showed a slightly positive deviation from ideality. Biggers and Muan⁴⁾ presented the relations in ortho-, and meta-silicate solid solutions found in the MnO-CoO-SiO_2 system at 1200 and 1250°C. On the basis of these results, Muan⁵⁾ emphasized the importance of the conjugation lines between co-existing solid solutions. However, the activity-composition relations to the olivine and pyroxene in the FeO-MgO-SiO_2 system has not yet been experimentally studied.

Generally, it has been assumed that the olivine composing of iron and magnesium may behave ideally, and the various thermodynamic calculations have

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1) K. Schwerdtfeger and A. Muan, *Trans. AIME*, **236**, 201 (1966).
2) L. S. Darken and K. Schwerdtfeger, *ibid.*, **236**, 208 (1966).
3) D. P. Masse, E. Rosen and A. Muan, *J. Am. Ceram. Soc.*, **49**, 328 (1966).
4) J. V. Biggers and A. Muan, *ibid.*, **50**, 230 (1967).
5) A. Muan, *Am. Min.*, **52**, 797 (1967).

been made on the basis of the ideality. For instance, Bowen and Schairer⁶⁾ calculated the molal heat of fusion of fayalite (Fe_2SiO_4) and forsterite (Mg_2SiO_4) in their classical paper, and Lamberg and DeVore⁷⁾ also postulated the ideality to calculate the distribution constant of iron and magnesium in co-existing olivine and pyroxene by using mole fraction. Bradley⁸⁾ found that the olivine solid solution is ideal, on the basis of the molal heat of fusions of fayalite and forsterite. Sahama and Torgesson⁹⁾ also presented the linearity found in the relationship between the heat of solution and the Mg/Fe ratio in the natural forsterite-fayalite series by means of the solution calorimetry, and indicated that the replacement of Fe and Mg in the olivine structure is thermally perfect. They also stated that the replacement of Fe to Mg in orthorhombic pyroxene structure is perfect too.

The present objectives are to find the activity-composition relations in the olivine and the pyroxene solid solutions in the FeO-MgO-SiO_2 system and to confirm whether or not these solid solution aresideal just as expected by many investigators.

Methods of Calculation of the Activities

The approximate diagram for the subsolidus phase equilibria in the FeO-MgO-SiO_2 system is known from the study by Bowen and Schairer⁶⁾ under low oxygen partial pressures, and Fig. 1 shows an isothermal section at 1204°C. In this system, there exist three solid solution series; the oxide, MgO-FeO, the olivine, Fe_2SiO_4-Mg_2SiO_4, and the pyroxene, $FeSiO_3$-$MgSiO_3$. The oxide and olivine solid solutions are continuous, but the pyroxene solid solution is a limiting as shown in Fig. 1, because of the instability of ferrosilite in ordinary temperature and pressure. From the present study, we found a point A and a point B in Fig. 1 to be 62 mol% fayalite and 48 mol% ferrosilite at 1204°C, respectively. The activity-composition relation in the oxide solid solution, FeO-MgO, has already been studied by Hahn, Jr., and Muan¹⁰⁾ in the temperature interval from 1000 to 1300°C, and they concluded that the system showed a considerable positive deviation from the Raoult's law.

Based on Fig. 1, it may be convenient to calculate the activity of the component Fe_2SiO_4, $a_{FeSi_{0.5}O_2}$, in the olivine solid solution and the activity of the component $FeSiO_3$, a_{FeSiO_3}, in the pyroxene solid solution as follows:

1) The Activity of Fe_2SiO_4 in Composition Ranging from Pure Fe_2SiO_4 to a Point A. Consider the following reaction,

$$FeSi_{0.5}O_2 = Fe + \tfrac{1}{2}\,SiO_2 + \tfrac{1}{2}\,O_2 \qquad (1)$$

in which pure fayalite dissociates to metallic iron, silica, and oxygen gas. For this reaction, the equilibrium constant, K_1, is expressed as

$$K_1 = [a_{Fe}\cdot a^{1/2}_{SiO_2}\cdot P^{1/2}_{O_2}(1)]/a_{FeSi_{0.5}O_2\text{-}(p)} \qquad (2)$$

where a represents the activity of each component shown by subscripts, in which $FeSi_{0.5}O_2$-(p) means for pure fayalite, and where $P_{O_2}(1)$ implies an oxygen partial pressure. Since the composition of fayalite is stoichiometric as confirmed by Kitayama and Katsura,¹¹⁾ then the equilibrium constant, K_1, may be written as

$$K_1 = P^{1/2}_{O_2}(1) \qquad (3)$$

In the case of the solid solution, the same treatment is applied as follows,

$$(FeSi_{0.5}O_2)_{ss} = Fe + \tfrac{1}{2}\,SiO_2 + \tfrac{1}{2}\,O_2 \qquad (4)$$

in which the fayalite component in the olivine dissociates to form pure metallic ion and pure silica as in the reaction (1). The subscript ss means a solid solution, and the equilibrium constant, K_4, is also expressed as

$$K_4 = P^{1/2}_{O_2}(4)/a_{(FeSi_{0.5}O_2)_{ss}\text{-}(1)} \qquad (5)$$

where the subscript $(FeSi_{0.5}O_2)_{ss}$-(1) means the limiting solid solution from pure fayalite to the point A. From Eqs. (3) and (5), we get the following relation by using pure fayalite as the standard state for the activity of $FeSi_{0.5}O_2$,

$$a_{(FeSi_{0.5}O_2)_{ss}\text{-}(1)} = P^{1/2}_{O_2}(4)/P^{1/2}_{O_2}(1) \qquad (6)$$

because K_4 is equal to K_1.

2) The Activity of Fe_2SiO_4 in Composition Ranging from the Point A to Pure Mg_2SiO_4. In this region, the reaction of olivine is different from that of Eq. (4). If we follow experimentally the appearance of metallic iron by changing the oxygen partial pressure, then olivine solid solution may first dissociate as follows,

$$\begin{aligned}(FeSi_{0.5}O_2)_{ss} =\\ &\tfrac{1}{2}\,Fe + \tfrac{1}{2}\,(FeSiO_3)_{ss} + \tfrac{1}{4}\,O_2 \qquad (7)\end{aligned}$$

The equilibrium constant, K_7, is

$$K_7 = [a^{1/2}_{(FeSiO_3)_{ss}}\cdot P^{1/2}_{O_2}(7)]/a_{(FeSi_{0.5}O_2)_{ss}\text{-}(2)} \qquad (8)$$

where the subscript $(FeSi_{0.5}O_2)_{ss}$-(2) means the range from the point A to pure Mg_2SiO_4. The pyroxene thus appeared will subsequently decompose at an oxygen partial pressure defined by the following Eq. (9),

$$\tfrac{1}{2}\,(FeSiO_3)_{ss} = \tfrac{1}{2}\,Fe + \tfrac{1}{2}\,SiO_2 + \tfrac{1}{4}\,O_2 \qquad (9)$$

The equilibrium constant, K_9, is expressed as

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6) N. L. Bowen and J. F. Schairer, *Am. J. Sci.*, **29**, 151 (1935).

7) H. Lamberg and G. DeVore, *J. Geol.*, **59**, 193 (1951).

8) R. S. Bradley, *Am. J. Sci.*, **260**, 550 (1962).

9) Th. G. Sahama and D. R. Torgesson, *J. Geol.*, **57**, 255 (1949).

10) W. C. Hahn, Jr., and A. Muan, *Trans. AIME*, **224**, 416 (1962).

11) K. Kitayama and T. Katsura, This Bulletin, **41**, 525 (1968).

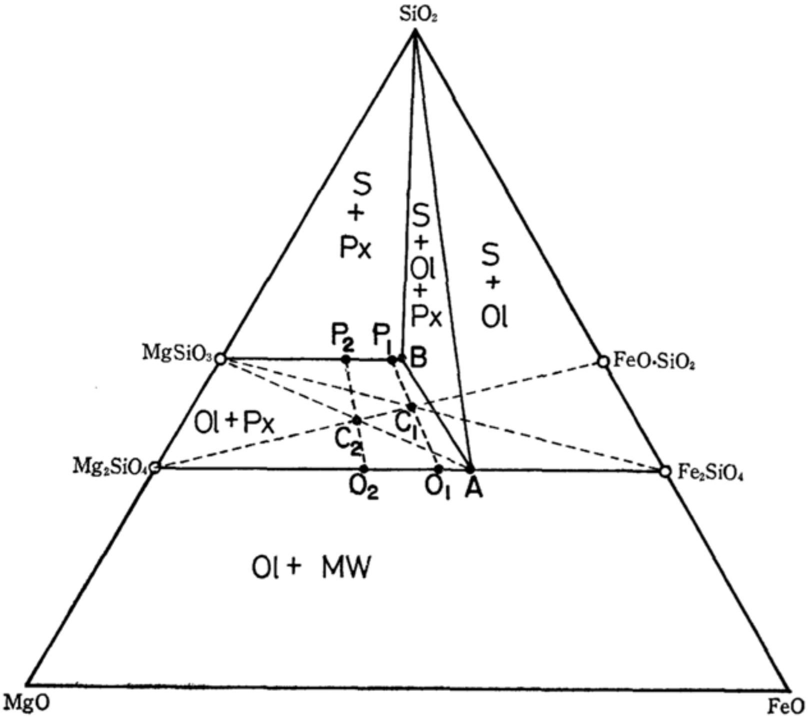

Fig. 1. The isothermal section for the system MgO-FeO-SiO$_2$ at 1204°C.
S: silica, Px: pyroxene, Ol: olivine, MW: magnesiowüstite

$$K_9 = P_{\mathrm{O}_2}^{1/4}(9)/a_{(\mathrm{FeSiO}_3)_{ss}}^{1/2} \qquad (10)$$

In the reaction (9), pure silica and iron appear as shown *in* Fig. *1*, and *there exists* a relation, $K_4 = K_7 \cdot K_9$. Thus, we may obtain the Eq. (11), taking the pure fayalite as the standard state,

$$a_{(\mathrm{FeSi}_{0.5}\mathrm{O}_2)_{ss}} = [P_{\mathrm{O}_2}^{1/4}(7) \cdot P_{\mathrm{O}_2}^{1/4}(9)]/P_{\mathrm{O}_2}^{1/2}(1) \qquad (11)$$

3) The Activity of FeSiO$_3$ in the Pyroxene Solid Solution. The activity of FeSiO$_3$ in the pyroxene solid solution is obtained by the same method as described above. As for the solid solution is concerned, the activity of FeSiO$_3$ is given by Eq. (10), taking an arbitrary composition as the standard state for the component FeSiO$_3$. If we want to take pure ferrosilite as the standard state, then we have to apply the extrapolation method. Here, we may apply the α-function method[12,13] to determine an oxygen partial pressure at which ferrosilite may decompose as shown in Eq. (9). After obtaining the oxygen partial pressure for pure ferrosilite, P_{O_2}(9-p), the activity of the component FeSiO$_2$ in pyroxene solid solution may be derived as

$$a_{(\mathrm{FeSiO}_3)_{ss}} = P_{\mathrm{O}_2}^{1/2}(9)/P_{\mathrm{O}_2}^{1/2}(9\text{-p}) \qquad (12)$$

Experimental

Preparation of Olivine Solid Solution. Reagent grade chemicals are used. Ferric oxide is reduced to ferrous at 1200°C in an atmosphere of CO$_2$/H$_2$=1. After analyzing the ferrous content, the oxide is mixed with silica to prepare the stoichiometric fayalite having the Fe/Si ratio 1/2. The mixture is then heated at 1300°C to prepare the fayalite in the same atmosphere by using a Pt alloy (20%Rh) as a container which was previously saturated with iron. The melt is quenched and powdered. Forsterite is prepared as follows; Silica and magnesium oxide are stoichiometrically mixed and made uniform by using an alumina pot mill. The powder is heated at 1700°C by using a zirconia or a Pt alloy container. The quenched sample is powdered, and repeatedly heated at 1700°C. The iron content in fayalite and the magnesium in forsterite are analyzed by potassium permanganate and EDTA titration methods respectively. Both samples with various mole fractions are mixed to prepare the olivine solid solution.

About 5 g of each mixture is heated for 5 hr at 1200 to 1300°C by using a Pt alloy container under the atmosphere of CO$_2$/H$_2$=1. The prepared olivine solid solutions are checked by X-ray diffraction method and by chemical analysis. Yoder and Sahama,[14] and Eliseev[15] measured the d$_{130}$ spacing of natural and

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12) L. S. Darken and R. W. Gurry, " Physical Chemistry of Metals," McGraw-Hill, New York (1953), p. 264.

13) A. Muan, R. H. Nafziger and P. L. Roeder, *Nature*, **202**, 688 (1964).

14) H. S. Yoder, Jr., and Th. G. Sahama, *Am. Min.*, **42**, 475 (1957).

15) E. Eliseev, *Zapiski Vsesoyuz. Min. Obshchestva* **86**, 657 (1957) (Cited from the " Silicate Science," Vol. III, W. Eitel, Academic Press, New York (1965) p. 406.

synthetic olivines, and showed the linearity between the d_{130} value and the composition. The relationship between the d_{130} value and the composition by the present study is in good accordance with those of the literature.

Preparation of Pyroxene Solid Solution. The silica and magnesium oxide are thouroughly mixed by a pot mill to prepare enstatite ($MgSiO_3$). The mixture is repeatedly heated at 1700°C by using a Pt alloy container to make it homogeneous solution. The glass thus obtained is finally crystallized at 1200°C to get the monoclinic structure. Since ferrosilite cannot synthesize in the present conditions, then ferrous oxide is mixed with silica so as to maintain the Fe/Si ratio of 1 for the " ferrosilite." The mixture with various ratios of enstatite and " ferrosilite " are heated at 1200°C to prepare the homogeneous pyroxene solid solutions. The pattern of the X-ray diffraction of the solid solution is complicated, but systematically changes with increasing ferrosilite component. The problem of the structure of pyroxene has not yet been solved as summarized by Morimoto,[16] but Dr. Kushiro[17] found the proto-type pyroxene in the present samples.

Apparatus. The furnace, the gas mixer, the electric controller system for temperature are the same as those used in a previously study.[18] Mixed gases of CO_2 and H_2 are used to obtain the oxygen partial pressure.

Procedure. The standard quenching techniques are adopted under controlled atmospheric condition. A sample of either olivine or pyroxene solid solution is kept at 1204±2°C and at a desired level of the oxygen partial pressure. After 24 hr, the sample is quenched in the brass tube connected to the bottom of the furnace tube. Then an oxygen partial pressure, at which metallic iron appears in the sample, is determined. The presence of metallic iron is detected by dipping the sample into a dilute hydrochloric acid solution as previously described.[19]

A Direct Determination of the Oxygen Partial Pressure. The actual oxygen partial pressure of the gas phase is determined by a solid electrolyte cell, and the details of the design and the measurement were described by Katsura and Hasegawa.[20]

Results and Discussion

Determination of Conjugation Lines between Olivine and Pyroxene Solid Solution. In order to determine the activity of $a_{(FeSi_{0.5}O_2)\text{-}(2)}$, the conjugation lines between olivine and pyroxene solid solutions must be determined; for this purpose, various mixtures of Mg_2SiO_4 and " ferrosilite," or of Fe_2SiO_4 and $MgSiO_3$ are heated at 1204°C and at an oxygen partial pressure of $10^{-11.0}$ atm to avoid an appearance of metallic iron or ferric oxide. The samples are quenched after a reasonable period of time, and the d_{130} value of the olivine phase coexisting with pyroxene is measured to determine the composition of the olivine by comparing with the d_{130} of the standard. In order to criticise the reasonable period of time for the equilibrium state, different combinations of the two solid solution series, but with the same bulk composition are used just at the same conditions. Examples are illustrated in Fig. 1 as points C_1 and C_2. From the careful measurement of d_{130} value, it was found that 48 hr heating is sufficient to the equilibrium state throughout the study. The conjugation lines are, then, drawn so as to pass the two points, for example, C_1–O_1, or C_2–O_2 in Fig. 1 to determine the composition of pyroxene solid solution, P_1 or P_2. The result of the equilibrium co-existence of olivine and pyroxene solid solutions are graphically illustrated in Fig. 2.

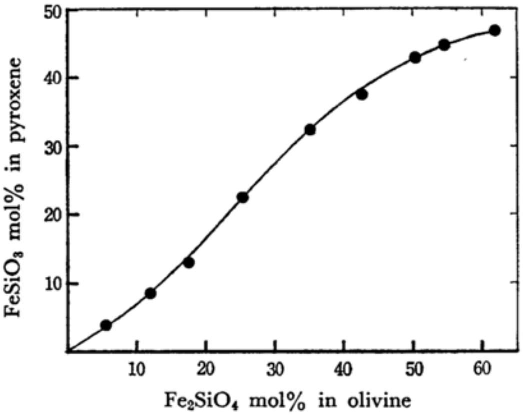

Fig. 2. The equilibrium composition between olivine and pyroxene solid solutions in terms of fayalite component in olivine and of ferrosilite component in pyroxene.

The Pyroxene Solid Solution. The values of the oxygen partial pressures of P_{O_2} (9) are given in Table 1, with the width of experimental errors. Activities calculated on choosing the composition of 48 mol% ferrosilite as an arbitrarily selected standard are also given in Table 1. The relationship between $[\log N_{FeSiO_3} - \frac{1}{2}\log P_{O_2}(9)]$ and $(1-N_{FeSiO_3})^2$, which is related to the α-function,[13] are illustrated in Fig. 3. An extrapolated value of $\log P_{O_2}(9\text{-p})$ for pure ferrosilite is determined to be -12.35 ± 0.03.

TABLE 1. ACTIVITY OF PYROXENE

N_{FeSiO_3}	$-\log P_{O_2}(9)$ (atm)	a_{FeSiO_3}*	a_{FeSiO_3}**
0.10	14.00±0.02	0.15±0.01	0.26±0.01
0.20	13.42±0.03	0.29±0.02	0.50±0.02
0.30	13.10±0.03	0.42±0.03	0.73±0.03
0.39	12.94±0.03	0.51±0.03	0.87±0.03
0.48	12.82±0.02	0.58±0.03	1.00

* Based on the pure ferrosilite as standard.

** Based on the composition 48 mo% ferrosilite as standard.

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[16] N. Morimoto, *Yogyo Kyokai Shi*, **74**, 3 (1966).

[17] Private communication.

[18] T. Katsura and S. Kimura, This Bulletin, **38**, 1664 (1964).

[19] T. Katsura, B. Iwasaki, S. Kimura and S. Akimoto, *J. Chem. Phys.*, **47**, 4559 (1967).

[20] T. Katsura and M. Hasegawa, This Bulletin, **40**, 561 (1967).

Activities calculated on the basis of choosing pure ferrosilite as standard are given in Table 1, and activity-composition relations are illustrated in Fig. 4, together with a curve for a_{MgSiO_3} calculated by a graphical integration of the Gibbs-Duhem equation. As may be seen in Fig. 4, the pyroxene system shows a significant positive deviation from ideality.

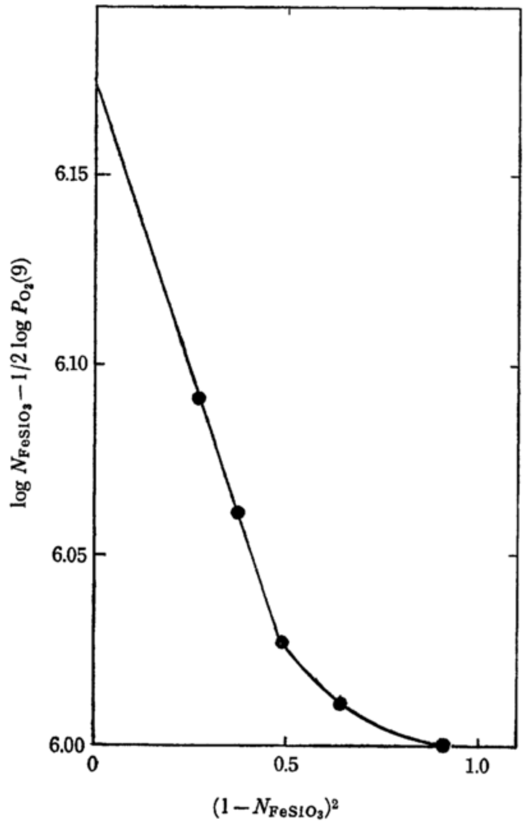

Fig. 3. Relationship between [$\log N_{FeSiO_3} - \frac{1}{2} \log P_{O_2}(9)$] and $(1-N_{FeSiO_3})^2$.

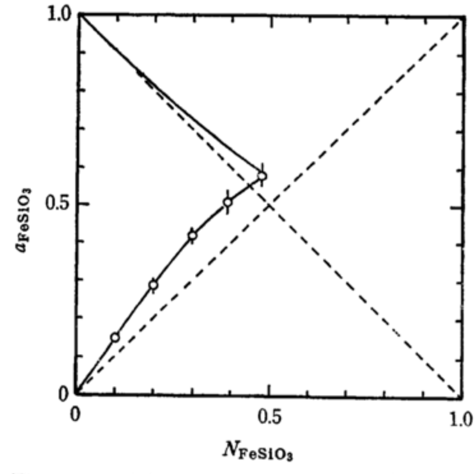

Fig. 4. Activity-composition relations in pyroxene solid solution at 1204°C.

Using the value of P_{O_2}(9-p), the standard free energy change of formation of ferrosilite, Fe(metal) + SiO_2(tridymite) + $\frac{1}{2}O_2 = FeSiO_3$, is calculated to be -41.7 ± 0.2 kcal/mol at 1204°C. Combining this with the value of the standard free energy change of formation of wüstite at 1204°C obtained by Darken and Gurry,[21] the free energy change of formation of ferrosilite from wüstite and silica is determined to be -1.6 kcal/mol. Akimoto *et al.*[22] gave the value of -1.4 kcal/mol at 1204°C on the basis of their high pressure synthesis of orthoferrosilite, Schwerdtfeger and Muan[1] gave -1.3 ± 0.3 kcal/mol at 1150°C, and Muan *et al.*[18] gave -1.3 ± 0.3 kcal/mol for the same reaction. Thus the present value is agreed well with those values obtained by different methods of determination.

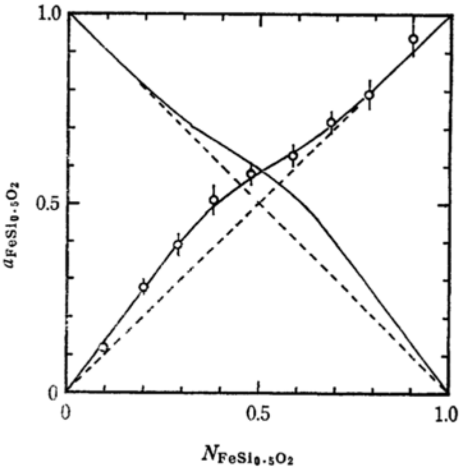

Fig. 5. Activity-composition relations in olivine solid solution at 1204°C.

The Olivine Solid Solution. The results for the olivine solid solution are given in Table 2. The values in the second and third columns are of the oxygen partial pressures of $P_{O_2}(7)$ and $P_{O_2}(4)$, respectively. The fourth column shows the composition of pyroxene co-existing with olivine with the composition in the first column, and obtained from Fig. 2. The fifth column shows the values of the $P_{O_2}(9)$ obtained by interpolation of the values in Table 1.

The activity-composition relation in olivine solid solution is graphically illustrated in Fig. 5 with the experimental errors. A curve for $a_{MgSi_{0.5}O_2}$ is also drawn by a graphical integration of the Gibbs-Duhem equation. As may be seen in Fig. 5, the system displays a significant positive deviation from the ideality.

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[21] L. S. Darken and R. W. Gurry, *J. Am. Chem. Soc.*, **67**, 1398 (1945).

[22] S. Akimoto, T. Katsura, Y. Syono, H. Fujisawa and E. Komada, *J. Geophys. Res.*, **70**, 5269 (1965).

TABLE 2. ACTIVITY OF OLIVINE*

$N_{Fe_2SiO_4}$	$-\log P_{O_2}(7)$ (atm)	$-\log P_{O_2}(4)$ (atm)	N_{FeSiO_3} (± 0.08)	$-\log P_{O_2}(9)$ (atm)	$a_{FeSi_{0.5}O_2}$
0.10	14.13±0.02		0.077	14.26±0.08	0.12±0.01
0.20	13.45±0.02		0.175	13.52±0.06	0.28±0.02
0.29	13.19±0.02		0.267	13.19±0.05	0.39±0.03
0.38	12.93±0.03		0.348	13.01±0.04	0.51±0.04
0.48	12.80±0.02		0.415	12.90±0.04	0.58±0.03
0.59	12.73±0.03		0.468	12.83±0.03	0.63±0.03
0.69		12.66±0.02			0.72±0.03
0.79		12.58±0.02			0.79±0.04
0.90		12.43±0.03			0.94±0.05

* The value of $-\log P_{O_2}(1)$ was determined to be -12.38 ± 0.02.11)

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