

Ni-Mg partitioning between synthetic olivines and orthopyroxenes: Application to geothermometry

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ABSTRACT

The partitioning of Ni and Mg between olivine and orthopyroxene is described by the exchange equilibrium



Previous studies on natural ultramafic rocks showed that this equilibrium is very sensitive to crystallization temperature but is reset slowly enough to bear some interest as a geothermometer. On the contrary, the small volume change for the reaction ($\Delta V_{\text{exch}} \approx 0.08 \text{ cm}^3$) suggests only small dependence on pressure.

The temperature dependence of the exchange reaction was studied with Mg-Fe-Ni olivines and orthopyroxenes synthesized at atmospheric pressure, under reducing conditions, and between 1075 and 1225 °C. Fe was introduced in order to obtain *Pbca* orthopyroxene and to avoid the crystallization of *Pbcn* protopyroxene, which is the stable low-pressure, high-temperature polymorph of magnesian pyroxenes. In some cases both polymorphs were obtained, but were discriminated by their compositional differences.

The distribution coefficient

$$k_{\text{Ni-Mg}} = (\text{Ni/Mg})_{\text{Ol}} : (\text{Ni/Mg})_{\text{Opx}}$$

was found to be independent of composition at constant temperature in the experimental range. The thermometric relation

$$\ln k_{\text{Ni-Mg}} = [3801/T] - 1.815$$

is in close agreement with a previous calibration on naturally equilibrated samples.

Although Ni does not behave ideally in olivines (strong ordering on M1 sites), the equilibrium relation may be approximated with an ideal disordered model in a compositional range much larger than that encountered in natural mafic and ultramafic rocks.

INTRODUCTION

Geothermometers are very useful in the petrologic study of ultramafic rocks, but only a very few different temperature-sensitive phase equilibria have been calibrated so far. The two most popular ones are the orthopyroxene-clinopyroxene (Opx-Cpx) equilibrium (first calibrated by Wood and Banno, 1973; numerous reports of experimental data and calibration since then) and the Fe-Mg partitioning between olivine and spinel (first proposed by Irvine, 1965). The latter has been proved able to re-equilibrate in a matter of days, at magmatic temperatures (Lehmann, 1983; Ozawa, 1983), whereas the former is thought to be extremely inert, i.e., rather insensitive to short thermal events.

The Ni-Mg partitioning between olivine and orthopyroxene has been proposed as a semi-empirical geothermometer by Berger and Vannier (1978). This proposal was based on the study of lherzolite xenoliths collected from the Quaternary basalts of the southern French Mas-

sif Central. The authors showed that in samples with homogeneous phase chemistry, the Ni-Mg partitioning between olivine and orthopyroxene is a simple function of the temperature as estimated from the Opx-Cpx equilibrium (Wood and Banno, 1973; Mercier, 1976):

$$\ln k_{\text{Ni-Mg}} = [3820/T] - 1.822,$$

where $k_{\text{Ni-Mg}} = (\text{Ni/Mg})_{\text{Ol}} : (\text{Ni/Mg})_{\text{Opx}}$.

The discussion of this geothermometer, and especially of its kinetics, led to the conclusion that the calculated temperatures give roughly the same type of information as Wood and Banno's equilibrium (i.e., "fossil" temperatures, insensitive to brief thermal events: Berger and Vannier, 1984). This equilibrium is thus of particular interest for the study of Cpx-free ultramafic rocks and of some lherzolites in which textural or chemical evidence suggests that Cpx may have resulted from late solid-state reaction or magma infiltration.

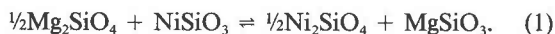
The aim of the present study is to reassess Ni-Mg partitioning between olivine and orthopyroxene on the basis

of experimental data in order to improve the calibration of the geothermometer.

THEORETICAL BACKGROUND

General thermobarometric relation

Ni-Mg partitioning between olivine and orthopyroxene is described by the exchange equilibrium



Thermodynamic equilibrium is realized when

$$K_{\text{Ni-Mg}} = (a_{\text{NiSiO}_3}/a_{\text{MgSiO}_3})/(a_{\text{Ni}_2\text{SiO}_4}/a_{\text{Mg}_2\text{SiO}_4})^{1/2} = \exp(-\Delta G_{\text{exch}}/RT),$$

where a_i is the activity of component i in its phase and ΔG_{exch} is the standard-state Gibbs free energy of Equilibrium 1. As most natural olivines and orthopyroxenes are magnesian and contain only small amounts of Ni, the implicit standard state for both Ni end members is the infinitely diluted component in its phase (i.e., Henry's law component), whereas Mg end-member activities are referred to pure components.

Activity coefficients are defined as

$$\begin{aligned} \gamma_{\text{Ni}_2\text{SiO}_4} &= a_{\text{Ni}_2\text{SiO}_4}/(X_{\text{Ni}}^{\text{ol}})^2 \\ \gamma_{\text{NiSiO}_3} &= a_{\text{NiSiO}_3}/(X_{\text{Ni}}^{\text{opx}}), \end{aligned}$$

etc., so that the equilibrium condition may be written

$$K_{\text{Ni-Mg}} = k_{\text{Ni-Mg}} K_\gamma = \exp(-\Delta G_{\text{exch}}/RT), \quad (2)$$

where $k_{\text{Ni-Mg}}$ is the distribution coefficient and K_γ characterizes the energetic contribution of the nonideality of olivine and/or orthopyroxene solid solutions.

As Equilibrium 1 only involves two condensed phases, associated variations of heat capacity, compressibility, and thermal expansion may be neglected:

$$\Delta G_{\text{exch}} = \Delta U_{\text{exch}} - T\Delta S_{\text{exch}} + P\Delta V_{\text{exch}} \quad (3)$$

where internal energy, entropy, and volume variations are given at conventional P - T conditions.

Combination of Equations 2 and 3 leads to the general thermobarometric relation

$$\ln k_{\text{Ni-Mg}} + \ln K_\gamma = -[(\Delta U_{\text{exch}} + P\Delta V_{\text{exch}})/RT - \Delta S_{\text{exch}}/R].$$

Role of pressure

The influence of pressure over the exchange reaction is characterized by the volume change ΔV_{exch} :

$$(\partial \ln K_{\text{Ni-Mg}}/\partial P)_T = -\Delta V_{\text{exch}}/RT.$$

ΔV_{exch} is the algebraic sum of the molar volumes of components in their standard state.

Numerous X-ray diffraction studies of Mg-Fe olivines and orthopyroxenes (see Cameron and Papike, 1980; Brown, 1982) showed that they obey fairly well Végard's law. Ni-Mg olivines, on the contrary, show a clear deviation from the law; the molar volume of pure liebenbergite ($\bar{V}_{\text{Ni}_2\text{SiO}_4}^0 = 42.57 \text{ cm}^3$) is significantly lower than its partial

molar volume in Ni-poor olivines ($\bar{V}_{\text{Ni}_2\text{SiO}_4, \text{s.s.}}^0 = 42.91 \text{ cm}^3$; Matsui and Syono, 1968; Bish, 1981; Robie et al., 1984).

The molar volume of pure NiSiO₃ is not known, since this pyroxene is not stable, either at standard conditions or at high pressure (up to 40 kbar), and breaks down to olivine and silica. Direct measurements of crystallographic parameters (Matsui et al., 1968) led to an extrapolated molar volume $\bar{V}_{\text{NiSiO}_3, \text{s.s.}}^0 = 30.56 \text{ cm}^3$ in Ni-poor magnesian orthopyroxenes synthesized at 40 kbar, 1300 °C. No significant departure from Végard's law was observed when adopting this value for pure NiSiO₃.

With these results, an estimation of ΔV_{exch} can be derived:

$$\begin{aligned} \Delta V_{\text{exch}} &= 0.5(\bar{V}_{\text{Ni}_2\text{SiO}_4}^0 - \bar{V}_{\text{Mg}_2\text{SiO}_4, \text{s.s.}}^0) + (\bar{V}_{\text{MgSiO}_3, \text{s.s.}}^0 - \bar{V}_{\text{NiSiO}_3}^0) \\ &= 0.08 \pm 0.05 \text{ cm}^3. \end{aligned}$$

The stated uncertainty reflects only discrepancies between published data for the Mg end members (see Cameron and Papike, 1980; Brown, 1982) and is thus underestimated.

The change in volume appears very small, indicating that the exchange reaction is almost independent of pressure. For instance, a 10-kbar pressure increase at constant $T = 1400 \text{ K}$ would cause a 0.7% decrease of $K_{\text{Ni-Mg}}$, a difference lower than the predicted analytical error on a partition coefficient involving a minor element.

Moreover, the assumption that K_γ is independent of pressure is fairly reasonable, considering that most olivine and orthopyroxene models (e.g., Nafziger and Muan, 1967; Sack, 1980) have small dependence of activity coefficients on pressure, if at all. Nevertheless, the behavior of Ni in orthopyroxene is still poorly known, and definite conclusions would require additional high-pressure experimentation.

Thermodynamical interpretation of Berger and Vannier's empirical calibration

Berger and Vannier (1978) described the exchange reaction using an ideal model for both olivine and orthopyroxene (i.e., $K_\gamma = 1$). They obtained a good linear correlation between $\ln k_{\text{Ni-Mg}}$ and $1/T$, and this thermometric relation was successfully tested against a previous experimental result concerning a Ni-rich olivine-orthopyroxene equilibrium at 1400 °C in the system MgO-NiO-SiO₂ (Campbell and Roeder, 1968). They estimated

$$\Delta G_{\text{exch}} = -31782 + 15.16T$$

and noticed that the apparent ΔS_{exch} value appears surprisingly large for such a solid-solid equilibrium. This remark suggests that the estimated entropy variation presumably includes a term related to excess mixing entropies of the olivine and/or orthopyroxene solid solutions. As a comparison they quoted a value of $\Delta S = 3.8 \text{ J/K}$ estimated for the equivalent Mg-Fe exchange equilibrium, which appears roughly ideal at temperatures over 1000 °C (Sack, 1980). Moreover, the departure of Ni-Mg olivines from Végard's law and numerous order-disorder studies (Matsui and Syono, 1968; Rajamani et al., 1975;

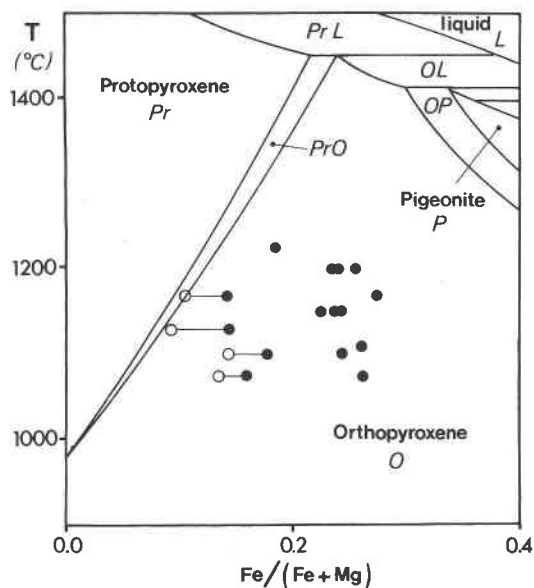


Fig. 1. Pyroxene polymorphism at atmospheric pressure in the system $Mg_2Si_2O_6-Fe_2Si_2O_6$ (after Buseck et al., 1980) and projection of synthesized pyroxenes. Tie-lines join sets of coexisting pyroxenes in the same sample. The protoenstatite to clinoenstatite inversion occurs at temperatures lower than 800 °C.

Bish, 1981; Annersten et al., 1982; Nord et al., 1982) show that, at least for olivines, an ideal model is a rough approximation.

EXPERIMENTAL STUDY

Ni-Mg partitioning between synthetic Mg-Fe-Ni olivines and orthopyroxenes was studied at atmospheric pressure, between 1075 and 1225 °C. Fe was added in order to obtain *Pbca* orthopyroxene crystallization and avoid the formation of *Pbcn* protopyroxene, which is the stable low-pressure, high-temperature polymorph of magnesian pyroxenes (Fig. 1).

Choice of synthesis experiments

When dealing with solid-solid equilibria, the use of reversal experiments provides a way of testing the equilibration state of the charges and is thus usually preferred to synthesis experiments.

Some observations show, nevertheless, that reversal experiments are not necessarily well adapted to the study of an equilibrium that is supposed to behave as a geothermometer, unless they are made at temperatures much higher than that encountered in geologically reasonable situations.

Preliminary experiments described by Berger (1981) showed that no significant Ni-Mg interdiffusion between olivine and orthopyroxene occurred when reheating a natural harzburgite at 1100 °C for 27 d and 1200 °C for 7 d, whereas the initial equilibration temperature was estimated to 1000 ± 50 °C. In the same way, studies of peridotite xenoliths in alkali basalts (e.g., Berger and Vannier, 1984) show that Ni-Mg re-equilibration is gen-

erally not achieved although the reheating suffered by these rocks probably lasted much longer than most experimental runs.

These observations show that the idea that this exchange reaction is a geothermometer is not unreasonable. In other terms, if total re-equilibration had occurred in Berger's experiments, it would have meant that the reaction, although a good thermometer, is not able to keep any information on fossil equilibrium temperatures and will only provide "closure" temperatures that essentially depend on the cooling rate of the samples (Hart, 1981). This conclusion would have been in contradiction with the observed state of most peridotite xenoliths.

As a result of this preliminary discussion, the exchange reaction appears quite inert and thus should be very difficult to reverse at geologically reasonable temperatures in the laboratory. One could then be tempted to try and reverse the exchange reaction using a fluxing component, in order to accelerate the diffusion process. But such experiments would be almost impossible to interpret. In hypersolidus conditions, the original set of minerals would be submitted to partial melting and/or epitaxial growth. The final set of minerals would contain an unpredictable amount of new (i.e., synthesized) minerals, so that such an experiment should not be interpreted as a reversal *sensu stricto* (i.e., re-equilibration by interdiffusion). Anyhow, the presence of a liquid should have little or no influence on the values of diffusion coefficients in the solids, which definitely may be low.

The present study only reports synthesis experiments, which, as mentioned before, are not a wholly satisfactory way to proceed. In order to avoid ambiguity, the choice was made of a simple and unique equilibrium criterion (chemical homogeneity of all present phases at crystal and sample scales). This test appeared quite selective, as it was only passed by 17 out of the 44 charges in which the synthesized minerals were large enough to be analyzed in good conditions (i.e., most crystals exceeding $20 \mu m \times 20 \mu m$).

Experimental procedure

The starting mixtures consisted of pure silica, MgO- Fe_2O_3 -NiO gels, and 2% to 8% flux. Preliminary experiments showed that, without a flux, solid-state reactions were very slow and that samples still contained half of the original reactants after one week at 1200 °C. The same difficulties are mentioned by Ringwood (1956) and Campbell and Roeder (1968). Magnesium fluoride and disodium tetraborate mixtures were chosen as a flux because Na, B, and F are not accepted by olivine and orthopyroxene crystal lattices.

Metallic oxide gels were prepared as follows: hydroxides were coprecipitated in a NaOH solution from a nickel sulfate-iron sulfate-magnesium chloride solution. After filtration the gel was washed with ethanol in order to dissolve most of the excess NaOH, desiccated at 110 °C for 12 h and dehydrated at 700 °C for 2 h. The gels were extremely hygroscopic; that is, they were able to adsorb

up to 0.5% water after 1-min exposure to ambient air. Mass balance allowed the estimation of their water contents, which always exceeded 5% although the gels had been immediately isolated in air-tight bottles.

The Mg:Fe:Ni ratios of the gels used are given in Table 1. In a few experiments, some pure NiO was added in order to explore a larger range of mineral compositions. The compositions of the charges were chosen in order to obtain minerals with quite low Ni contents. With bulk NiO contents of the charges ranging from 0.6% to 7.3%, synthesized orthopyroxenes contained 0.15 to 3.7% NiO, and olivines, 0.5% to 10.2%. Taking into account the silica-rich liquid resulting from the reaction, the molar silicon : metal ratio was chosen close to 0.8, a little higher than the value, close to 0.7, that characterizes a 50% olivine–50% orthopyroxene mineral association.

The reactants were ground under acetone, pelletized, and put in alumina crucibles. The runs were carried out in furnaces using Kanthal A1 or Pt wires. Temperature was measured by Pt-Pt₉₀Rh₁₀ thermocouples. The temperature gradient did not exceed 5 °C over the sample volume. Reducing conditions were obtained with a 37.5% CO₂–2.3% H₂–60.2% Ar gas flow renewing the atmosphere in the furnace every 20 min as a mean. Dilution with Ar was meant to deplete water condensation at the exit of the furnace. Runs of 110 h as a mean yielded in most cases olivine and pyroxene crystals mostly exceeding a 20 μm size and thus large enough to be analyzed in good conditions. Nevertheless, at temperatures lower than 1100 °C, runs had to be stopped several times and the sample reground and pelletized in order to approach equilibrium.

At the temperatures of the experiments, the reaction rate between the pellet and the crucible was quite slow, and crystallization of aluminous spinel at the rim of the sample occurred only at temperatures over 1200 °C.

At the end of the runs, the samples showed a 6 to 8% weight loss essentially due to dehydration, reduction of Fe₂O₃, and vaporization of F, probably as SiF₄ (Hinz and Kunth, 1960). The samples were split into two parts, one powdered and analyzed by X-ray diffraction, the other polished for electron-microprobe analysis.

Microprobe analytical procedure

Minerals and glasses were analyzed with a CAMEBAX electron microprobe using the “double measurement” method (Marion and Vannier, 1983). This method is meant to reduce the imprecision due to imperfect repositioning of the spectrometers. Operating conditions were 15-kV acceleration tension, 15-nA absorbed current. The probe diameter was close to 1 μm for silicates, whereas 2 × 2 μm or 5 × 5 μm scanning was used for glasses. The analytical standards were an olivine from San Carlos (Arizona) for Si, an albite from Amelia County (Virginia) for Na, and pure MgO, NiO, Fe₂O₃, and Al₂O₃ for the remaining elements. B and F were not determined. Counting times were chosen in order to obtain a ±2σ precision estimated to be better than 1% on Si and Mg and better

TABLE 1. Mg:Fe:Ni atomic ratios in the metallic oxides gels

Gel	Mg	Fe	Ni
CP 02	0.764	0.191	0.045
CP 05	0.667	0.292	0.042
CP 06	0.690	0.297	0.010
CP 07	0.577	0.385	0.038

than 1.5% on Fe for silicate analysis. The ±2σ precision on Ni was usually better than 4% except for the charges with the lowest Ni content (for instance, in charge LPF30, the imprecision was estimated to be 9% for orthopyroxene (NiO 0.44 ± 0.04%) and 5% for olivine (NiO 1.25 ± 0.06%)). A ZAF correction procedure with modified absorption coefficients (Vannier, unpub. data) was used. Analyses were usually performed on crystals larger than 50 × 50 μm and systematically at more than 10 μm from crystal edges.

Mg:Fe ratios were computed assuming that Fe is entirely bivalent. Such an assumption is appropriate for magnesian olivines. In the studied pyroxenes, apart from the reducing conditions imposed, it was adopted for crystal-chemical reasons: their low Na and Al contents (Al₂O₃ < 0.15%; Na₂O not significant) do not allow for Fe³⁺ by stoichiometric substitutions.

Mineralogy and equilibrium state of the charges

Charges run with a flux showed no trace of the original reactants. Their phases consisted of olivine, one or several pyroxene(s), and 5 to 30% interstitial glass.

As stated before, the chemical homogeneity of minerals and glasses was taken as an equilibrium criterion. This criterion was considered satisfied when the relative dispersion was lower than 5% for MgO and FeO, 8% for NiO in the silicates, and 5% for SiO₂, Al₂O₃, MgO, total FeO, and Na₂O in the glass. In some cases, a chemical gradient was observed in the glass, in the vicinity (100–200 μm) of the crucible. This zone was generally deprived of crystals and was not considered in this test.

First series of runs. A major concern was to ascertain that analyzed pyroxenes were *Pbca* orthopyroxenes and not *Pbcn* protopyroxenes partially transformed to *P2₁/c* clinostatite. X-ray diffraction patterns failed several times to provide definite information on sample mineralogy because diffraction characteristics of pyroxene polymorphs are partly hidden by the main peaks of olivine. Peaks of lower intensity had to be used and suggested that both ortho- and clinostatite were present in the first series of charges. Microprobe study of the charges that appeared best equilibrated showed that two sets of chemically different pyroxenes could be discriminated, mostly by their Mg:Fe ratio (Table 2). In each charge, “low-Mg” pyroxenes formed a chemically homogeneous set, whereas “high-Mg” pyroxenes were more scattered and were surprisingly difficult to analyze (bad reproducibility and analytical totals, which may reflect surface defects or small-scale heterogeneity). Projection of the composition of the coexisting pyroxenes on the

Mg₂Si₂O₆-Fe₂Si₂O₆ diagram (Fig. 1) falls close to the field where ortho- and protopyroxene coexist at atmospheric pressure (Buseck et al., 1980). In this domain, protopyroxene is slightly richer in Mg than is associated Opx. As the occurrence of clinoenstatite is ascribed to isochemical "inversion" of protopyroxene at low temperature (Buseck et al., 1980), the "high-Mg" pyroxenes were interpreted as partially inverted protopyroxene, whereas the "low-Mg" pyroxenes were considered as orthopyroxene. With such an assumption, one can compare the Ni:Mg ratios of coexisting polymorphs (Table 2). On the average, the values for orthopyroxene and protopyroxene do not differ significantly.

Numerous pyroxenes were analyzed in these charges, and only the "low-Mg" homogeneous set of analyses was considered as valid data. In two cases, the chemical bimodality was not apparent, and the charges were discarded. As a result, only 4 out of a series of 12 experiments were considered satisfactory.

Second series of runs. In order to avoid ambiguities resulting from mixtures of pyroxene polymorphs, the subsequent runs were carried out with bulk compositions richer in Fe. For example, the fayalite content of olivines in run products was raised from 18–20% to 28–35%. X-ray diffraction patterns then confirmed orthopyroxene crystallization and seldom suggested the presence of clinoenstatite. Pyroxene analyses were homogeneous, showing that the previous mineralogical ambiguity had been avoided.

EXCHANGE DATA

In the experimental compositional interval (Figs. 1 and 2), the Mg-Fe and Ni-Mg distribution coefficients do not show any significant variation with silicate composition at constant temperature (Table 3). This result is not surprising for Mg-Fe partitioning as most authors consider that the Mg-Fe exchange equilibrium may be treated as ideal in our experimental range. At temperatures over 1000 °C, the composition dependence of $k_{\text{Mg-Fe}}$ is noticeable only for a much wider range of compositions (Sack, 1980). Concerning the Ni-Mg partitioning, this result is very satisfying for it indicates that the K_γ nonideal contribution to $K_{\text{Ni-Mg}}$

$$K_\gamma = (\gamma_{\text{Ni}_2\text{SiO}_4}/\gamma_{\text{Mg}_2\text{SiO}_4})^{1/2}/(\gamma_{\text{NiSiO}_3}/\gamma_{\text{MgSiO}_3})$$

is independent of composition in the experimental ranges of composition and temperature.

Mg-Fe partitioning

The results (Fig. 3) are in good agreement with published data (e.g., Sack, 1980) and show that $k_{\text{Mg-Fe}} = (\text{Mg/Fe})_{\text{Opx}}/(\text{Mg/Fe})_{\text{Ol}}$ is almost independent of temperature ($k_{\text{Mg-Fe}} = 1.33 \pm 0.11$).

Ni-Mg partitioning

Experiments confirm that $k_{\text{Ni-Mg}}$ is quite dependent on temperature (Fig. 3), allowing discrimination of runs carried out at 25 °C intervals. Linear regression between $\ln(k_{\text{Ni-Mg}})$ and $1/T$ leads to

$$\ln(k_{\text{Ni-Mg}}) = [(3801 \pm 222)/T] - (1.815 \pm 0.157)$$

with a 0.979 correlation coefficient. Estimated residual error on $\ln(k_{\text{Ni-Mg}})$ is 0.020, meaning that this regression statistically accounts for 98% of $k_{\text{Ni-Mg}}$ variation.

This result is in close agreement with Berger and Vanier's calibration.

DISCUSSION

This agreement suggests that the composition interval over which K_γ appears to be independent of composition may be extended to natural compositions. The thermometric relation obtained can be interpreted as

$$-\Delta G_{\text{exch}} - RT \ln K_\gamma = RT \ln k_{\text{Ni-Mg}} = 31603 - 15.09T.$$

We mentioned earlier that, when adopting an ideal model for both solid solutions (i.e., $K_\gamma = 1$), the apparent entropy value (15.09 J/K) was anomalously large. It can be compared for instance to the value $R \ln k_{\text{Mg-Fe}} = 2.4 \pm 0.2$ J/K relative to the Mg-Fe partitioning in the same minerals.

This remark suggests that excess mixing entropies should give a significant contribution to the apparent entropy of the Ni-Mg exchange reaction.

Numerous studies (Matsui and Syono, 1968; Rajamani et al., 1975; Bish, 1981; Annersten et al., 1982; Nord et al., 1982) showed that in olivines, Ni shows a strong preference for M1 sites. Nevertheless, Seifert and O'Neill (1987) showed that only a small positive deviation from ideality accounts for activity-composition relations in Ni-Mg olivines. This result suggests only little contribution of olivine to K_γ .

The results of Ghose et al. (1974) indicate little if any ordering in Ni-Mg orthopyroxenes. High-pressure experimentation would be needed in order to characterize the

TABLE 2. Chemical bimodality of pyroxenes synthesized in the first series of runs

Run	T (°C)	Ortho group			Proto and clino group		
		n*	Mg/Fe**	Ni/Mg**	n*	Mg/Fe**	Ni/Mg**
LPF14	1075	2	5.14(23)	0.0324(9)	2	6.31(65)	0.0312(7)
LPF11	1100	4	4.82(20)	0.0322(12)	3	5.99(61)	0.0285(20)
LPF09	1130	4	6.14(59)	0.2056(5)	3	9.08(44)	0.0259(44)
LPF10	1170	5	6.08(28)	0.0260(10)	3	8.51(33)	0.0254(10)

* Number of analyses.

** Atomic ratios.

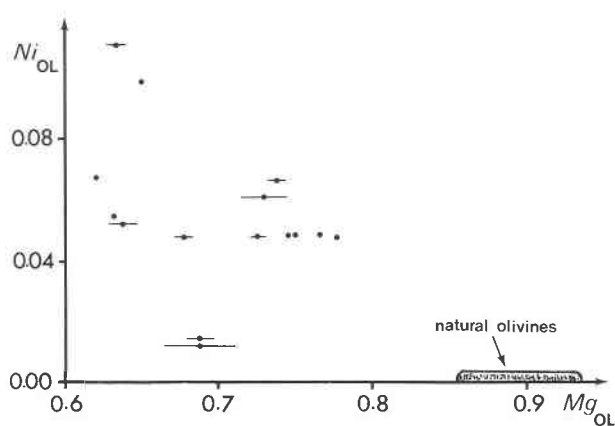


Fig. 2. Composition of the synthesized olivines in the diagram X_{Mg} vs. X_{Ni} .

mixing properties of $NiSiO_3$ in orthopyroxenes, but this discussion suggests that some excess mixing entropy should probably be considered.

Nevertheless, the exchange data show that Ni-Mg partitioning may be approximated with an ideal disordered model for both solid solutions, even though the Gibbs free energy estimated with this model should not be interpreted without precaution as the standard-state Gibbs free energy of the exchange reaction.

APPLICATION TO GEOTHERMOMETRY

Further approximation is needed in order to extrapolate the proposed geothermometer (T in kelvins),

$$T = 3801 / (1.815 + \ln k_{Ni-Mg}),$$

to natural samples, as natural olivines and orthopyroxenes do contain elements such as Ca, Al, Cr, Mn, and Ti that may alter activity-composition relations. Reversals on natural samples at high temperature could thus im-

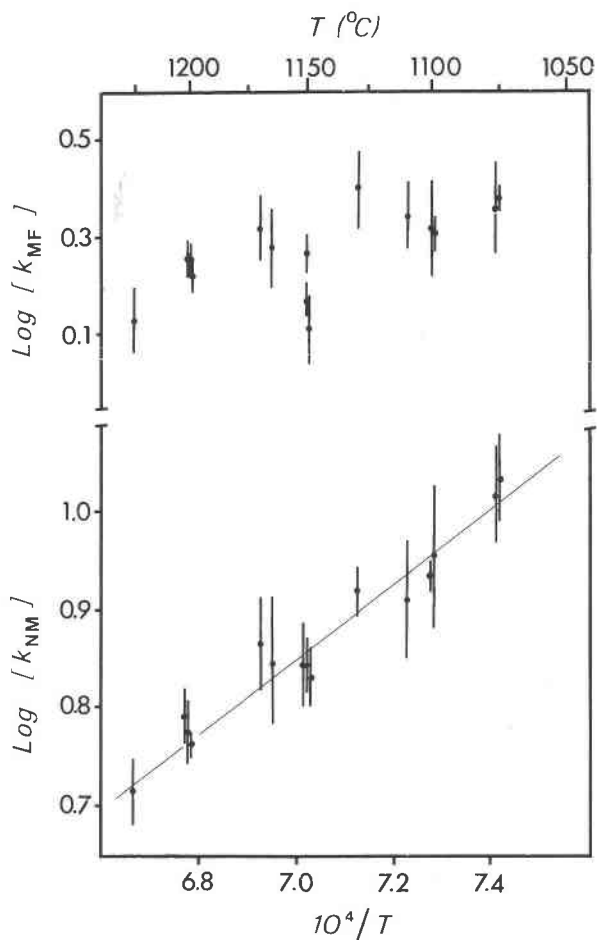


Fig. 3. Experimental Mg-Fe and Ni-Mg partitioning between olivine and orthopyroxene as functions of temperature.

TABLE 3. Experimental data on Mg-Fe-Ni partitioning between olivine and orthopyroxene

Run	d^*	T (°C)	$\log_{10} f_{O_2}$	n^{**}	Ni/Mg in Ol†	Ni/Mg in Opx†	X_{Mg}^{Cl}	X_{Mg}^{Opx}	k_{Ni-Mg}	k_{Mg-Fe}
LPF14‡	118	1075	-10.4	3	0.0893(27)	0.0324(9)	0.738(5)	0.820(11)	2.76(14)	1.44(15)
LPF26	114	1075	-10.5	4	0.1090(9)	0.0388(16)	0.620(2)	0.723(4)	2.82(13)	1.46(3)
LPF11‡	100	1100	-10.0	4	0.0838(60)	0.0322(12)	0.730(15)	0.805(6)	2.60(21)	1.38(14)
LPF29	116	1100	-10.1	3	0.0181(15)	0.0071(6)	0.687(22)	0.753(15)	2.54(3)	1.36(3)
LPF20	158	1110	-10.0	5	0.0824(43)	0.0332(31)	0.638(11)	0.727(21)	2.49(16)	1.43(10)
LPF09‡	145	1130	-9.5	3	0.0642(6)	0.0256(5)	0.765(1)	0.841(12)	2.51(6)	1.50(13)
LPF15	135	1150	-9.3	3	0.0656(3)	0.0284(11)	0.749(2)	0.760(35)	2.31(10)	1.12(8)
LPF18	137	1150	-9.3	2	0.0665(9)	0.0291(13)	0.725(4)	0.752(4)	2.29(7)	1.18(1)
LPF25B	114	1150	-9.3	4	0.1759(8)	0.0756(25)	0.631(4)	0.721(6)	2.33(7)	1.31(1)
LPF21	158	1165	-9.1	5	0.0870(13)	0.0375(25)	0.631(1)	0.709(18)	2.33(16)	1.33(11)
LPF10‡	73	1170	-9.0	3	0.0616(14)	0.0260(10)	0.779(5)	0.841(6)	2.37(12)	1.37(9)
LPF22B	112	1200	-8.7	3	0.1526(21)	0.0710(16)	0.650(3)	0.724(9)	2.15(3)	1.25(3)
LPF23	135	1200	-8.7	6	0.0719(24)	0.0325(15)	0.677(7)	0.744(13)	2.21(6)	1.30(5)
LPF30	115	1200	-8.7	4	0.0191(6)	0.0088(2)	0.687(7)	0.743(10)	2.17(7)	1.30(4)
LPF27	114	1225	-8.3	5	0.0647(26)	0.0324(23)	0.757(11)	0.796(17)	2.05(7)	1.14(6)

* Duration of experiments (h).

** Number of olivine-orthopyroxene pairs.

† Atomic ratios.

‡ Data from the first series of runs.

prove the calibration of the thermometer, but Berger's experiments (1981), already mentioned, show that run durations much longer than one month would probably be needed at temperatures as high as 1200 °C.

At the same time, the slow kinetics justify the geological interest in the equilibrium. The primary (metastable) equilibrium conditions are preserved reasonably well during the *P-T* path of the sample up to the Earth's surface, whereas "rapid" equilibria such as the Mg-Fe partitioning between olivine and spinel will only reveal the last thermal episode of the sample's history.

At this stage, however, some qualitative arguments may be proposed to justify the application of the geothermometer to natural samples. In olivines, only minor elements (Mn, Ca) have not been taken into account, and one can assume that they do not notably modify the $\gamma_{\text{Ni}_2\text{SiO}_4}/\gamma_{\text{Mg}_2\text{SiO}_4}$ ratio. In orthopyroxenes, Al, Fe³⁺, and Ca can be present in more than trace amounts. The little ordering found in (Ni,Mg)SiO₃ crystals (Ghose et al., 1974) accounts for the similarity of Ni²⁺ and Mg²⁺ behavior in this mineral, suggesting that the influence of "foreign" elements on the $\gamma_{\text{NiSiO}_3}/\gamma_{\text{MgSiO}_3}$ ratio should be weak.

Analytical accuracy appears critical for the use of this geothermometer. Terrestrial orthopyroxenes seldom contain more than 0.14% NiO, whereas NiO content in olivines is generally lower than 0.45%. Using usual analytical routines, olivine-orthopyroxene pairs will lead to a quite large uncertainty on temperature estimation. Yet, the required refinements can be achieved and then allow the estimation of "fossil" equilibrium temperatures in clinopyroxene-free ultramafic rocks.

ACKNOWLEDGMENTS

I wish to thank M. Vannier for his constant help and advice and E. Berger and C. Campiglio for reviewing the manuscript. X-ray diffraction analyses were performed by N. Forette, and microprobe analyses by M. C. Forette and G. Frot.

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MANUSCRIPT RECEIVED NOVEMBER 10, 1986

MANUSCRIPT ACCEPTED OCTOBER 21, 1987