

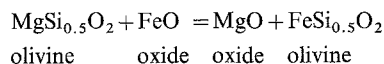
Experimental determination of activities in Fe–Mg olivine at 1400 K

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Received September 20, 1989 / Accepted December 4, 1990

Abstract. The exchange equilibrium



has been used to measure activity-composition relations along the olivine join $\text{FeSi}_{0.5}\text{O}_2 - \text{MgSi}_{0.5}\text{O}_2$ at 1400 K and 1 atm pressure. Equilibrium Fe–Mg partitioning between the two phases was determined by reversing the compositions of olivine coexisting with oxide and metallic iron over the composition range Fo_{23} to Fo_{92} . A detailed study of the thermodynamic properties of the oxide phase has recently been made by Srećec et al. and we have confirmed their results in the composition range of interest. Application of the oxide data to the exchange equilibrium enables the properties of olivine to be determined. Within experimental uncertainty (Fe, Mg) $\text{Si}_{0.5}\text{O}_2$ olivine can, at 1400 K, be treated as a symmetric solution with $W_{\text{Fe-Mg}}^{\text{ol}}$ of 3.7 ± 0.8 kJ/mol. The data permit the presence of only very slight asymmetry in the series. The data do not support recent assertions that olivine is highly non-ideal ($W \approx 10$ kJ/mol) under these conditions.

Introduction

Olivine is an important constituent of many igneous and metamorphic rocks and is, of course, dominant in the upper mantle. It comprises the only $\text{Fe}^{2+} - \text{Mg}^{2+}$ solid solution series that is essentially binary in natural assemblages, generally containing <2% of other substituents. The common occurrence of olivine and its relative compositional simplicity have led to its being used widely in geothermometry and barometry. Although this is particularly true of redox equilibria such as fayalite-magnetite-quartz (FMQ), and olivine-spinel-orthopyroxene, a large number of other pressure-temperature dependent equilibria involving olivine have also been calibrated (e.g. Irvine 1965; O'Neill and Wood 1979; Bohlen et al. 1980;

Frost et al. 1988). Application of these equilibria to rocks requires, at minimum, an understanding of the mixing properties of $(\text{Fe, Mg})_2\text{SiO}_4$ solid solutions. In the ideal case, a complete internally consistent thermodynamic base for all Fe- and Mg-end members of concern would be available.

Measurements of the thermodynamic properties of olivine commenced with heat capacity and enthalpy measurements on forsterite (Torgeson and Sahama 1948; Orr 1953) and has recently been extended through similar measurements on fayalite (Robie et al. 1982) and on $(\text{Fe, Mg})_2\text{SiO}_4$ solid solutions (Wood and Kleppa 1981). There have been numerous efforts to integrate these experimental results into internally consistent data sets (e.g. Helgeson et al. 1978). Some of the most recent are that of Berman (1988), which considers stoichiometric minerals only, and those of Wood (1987) and Sack and Ghiorso (1989) which account for the properties of end-members and solid solutions.

Experiments on Fe–Mg mixing properties in fayalite-forsterite solid solutions have been performed by equilibrating these mixtures with oxides and silicates whose properties are known or are derivable independently. The data of Nafziger and Muan (1967) and Kitayama and Katsura (1968) may be interpreted (Williams 1971) as indicating small positive deviations from the ideal with an activity coefficient for the $\text{FeSi}_{0.5}\text{O}_2$ component given by the symmetric regular solution equation:

$$RT \ln \gamma_{\text{FeSi}_{0.5}\text{O}_2} = W(1 - X_{\text{FeSi}_{0.5}\text{O}_2})^2 \quad (1)$$

where $W = 1.9$ kJ/mol. A more detailed analysis by Williams (1972) of the experimental data has led to his suggestion that olivines are slightly asymmetric with activity coefficients given by:

$$RT \ln \gamma_{\text{FeSi}_{0.5}\text{O}_2} = [W_{\text{Fe}} + 2X_{\text{Fe}}(W_{\text{Mg}} - W_{\text{Fe}})](1 - X_{\text{Fe}})^2 \quad (2a)$$

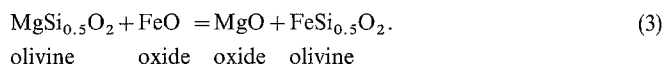
$$RT \ln \gamma_{\text{MgSi}_{0.5}\text{O}_2} = [W_{\text{Mg}} + 2X_{\text{Mg}}(W_{\text{Fe}} - W_{\text{Mg}})](1 - X_{\text{Mg}})^2 \quad (2b)$$

where W_{Fe} and W_{Mg} are temperature dependent and have values of approximately 7.1 and 5.0 kJ/mol, respectively,

at 1200° C. Most recent studies agree with Williams' work, although exact values of the interaction parameters W_{Fe} and W_{Mg} are not well constrained. Wood and Kleppa (1981) showed, for example, that temperature-independent values of W_{Fe} and W_{Mg} of 4.2 and 8.4 kJ/mol respectively would fit all of the enthalpy and activity-composition data. O'Neill and Wall (1987) argued that a symmetric value of 5.0 ± 2.0 kJ/mol is consistent with all of the available data while Wood and Virgo (1989) adopted a symmetric value of 4.2 kJ/mol with an estimated uncertainty of ± 1.25 kJ/mol. Experimental data of O'Neill and Wood (1979), Davidson and Mukhopadhyay (1984) and Kawasaki and Matsui (1983) were fitted by the authors concerned to derive symmetric W values of 4.1, 3.5, and 6.9 kJ/mol respectively, all with small apparent uncertainties.

It is clear that a large number of experimental and theoretical analyses have led to similar conclusions about olivine solid solutions. Deviations from ideality are small and a symmetric model with W of about 5 kJ/mol fits the data. This conclusion has been called into question, however, in a recent study by Sack and Ghiorso (1989) who have attempted to integrate end-member properties and mixing parameters into an internally consistent data base for the system $\text{Mg}_2\text{SiO}_4 - \text{Fe}_2\text{SiO}_4 - \text{SiO}_2$. They consider that the mixing properties of $(\text{Fe}, \text{Mg})\text{Si}_{0.5}\text{O}_2$ olivines are well constrained by the wide range of experimental data available and that this series is much more nonideal than previously believed. Specifically, they give a symmetric mixing parameter, W , of 10.17 ± 0.25 kJ/mol on a one (Mg, Fe) atom basis. This value is so much larger than the others discussed above that it would have a great impact on geothermobarometry involving olivine solid solutions. Taking the olivine-spinel-orthopyroxene oxygen barometer (Mattioli and Wood, 1988) as an example, adoption of the Sack and Ghiorso properties for olivine and orthopyroxene would lower calculated oxygen fugacities for mantle compositions by about 0.7 log units, significantly affecting calculated fluid compositions. Barometers and thermometers with small entropy and volume changes would be even more greatly affected.

In view of the geological importance of olivine solid solutions we have attempted to resolve this question by measurement of activity-composition relations along the Fe–Mg olivine join at 1400 K. The experimental approach involves an investigation of the equilibrium:



We have reversed Fe–Mg partitioning between olivine and oxide phases at 1400 K for assemblages both saturated and slightly undersaturated in metallic iron. We also checked the activity-composition relations in $(\text{Fe}, \text{Mg})_{1-x}\text{O}$ oxide recently measured under these conditions by Srečec et al. (1987). Use of measured oxide properties in conjunction with tight brackets on iron-magnesium partitioning between the two phases enables activity-composition relations on the olivine join to be determined.

Experimental methods

Olivines $(\text{Fe}_x\text{Mg}_{1-x})\text{Si}_{0.5}\text{O}_2$ with $x=0.8, 0.6, 0.4, 0.2$ and 0.0 were the same samples as those used in the calorimetric study of Wood and Kleppa (1981). They were synthesized hydrothermally at 800° C and 1 kbar then ground, pressed into pellets and held for 24 hours at 1150° C and 1 atm pressure at an f_{O_2} slightly above the iron-wustite buffer (IW). Samples with $x=0.50$ and 0.75 were the same as those prepared for the garnet mixing property study of Hackler and Wood (1989). They were synthesized at about 100° C below the olivine solidus at 1 atm and about 0.05 log units below IW. Magnesiowustite (mw) samples $(\text{Fe}_x\text{Mg}_{1-x})\text{O}$ were prepared for x values of 0.25, 0.3, 0.33, 0.5, 0.8, 0.9 and 0.95. They were made from appropriate amounts of analytical grade MgO (from decarbonated magnesium carbonate), Fe_2O_3 and metallic Fe. All mixtures were ground in an agate mortar under acetone and pressed into approximately 1 g pellets with one drop of butyl acetate glue added as a bonding agent. The samples were sintered at 1200° C in a vertical quench furnace for a minimum of four hours then ground, re-pressed and sintered again for a total of either two or three cycles. Oxygen fugacity during sintering was kept approximately midway between the iron-wustite and wustite-magnetite boundaries by flowing a CO/CO_2 gas mixture at 1 cm/sec velocity through the furnace tube. Cycles of sintering and grinding were made until the samples were found, by X-ray diffraction, to be single-phase and well-homogenized. Cell edges were measured and found to be in good agreement with the measurements of Nafziger and Muan (1967).

Oxide, olivine and metallic Fe were mixed in approximately equimolar amounts for the experiments. In order to reverse Fe–Mg partitioning between olivine and oxide, each oxide solid solution was mixed, in separate starting compositions, with olivines estimated to be both more and less iron-rich than the equilibrium value. Initial estimates of equilibrium compositions were made from the unreversed experimental data of Nafziger and Muan (1967).

The first two experiments comprised suspending three small (100 mg) pellets in the hot zone of the vertical furnace. One pellet contained oxide, Fe-rich olivine, and metal, a second contained oxide, Fe-poor olivine and metal, and the third was oxide plus metal alone. Later experiments used mixtures of oxide and metal only or oxide and olivine only in order to check activity-composition relations for the latter two phases. Temperature was measured via a $Pt_{100}/Pt_{90}Rh_{10}$ thermocouple situated adjacent to the samples, while oxygen fugacity was continuously monitored with an yttria-stabilized zirconia electrolyte (from Ceramic Oxide Fabrications Pty, Victoria, Australia) also located next to the samples. Fluctuations on the order of ± 0.04 log units in f_{O_2} were observed. Experiments were performed for 5 days at temperatures close to 1400 K. Oxygen fugacities were controlled by CO/CO_2 gas mixtures passed through the furnace at velocities of about 1 cm/sec. The oxygen fugacity selected for each experiment was that calculated to correspond to equilibrium between the starting oxide composition and metallic iron using the data of Srečec et al. (1987) on

Table 1. Magnesiowustite-iron equilibration at 1400 K

Initial composition	Final composition	Microprobe data		$\log f_{\text{O}_2}$
		FeO	MgO	
$W_0 + \text{Fe(m)}$	$W_{9.6}$	16.00 (0.94)	84.71 (2.64)	–14.27
$W_{25} + \text{Fe(m)}$	$W_{10.0}$	16.87 (0.36)	85.38 (0.89)	–14.27
$W_{30} + \text{Fe(m)}$	$W_{29.1}$	42.51 (0.48)	58.02 (0.41)	–13.55
$W_{80} + \text{Fe(m)}$	$W_{44.3}$	58.45 (1.41)	41.25 (0.77)	–13.34
$W_{25} + \text{Fe(m)}$	$W_{41.7}$	55.88 (1.01)	43.85 (0.86)	–13.34
$W_{80} + \text{Fe(m)}$	$W_{78.0}$	85.17 (0.85)	13.45 (0.11)	–13.05
$W_{29} + \text{Fa}_0 + \text{Fe(m)}$	$W_{30.8}$	45.56 (0.43)	57.38 (0.35)	–13.43

Value in brackets is 1 standard deviation.

Table 2. Results from olivine-magnesiowustite reaction at iron saturation

Initial composition	Weight % data from microprobe				Final composition	$\log f_{\text{O}_2}$	
		Oxide	wt. %	SD			
$\text{W}_{30} + \text{Fa}_{20} + \text{Fe(m)}$	MW phase	FeO	42.17	0.56	$\text{W}_{29} + \text{Fa}_{08} + \text{Fe(m)}$	-13.55	
		MgO	57.88	0.70			
Olivine phase	FeO	7.85	0.28				
	MgO	50.69	0.42				
$\text{W}_{30} + \text{Fa}_0 + \text{Fe(m)}$	MW phase	FeO	41.91	0.32	$\text{W}_{29} + \text{Fa}_{08} + \text{Fe(m)}$		
		MgO	57.89	0.58			
Olivine phase	FeO	7.64	0.25				
	MgO	50.63	0.50				
$\text{W}_{80} + \text{Fa}_{40} + \text{Fe(m)}$	MW phase	FeO	84.94	0.55	$\text{W}_{79} + \text{Fa}_{25} + \text{Fe(m)}$		-13.05
		MgO	13.02	0.23			
Olivine phase	FeO	23.12	0.64				
	MgO	38.46	0.53				
$\text{W}_{80} + \text{Fa}_{20} + \text{Fe(m)}$	MW phase	FeO	84.84	0.38	$\text{W}_{78} + \text{Fa}_{25} + \text{Fe(m)}$		
		MgO	13.53	0.16			
Olivine phase	FeO	23.02	0.66				
	MgO	39.40	0.43				
$\text{W}_{90} + \text{Fa}_{60} + \text{Fe(m)}$	MW phase	FeO	93.65	0.59	$\text{W}_{91} + \text{Fa}_{48} + \text{Fe(m)}$	-12.96	
		MgO	5.12	0.57			
Olivine phase	FeO	40.02	0.69				
	MgO	24.79	0.57				
$\text{W}_{90} + \text{Fa}_{40} + \text{Fe(m)}$	MW phase	FeO	92.00	0.61	$\text{W}_{88} + \text{Fa}_{38} + \text{Fe(m)}$		
		MgO	6.84	0.15			
Olivine phase	FeO	33.41	0.43				
	MgO	30.82	0.41				
$\text{W}_{95} + \text{Fa}_{80} + \text{Fe(m)}$	MW phase	FeO	97.94	0.74	$\text{W}_{98} + \text{Fa}_{77} + \text{Fe(m)}$		-12.89
		MgO	1.41	0.04			
Olivine phase	FeO	57.79	0.63				
	MgO	9.71	0.22				
$\text{W}_{95} + \text{Fa}_{60} + \text{Fe(m)}$	MW phase	FeO	96.82	0.59	$\text{W}_{96} + \text{Fa}_{65} + \text{Fe(m)}$		
		MgO	2.46	0.05			
Olivine phase	FeO	51.10	0.65				
	MgO	15.59	0.25				
$\text{W}_{95} + \text{Fa}_{40} + \text{Fe(m)}$	MW phase	FeO	94.77	0.53	$\text{W}_{93} + \text{Fa}_{52} + \text{Fe(m)}$		
		MgO	3.99	0.09			
Olivine phase	FeO	42.85	0.68				
	MgO	21.99	0.26				

oxide properties and O'Neill (1988) on the f_{O_2} of the iron-wustite buffer. The f_{O_2} was monitored continuously using the electrolyte with air ($f_{\text{O}_2}=0.21$) as a reference and small adjustments made as required during the experiment. This experimental arrangement reproduces the f_{O_2} of the iron-wustite buffer (O'Neill 1988) to within 0.06 log units and as can be seen from Table 2, magnesiowustite compositions did not change substantially and Fe(metal) did not disappear during the experiments. These observations demonstrate that our data are consistent with the results of Srećec et al. (1987) and O'Neill (1988).

Samples were quenched by pulling them to the top of the furnace and allowing them to cool in the reducing gas mixture before removal. The products were then analyzed with the JEOL 733 Superprobe at Northwestern University under the following conditions: accelerating voltage 15 kV; beam current 30 nA. Standards: Fe—synthetic fayalite; Mg, Si—natural forsteritic olivine. Correction program—ZAF.

Results

Magnesiowustite activity-composition relationships

The success of our approach depends, of course, on the accuracy of the microprobe data, but even more critical are the thermodynamic data for the oxide phase. Srećec et al. (1987) report the results of more than 280 emf and gas equilibration measurements made on magnesiowustite solid solutions coexisting with metallic iron in two different laboratories over the temperature range 1050–1573 K. They used the results to derive activity-composition relations for the ternary oxide solid solution $\text{MgO}-\text{FeO}-\text{Fe}_{2/3}\text{O}$ under conditions of iron saturation. We show their derived best-fit curve at 1400 K in Fig. 1, a plot of $(\text{Fe}/\text{Fe}+\text{Mg})$ in magnesiowustite versus $-\Delta \log f_{\text{O}_2}$, the difference in $\log f_{\text{O}_2}$ between iron-magnesiowustite equilibrium and iron-wustite equilibrium. As can also be seen, the earlier data of Hahn and Muan (1962) (at 1373 K) differ slightly from the Srećec et al. curve implying that magnesiowustite is less ideal than was found in the recent study. We must begin, therefore, by considering the reasons for this small discrepancy and its possible implication.

The Hahn and Muan (1962) data lie below the curve of Srećec et al. by about 0.05 mol fraction Fe or about 0.08 log units in f_{O_2} over most of the composition range studied. Hahn and Muan measured the end-member iron-wustite (IW) curve to ± 0.02 log units and quote all experimental oxygen fugacities to 0.01 log units. In our experience, however, fluctuations in f_{O_2} of the order of 0.02–0.04 commonly occur with capillary flow meters so that a cumulative uncertainty of ± 0.05 log units in $\Delta \log f_{\text{O}_2}$ is possible, particularly since Hahn and Muan did not independently measure f_{O_2} in the furnace. Another considerable source of uncertainty lies in the X-ray method used to determine oxide composition. Hahn and Muan synthesized a series of oxides on the $\text{MgO}-\text{FeO}_{1+y}$ join at 1300° C and f_{O_2} slightly above IW and calibrated the (200) spacing as a function of composition. Applying the calibration to their 1100° C products they quote an uncertainty of ± 0.03 mol fraction at high FeO contents and 0.015 mol fraction at low FeO contents. These, combined with the f_{O_2} uncertainties are virtually

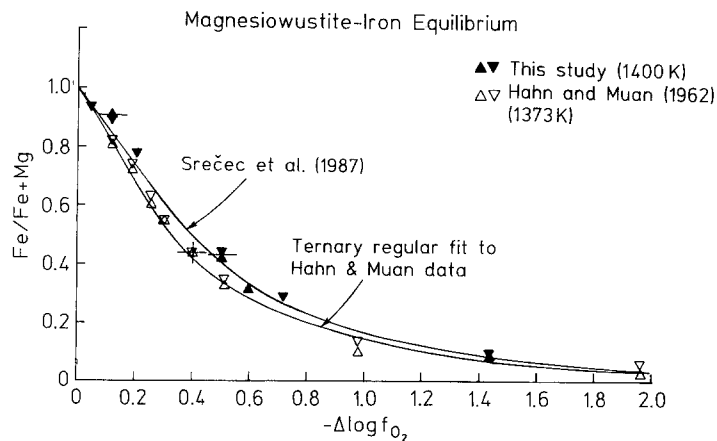


Fig. 1. Plot of the atomic fraction of iron $[n_{\text{Fe}}/(n_{\text{Fe}}+n_{\text{Mg}})]$ in magnesiowustite equilibrated with iron metal vs. $\log_{10}(f_{\text{O}_2}/f_{\text{O}_2}^{\text{IW}})$ where $f_{\text{O}_2}^{\text{IW}}$ is that of iron-wustite equilibrium (IW). Closed symbols are data from this work with arrows indicating direction of approach to equilibrium. Open symbols are data of Hahn and Muan (1962) with arrows as before. Error bars represent cumulative uncertainties in f_{O_2} and composition (see text). Curves are from Srećec et al. (1987) and a ternary fit to the Hahn and Muan data (see text)

sufficient to bring the Hahn and Muan data into agreement with the curve of Srećec et al. (1987) (Fig. 1). There is, however, an additional source of uncertainty in the X-ray method. It is now known that the cell edges of magnesiowustites measured at room temperature depend on the temperature from which the samples are quenched (Biggar 1974). The effect described by Biggar (1974) is sufficient to cause several mole percent error in apparent composition when there is a 100° C or more difference between calibration temperature and unknown sample temperature. In this case 1300° C sintered samples were used to measure 1100° C unknowns. Our initial inclination was, therefore, to accept the data of Srećec et al. (1987), particularly since the results of Berthet and Perrot (1970) are in very good agreement with them. If, for example, we take the Berthet and Perrot value of $W_{\text{Fe-Mg}}^{\text{oxide}}$ at 850° C and calculate the expected value of $\Delta \log f_{\text{O}_2}$ at 1400 K with it, we obtain a curve which is within 0.02 log units in f_{O_2} of that of Srećec et al. (1987). Berthet and Perrot established magnesiowustite-iron equilibrium by determining the oxygen contents of quenched mixtures rather than by measuring composition by an X-ray method.

As a final check on the applicability of the magnesiowustite data of Srećec et al. (1987), we performed measurements of the compositions of magnesiowustite coexisting with iron as a function of f_{O_2} using exactly the same experimental procedures as those used for the olivine-oxide equilibration experiments. Iron-wustite equilibrium was determined to be at $-12.84 \pm 0.03 \log f_{\text{O}_2}$ at 1400 K, a result in good agreement with the O'Neill (1988) value of -12.90 . Reversals at 0.5 and 1.43 log units in f_{O_2} below IW yielded (by microprobe) oxide compositions in excellent agreement with those predicted from the Srećec et al. curve (Fig. 1). Half-reversals at Fe/Fe+Mg of 0.29 and 0.78 were obtained from oxide+iron pellets sintered at the same time as olivine+ox-

Table 3. Results from olivine-magnesiowustite reaction without iron saturation

Initial composition	Weight % data from microprobe			Final composition	$\log f_{O_2}$	
	Oxide	wt. %	SD			
$W_{33} + Fa_0$	MW phase	FeO	45.56	0.43	$W_{31} + Fa_{08}$	-13.43
		MgO	57.38	0.35		
Olivine phase	FeO	8.52	0.37			
	MgO	52.02	0.54			
$W_{95} + Fa_{100}$	MW phase	FeO	96.67	0.66	$W_{97} + Fa_{76}$	
		MgO	1.50	0.03		
	Olivine phase	FeO	57.61	0.59		
		MgO	9.95	0.14		
$W_{95} + Fa_{70}$	MW phase	FeO	96.12	1.02	$W_{96} + Fa_{65}$	-12.74
		MgO	2.53	0.07		
	Olivine phase	FeO	51.75	0.63		
		MgO	15.74	0.23		
$W_{95} + Fa_{50}$	MW phase	FeO	95.86	0.63	$W_{94} + Fa_{57}$	
		MgO	3.41	0.19		
	Olivine phase	FeO	46.74	0.65		
		MgO	19.72	0.35		

ide + iron pellets and, for completeness, several oxide compositions from olivine + oxide + iron experiments are also shown as half-reversals in Fig. 1. It is clear that our results, which have very small uncertainties in Fe/Mg ratio, and uncertainties in $\Delta \log f_{O_2}$ of about 0.05 are in excellent agreement with the Srećec et al. curve and cannot be consistent with the midpoints of the data of Hahn and Muan (1962). The agreement between our results, those of Srećec et al. (1987) and those of Berthet and Perrot (1970) indicates that the Srećec et al. curve is correct to within ± 0.02 – 0.03 log units in f_{O_2} . This enables us to make a reasonable estimate of the uncertainties in the olivine properties derived from our Fe–Mg exchange data. A very conservative uncertainty estimate may be obtained by assuming that the Hahn and Muan data are correct and to that end, we have fitted a solution model to their data (Fig. 1). The propagation of errors in oxide properties into uncertainties in olivine mixing parameters is discussed further.

Olivine-oxide exchange data

The results of between 10 and 20 analyses each on all product oxides and olivines indicate that both phases were well-reacted and essentially homogeneous. The first two experiments contained a pellet of oxide + iron alone, in addition to the olivine + oxide + metallic iron pellets. This was to check that the oxide composition reached the equilibrium value under the temperature and f_{O_2} conditions of the experiment. If equilibrium is achieved, the

oxide should be the same composition in all three pellets (with and without olivine). As can be seen from Table 2, the oxides in all three pellets of the experiments which began with $(Fe_{0.3}Mg_{0.7})O_{1+y}$ and $(Fe_{0.8}Mg_{0.2})O_{1+y}$ are of the same composition within analytical uncertainty. Larger differences were observed between pellets when the starting oxides were more iron-rich, $(Fe_{0.9}Mg_{0.1})O_{1+y}$ and $(Fe_{0.95}Mg_{0.05})O_{1+y}$. In these cases, the products were homogeneous as evinced from the small standard deviations of the microprobe data (Tables 2 and 3), but varied by several mole percent (e.g. from $(Fe_{0.93}Mg_{0.07})O_{1+y}$ to $(Fe_{0.975}Mg_{0.025})O_{1+y}$) in the experiment starting with $(Fe_{0.95}Mg_{0.05})O_{1+y}$. The reason for this is that these experiments were performed essentially at only 0.05 log units below the iron-wustite boundary. Small fluctuations in temperature and f_{O_2} this close to the iron wustite boundary cause the "instantaneous" equilibrium oxide composition to cycle between about $(Fe_{0.92}Mg_{0.08})O_{1+y}$ and $(Fe_{1.0}Mg_{0.0})O_{1+y}$. Thus, the small compositional differences observed in different pellets are, within experimental uncertainty, acceptable under f_{O_2} conditions very close to the iron-wustite boundary.

Our first series of experiments (Table 2), produced data which have been criticised as not being "normal" reversals because in several cases the oxide and olivine phases both became depleted in iron as the metal acted as a sink. In these cases, however, the olivine-oxide Fe–Mg partitioning converged from high and low values of K_D to essentially the same value and the oxide composition was the same in the pellets with olivine and those without olivine (Tables 1 and 2). It is very difficult

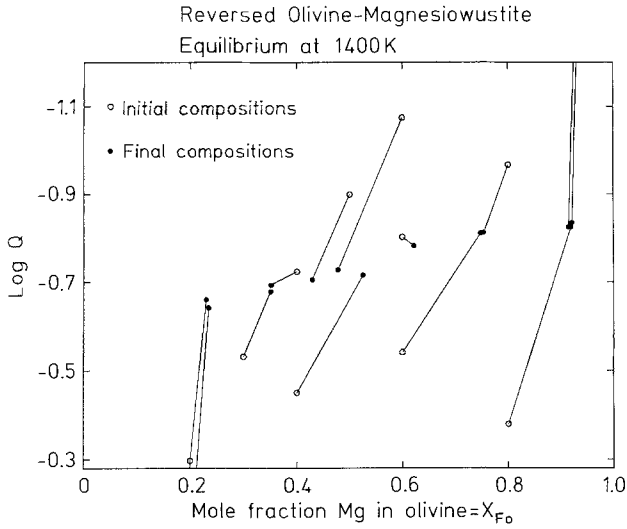


Fig. 2. Plot of $\log_{10} Q$ [$Q = \frac{a_{\text{MgO}}^{\text{oxide}} \cdot X_{\text{Fay}}^{\text{ol}}}{a_{\text{FeO}}^{\text{oxide}} \cdot X_{\text{Fo}}^{\text{ol}}}$] vs. mole fraction $\text{MgSi}_{0.5}\text{O}_2$ in olivine. Approach toward equilibrium is shown by lines connecting the *open symbols* (starting compositions) to the *closed symbols* (final compositions)

under these circumstances to argue that the three phases olivine, oxide and metal are not extremely close to equilibrium. As an additional test, however, we duplicated several experiments without Fe metal and performed them at about 0.1 log units in f_{O_2} above Fe-saturation (Table 3) to ensure that the $\text{Fe}_{2/3}\text{O}$ content of the magnesiowustite was essentially the same as at iron-saturation. The four data (Table 3, Fig. 2) are in perfect agreement with the experiments performed at Fe-saturation and provide “normal” brackets of Fe–Mg partitioning at low and high Fe/Fe + Mg ratios in olivine (0.08 and 0.65 approximately).

Treatment of data

The condition of equilibrium between oxide and olivine, as derived from Eq. 3 is:

$$\Delta G_{(3)}^0 = -RT \ln \left[\frac{a_{\text{MgO}}^{\text{mw}} a_{\text{FeSi}_{0.5}\text{O}_2}^{\text{ol}}}{a_{\text{FeO}}^{\text{mw}} a_{\text{MgSi}_{0.5}\text{O}_2}^{\text{ol}}} \right]. \quad (4)$$

We have confirmed Srećec et al.’s (1987) measurement of the activity-composition relations in $\text{MgO} - \text{FeO} - \text{Fe}_{2/3}\text{O}$ magnesiowustite solid solutions at 1400 K and 1 atm pressure in equilibrium with metallic iron. We can thus rearrange Eq. 4 as follows:

$$\begin{aligned} \frac{\Delta G_{(3)}^0}{2.303RT} &= -\log \left[\frac{a_{\text{MgO}}^{\text{mw}} X_{\text{Fay}}^{\text{ol}}}{a_{\text{FeO}}^{\text{mw}} X_{\text{Fo}}^{\text{ol}}} \right] - \log \gamma_{\text{Fay}}^{\text{ol}} + \log \gamma_{\text{Fo}}^{\text{ol}} \\ &= -\log Q - \log \gamma_{\text{Fay}}^{\text{ol}} + \log \gamma_{\text{Fo}}^{\text{ol}} \end{aligned} \quad (5)$$

where Fay and Fo are used as abbreviations for $\text{FeSi}_{0.5}\text{O}_2$ and $\text{MgSi}_{0.5}\text{O}_2$ components, respectively. Differentiating Eq. 5 at constant temperature and applying the Gibbs-Duhem equation we obtain:

$$d \log \gamma_{\text{Fay}}^{\text{ol}} = -X_{\text{Fo}}^{\text{ol}} d \log Q. \quad (6)$$

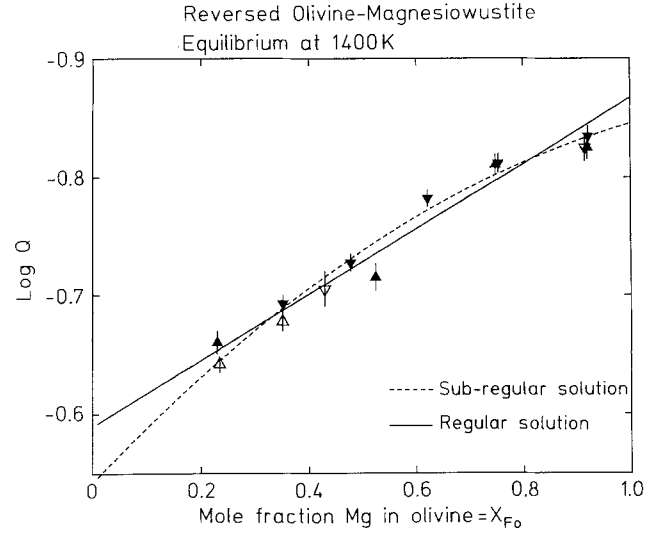


Fig. 3. Plot of $\log_{10} Q$ vs. mole fraction $\text{MgSi}_{0.5}\text{O}_2$ in olivine. Approach toward equilibrium is shown schematically. *Closed symbols* represent products equilibrated with metallic iron; *open symbols* represent products equilibrated without metallic iron. The *solid line* represents a regular solution fit to the data, yielding the symmetric interaction parameter $W_{\text{Fe-Mg}}^{\text{ol}} = 3.72$ kJ/mol. The *dashed line* is a sub-regular fit to the data, with the asymmetric parameters $W_{\text{Fe}} = 3.26 \pm 1.67$ kJ/mol and $W_{\text{Mg}} = 4.87 \pm 1.27$ kJ/mol. *Error bars* represent 2 standard errors in $\log_{10} Q$. Uncertainty in X_{Fo} is smaller than the width of each error bar

Integration by parts leads to:

$$\log \gamma_{\text{Fay}}^{\text{ol}} = -X_{\text{Fo}}^{\text{ol}} \log Q + \int_0^{X_{\text{Fo}}^{\text{ol}}} \log Q dX_{\text{Fo}}^{\text{ol}}. \quad (7)$$

Similarly for the $\text{MgSi}_{0.5}\text{O}_2$ component we obtain:

$$\log \gamma_{\text{Fo}}^{\text{ol}} = \log Q (1 - X_{\text{Fo}}^{\text{ol}}) + \int_1^{X_{\text{Fo}}^{\text{ol}}} \log Q dX_{\text{Fo}}^{\text{ol}}. \quad (8)$$

Q may be obtained from the compositions of coexisting olivine and oxide using the activity-composition relations for the latter phase of Srećec et al. (1987). The integrals on the right-hand side of Eqs. 7 and 8 were obtained graphically from a plot of $\log Q$ against $X_{\text{Fo}}^{\text{ol}}$ such as those shown in Figs. 2 and 3. Figure 2 shows the actual compositional changes towards equilibrium in $\log Q$ -composition space while Fig. 3 shows schematic approach, with either upward-pointing or downward-pointing arrows. In Fig. 3, open symbols represent product compositions reacted in the absence of metallic iron, whereas solid symbols show product compositions reacted with metallic iron present.

Assigning uncertainties of ± 2 standard errors to each of the experimentally-derived values of $\log Q$, maximum and minimum possible values of $\log \gamma_{\text{Fo}}^{\text{ol}}$ and $\log \gamma_{\text{Fay}}^{\text{ol}}$ were obtained by connecting the experimental points in such a way as to give maximum and minimum values of $d \log Q / dX_{\text{Fo}}^{\text{ol}}$. Thus we obtain the activities of $\text{FeSi}_{0.5}\text{O}_2$ and $\text{MgSi}_{0.5}\text{O}_2$ component shown in Fig. 4.

There are two straightforward ways to compare the activity-composition data with regular and subregular

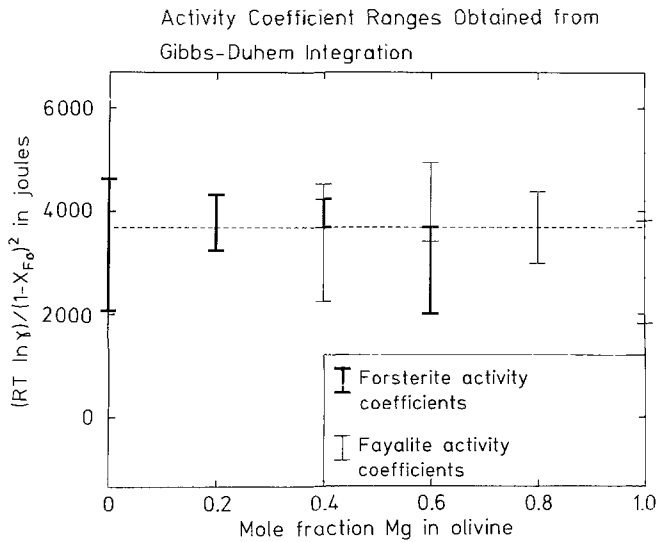


Fig. 4. Plot of the range of values for $2.303 RT \log_{10} \gamma_{Fe}^{ol}/(1-X_{Fe})^2$ (**bold strikes**) and $2.303 RT \log_{10} \gamma_{Mg}^{ol}/(1-X_{Mg})^2$ (**thin strikes**) vs. mole fraction of forsterite in olivine. The zone delineated as the **dashed line** is the allowed range of regular solution fit parameters. It is about 10 J wide. A value for symmetric W_{Fe-Mg}^{ol} of 3.68 ± 0.001 kJ/mol (ignoring uncertainties in oxide properties) is calculated. The permitted asymmetry in this plot is from $W_{Fe} = 2.63$ and $W_{Mg} = 4.63$ kJ/mol to $W_{Fe} = 3.73$ and $W_{Mg} = 3.65$ kJ/mol

models. One is to rearrange Eq. 4, substituting either (1) regular, or (2) subregular models for the activity coefficients of $FeSi_{0.5}O_2$ and $MgSi_{0.5}O_2$ components. In the former (regular) case, $\log Q$ should be a linear function of X_{Fe}^{ol} and a best fit line gives (ignoring uncertainties in oxide properties) a W_{Fe-Mg}^{ol} of 3.72 ± 0.22 kJ/mol. The linear fit misses two of the data points on the wrong side, however, implying slight asymmetry in the solid solution. In the subregular model, $\log Q$ is a quadratic function of X_{Fe}^{ol} and Fig. 3 shows a tightly constrained quadratic which yields $W_{Fe} = 3.26 \pm 1.67$ kJ/mol and $W_{Mg} = 4.87 \pm 1.27$ kJ/mol. As can be seen, the data constrain well the magnitude of W and the extent of asymmetry in the solution.

An alternate method which gives slightly smaller apparent uncertainties involves plotting $2.303 RT \log \gamma/(1-X)^2$ versus mole fraction as in Fig. 4. If the solid solution is regular, $2.303 RT \log \gamma/(1-X)^2$ should be constant and the same for both components. As can be seen from Fig. 4, a small range of regular solution parameters provide acceptable fits to the data, giving W_{Fe-Mg}^{ol} of 3.68 kJ/mol. The acceptable extent of asymmetry is from $W_{Fe} = 2.63$ and $W_{Mg} = 4.63$ kJ/mol to $W_{Fe} = 3.73$ and $W_{Mg} = 3.65$ kJ/mol. These results and conclusions are in excellent agreement with the earlier experimental data of Nafziger and Muan (1967) and Kitayama and Katsura (1968) and the summary of Williams (1972), but disagree markedly with the conclusions of Sack and Ghiorso (1989) who argue for a value of W_{Fe-Mg}^{ol} of 10.17 ± 0.25 kJ.

Apart from the analytical uncertainties and uncertainties in the Gibbs-Duhem integrations which are discussed above, errors in the derived values of olivine properties accrue from errors in the assumed mixing properties of the magnesiowustite phase. These may be assessed

by assigning uncertainties to the $f_{O_2} - X_{FeO}^{mw}$ curve of Srećec et al. (1987) for magnesiowustite-iron equilibrium. The latter was derived almost entirely from emf measurements relative to the iron wustite buffer, and has extremely small formal uncertainties ($\ll 0.01 \log f_{O_2}$ units) which would contribute negligibly to uncertainties in W_{Fe-Mg}^{ol} . A reasonable upper bound to the uncertainties in Srećec et al.'s curve is however, provided by its comparison with our reversal data and the experiments of Berthet and Perrot (1970). These imply, as discussed earlier, that the Srećec et al. $\log f_{O_2} - X_{FeO}^{mw}$ curve is correct to within $\pm 0.02 - 0.03 \log f_{O_2}$ units at low FeO contents of magnesiowustite. Applying this uncertainty, with the constraint that $\Delta \log f_{O_2}$ relative to IW must approach 0.00 at the pure Fe-end of the series, yields an accrued uncertainty in W_{Fe-Mg}^{ol} of approximately ± 0.8 kJ/mol, i.e. W_{Fe-Mg}^{ol} of 3.7 ± 0.8 kJ/mol. If, on the other hand, we make the extremely conservative assumption that the Hahn and Muan (1962) data are correct and all the other results wrong, then the former may be fitted with a ternary regular solution, as shown in Fig. 1 and W_{Fe-Mg}^{ol} re-derived as before. This procedure yields a best-fit value of W_{Fe-Mg}^{ol} which is 1.54 kJ/mol larger than that obtained from the Srećec et al. data, i.e. 5.26 kJ/mol. There appears to be no plausible way in which W_{Fe-Mg}^{ol} values substantially greater than 5 kJ/mol can be obtained.

Our results indicate that $(Mg, Fe)Si_{0.5}O_2$ olivines may be treated, at 1400 K, as symmetric solutions with W_{Fe-Mg}^{ol} of 3.7 ± 0.8 kJ/mol. Although this result should be adequate for most petrologic purposes, small extents of asymmetry are permitted by the data, and Fig. 4 yields, in this case, $(W_{Mg}^{ol} - W_{Fe}^{ol})$ of -0.1 to $+2.0$ kJ/mol.

Acknowledgements. We wish to thank Johannes Nell, Taras Bryndzia and Roderick Hackler for their useful comments during this project. We also thank Kara McGuirk and Huang Zhixin for their contributions in the laboratory. This project was initiated with support from NSF at Northwestern and completed with a grant from NERC at Bristol.

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Editorial responsibility: I.S.E. Carmichael