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The distribution of Mg and Fe^{2+} between olivine and spinel at 1300°C

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Abstract

The equilibrium distribution of magnesium and ferrous iron between olivine and aluminate spinel, and between olivine and ferrite spinel, was determined at 1300°C in order to understand the relationship between these phases in mafic and ultramafic rocks. A series of olivines (Mg_2SiO_4–Fe_2SiO_4) were equilibrated with aluminate spinels ($MgAl_2O_4$–$FeAl_2O_4$) in the presence of metallic iron. The distribution coefficient $K_d^{ol-al} = (X_{Mg}^{ol}/X_{Fe^{2+}}^{ol}) \cdot (X_{Fe^{2+}}^{al}/X_{Mg}^{al})$ is close to one at 1300°C: it varies between 0.94 and 1.23, and increases with X_{Mg}^{al}. Olivines were equilibrated with ferrite spinels ($MgFe_2O_4$) (Mf) – Fe_3O_4 (Mt)) as two-phase assemblages, or with pyroxene or liquid as three-phase assemblages in the system MgO–SiO_2–FeO–Fe_2O_3. Magnesium is preferentially partitioned into olivine relative to ferrite spinel, and the distribution coefficient $K_d^{ol-ft} = (X_{Mg}^{ol}/X_{Fe^{2+}}^{ol})\ (X_{Fe^{2+}}^{ft}/X_{Mg}^{ft})$ varies between 6.7 and 9.3 at 1300°C.

The systematic variation of the distribution coefficient with spinel composition was used to calculate the activity–composition relations of both the aluminate and the ferrite solid solutions. It was assumed that the olivine solid solution is ideal, and that the spinel solid solutions are regular and single-sited, with respect to magnesium and ferrous iron, at 1300°C. The experimental results show that the aluminates are nearly ideal, and can be well described by a regular, symmetric solution model with an interaction parameter W_{al} of -3.1 ± 0.6 kJ/mole, and equilibrium constant $K^{ol-al} = 0.97 \pm 0.08$ at 1300°C. The ferrite solid solution appears to fit an asymmetric model with $W_{Mf} = 2 \pm 2$ kJ/mole and $W_{Mt} = 7 \pm 4$ kJ/mole, and equilibrium constant $K^{ol-ft} = 7 \pm 1$ at 1300°C. If the spinel solution properties are recalculated assuming non-ideal olivines with $W_{ol} = 4.2$ kJ/mole, neither activity–composition relations nor the equilibrium constants are changed significantly.

These new thermodynamic data may be applied to: (1) calibration of the olivine–spinel geothermometer, (2) calibration of the olivine–orthopyroxene–spinel and olivine–silica–spinel oxygen geobarometers, and (3) calculation of other reactions in mantle assemblages.

Introduction

The olivine–spinel geothermometer

Natural spinel is generous in its range of solid solution and persistent in its occurrence in a wide variety of rock types; two features which promote this mineral as a potentially useful petrogenetic indicator. A number of petrologists, notably Irvine (1965, 1967) and Evans and Frost (1975), have observed that the distribution of Mg and Fe^{+2} between olivine and spinel depends, in a systematic way, on the identity of the other cations in the spinel structure such as Cr, Al and Fe^{3+}, and on the interpreted temperature of equilibration. This has led to the suggestion that the composition of coexisting olivine and spinel can be used as a geothermometer, and to many attempts to calibrate it (Jackson, 1969; Fujii, 1978; Engi, 1978; Wood and Nicholls, 1978; Fabriès, 1979; Roeder et al., 1979; Fujii and Scarfe, 1982; Wilson, 1982). Calibrations constructed from thermodynamic data on end-member components in the complex spinel solutions suffer because of the imprecision of published values (see discussion in Roeder et al., 1979), while calibrations based on natural assemblages require independent information about equilibration temperatures and confidence that those represent blocking temperatures for the olivine–spinel cation exchange. Applicability of the olivine–spinel geothermometer must be assessed in the context of evidence that although mineral pairs in quickly-quenched volcanic rocks probably record magmatic temperatures, there is considerable re-equilibration between oxide and silicate under conditions of slow cooling, as in large layered intrusions (Irvine, 1965; Clark, 1978; Roeder et al., 1979; Wilson, 1982).

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Scope of present work

In order to understand in detail how Mg–Fe^{2+} distribution between olivine and spinel depends on the identity of the trivalent cation, and in order to provide a partial experimental calibration of the geothermometer, we have conducted two series of experiments equilibrating olivine and spinel at 1300°C. In the first series, the composition of coexisting olivine and pure aluminate spinel was determined for a range of Mg/Fe^{2+} ratios. The equilibria can be expressed by the following exchange reaction and distribution coefficient:

$$\underset{\substack{\text{spinel}\\ \text{(sensu stricto)}}}{MgAl_2O_4} + \underset{\text{fayalite}}{FeSi_{0.5}O_2} = \underset{\text{hercynite}}{FeAl_2O_4} + \underset{\text{forsterite}}{MgSi_{0.5}O_2} \quad (1)$$

$$K_d^{ol\text{-}al} = \frac{X_{Mg}^{ol}\,X_{Fe^{2+}}^{al}}{X_{Fe^{2+}}^{ol}\,X_{Mg}^{al}}$$

where X_{Mg}^{ol} refers to the atom fraction Mg/(Mg+Fe^{2+}) in olivine, and all other terms are defined analogously. In the second series, olivine was equilibrated with ferrite spinel, again over a range of Mg/Fe^{2+} values.

$$\underset{\text{magnesioferrite}}{MgFe_2O_4} + \underset{\text{fayalite}}{FeSi_{0.5}O_2} = \underset{\text{magnetite}}{Fe_3O_4} + \underset{\text{forsterite}}{MgSi_{0.5}O_2} \quad (2)$$

$$K_d^{ol\text{-}ft} = \frac{X_{Mg}^{ol}\,X_{Fe^{2+}}^{ft}}{X_{Fe^{2+}}^{ol}\,X_{Mg}^{ft}}$$

The temperature of 1300°C, which is close to the liquidus of mafic rocks, was chosen because equilibrium could be confidently achieved in a reasonable time and because published phase relations are available for pertinent systems at 1300°C. Aluminate and ferrite are significant components of spinel solutions which coexist with olivine in nature. The effect of the chromite component on olivine–spinel equilibria has been investigated at lower temperatures (Engi, 1978) but not at magmatic temperatures.

Applications

Irvine (1965) and Wood and Nicholls (1978) have shown that in order to calibrate the olivine–spinel geothermometer for application to natural samples where the spinel phase is a member of the multicomponent solid solution (Mg,Fe^{2+}) (Al,Fe^{3+},Cr)$_2$O$_4$, the equilibrium constants $K^{ol\text{-}al}$, $K^{ol\text{-}ft}$ and $K^{ol\text{-}cr}$, which correspond to exchange reactions between olivine and pure aluminate, ferrite and chromite spinel respectively, must be evaluated for the range of geologically-interesting temperatures. Our experimental data provide high-temperature values for the first two parameters. These equilibrium constants are independent of Mg/Fe^{2+} ratios, incorporate deviations from ideality in both olivine and binary spinel solutions and do not depend on external sources of thermodynamic data. Aside from the calibration of the geothermometer, the experimentally-determined values of $K^{ol\text{-}al}$, $K^{ol\text{-}ft}$ and the derived $K^{al\text{-}ft}$ (which represents the exchange equation between the aluminate and ferrite components of spinel solution) may be useful for the calculation of physical conditions constrained by other equilibria in mafic and ultramafic rocks (e.g., O'Neill, 1981; Nicholls, 1977).

Any comprehensive calibration of the olivine-spinel geothermometer must include the evaluation of activity coefficients for both olivine and multi-component spinel solid solutions over an appropriate range of temperature. The activity–composition relations of olivine solid solutions have been examined in a number of studies (Nafziger and Muan, 1967; Williams, 1972; Obata et al., 1974; Kawasaki and Matsui, 1977; O'Neill and Wood, 1979; Sack, 1980; Engi, 1980; Wood and Kleppa, 1981) with similar, if not entirely coincident, conclusions. Sack (1982) has taken the available experimental data on spinel solid solutions and constructed a thermodynamic model which allows the calculation of the activities of various molecular species in a complex spinel. He uses a Temkin type model for the configurational entropy together with published experimental data on Fe–Mg exchange between spinel and olivine, and on spinel miscibility gaps.

The spinel minerals exhibit variation in the pattern of cation distribution in a structure that contains twice as many octahedral as tetrahedral sites available for occupancy, the limiting cases being the "normal" distribution A(B)$_2$O$_4$ and the "inverse" distribution B(AB)$_2$O$_4$, where the cations in parentheses represent the octahedral sites. Intermediate cases are known, but cation distribution is difficult to measure and its variation with spinel composition, temperature and thermal history is only beginning to be understood (Osborne et al., 1981). The cation distributions of the aluminate and ferrite spinels of the present experiments are not known. From our experimental results the variation of $K_d^{ol\text{-}al}$ and $K_d^{ol\text{-}ft}$ with the Mg/Fe^{2+} ratio of the spinel has been used to calculate, in addition to the equilibrium constants, the activity–composition relations for the MgAl$_2$O$_4$–FeAl$_2$O$_4$ and the MgFe$_2$O$_4$–Fe$_3$O$_4$ solid solutions at 1300°C, assuming that mixing takes place on one lattice site.

Experimental methods

Procedures

Each experiment was conducted by hanging a sample of approximately 100 mg of starting material, mounted on a wire loop, in the predetermined thermal center of a vertical quench furnace with a 1-inch diameter alumina furnace tube. Iron wire was used for the olivine–aluminate equilibration experiments and platinum wire for the olivine–ferrite experiments. A Pt/Pt$_{90}$Rh$_{10}$ thermocouple, calibrated at the melting points of gold and diopside, was used to measure the temperature at the beginning and end of each run.

For most of the runs, the oxygen fugacity of the atmosphere within the furnace was controlled by mixing carbon dioxide and hydrogen in known proportions. In other cases, the furnace atmosphere was air or pure CO_2. The oxygen fugacity corresponding to each gas mixture, and to pure CO_2, was checked with a ceramic electrolyte cell. The iron–wüstite transition at 1200 and 1300°C was used to check the fo_2 control, and found to be within 0.1 log units of the values reported by Nafziger (1966) and Presnall (1966).

The experiments were run for 24 hours and the achievement of chemical equilibrium was tested by the techniques described in a following section. Both temperature and oxygen fugacity were monitored for at least an hour at the begining and end of each run, and varied by less than 2°C and 0.1 log units, respectively, over the 24-hour run period.

Analysis

All samples were analyzed using an Applied Research Laboratories electron microprobe in the energy dispersive mode with a lithium-drifted silicon detector. An accelerating voltage of 15 kV and a counting time of 120 seconds were used. The X-ray intensities were corrected on-line employing a multiple least-squares program that compared sample spectra to stored spectra for each element, and corrected apparent concentrations using the techniques described by Bence and Albee (1968) and the correction factors of Albee and Ray (1970). Eleven synthetic olivines ranging in composition from forsterite to fayalite (supplied by C. Smith, Geological Survey of Canada) were used as analytical standards for olivine analysis. Synthetic periclase, fayalite and corundum were used as analytical standards for the aluminate and ferrite spinels. The relative proportions of ferrous and ferric iron in the spinels were calculated assuming that they correspond to the stoichiometric formula $M^{2+}M_2^{3+}O_4$; the validity of this assumption is discussed in a later section. To test reproduciblity, a standard olivine was analyzed with every set of samples over the period of approximately a year. The observed variation, expressed as a single standard deviation from a mean value of mole% forsterite, was 0.3% for a natural forsteritic olivine (supplied by B. Evans, University of Washington). A more detailed discussion of analytical procedure and the quality of analytical results, in terms of the precision and accuracy obtained on standard materials that are mineralogically similar to the samples, is given by Jamieson (1981).

Design and demonstration of equilibrium

The following procedure was designed with the aim of (1) producing olivine and spinel crystals large enough to analyze confidently by electron microprobe, and (2) approaching the equilibrium compositions of coexisting phases from two directions. This ensured that any change in K_d with the Mg/(Mg+Fe^{2+}) value of the spinel was not an artifact of either analytical technique or difficulty reaching equilibrium. Our experimental design benefitted from previous work on pertinent systems, notably the work of Muan and Osborn (1956), Nafziger (1966), Speidel and Osborn (1967), Speidel (1967) and Ulmer (1964, 1969).

Olivine-aluminate equilibration experiments. The olivines and aluminates were equilibrated with metallic iron to guarantee that each aluminate was the most reduced spinel for that particular bulk composition. The starting material for each run consisted of olivine of known composition, aluminate of known composition, and a flux[2], mixed together in known proportions and mounted on an iron wire spring. A flux was necessary to produce sufficiently large aluminate spinel crystals. The composition of the flux (close to that of basalt) was chosen so that it contained no elements other than Fe, Mg, Si and Al that would enter the structures of either olivine or aluminate in significant amounts. Crystalline starting materials were olivines and aluminates synthesized at 1300°C from SiO_2, MgO, Al_2O_3 and Fe_2O_3, in proportions required to give stoichiometric phases. The Mg/Fe ratio for coexisting olivine and aluminate spinel was varied by changing the oxygen fugacity. This changed the amount of metallic iron relative to that of the rest of the sample so that the proportion of ferrous iron and magnesium available to be incorporated into the crystalline phases was altered.

To demonstrate that the olivine–aluminate compositions from a run at a particular oxygen fugacity at 1300°C represented the equilibrium assemblage for those conditions, pairs of mixtures with starting materials of similar bulk composition were run simultaneously. One mixture contained a Mg-rich olivine and a Fe^{2+}-rich aluminate, and the other contained a Fe^{2+}-rich olivine and a Mg-rich aluminate. In other words, the equilibrium tie-line was determined by the process of (1) an olivine becoming more Fe^{2+}-rich and an aluminate more Mg-rich, or (2) an olivine becoming more Mg-rich and an aluminate more Fe^{2+}-rich. For a particular temperature and oxygen fugacity, two samples of identical bulk composition, but different starting materials, should define a single tie-line between coexisting olivine and aluminate spinel.

Olivine–ferrite equilibration experiments. In the experiments designed to equilibrate olivine and ferrite spinel, sufficiently large crystals could be grown without the use of a flux. Consequently, the bulk composition of all the samples can be described by the system MgO–SiO_2–FeO–Fe_2O_3. The starting material for each experiment in this series was an assemblage of olivine and ferrite of different composition from that finally equilibrated during the experimental run. This was achieved by prefiring a chosen bulk composition at a higher temperature than 1300°C, or at a different oxygen fugacity than that chosen for the run. The bulk composition and the oxygen fugacity were varied to produce coexisting olivine and ferrite with various Mg/Fe^{2+} ratios.

To test the attainment of equilibrium, starting material containing Mg-rich olivine and ferrite was run simultaneously with starting material containing Fe^{2+}-rich olivine and magnesioferrite, both samples having the same bulk composition in terms of Mg–Si-total Fe, under conditions which produced an olivine–ferrite pair with Mg/Fe^{2+} ratios intermediate to those of the starting materials. In other words, a relatively oxidized and a relatively reduced assemblage were equilibrated at an intermediate oxygen fugacity. In the case of the three-phase assemblage where pyroxene coexists with olivine and ferrite, equilibrium was also tested by running starting materials of different bulk composition at the same oxygen fugacity. Detailed phase relations are described by Jamieson (1981).

Results

Table 1 shows the results of (a) olivine–aluminate, and (b) olivine–ferrite equilibration experiments, in terms of the composition of coexisting olivine and spinel, and the distribution coefficient calculated according to equations (1) and (2) in each case. The listed values of mole% Mg_2SiO_4, $MgAl_2O_4$ and $MgFe_2O_4$ are the means of at least five analyzed crystals of each phase. The uncertain-

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[2] Flux composition is MgO = 15, Al_2O_3 = 20, SiO_2 = 45, CaO = 8 and FeO = 12 wt.%.

Table 1. Results of (a) olivine–aluminate, and (b) olivine–ferrite, equilibration experiments at 1300°C. Bracketed samples identified by symbols are those used to test the achievement of equilibrium. O = olivine, F = ferrite spinel, P = pyroxene, L = liquid.

(a) Olivine-Aluminate

		Furnace Atmosphere		Run Products		
	Sample No.	CO_2/H_2	$-\log f_{O_2}$	mole % Mg_2SiO_4	mole % $MgAl_2O_4$	K_d^{ol-al}
□	A-1	0.05	13.2	92.4 (0.1)	91.8 (0.1)	1.09 (0.02)
	A-2	0.05	13.2	92.0 (0.2)	90.3 (0.3)	1.23 (0.06)
○	A-3	0.10	12.6	86.1 (0.1)	84.4 (0.2)	1.14 (0.02)
	A-4	0.10	12.6	86.1 (0.2)	84.3 (0.3)	1.15 (0.03)
△	A-5	0.15	12.2	81.4 (0.1)	79.8 (0.2)	1.11 (0.02)
	A-6	0.15	12.2	81.4 (0.2)	79.2 (0.7)	1.15 (0.05)
⬡	A-7	0.20	11.9	71.3 (0.7)	71.7 (0.7)	0.98 (0.05)
	A-8	0.20	11.9	72.0 (0.3)	70.7 (0.4)	1.07 (0.03)
	A-9	0.20	11.9	71.5 (0.3)	70.9 (0.3)	1.03 (0.02)
◇	A-10	0.25	11.7	63.1 (0.3)	62.2 (0.2)	1.04 (0.01)
	A-11	0.25	11.7	62.9 (0.1)	62.2 (0.4)	1.04 (0.02)
	A-12	0.34	11.4	59.7 (0.2)	58.6 (0.5)	1.04 (0.02)
	A-13	0.40	11.2	52.8 (0.3)	54.2 (0.4)	0.94 (0.02)
	A-14	0.40	11.2	51.7 (1.0)	53.3 (1.0)	0.94 (0.07)
	A-15	0.40	11.2	52.5 (0.3)	52.5 (0.8)	1.00 (0.03)
	A-16	0.40	11.2	51.6 (0.2)	52.2 (0.5)	0.98 (0.02)
	A-17	0.40	11.2	51.5 (0.1)	51.2 (0.2)	1.01 (0.01)
	A-18	0.40	11.2	46.4 (0.2)	47.7 (0.4)	0.95 (0.01)

(b) Olivine-Ferrite

	Sample No.	CO_2/H_2	$-\log f_{O_2}$	Phases	mole % Mg_2SiO_4	mole % $MgFe_2O_4$	K_d^{ol-ft}
■	F-1	air	0.7	OFP	94.8 (0.1)	73.2 (0.2)	6.7 (0.1)
	F-2	air	0.7	OFP	94.4 (0.2)	69.7 (0.4)	7.3 (0.3)
	F-3	CO2	2.8	OFP	86.5 (0.2)	43.5 (0.5)	8.4 (0.2)
●	F-4	CO2	2.5	OFP	86.3 (0.1)	41.7 (0.6)	8.8 (0.2)
	F-5	CO2	2.5	OFP	85.8 (0.1)	40.3 (0.8)	8.9 (0.2)
	F-6	CO2	2.5	OFP	84.7 (0.3)	40.0 (0.7)	8.3 (0.3)
	F-7	41.5	6.3	OF	78.2 (0.2)	30.7 (0.4)	8.1 (0.2)
	F-8	23.6	6.8	OF	76.6 (0.4)	28.2 (0.3)	8.3 (0.2)
▲	F-9	23.6	6.8	OF	76.7 (0.6)	26.0 (0.8)	9.3 (0.5)
	F-10	23.6	6.8	OF	75.8 (0.7)	25.4 (0.7)	9.2 (0.5)
	F-11	23.6	6.8	OF	66.3 (0.8)	18.7 (0.6)	8.5 (0.3)
⬢	F-12	41.5	6.3	OFL	46.8 (0.1)	11.2 (0.3)	7.0 (0.2)
	F-13	41.5	6.3	OFL	47.0 (0.2)	10.9 (0.4)	7.3 (0.3)
◆	F-14	13.6	7.4	OFL	43.6 (0.2)	10.2 (0.5)	6.8 (0.3)
	F-15	13.6	7.4	OFL	42.3 (0.2)	9.6 (0.3)	7.1 (0.2)

ties in parentheses represent the single standard errors of these means, and have been propagated through the calculation of K_d^{ol-al} and K_d^{ol-ft}. The sample groups bracketed and identified by symbols in the first column of each table are those cases where the attainment of equilibrium was tested by one of the methods described in the previous section, and which would be expected to correspond to a single tie-line.

Figure 1 shows tie-lines between the solid solutions of (a) olivine and aluminate spinel, and (b) olivine and ferrite spinel. Small arrows identify the direction of compositional change from the starting materials to the final assemblage. It can be seen that equilibrium was closely approached and, in fact, for the pairs (A-3, A-4), (A-10, A-11), and (F-12, F-13) the tie-lines of the reversed pair are coincident. It was not possible to establish tie-lines

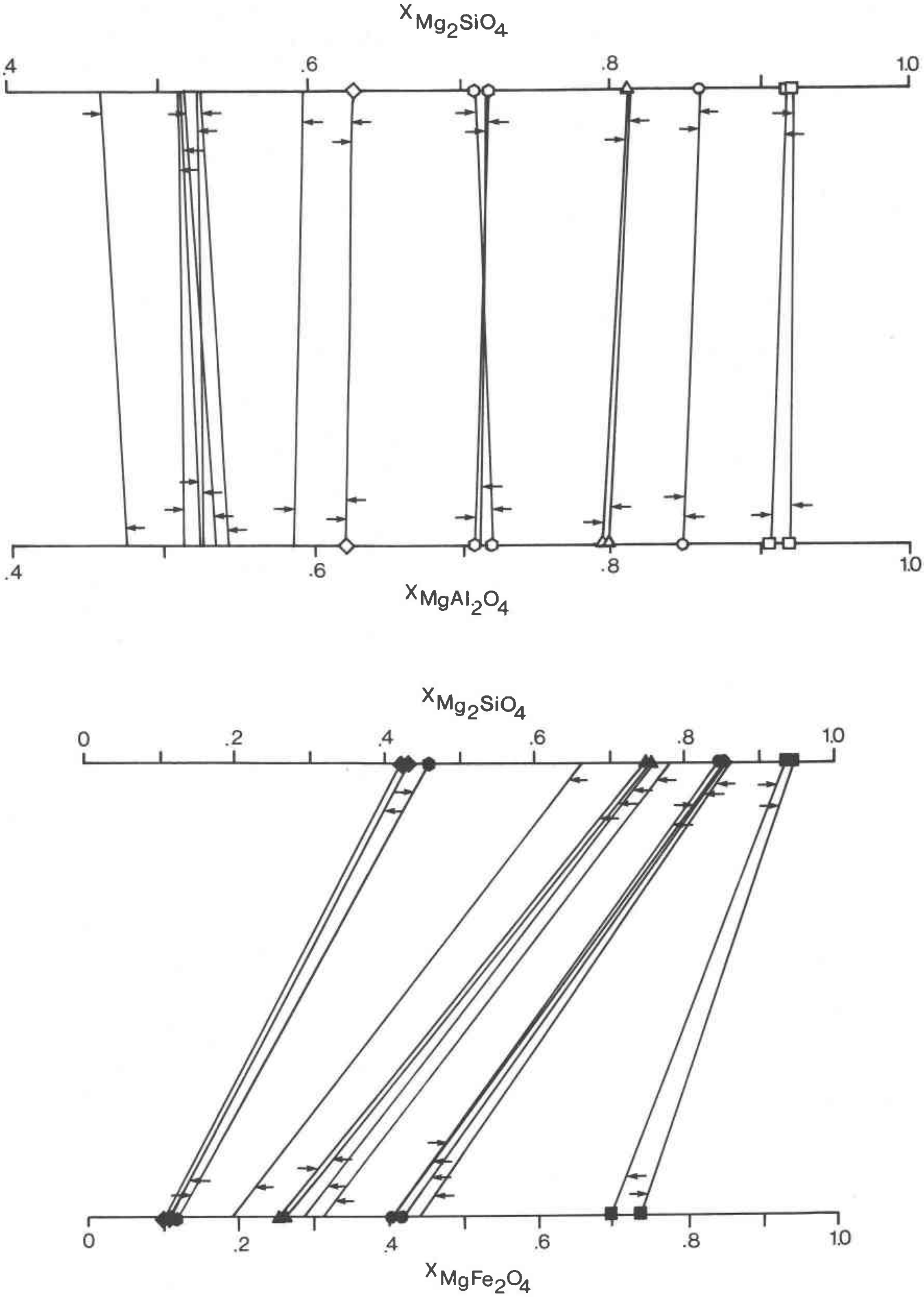

Fig. 1. Tie-lines between (a) olivine and aluminate spinel, and (b) olivine and ferrite spinel, at 1300°C. Symbols correspond to the groups of samples, bracketed in Tables 1(a) and (b), whose tie lines are expected to be coincident.

for phase compositions richer in iron than those shown in Figure 1, because 1300° C is above the melting point of iron-rich olivines.

The experimental results demonstrate how the partitioning of magnesium and ferrous iron between olivine and spinel depends on the identity of the other cation in the spinel structure. Table 1a and Figure 1a show that at 1300°C magnesium, relative to ferrous iron, is incorporated into olivine and aluminate spinel with little discrimination between the two structures. This is illustrated by the nearly vertical tie-lines between olivine and aluminate, and the proximity of the K_d^{ol-al} values to 1. On the other hand, the orientation of the tie-lines between olivine and ferrite in Figure 1b, and the positive values of K_d^{al-ft} listed in Table 1b, indicate that magnesium, relative to ferrous iron, is incorporated into olivine in preference to ferrite spinel at 1300°C.

Stoichiometry of the spinel phases

Electron microprobe analysis of the spinels from the experimental runs defines their compositions in terms of magnesium, aluminum (for the aluminates), and total iron, but since the relative proportions of ferrous and ferric iron cannot be distinguished, and since spinel solid solutions in the system $MgO–Al_2O_3$-$FeO–Fe_2O_3$ at 1300°C are thought to include cation-deficient compositions (Speidel, 1967; Ulmer, 1964; Atlas and Sumida, 1958; Kwestroo, 1959), it was necessary to make some assumption about spinel stoichiometry.

The mineral formulae of the aluminate spinels, which represent compositions in equilibrium with metallic iron, were calculated according to $M^{2+}M_2^{3+}O_4$ stoichiometry, and indicate the presence of a small amount of ferric iron, which increases systematically with total iron content and oxygen fugacity to a maximum of 6 atomic% of the total aluminum plus ferric iron. Ulmer (1964) has suggested that Mg–Fe aluminate spinels in equilibrium with iron at 1300°C are slightly cation-deficient, a deviation from stoichiometry which would lower the calculated $Fe^{2+}/(Fe^{2+}+Mg)$ atom proportion of aluminate from, for example, 0.50 to 0.45, although the total iron to magnesium ratio would remain the same.

Speidel (1967) found that at 1300°C the most reduced ferrite spinels in the system $MgO–FeO–Fe_2O_3$ are stoichiometric but the more oxidized ferrites are cation-deficient. Deviation from stoichiometry assessed by Speidel's isobars would lower the calculated $Fe^{2+}/(Fe^{2+}+Mg)$ of the ferrite for sample F-1 from 0.76 to 0.73. This effect decreases with increasing iron content of the spinels, and ferrites equilibrated at oxygen fugacities lower than that of pure CO_2 (F-7 to F-15) would be stoichiometric.

Not only are these possible deviations from stoichiometry small, but the significance of cation-deficient spinels to the $Mg–Fe^{2+}$ distribution between olivine and spinel is not readily predictable. In the present investigation it has been assumed that small departures from stoichiometry do not affect the proportions of magnesium and ferrous iron involved in cation exchange with olivine, and the stoichiometric spinel compositions are used for calculation of the distribution coefficients.

Calculation of equilibrium constants and activity coefficients

Method

The composition of coexisting olivine and spinel, or more specifically, the variation of the olivine–spinel distribution coefficient with the $Mg/(Mg+Fe^{2+})$ of the spinel, can be used to determine the equilibrium constants for equations (1) and (2), and the activity–composition relations for the two spinel solid solutions. Appropriate solution models must be chosen and the thermodynamic properties of the olivines must be known.

Here both the aluminates and the ferrites are considered to be single-sited, regular (in the sense of Thompson, 1967) solid solutions. The standard states for the spinel phases are pure spinel ($MgAl_2O_4$) and hercynite ($FeAl_2O_4$) with normal cation distribution, and pure magnesioferrite ($MgFe_2O_4$) and magnetite (Fe_3O_4) with inverse cation distribution, all at 1300°C and 1 atmosphere. Aside from the fact that where cation distributions have been measured (Navrotsky and Kleppa, 1967; Osborne et al., 1981), $Mg–Fe^{2+}$ aluminates are essentially normal spinels and $Mg–Fe^{2+}$ ferrites are essentially inverse spinels, choosing these particular standard states with regard to structural state provides a simple relation between activity and mole fraction, for example: $a_{Hc}^{al} = X_{Hc}^{al}\, \gamma_{Hc}^{al}$, where a is activity and γ is the activity coefficient. The olivine solid solution is assumed to behave ideally at 1300 C. The conclusions of a number of studies on olivine mixing properties indicate ideal or nearly ideal behavior at high temperatures (Sack, 1980; Engi, 1981) and, as will be shown later, the small positive deviation from ideality suggested by other studies (O'Neill and Wood, 1979; Wood and Kleppa, 1981) does not significantly affect the spinel activity–composition relations or the equilibrium constants calculated in the present work.

The difference between the distribution coefficient and the equlibrium constant can be expressed in terms of the activity coefficients of the spinel components, using the olivine–aluminate equilibria as an example:

$$\ln K_d^{ol-al} = \ln K^{ol-al} - \ln \gamma_{Hc} + \ln \gamma_{Sp} \qquad (3)$$

For a symmetric or one-parameter solution model (Thompson, 1967), the activity coefficient is related to the interaction parameter W_{al} as follows:

$$\ln \gamma_{Hc} = \frac{W_{al}}{RT} X_{Sp}{}^2 \qquad (4)$$

Substituting (4), and the relation $X_{Hc} = (1–X_{Sp})$, in equation (3) results in the following linear equation:

$$\ln K_d^{\text{ol-al}} = \left[\ln K^{\text{ol-al}} + \frac{W_{\text{al}}}{RT}\right] - \left[\frac{2W_{\text{al}}}{RT}\right] X_{\text{Sp}} \quad (5)$$

For asymmetric solid solution models, two interaction parameters are needed, and the relation between the activity coefficient and these parameters (Thompson, 1967) is:

$$\ln \gamma_{\text{Hc}} = \frac{X_{\text{Sp}}^2}{RT}\left[W_{\text{Hc}} + 2X_{\text{Hc}}\,(W_{\text{Sp}} - W_{\text{Hc}})\right] \quad (6)$$

If equation (6) is substituted into (3), the variation of the distribution coefficient with spinel composition has the form of a second-degree polynomial equation:

$$\ln K_d^{\text{ol-al}} = \left[\ln K^{\text{ol-al}} + \frac{W_{\text{Hc}}}{RT}\right] + \left[\frac{2W_{\text{Sp}} - 4W_{\text{Hc}}}{RT}\right] X_{\text{Sp}} + \left[\frac{3W_{\text{Hc}} - 3W_{\text{Sp}}}{RT}\right] X_{\text{Sp}}^2 \quad (7)$$

Calculations from olivine–aluminate results

Figure 2a shows the relation between ln $K_d^{\text{ol-al}}$ and X_{Sp} determined by the olivine–aluminate equilibration experiments. The distribution of the data approximates a straight line which suggests that, if olivines are ideal at 1300°C, the aluminate solid solution can be well described as a symmetric regular solution. Since the uncertainty in the determination of X_{Sp} is much less than that of ln $K_d^{\text{ol-al}}$, a straight line was fitted to the data using a least-squares fit with the individual data points weighted by factors proportional to the calculated uncertainties in the ln $K_d^{\text{ol-al}}$ values. The error bar on each point represents analytical uncertainty or heterogeneity within any one sample. The linear correlation coefficient is 0.95. In Figure 2b the calculated activity–composition relations for the aluminates at 1300°C illustrate the small symmetric negative deviation from ideality. The value of the equilibrium constant $K^{\text{ol-al}}$ and the interaction parameter W_{al}, which have been calculated from the fitted line, are also shown. The uncertainties associated with these two parameters, and an example of the uncertainty associated with the activity values shown by the vertical error bar, were determined by propagation of both the analytical uncertainties and the quality of the fit.

Calculations from olivine–ferrite results

Figure 3a shows that the variation of ln $K_d^{\text{ol-ft}}$ with X_{Mf}, as measured by the olivine–ferrite equilibration experiments, is more complicated than the olivine–aluminate case, but can be reasonably well described by a second-degree polynomial curve, corresponding to an asymmetric regular solution model for the ferrites. The curve shown has been fitted to the weighted data and has a correlation coefficient of 0.88. The pattern of the distribution might be clarified by more information in the Mg-rich part of the system, but this is a difficult region to explore experimentally due to the high oxygen fugacities and the difficulty of quenching magnesiowustite which coexists with very Mg-rich olivines and ferrites (Jamieson, 1981). The calculated activity–composition relations corresponding to this asymmetric solution model, the value of the equilibrium constant $K^{\text{ol-ft}}$ at 1300°C, the two interaction parameters, and associated uncertainties are shown in Figure 3b.

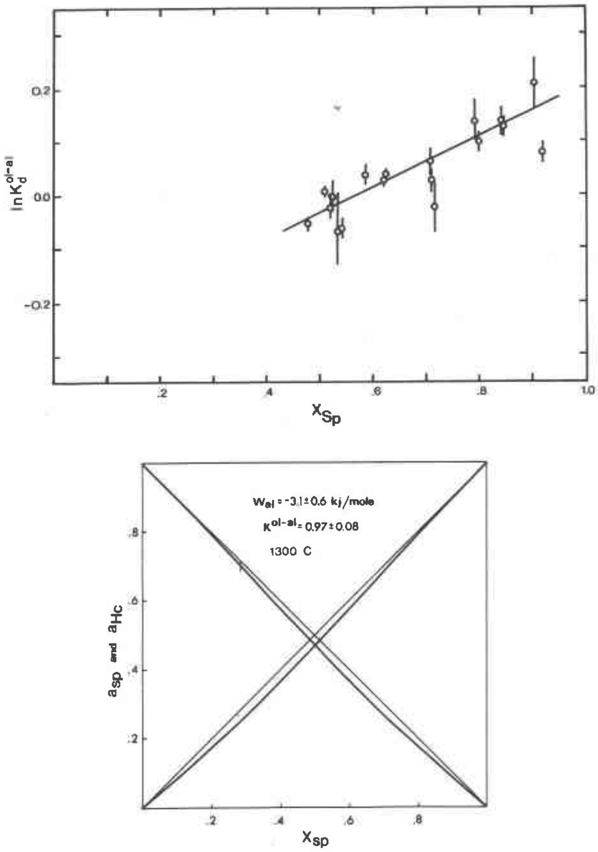

Fig. 2. (a) The variation of ln $K_d^{\text{ol-al}}$ with aluminate spinel composition, and (b) the activity–composition relations for the $MgAl_2O_4$–$FeAl_2O_4$ solid solution at 1300°C, as calculated from equations given in the text. An example of the uncertainty associated with the calculated activity values is shown.

If site occupancies for the $MgFe_2O_4$–Fe_3O_4 solid solution were known, these experimental data might be explained by a simpler model that related cation ordering directly to thermodynamic parameters, possibly involving a discontinuous function of ln K_d with spinel composition.

Effect of non-ideal olivines

If the thermodynamic parameters determined in the procedure described above are recalculated assuming a

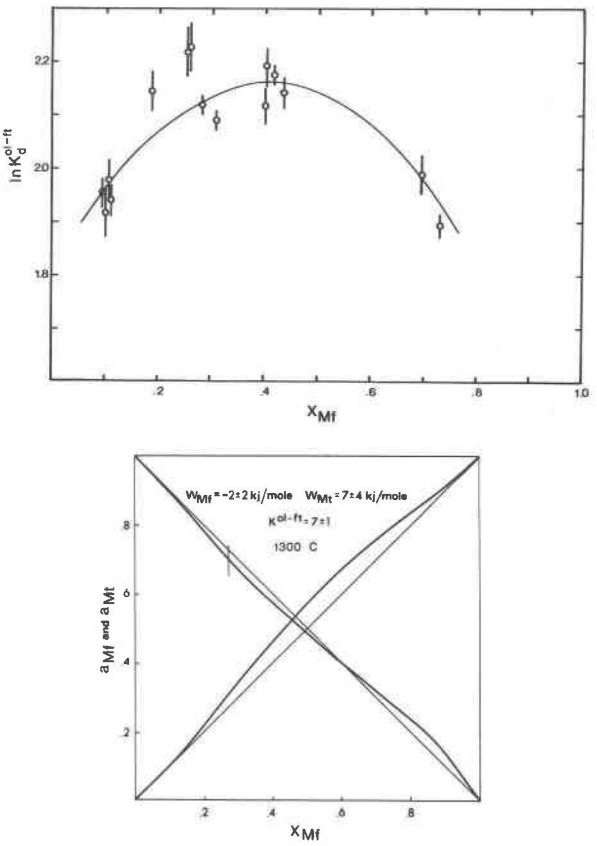

Fig. 3. (a) The variation of ln K_d^{ol-ft} with ferrite spinel composition, and (b) the activity–composiltion relations for the $MgFe_2O_4$–Fe_3O_4 solid solution at 1300°C, as calculated from equations given in the text. An example of the uncertainty associated with the activities is shown.

positive deviation from ideality for the olivine solid solution such that W_{ol} = 4.2 kJ/mole at 1300°C, the changes are very small, as follows: K^{ol-al} remains essentially unchanged at 0.98±0.8 and the aluminates show a very slight positive deviation from ideality with W_{al} = 1.3±0.6 kJ/mole, K^{ol-ft} drops marginally from 7±1 to 6±1 and the degree of asymmetry in the ferrite solid solution is decreased, but the values of the interaction parameters remain unchanged within the uncertainty ranges indicated.

Conclusion

Experiments equilibrating olivine and aluminate spinel, and olivine and ferrite spinel, at 1300°C, define how the distribution of magnesium and ferrous iron between olivine and spinel depends on spinel composition. If aluminum is the only trivalent or B cation in the spinel structure, there is little preferential partitioning of magnesium, relative to Fe^{2+}, between the two phases. The Mg–Fe^{2+} distribution varies slightly and systematically with the Mg/(Mg+Fe^{2+}) of the aluminate, so that if olivines are ideal at 1300°C, the $MgAl_2O_4$–$FeAl_2O_4$ solid solution can be well described as a regular, symmetric solution with a small negative departure from ideality. The equilibrium constant K^{ol-al} is 0.97±0.08 at 1300°C. The free energy of reaction associated with the olivine–aluminate exchange equation (1) is 0±1 kJ/mole. If the B cation in the spinel structure is ferric iron, there is considerable preferential partitioning of Mg, relative to Fe^{2+}, into the olivine structure. This partitioning is highest at intermediate values of Mg/(Mg+Fe^{2+}) and, assuming ideal olivines, the $MgFe_2O_4$–Fe_3O_4 solid solution appears to conform to an asymmetric, regular solution model, with a calculated equilibrium constant K^{ol-ft} of 7±1 and $\Delta G_R^{o\,ol-ft}$ for exchange reaction (2) of −25±2 kJ/mole. These experimentally-determined equilibrium constants can be used to partially calibrate the olivine–spinel geothermometer at high temperatures. The results of Engi (1978) on olivine–chromite and olivine–aluminate exchange reactions contribute to the low-temperature calibration. A reliable value for K^{ol-cr} at high temperatures, the variation of K^{ol-ft} with temperature, and a comprehensive assessment of the thermodynamic mixing properties of complex spinels are needed to complete the calibration of the olivine–spinel geothermometer.

The equilibrium constants for the olivine–ferrite and olivine–aluminate equations can be combined to give K^{al-ft} = 0.14 for the following spinel exchange equation.

$$MgAl_2O_4 + Fe_3O_4 = FeAl_2O_4 + MgFe_2O_4$$

The free energy change for this equation, calculated from the present study, is equal to +25 kJ/mole, compared to +22 kJ/mole calculated from the equation given by Sack (1982). The positive free energy change reflects the strong affinity between magnesium and aluminum, and between ferrous and ferric iron in the spinel structure. This, in part, explains the high aluminum content of spinels which crystallize from basaltic liquids with high Mg/(Mg+Fe^{2+}) (usually at high temperatures), and the more ferric nature of the spinels which crystallize from basaltic liquids with lower values of Mg/(Mg+Fe^{2+}).

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