

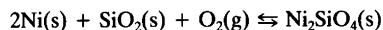
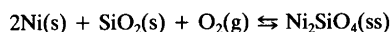
Determination of Activity–Composition Relations in (Ni, Mg)₂SiO₄ Solid Solutions at 1200–1600 K by Solid-State Emf Measurements

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Activity–composition relations in the olivine system Ni₂SiO₄–Mg₂SiO₄ were determined in the temperature range 1200–1600 K. The following equilibria were studied:

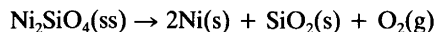


The oxygen pressures for different olivine compositions, including the end component Ni₂SiO₄(s), were measured using oxygen concentration cells involving stabilized zirconia as solid electrolyte. The activity values obtained for Ni₂SiO₄ show negative deviation from ideality at 1200 K, while at 1400 K slight positive deviation is observed.

The cation Ni²⁺ is a common minor constituent in natural olivines. A knowledge of the thermodynamic and structural properties of the system Ni₂SiO₄–Mg₂SiO₄ is therefore quite essential for the understanding of several important rock-forming processes.

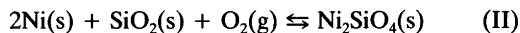
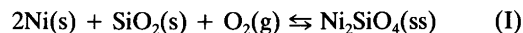
From structural studies of both natural and synthetic Ni–Mg olivines it was shown that Ni²⁺ and Mg²⁺ exhibit a considerable degree of cation ordering.^{1,2,3} It turned out that the Ni²⁺ ions prefer M1 sites to M2 sites in Ni–Mg olivines. This structural deviation from ideal solid solutions should have a substantial impact on the energetics of the solid solution series (Ni, Mg)₂SiO₄. To find out how this cation ordering will effect the macroscopic thermodynamic activities, accurate activity values are needed.

The solid solution series Ni₂SiO₄–Mg₂SiO₄ has been investigated previously by Campbell and Roeder,⁴ who studied the reaction:



at 1673 K using a CO₂/H₂-gas equilibration method. They found the activity values for Ni₂SiO₄ to be slightly positive at low Ni²⁺ concentrations. Seifert and O'Neill⁵ carried out an equilibration study in which the cation compositions of the coexisting phases (Ni, Mg)O(ss) and (Ni, Mg)₂SiO₄(ss) were determined at 1573 K and 0.5 GPa. They also found a small positive deviation of the activity values for Ni₂SiO₄ assuming the solid solution (Ni, Mg)O to be ideal.

The present study was undertaken in order to obtain improved activity–composition data for the Ni₂SiO₄–Mg₂SiO₄ olivine system in the temperature range 1200–1600 K. The following equilibrium reactions were then investigated:



Equilibrium (I) could be studied at olivine compositions $X(\text{Ni}^{2+}) \geq 0.18$ where SiO₂(s) and

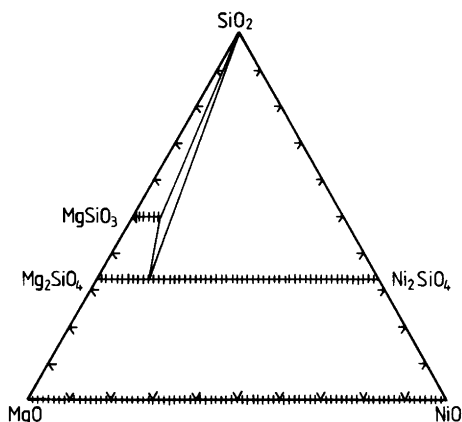


Fig. 1. The MgO–NiO–SiO₂ phase diagram at 1673 K. Modified from Campbell and Roeder.⁴

(Ni, Mg)₂SiO₄ solid solutions occur together (see Fig. 1). The equilibrium oxygen pressures were measured using oxygen concentration cells with calcia-stabilized zirconia (CSZ) and yttria-stabilized zirconia (YSZ) respectively, as the solid electrolyte. The solid-state emf technique has proved to be a very accurate and efficient method for studying oxide solid solutions.^{6,7}

Experimental

Chemicals. The SiO₂ used was made by heating silicic acid (Fisher certified reagent) to 1300 K, and the NiO by heating basic nickel (II) carbonate (Fluka *p.a.*) to 1100 K. Samples of the solid

solutions with different compositions were prepared using the gelling technique.⁸ Stock solutions of Ni²⁺ and Mg²⁺ were prepared by dissolving appropriate amounts of NiCO₃ (Baker Analyzed Reagent) and MgO (Merck *p.a.*), respectively, in concentrated HNO₃. Known volumes of the nitrate solutions and a small excess of TEOS (tetraethylorthosilicate, Merck *p.a.*) were mixed with ethanol to obtain a homogeneous solution. An excess of concentrated aqueous NH₃ was added, and the gel produced was sealed in beakers and left overnight. After drying at 350 K for two days, the gel was slowly heated to 450 K. The temperature was then raised stepwise to about 500 K, 800 K and 1200 K. Finally, the samples were fired several times at about 1400 K, ground and examined by X-ray powder diffraction. Any remaining NiO was removed by treatment with hot dilute HNO₃.

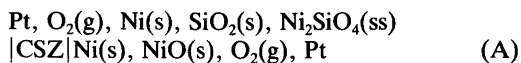
The various solid solutions prepared were checked by ICP (Inductively Coupled Plasma discharge) analysis (see Table 1). Compositions obtained in this way were found to be close to the starting "volumetric" values. Impurities such as Fe, Ca, Zn and Co were present in maximum concentrations of 0.03, 0.06, 0.005 and 0.06 mol %, respectively.

The emf methods used. Solid state emf methods for the determination of activity–composition relations for oxide solid solutions, such as the "single" and "double" tube emf cell arrangements, are thoroughly described by Pejryd.⁷ In the present study, the "double tube" arrangement was

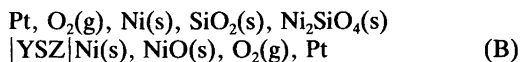
Table 1. Olivine compositions, $E(T)$ relationships and calculated standard deviations of the fit (s_f) obtained for the various samples.

Sample	$X(\text{Ni}^{2+})$		$E/\text{mV} = a + b T$		Number of measured values	Temperature interval	s_f/mV
	Initial composition. ICP-analysis	Equilibrium composition. X-ray analysis	a	b			
ZP(18)	19.5(2)	18.3	161.0	-0.0326	11	1178–1448 K	1.6
ZP(33)	31.5(2)	32.8	109.6	-0.0202	14	1230–1415 K	0.76
ZP(51)	50.6(2)	–	135.8	-0.0620	10	1177–1406 K	0.98
DT(65)	60.2(4)	64.7	94.4	-0.0424	12	1283–1565 K	0.99
DT(71)	69.8(5)	70.6	102.3	-0.0538	16	1209–1538 K	0.93
DT(79)	80.3(1.1)	79.2	77.7	-0.0403	14	1119–1460 K	0.64
DT(90)	90.0(1.5)	90.0	65.3	-0.0361	14	1130–1459 K	0.37
DT(100)	–	–	46.6	-0.0255	13	1368–1605 K	0.64

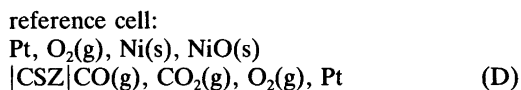
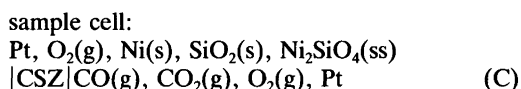
used to measure the samples designated DT(65), DT(71), DT(79) and DT(90). The cell configuration can here be written:



For the sample mixture containing the end component $\text{Ni}_2\text{SiO}_4(\text{s})$ [labelled DT(100)] the following cell configuration was used:



The reason for choosing (Ni, NiO) as reference system instead of combining cell (A) and cell (B) was the very sluggish reaction of equilibrium (II). Although this choice of reference system improved the measurements, it was still difficult to obtain reproducible emf values at lower Ni^{2+} contents. Here, the emf values drifted, probably due to transport of oxygen through the electrolyte; the latter phenomenon is enhanced with increase in the difference in the oxygen pressures on each side of the solid electrolyte. To overcome these difficulties, the measuring technique was modified and the "zero-point" emf technique (see Ref. 9 for details) was used for the samples designated ZP(18), ZP(33) and ZP(51). The cell configuration for the "zero-point" method can be written:



The cell arrangements (C) and (D) were assembled in the same furnace and thus equilibrated with the same CO/CO_2 gas mixture. The basic idea was to change the reference O_2 pressure by adjusting the CO/CO_2 ratios until the emf of the sample cell approached zero. The O_2 pressure of the sample is then equivalent to the O_2 pressure in the gas mixture which is determined by the reference cell.

The cells were heated in two different types of resistance furnace. For temperatures up to 1400 K a furnace with Kanthal A-1 resistance

wire was used, and for temperatures up to 1600 K a Pt (40 mass % Rh) resistance furnace. Cell emf's and thermo-emf's were measured with a Solartron 7075 digital voltmeter with a high input impedance ($10^{10} \Omega$). The thermocouple used consisted of Pt/Pt(10 mass % Rh).

Measuring procedure. The samples were prepared by thoroughly mixing nickel metal powder (Merck *p. a.*), SiO_2 and olivine in a weight ratio of about 10:2:1 and to a total amount of 1–1.5 g. The mixtures were then dried before placing them in the CSZ tubes. The reference systems were prepared in a similar manner by mixing nickel powder and NiO in a weight ratio of about 1:1.

The sample cells or cell compartments (depending on whether the "zero-point" technique or the "double tube" arrangement was used) were evacuated and filled with H_2 several times prior to final evacuation. The electrolyte tube thus contained a small amount of H_2 to react with the remaining O_2 in the cell to produce a $\text{H}_2/\text{H}_2\text{O}$ gas mixture.

In a typical run the furnace temperature was raised slowly at a rate of $\sim 100 \text{ K h}^{-1}$ to about 1350 K. The cells were then kept at this temperature for one day to equilibrate. The sample temperature was then lowered (and later raised) in steps of about 25–50 K, and the emf's were measured. The equilibration times at each temperature varied from 12 hours to a couple of days. The emf values obtained on repeatedly lowering

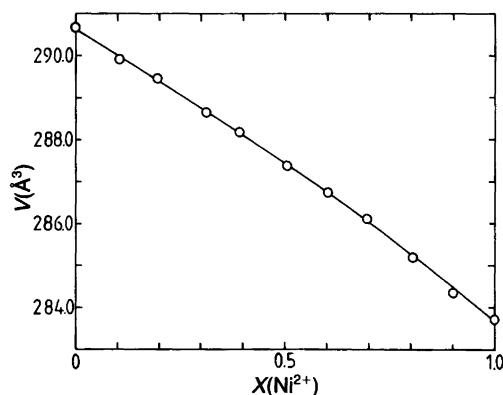


Fig. 2. Unit cell volumes obtained as a function of the olivine compositions. The solid line represents a least-squares fit.

and raising the temperature resulted in reproducible curves of emf vs. temperature. The measurements were interrupted when enough reproducible data had been collected (after 2–5 weeks) or when the emf values showed a tendency to drift.

After each run, the composition of each olivine sample was checked by X-ray powder diffraction, using the “calibration curve” shown in Fig. 2. This curve was established as follows: 9 different solid solutions with known compositions, as well as the end components, were analysed on a Rigaku X-ray powder diffractometer. Diffraction peaks in the range 61–107° in 2 θ (CuK α radiation) were collected with a scan-speed of 0.06° min⁻¹. Unit cell volumes of the olivines were then refined using the least-squares program PI-RUM.¹⁰

The equilibrium olivine compositions given in Table 1 (determined by X-ray powder diffraction) show good agreement with the initial compositions found by the ICP analysis. One exception is the olivine composition in sample DT(65), in which the Ni²⁺ content increased from 60.2 mol % to 64.7 mol %. This drift in cation composition was probably caused by oxygen diffusion through the electrolyte tube and subsequent oxidation of Ni metal according to reaction (I).

Results and calculations

Emf values obtained. For each of the various compositions in the olivine solid solution series (including the end component Ni₂SiO₄), 10–15 pairs of (*E*/mV, *T*/K) data were measured in the temperature interval 1100–1600 K. For the compositions for which the “double tube” arrangement was used, the *E* values represent emf values obtained with cell configurations (A) and (B). In cases where the “zero-point” method was used, the *E* values correspond to the differences between measured emf values for cell configurations (C) and (D):

$$E = \text{emf}(C) - \text{emf}(D)$$

For each composition, the measured values were fitted by an equation of the type $E = a + bT$ and the parameters *a* and *b* were determined by a least-squares treatment. The results thus obtained are given in Table 1 and displayed in Fig.

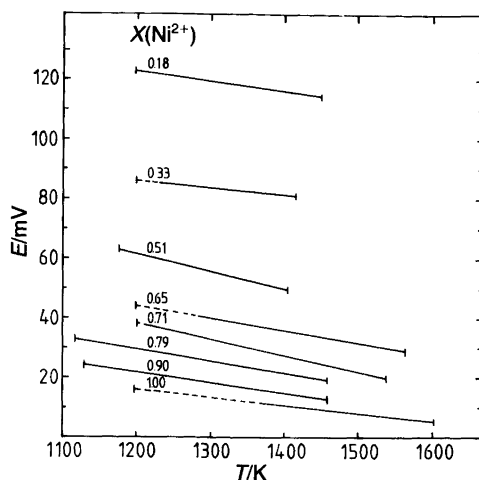


Fig. 3. $E(T)$ lines for the various olivine compositions. Solid lines show measured temperature intervals, and broken lines extrapolated ranges.

3. The calculated standard deviations of the fit were in most cases 0.5–1.0 mV.

It should be mentioned that the analysis of sample ZP(51) was ruined by the appearance of a crack in the electrolyte tube at the end of the measurement run. In addition, it was not necessary to analyse sample DT(100) as it contained the end component Ni₂SiO₄.

Calculation of activities. By applying the law of mass action to the equilibria (I) and (II), the activity of Ni₂SiO₄ in (Ni, Mg)₂SiO₄ solid solutions can be derived as follows:

$$a(\text{Ni}_2\text{SiO}_4) = p(\text{O}_2, \text{I})/p(\text{O}_2, \text{II})$$

where $p(\text{O}_2, \text{I})$ and $p(\text{O}_2, \text{II})$ are the equilibrium oxygen pressures for equilibria (I) and (II), respectively. However, for the evaluation of the results it is advantageous to consider the unit NiSi_{0.5}O₂, whence ideal activities are linearly dependent on $X(\text{Ni}^{2+})$. The activity, $a(\text{NiSi}_{0.5}\text{O}_2)$, is then defined as

$$a(\text{NiSi}_{0.5}\text{O}_2) = \left(\frac{p(\text{O}_2, \text{I})}{p(\text{O}_2, \text{II})} \right)^{1/2} \quad (1)$$

The calculation of $a(\text{NiSi}_{0.5}\text{O}_2)$ is based on the difference between *E* for the sample containing the end component Ni₂SiO₄, [from cell configuration (B)], and *E* for the samples with various

solid solutions [from cell configuration (A)] at the same temperature:

$$E(\text{diff}) = E(A) - E(B) \quad (2)$$

It should be noted that the emf contribution from the Ni-NiO system will be eliminated by the relationship in eqn. (2).

For a solid state galvanic cell an equilibrium emf value (E/mV) is related to the sample oxygen partial pressure ($p(O_2)/\text{atm}$), the reference oxygen partial pressure [$p'(O_2)/\text{atm}$] and the temperature (T/K) through the relationship

$$E = -\frac{RT}{4F} \ln \left[\frac{p(O_2)}{p'(O_2)} \right] \quad (3)$$

where $F = 96484.56$ coulomb mol^{-1} is the Faraday constant and $R = 8.31441$ $\text{J K}^{-1} \text{mol}^{-1}$ is the gas constant (1 atm = 101.325 kPa). Performing the operation as indicated by eqn. (2), the following equation is derived:

$$E(\text{diff}) = -\frac{RT}{4F} \ln \left[\frac{p(O_2, \text{I})}{p(O_2, \text{II})} \right] \quad (4)$$

Insertion of eqn. (1) into eqn. (4) and rearrangement gives

$$\ln a(\text{NiSi}_{0.5}\text{O}_2) = -\frac{2F}{R} \cdot \frac{E(\text{diff})}{T} \quad (5)$$

where $a(\text{NiSi}_{0.5}\text{O}_2) = 1$ or $\text{Ni}_2\text{SiO}_4(\text{s})$ in equilibrium with $\text{Ni}(\text{s})$ and $\text{SiO}_2(\text{s})$.

Starting with the $E(T)$ relationships given in

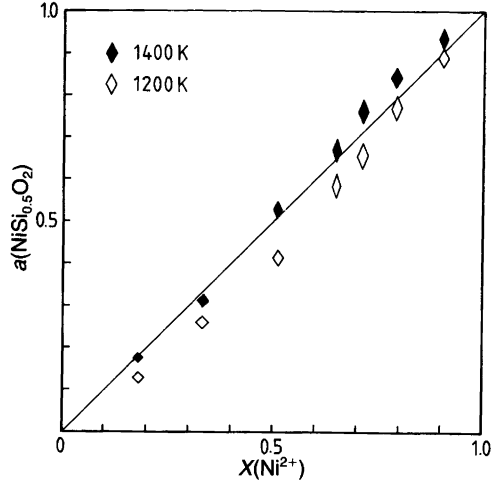


Fig. 4. Activities versus olivine composition at two temperatures, 1200 and 1400 K. The extension of the symbols corresponds to the estimated uncertainties.

Table 1, and using eqns. (2) and (5), the temperature dependence of the activities could be calculated. These relationships for the various compositions are summarized in Table 2, as well as estimated uncertainties in $a(\text{NiSi}_{0.5}\text{O}_2)$. In Fig. 4, the activity values at 1200 K and 1400 K are plotted against the solid solution composition, $X(\text{Ni}^{2+})$.

Calculation of Gibbs free energy. The Gibbs free energy ($\Delta G^\circ/\text{J mol}^{-1}$) for equilibrium reaction (II) is related to $p(O_2, \text{II})$ according to the relationship:

Table 2. Temperature dependence of $\ln a(\text{NiSi}_{0.5}\text{O}_2)$ for different mole fractions $X(\text{Ni}^{2+})$.

$X(\text{Ni}^{2+})$	$\ln a(\text{NiSi}_{0.5}\text{O}_2) = c+d/T$		Estimated uncertainty in $a(\text{NiSi}_{0.5}\text{O}_2)$ at 1200 K	Temperature interval
	c	d		
0.18	0.1648	-2655.	± 0.008	1178-1448 K
0.33	-0.1230	-1462.	± 0.010	1230-1415 K
0.51	0.8471	-2070.	± 0.019	1177-1406 K
0.65	0.3922	-1109.	± 0.027	1283-1565 K
0.71	0.6568	-1293.	± 0.029	1209-1538 K
0.79	0.3435	- 721.8	± 0.027	1119-1460 K
0.90	0.2460	- 434.0	± 0.026	1130-1459 K

$$\Delta G^\circ(\text{II}) = RT \ln 10 \log p(\text{O}_2, \text{II}) \quad (6)$$

For sample DT(100), eqn. (3) can be written in the form:

$$E = -\frac{RT \ln 10}{4F} \log \left[\frac{p(\text{O}_2, \text{II})}{p(\text{O}_2, \text{Ni}, \text{NiO})} \right] \quad (7)$$

As seen in Table 1, the relationship

$$E = 46.6 - 0.0255T \quad (8)$$

was obtained. Therefore, using the equation

$$\log p(\text{O}_2, \text{Ni}, \text{NiO}) = 8.055 - 24274/T + 0.0984 \ln T \quad (9)$$

which describes the equilibrium oxygen pressure over an Ni–NiO mixture (Pejryd⁹), the following equation can be derived for equilibrium (II):

$$\log p(\text{O}_2, \text{II}) = -\frac{25213}{T} + 8.569 + 0.984 \ln T \quad (10)$$

Finally, introduction of eqn. (10) into eqn. (6), gives

$$\Delta G^\circ(\text{II}) = -482702 + 164.05T + 1.8838T \ln T \quad (11)$$

Considering the calculated uncertainty ($\sigma = \pm 0.64$ mV) for the cell configuration (B) and the uncertainty of ± 0.009 in $\log p(\text{O}_2, \text{Ni}, \text{NiO})$, the uncertainty in $\log p(\text{O}_2, \text{II})$ cannot exceed 0.02 log units, and thus ΔG° for equilibrium (II) should be accurate to within ± 500 J mol⁻¹. It can be mentioned that the calculated value of ΔG° (II) at 1400 K is -233930 J mol⁻¹, while the corresponding value according to O'Neill¹² is -234660 J mol⁻¹.

Decomposition temperature. At very high temperatures, Ni₂SiO₄ will decompose to the oxides NiO and SiO₂. By inserting $E = 0$ in eqn. (8), a decomposition temperature $T = 1827$ K is obtained. This value is in excellent agreement with experimental determinations of $T = 1818$ K, according to Phillips *et al.*,¹³ and $T = 1820 \pm 5$ K, according to O'Neill.¹⁰

Discussion

The kinetics of the system studied are known to be quite slow, and the sluggishness of reaction (II) is probably the main reason for the discrepancies in ΔG° values in the literature (see O'Neill¹¹ for a critical compilation). Furthermore, Campbell and Roeder,⁴ and Seifert and O'Neill⁵ mention difficulties in obtaining equilibrium conditions for reaction (I). The experimental complications that we have encountered are thus due mainly to the low rates of reactions (I) and (II). These conditions bring this system rather close to the limit where CSZ cells cannot be utilized. With this in mind, the uncertainties in the measured E values are quite acceptable.

Our results for the activity–composition relation in the Ni–Mg olivine solid solution comprise the compositional dependence of the activity for $X(\text{Ni}^{2+})$ values between 0.18 and 0.90, and the temperature dependence between ~ 1200 and 1400 K. Fig. 4 shows the activities at two temperatures, viz. 1200 and 1400 K. The uncertainties are approximately represented by the extension of the symbols (see also Table 2). The temperature effect on the activities is significant; at 1200 K there is a negative deviation from ideality, while at 1400 K the activities have increased, and become positive at medium and higher Ni compositions. As discussed by Bish,² a negative deviation can be explained by the strong cation ordering effect of Ni²⁺ and Mg²⁺ on the two available octahedral sites. The increase in activity with increasing temperature is expected since the cation ordering is less pronounced at higher temperatures (Boström^{3,14}). It should be noticed that the positive deviations found at temperature $T = 1400$ K cannot be explained by the two-site cation ordering feature, since the activity will approach that for ideality with increasing temperature. There ought, therefore, to be other structural features which can give positive contributions to the activity. In this respect, the formation of clusters or super-structures could be suggested.

The activity results obtained by Campbell and Roeder⁴ at 1643 K, as well as by Seifert and O'Neill⁵ at 1573 K, show slight positive deviations, while corresponding values extrapolated to these temperatures on the basis of the present study would be considerably higher. Moreover, Seifert and O'Neill⁵ did not observe the temper-

ature variation of the activities found in the present study.

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