

THE STABILITY OF OLIVINE AND PYROXENE IN THE
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ABSTRACT

The stability of olivine and pyroxene in the Ni-Mg-Si-O system was investigated at temperatures of 1300°–1500°C at controlled oxygen fugacities. The free energy of formation of nickel oxide varied from –24.4 Kcal./mole at 1300°C to –19.9 Kcal./mole at 1500°C. The free energy change for the reaction $2\text{Ni} + \text{SiO}_2 + \text{O}_2 = \text{Ni}_2\text{SiO}_4$ was determined at five temperatures and varied from –49.3 Kcal./mole at 1300°C to –40.1 Kcal./mole at 1500°C. The ideality of the magnesium-nickel olivine solid solution was measured and the close approach of the activity coefficients to unity (the maximum activity coefficient is 1.18) indicates a close approach to ideal behaviour. The oxygen fugacity for the univariant equilibrium between the most nickel rich (13 mole% NiSiO₃) pyroxene, olivine, cristobalite, metal and vapor at 1400°C is $10^{-7.46}$ atmospheres.

INTRODUCTION

Nickel, in common with other transition elements, can be found in a sulfide, silicate or metallic phase depending upon the environment during crystallization. Thus in an environment of low chemical potential of oxygen and sulfur such as is found in many meteorites, nickel is almost exclusively in the metallic phase. In ultrabasic and basic igneous rocks the higher chemical potential of sulfur and oxygen are responsible for the frequent occurrence of nickel in early formed olivine and pyroxene and in a sulfide phase. Processes such as sulfurization may cause redistribution of nickel between silicates and sulfides while serpentinization may cause redistribution between silicates, oxides and a metallic phase.

The present study was undertaken in order to determine the affect of varying oxygen chemical potential and temperature on the distribution of nickel between anhydrous silicates and a metallic phase and to determine the stability of the nickel-magnesium olivine (orthosilicate) and pyroxene (metasilicate) relative to the constituent oxides. The reactions of greatest interest in this study are:



Reaction (1) has been studied by many workers (Coughlin 1954, Kiukkola and Wagner 1957, Hahn and Muan 1961, Lebedev and Levitskii 1961, and Burdese *et al.*, 1963) and was undertaken in the present

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study as a check on the experimental method. The study of Hahn and Muan is of particular interest since they also determined the activity of NiO as a function of composition for the MgO-NiO solid solution series.

The equilibrium constant for reaction (2) was determined by Lebedev and Levitskii (1961) and Burdese *et al.*, (1963) at temperatures below 1200°C. There is complete solid solution between nickel and magnesium olivine as reported by Ringwood (1956) and Hayashi and Naka (1960). There is no information, however, on the equilibrium between Mg-Ni olivine, nickel metal, silica and oxygen. This equilibrium can be represented by equation (2) where Ni_2SiO_4 then refers to the nickel component in the olivine solid solution.

The pure nickel pyroxene is unstable relative to silica and the nickel olivine at a total pressure of one atmosphere. The nickel pyroxene may be similar to the iron analogue (ferrosilite) and only be stable at high confining pressures. Although pure NiSiO_3 is unstable, a Ni-Mg pyroxene solid solution containing less than 25 percent of the NiSiO_3 component has been described by Dilaktovskii (1941). Thus equation (3) is only relevant at atmospheric pressure for a fairly narrow pyroxene composition range.

In the present study the oxygen fugacity at equilibrium for reactions (1) and (2) were determined at temperatures of 1300°C to 1500°C. The standard free energy change and heat of these two reactions could then be calculated. The oxygen fugacity (f_{O_2}) at which Mg-Ni olivine (reaction 2) and Mg-Ni pyroxene (reaction 3) coexists with silica and metallic nickel was determined at a constant temperature of 1400°C. The composition of coexisting Mg-Ni pyroxene and olivine solid solution and the ideality of the Mg-Ni olivine solid solution could then be determined.

Experimental method. Mixtures of known composition were prepared from chemically pure silicic acid, magnesium oxide and nickel carbonate. The silicic acid was heated for 24 hours at 400°C and a correction was made for the remaining H_2O . Silica in this form was found to be much more reactive than that sintered at higher temperatures (Ringwood 1962). Nickel oxide was prepared by heating nickel carbonate at 600°C for 24 hours and magnesium oxide was heated at 1050°C for 48 hours. The oxide mixtures were first mixed in a ball mill and then ground by hand under acetone.

One of the major problems in this study was the difficulty in attaining equilibrium. Studies by Ringwood indicated that repeated heating and grinding and also a LiF flux were often necessary to insure equilibrium. Early experiments confirmed Ringwood's observations. In order to test the effectiveness of LiF as a flux and also to insure that a small amount of

LiF does not measurably effect the equilibrium the following experiments were conducted. Samples of composition Ni_2SiO_4 with 2 wt % LiF and without LiF were heated simultaneously at 1400°C . The f_{O_2} for reaction (2) was found to be $10^{-5.80}$ atm. for both the samples with LiF and without LiF; however, the samples without LiF often contained more phases than was possible at equilibrium. The amount of these unreacted phases was usually small for long runs (greater than 50 hours). Seven samples which contained approximately 2 wt % LiF before the experimental run were analyzed after the experimental run by flame photometry for lithium. The results in Table 4¹ indicate that less than half a percent of LiF remains after heat treatment. These results suggest that LiF does not measurably affect the equilibrium and that most of the LiF which is originally added is volatilized because of the relatively high vapor pressure of LiF (boiling point at 1 atm is about 1670°C).

In order to insure minimum reaction of the samples with a container the mixtures were made into pellets at 10,000–12,000 psi and suspended by platinum wire in the furnace. During the experimental runs the pellets were removed from the furnace twice, ground under acetone, pelletized and returned to the furnace. The total time in the furnace varied from six hours to five days depending on the difficulty in attaining equilibrium. The temperature of the furnace was controlled within $\pm 2^\circ\text{C}$ and was measured with a 90 percent Pt—10 percent Rh thermocouple periodically calibrated at the melting point of gold (1063°C) and diopside (1391°C).

The oxygen fugacity in the furnace was controlled by mixing CO_2 (bone dry grade) and H_2 (prepurified grade) in various proportions using a gas mixer as described by Darken and Gurry (1945). The calculated oxygen fugacities are believed to be accurate to $\log f_{\text{O}_2} = \pm .02$ atmospheres.

Experimental Results and Discussion

(a) Ni-O. The nickel-nickel oxide equilibrium as expressed by equation (1) was studied at 1300°C , 1400°C and 1500°C . The rate of reaction was very rapid compared to the rate for samples containing silica. The rapid melting of metallic nickel caused minor experimental problems at 1500°C .

The experimental data for the nickel-nickel oxide equilibrium is pre-

¹ Tables 1 through 4 have been deposited as Document No. 9738 with the American Documentation Institute, Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington, D. C. 205400. Copies may be secured by citing the document number, and remitting in advance \$1.25 for photoprints or \$1.25 for 35 mm. Microfilm.

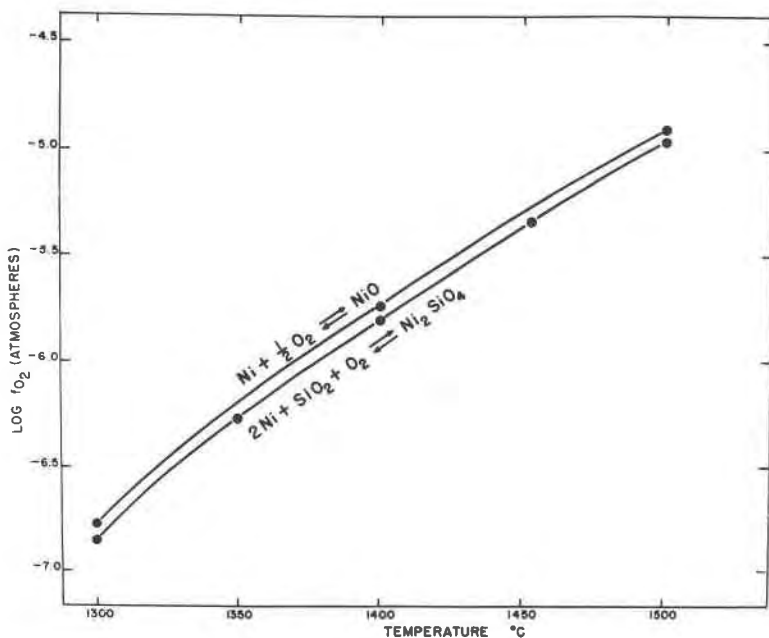


Fig. 1. A plot of $\log f_{O_2}$ vs temperature which shows the small affect silica has on oxidation-reduction behaviour of nickel.

sented in Table 1¹ and the dependence of the oxygen fugacity on temperature is shown in Figure 1. The standard free energy change for reaction (1) can be calculated by using the following relationship:

$$\Delta G^\circ_{(1)} = -RT \ln \frac{a_{NiO}}{a_{Ni}a_{O_2}^{1/2}} \quad (4)$$

Assuming the nickel oxide and nickel metal are in their standard state at equilibrium and if the fugacity of oxygen is substituted for activity:

$$\Delta G^\circ_{(1)} = -RT \ln \frac{1}{(f_{O_2})^{1/2}} \quad (5)$$

The standard free energy change calculated from the data in Table 1¹ is presented in Table 5. The free energy data are in excellent agreement with the previous data of Hahn and Muan (1961), Kiukkola and Wagner (1957) and Burdese *et al.*, (1963).

(b) Ni-Si-O. Reaction (2) was studied at temperatures of 1300°C to 1500°C.

¹ Deposited with ADI. See reference on p. 259.

¹ Deposited with ADI. See reference on p. 259.



Since the compound NiSiO_3 is unstable at atmospheric pressure, silica can coexist with the Ni olivine. Table 2¹ contains the critical experimental runs for this reaction. The experimental runs at 1500°C were different from those at lower temperatures in that the nickel at equilibrium was liquid.

The change in the equilibrium oxygen fugacity as a function of temperature for reactions (1) and (2) is shown in Figure 1. The two curves are parallel, with the Ni-NiO curve at a lower temperature and higher oxygen fugacity than the orthosilicate curve. If $\text{NiO} + \text{SiO}_2$ is a stable assemblage the Ni-NiO curve would lie below the orthosilicate curve.

The calculated free energy change for reaction 2 is tabulated in Table

TABLE 5. FREE ENERGY CHANGE IN Kcal. FOR THE FOLLOWING REACTIONS:

Temp. °C	(1) ^a $\text{Ni} + 1/2\text{O}_2$ = NiO	(2) $2\text{Ni} + \text{SiO}_2 + \text{O}_2$ = Ni_2SiO_4	(6) $2\text{NiO} + \text{SiO}_2$ = Ni_2SiO_4
1300	-24.4	-49.3	-0.5
1350	—	-46.6	—
1400	-22.1	-44.4	-0.2
1452	—	-42.0	—
1500	-19.9	-40.1	-0.3

^a Numbers in parentheses refer to equations in the text.

5 and plotted in Figure 2 together with data at lower temperatures by Lebedev *et al.*, (1961) and Burdese *et al.*, (1963). The results of the present study agree very well with the study by Burdese *et al.*, at lower temperatures. Lebedev *et al.*, (1961) and Burdese *et al.*, (1963) analyzed the gas phase in equilibrium with the condensed phases instead of using gas mixtures of known mixing ratio as in the present study.

The stability of the nickel orthosilicate relative to the oxides can be predicted by knowing the standard free energy change for reaction (6).



This can be calculated by combining the free energy change of reaction (1) and (2) as follows:

$$\Delta G_{(6)} = \Delta G_{(2)} - 2\Delta G_{(1)}$$

The values of $\Delta G_{(6)}$ are tabulated in Table 5. Ringwood (1956) found that Ni_2SiO_4 is stable up to the solidus at 1650°C. Phillips *et al.*, (1963) apparently were unaware of Ringwood's finding but reported Ni_2SiO_4 as

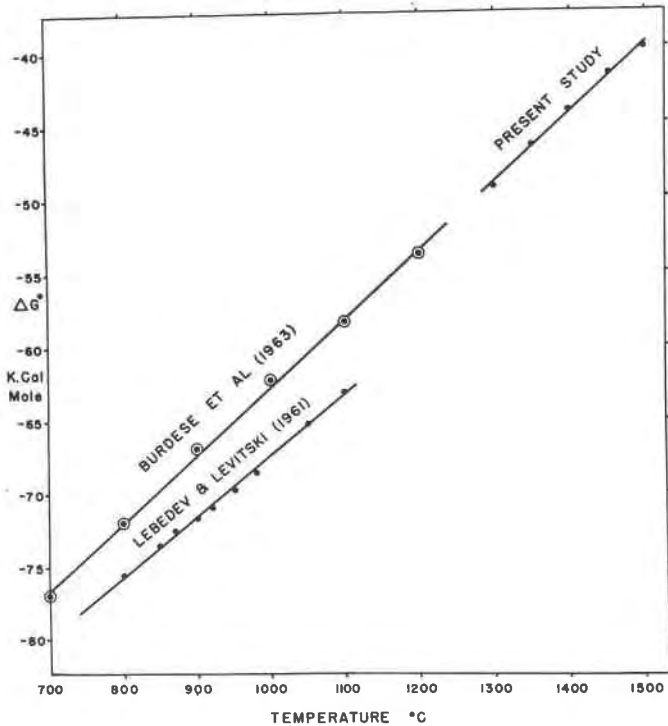


FIG. 2. The free energy change determined for the reaction $2\text{Ni} + \text{SiO}_2 + \text{O}_2 = \text{Ni}_2\text{SiO}_4$ as a function of temperature.

dissociating at 1545°C to $\text{NiO} + \text{SiO}_2$. Thus according to the data of Phillips et al $\Delta G_{(6)}^0$ should become zero at 1545°C . Some caution has to be exercised in using the free energy values for equation (6) since a reasonable margin of error in the determination of $\Delta G_{(1)}$ and $\Delta G_{(2)}$ is ± 0.1 Kcal/mole.

(c) Ni-Mg-Si-O. The compounds of interest in the Ni-Mg-Si-O system at 1400°C are shown in the schematic tetrahedron of Figure 3. Except for nickel metal all the compounds which are stable under the conditions of the present experiments lie on or very close to the MgO-NiO-SiO_2 plane. There is complete solid solution between MgO and NiO , between $\text{Mg}_2\text{-SiO}_4$ and Ni_2SiO_4 and partial metasilicate solid solution as shown by the solid line. O-X is a line of constant Mg:Ni:Si ratio picked at random and points (1), (2), and (3) on this line represent mixtures of different oxygen content but the same Ni:Mg:Si ratio. Thus if mixture O-X is heated at 1400° at an oxygen fugacity sufficient to oxidize all of the nickel to the +2 oxidation state the total composition of the mixture will be on the

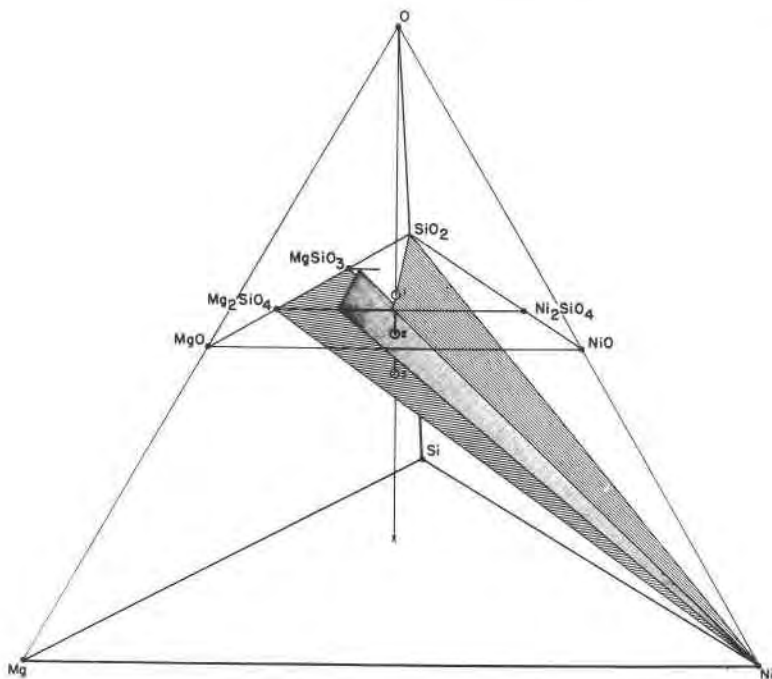


FIG. 3. A schematic tetrahedron showing the Ni-Mg-Si-O system at a constant temperature. The line O-X is a line of constant Mg:Ni:Si ratio and the points 1, 2, 3 on this line represent the mixture at different oxygen fugacities. The ruled and stippled planes connect the condensed phases in equilibrium at the oxygen fugacities 1, 2 and 3.

MgO-NiO-SiO₂ plane (point 1) on a tie line between olivine and silica. The amount of these two phases at equilibrium can be determined by using the "lever rule." If the oxygen fugacity is lowered such that some of the nickel is reduced to the metallic state the total composition will lie below the MgO-NiO-SiO₂ plane and the orthosilicate will contain less nickel. Point 2 represents the composition of the same mixture at an oxygen fugacity low enough so that nickel metal, olivine and pyroxene can coexist at equilibrium. The amount of these three crystalline phases is determined by the position of the O-X intercept in the three phase triangle (stippled plane) which connects the composition of the three phases. Point 3 represents the composition of the mixture when all the nickel has been reduced to the metallic state and coexists with a nickel free olivine and pyroxene.

The MgO-NiO-SiO₂ plane is shown separately in Figure 4. The solid dots in this figure represent the composition of the mixtures used in the

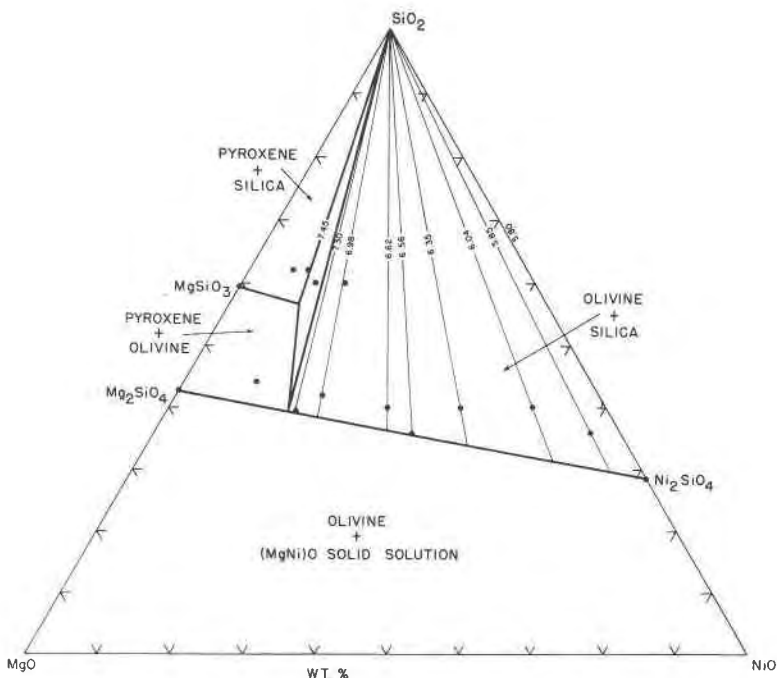


FIG. 4. The MgO-NiO-SiO₂ plane at 1400°C showing the phases present in equilibrium with metallic nickel. The numbers are the $-\log f_{O_2}$ for the equilibrium between nickel and the condensed phases shown on either end of the tie lines.

present study. The oxygen fugacity, the total time of the run at 1400°C and the phases present are tabulated in table 3.¹ These data can be used to calculate the equilibrium oxygen fugacity for reactions 2 and 3 at varying concentrations of Ni₂SiO₃ and NiSiO₃ in solid solution.

If it is assumed that the magnesium and nickel atoms in the olivine structure act as independent units and not as paired atomic units equation 2 should be rewritten as follows:



The variation of oxygen fugacity as a function of olivine composition for equation 7 is shown in Figure 4 by the numbered tie lines. The numbers correspond to the negative logarithm of the oxygen fugacity of the gas phase in equilibrium with the phases joined by the tie lines. Each of these tie lines is one edge of a three-phase triangle, such as triangle 1 in Figure 3

At low concentrations of Ni₂SiO₄ in the olivine, cristobalite² reacts

¹ Deposited with AD1. See reference on p. 259.

² The quenched samples contained cristobalite as determined by X-ray diffraction and not tridymite as might be expected at 1400°C.

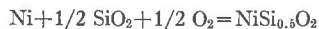
with olivine to form a pyroxene. The univariant equilibrium between pyroxene, olivine, cristobalite, metal and vapor at 1400°C is represented in Figure 4 by the three-phase triangle between olivine, pyroxene and cristobalite at an oxygen fugacity of $10^{-7.45}$ atmospheres. The maximum solubility of NiSiO₃ in the pyroxene solid solution at 1400°C is 13 mole % NiSiO₃. Muan, Nafziger and Roeder (1964) in their study of the Mg-Fe-Si-O system determined the standard free energy of formation of the unstable end member FeSiO₃. This was done by extrapolation of the fugacity data on the Mg-Fe pyroxene join to FeSiO₃ and by assuming a regular solution. The standard free energy of formation of NiSiO₃ could be calculated by the same method; however, the necessary extrapolation is much larger than was necessary for the iron analogue.

The equilibrium constant (K) for equation 7 can be calculated from the fugacity of oxygen at equilibrium when the activity of NiSiO_{0.5}O₂, SiO₂ and Ni is unity. This value of K can then be used to calculate with equation 8 the activity (a) and activity coefficient (γ) of NiSiO_{0.5}O₂ in nickel-magnesium olivine.

$$K_{1400^{\circ}\text{C}} = \frac{a_{\text{NiSi}_{0.5}\text{O}_2}}{f_{\text{O}_2}^{1/2}} = \frac{\gamma_{\text{NiSi}_{0.5}\text{O}_2} X_{\text{NiSi}_{0.5}\text{O}_2}}{f_{\text{O}_2}^{1/2}} = 794 \quad (8)$$

These are tabulated in Table 6 and the activity is plotted against mole fraction of Ni₂SiO₄ in Figure 5. The dashed line represents an ideal solid solution. The close approach of the experimental data to this line is an indication that the oxidation and reduction of nickel is controlled almost entirely by the oxygen fugacity and that there is very little structural control by changes in olivine composition. The assumption of constant activity of cristobalite and nickel metal with changing olivine composition and the assumption that the MgSi_{0.5}O₂ component of the olivine acts as a fairly inert solvent is reasonable.

TABLE 6. VALUES OF f_{O_2} , MOLE FRACTION (X), ACTIVITY AND ACTIVITY COEFFICIENTS OF NiSi_{0.5}O₂ IN Mg₂SiO₄-Ni₂SiO₄ SOLID SOLUTION AT 1400°C CALCULATED FROM THE FOLLOWING REACTION



log f_{O_2}	$X_{\text{Ni}_2\text{SiO}_4}$	activity	activity coefficient
-7.30 ± .02	0.18	0.18	1.00
-6.97 ± .02	0.22	0.26	1.18
-6.62 ± .02	0.35	0.39	1.11
-6.55 ± .02	0.40	0.42	1.05
-6.35 ± .02	0.52	0.53	1.04
-6.05 ± .02	0.72	0.75	1.04
-5.85 ± .02	0.89	0.93	1.05

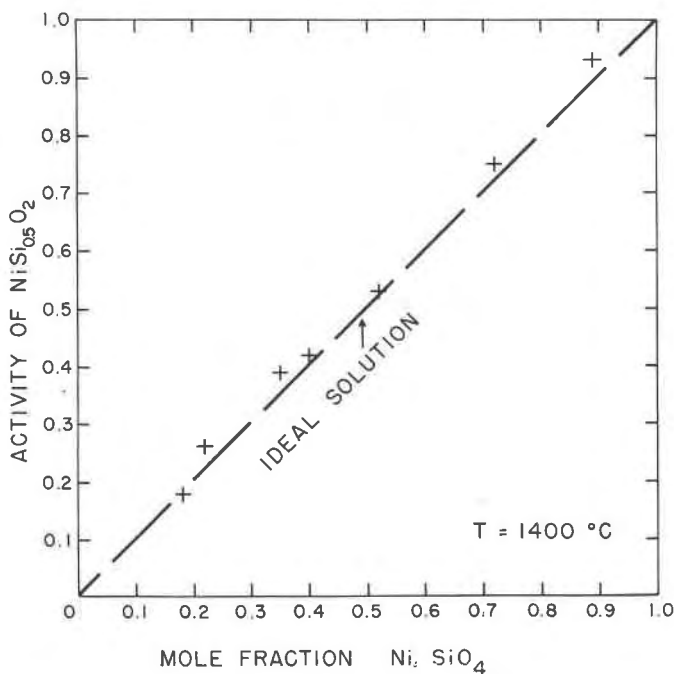


FIG. 5. The activity of $\text{NiSi}_{0.8}\text{O}_2$ in the olivine solid solution as a function of mole fraction at 1400°C .

Schwerdtfeger and Muan (1966) in a study of the iron-manganese olivine in equilibrium with silica, metallic iron and oxygen found that the olivine acted as an ideal solid solution. Nafziger (1966) found essentially the same thing for the magnesium-iron olivine. Since the Mn-Fe, Mg-Fe and Mg-Ni olivine series act as ideal solid solutions in equilibrium with cristobalite and a metallic phase, the oxygen fugacity necessary for the dissociation of orthosilicate is independent of other cations in the orthosilicate structure. Thus a model based on an ideal olivine solid solution and the extrapolation of thermodynamic data of end-member olivines is reasonable.

This suggests that the distribution of the elements Mn, Fe, Co, and Ni between olivine and a metallic phase in meteorites may be treated by using a fairly simple thermodynamic model.

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