An experimental study of Fe-Mg partitioning between olivine and orthopyroxene at 1173, 1273 and 1423 K and 1.6 GPa

Volker von Seckendorff and Hugh St.C. O'Neill

Bayerisches Geoinstitut, Universität Bayreuth, Postfach 10 12 51, W-8580 Bayreuth, Federal Republic of Germany

Abstract. The partitioning of Mg and Fe^{2+} between coexisting olivines and orthopyroxenes in the system MgO-FeO-SiO_2 has been investigated experimentally at 1173, 1273, 1423 K and 1.6 GPa over the whole range of Mg/Fe ratios. The use of barium borosilicate as a flux to promote grain growth, and the identification by back-scattered electron imaging of resulting growth rims suitable for analysis by electron microprobe, results in coexisting olivine and orthopyroxenene compositions determined to a precision of ± 0.003 to 0.004 in molar Fe/(Mg + Fe). Quasi-reversal experiments were performed starting with Mg-rich olivine and Fe-rich orthopyroxene (low K_D) and vice versa (high K_D), which produced indistinguishable results. The distribution coefficient, K_D, depends on composition and on temperature, but near Fe/(Mg + Fe) = 0.1 (i.e. mantle compositions) these effects cancel out, and K_D is insensitive to temperature. The results agree well with previous experimental investigations, and constrain the thermodynamic mixing properties of Mg $-$ Fe olivine solid solutions to show small near-symmetric deviations from ideality, with $W_{G_{Mg-Fe}^{ol}}$ between 2000 and 8000 J/mol. Multiple non-linear least squares regression of all data gave a best fit with $W_{G_{Mg-Fe}^{ol}}$ = 5625 ± 574 J/mol (implying 5450 J/mol at 1 bar) and $W_{G_{Mg-Fe}^{opx}}$ = 2145 ± 614 J/mol, but the two W_G parameters are so highly correlated with each other that our data are almost equally well fit with $W_{G_{Mg-Fe}^{ol}}$ = 3700 ± 800 J/mol, as obtained by Wiser and Wood. This value implies $W_{G_{Mg-Fe}^{opx}}$ = 280 ± 900 J/mol, apparently independent of temperature. Our experimental results are not compatible with the assessment of olivine-orthopyroxene equilibria of Sack and Ghiorso.

Introduction

The free energies involved in element partitioning reactions are typically small. For the partitioning of Mg and Fe^{2+} between co-existing ferromagnesian oxides and silicates they are of the order of a few kilojoules per mole of (Mg + Fe^{2+}). It is therefore usually not possible to predict such reactions from available thermochemical data, because these data are not accurate enough. The corollary of this is that the experimental study of partitioning reactions under controlled conditions can yield tight constraints on the thermochemical data, that is, both the standard state data for the end-members, as well as activity-composition relations. Here we report a new experimental investigation of the partitioning of Mg and Fe^{2+} between olivine and orthopyroxene in the system MgO-FeO-SiO_2.

Although the experimental data on Mg $-$ Fe olivine-orthopyroxene equilibria is relatively consistent (see Table 1 for a list of previous studies), recent attempts to extract activity-composition relations from these data have resulted in considerable disagreement. O'Neill and Wall (1987) reviewed a variety of data on activity-composition relations in Mg $-$ Fe olivines and concluded that virtually all were compatible with a simple regular solution model, with the regular solution interaction parameter $W_{G_{Mg-Fe}^{ol}}$ = 5000 J/mol (one atom basis). They estimated a probable uncertainty of ± 2000 J/mol. Since then, Wiser and Wood (1991) have determined the activity-composition relations in Mg $-$ Fe olivines from the exchange of Mg and Fe between olivine and co-existing magnesiowüstite solid solution with excess Fe metal, at 1400 K. Combined with the activity-composition relations for the magnesiowüstite solution in equilibrium with Fe metal determined by Srečeč et al. (1989), Wiser and Wood (1991) found $W_{G_{Mg-Fe}^{ol}}$ = 3700 ± 800 J/mol. While this value is compatible with the O'Neill and Wall (1987) appraisal, it is significantly less than the $W_{G_{Mg-Fe}^{ol}}$ = 10170 ± 250 J/mol suggested by Sack and Ghiorso (1989) from an assessment of the olivine-orthopyroxene partitioning data, mostly from naturally occurring mineral pairs. Most recently, Koch-Müller et al. (1992) reported results from new experiments on the partitioning of Mg and Fe between olivine and orthopyroxene at 1073, 1173 and 1273 K and 0.5 $-$ 1.5 GPa (including several experiments in the three phase field olivine + orthopyroxene + quartz at known pressure, which provide extra constraints on the

---

Correspondence to: V. von Seckendorff

Table 1. Compilation of previous experiments on olivine-orthopyroxene in the system $MgO-FeO-SiO_2$

| Author	T [K]	P [MPa]	Range X_{Fe}^{ol}	Analytical method
Nafziger and Muan (1967)	1473	0.1	0.0–0.6	XRD[b], Gas composition
Kitayama and Katsura (1968)	1477	0.1	0.0–0.5	XRD
Larimer (1968)	1573	0.1	0.0–0.2	EPMA[b]
Medaris (1969)[a]	1023	0.5	0.0–0.8	XRD
	1123	0.5	0.1–0.7	
Matsui and Nishizawa (1974)	1273	3000	0.0–0.7	EPMA
	1273	0.1	0.0–0.2	XRD, EPMA
Bohlen and Boettcher (1981)	1073	500–1000	0.92–0.93	XRD, EPMA
	1173	640–1100	0.92–0.97	
	1273	830–1240	0.91–0.96	
Fonarev (1981)	973	490	0.1–0.9	XRD
	1023	490–880	0.1–1.0	
	1073	98–490	0.1–0.9	
	1123	98–490	0.1–0.9	
Koch-Müller et al. (1992)	1073	500–1100	0.8–1.0	XRD, EPMA
	1173	500–1200	0.1–1.0	
	1273	500–1300	0.1–1.0	
Jamieson et al. (1992)	1573	1000	0.45–0.66	EPMA
	1623	1000	0.37–0.71	
	1673	1000	0.37–0.44	
	1723	0.1, 1000	0.16–0.33	

[a] Flux: H_2O, (Mg, Fe) Cl_2, Oxalate
[b] XRD: X-Ray diffraction; EPMA: electron microprobe analysis

mixing properties of olivine and orthopyroxene from the displacement of the fayalite-ferrosilite-quartz univariant equilibrium). Most of the experiments of Koch-Müller et al. (1992) were at the Fe-rich side of the system, but where there is compositional overlap, their results agree well with previous work. Combining their data with the previous data in the temperature range 1073 to 1273 K (see Table 1), they obtained, by non-linear least squares regression, $W_{G_{Mg-Fe}^{ol}} = 7120 \pm 1800$ J/mol and $W_{G_{Mg-Fe}^{ol}} = 3420 \pm 2000$ J/mol. Clearly there remains a disconcerting spread in inferred olivine and orthopyroxene mixing properties, which has prompted us to look again at this problem. We believe that another study of olivine and orthopyroxene Mg $-$ Fe partitioning is worthwhile and opportune because of two recent innovations in experimental method, which allow significantly greater accuracy to be achieved: firstly, the availability of back-scattered electron imaging in selecting areas for analysis by electron microprobe; and secondly, the use of a suitable flux to promote growth of relatively large, homogenous crystals.

Thermodynamic background

The partitioning of Mg and Fe between coexisting olivine and orthopyroxene may be represented by the reaction:

$$\frac{1}{2}Mg_2SiO_4 + \frac{1}{2}Fe_2Si_2O_6 = \frac{1}{2}Fe_2SiO_4 + \frac{1}{2}Mg_2Si_2O_6 \qquad (1)$$
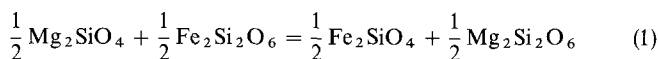
At equilibrium the free energy of the partitioning reaction, $\Delta G_{(T,P)}^{\circ}$, is related to the equilibrium constant $K_{(T,P)}$ by

$$RT\ln K_{(T,P)} = -\Delta G_{(T,P)}^{\circ} = -\Delta H_{(T,1)}^{\circ}$$
$$+ \Delta S_{(T,1)}^{\circ} \cdot T - \int_1^P \Delta V_{(T,P)}^{\circ} \cdot dP \qquad (2)$$

where $K_{(T,P)}$ is given by

$$K_{(T,P)} = \frac{(a_{Fe_2SiO_4}^{ol})^{1/2} (a_{Mg_2Si_2O_6}^{opx})^{1/2}}{(a_{Mg_2SiO_4}^{ol})^{1/2} (a_{Fe_2Si_2O_6}^{opx})^{1/2}} \qquad (3)$$

a_i^ϕ refers to the activity of component i in phase ϕ, which is related to the mole fraction X_i^ϕ by introducing the activity coefficient γ_i^ϕ such that

$$a_i^\phi = (X_i^\phi \cdot \gamma_i^\phi)^v \qquad (4)$$

where v is the number of structural sites per formula unit on which Mg and Fe mix–i.e. $v = 2$ for both olivine and orthopyroxene.

In both the olivine and the orthopyroxene structures, Mg and Fe^{2+} are distributed over two crystallographically distinct octahedrally coordinated sites, M1 and M2. Because these sites differ in geometry and size, some temperature-dependent ordering of Mg and Fe^{2+} between these sites may in principle be expected. In Mg $-$ Fe^{2+} olivines the ordering is so slight that it may be neglected (e.g. Ottonello et al. 1990). In contrast, ordering in Mg $-$ Fe^{2+} orthopyroxenes is substantial (e.g. Virgo and Hafner [1969]). There has been considerable speculation as to the relationship between such ordering and the macroscopic thermochemical mixing properties, which are the quantities of interest here. At present, such speculations suffer from neither the ordering nor the mixing properties being known with the necessary accuracy. For instance, most investigations on the ordering in Mg $-$ Fe^{2+} orthopyroxenes have used [57]Fe Mössbauer spectroscopy, but without any correction for the recoil-free fraction effect, resulting in systematic error (Seifert 1989). We therefore believe that any attempt at incorporating the possible effects of order/disorder into a solution model for Mg $-$ Fe^{2+} orthopyroxenes is premature. Instead, we aim for an empirical description of the mixing properties, with the hope that these may subsequently be matched with accurate order/disorder measurements in the development of a comprehensive mixing model. In using Eq. (4), we note that the effects of order/disorder will be subsumed into the γ term, which accordingly might show compositional and temperature dependences that appear anomalous when compared to simpler solid solutions without order/disorder. If so, this is a matter which needs to be established by experimental measurement, and we will initially employ, for both olivine and

orthopyroxene, the simplest empirical form for describing deviations from ideal mixing in binary solid solutions, namely the regular solution model (Thompson 1967), such that:

$$RT\ln\gamma_{Mg}^{ol} = (1 - X_{Mg}^{ol})^2 \cdot W_{G_{Mg-Fe}^{ol}} \tag{5}$$

and likewise for the other components.

The distribution coefficient K_D is defined as:

$$K_D = \frac{X_{Fe}^{ol} \cdot X_{Mg}^{opx}}{X_{Mg}^{ol} \cdot X_{Fe}^{opx}} \tag{6}$$

where $X_{Mg}^{\phi} = \left[\dfrac{n_{Mg}}{n_{Mg} + n_{Fe}} \right]_{\phi}$, and ϕ refers to either olivine or orthopyroxene.

Combining Eqs. (2) to (6) produces:

$$RT \cdot \ln K_D = -\Delta H_{(T,1)}^{\circ} + \Delta S_{(T,1)}^{\circ} \cdot T - \int_1^P \Delta V_{(T,P)}^{\circ} \cdot dP$$
$$+ (1 - 2 \cdot X_{Mg}^{ol}) \cdot W_{G_{Mg-Fe}^{ol}} - (1 - 2 \cdot X_{Mg}^{opx}) \cdot W_{G_{Mg-Fe}^{opx}} \tag{7}$$

The interaction parameter W may further be elaborated as function of temperature and pressure (Thompson 1967):

$$W_{G_i^{\phi}} = W_{H_i^{\phi}} - T \cdot W_{S_i^{\phi}} + P \cdot W_{V_i^{\phi}} \tag{8}$$

We take $W_{V_{Mg-Fe}^{ol}} = 108$ J/GPa from the excess molar volumes measured at 298 K and ambient pressure by Schwab and Küstner (1977). This value is small enough that little accuracy would be lost, were it to be ignored. $W_{V_{Mg-Fe}^{opx}} = 0$ (Turnock et al. 1973; Koch-Müller et al. 1992), although we note that excess volumes in orthopyroxenes depend on the state of order (e.g. Chatillon-Collinet et al. 1983).

Experimental

Olivine and orthopyroxene compositions were prepared by intimately grinding together pure (> 99.9%) MgO, Fe_2O_3 and SiO_2. The mixes were reacted to olivine, olivine plus silica, or pyroxene in a vertical tube furnace with fO_2 controlled using a mixture of CO and CO_2 at the ratio 4:1. Synthesis temperatures were chosen according to composition between 1673 K (Mg-rich) and 1373 K (Fe-rich). For quenching the samples were cooled down to 1073 K and dropped onto dry ice while still under the CO-CO_2 atmosphere. If necessary the starting materials were reground and rerun several times until homogeneity was achieved, with total run times between 48 h and 10 days. Fe-rich orthopyroxenes are not stable at atmospheric pressure, and therefore all orthopyroxene compositions were further reacted at 1273 K and about 2 GPa for approximately 24 hours in the piston-cylinder apparatus, using graphite capsules.

High pressure experiments were performed in a conventional 3/4″ piston-cylinder apparatus (Boyd and England 1960). Olivine-orthopyroxene K_D is relatively insensitive to pressure, so the precise control of pressure is not the most important of experimental considerations. We therefore used the traditional talc-pyrex pressure cell, which consisted of concentric tubes of talc (outermost) and borosilicate glass, and a tapered graphite heater (innermost) with top and bottom plugs of crushable alumina. The tapering is to minimize temperature gradients (Kushiro 1976). The capsules, made of high purity graphite, were placed between cylinders of soft fired (1173 K) pyrophyllite which fitted tightly into a soft fired pyrophyllite sleeve. This avoided any contamination from the injection of the crushable alumina through cracks in the graphite, which occurred in some preliminary runs, presumably during the initial pressurization of the cell.

For starting mixtures synthesized olivines and orthopyroxenes were ground together and mixed with BaO-B_2O_3 flux (78 wt.% BaO, 22 wt.% B_2O_3; Hauptmann et al. 1973; Linares 1962) in different ratios (opx : ol : flux), according to the run temperature and the bulk composition. Compositions were selected to obtain a fairly even density of data over the entire range of Fe/Mg ratios, starting with both Mg-rich olivine and Mg-poor pyroxene, and vice versa,

corresponding to quasi-reversals. BaO-B_2O_3 was chosen as a flux for the following reasons: (1) Ba and B are not incorporated into olivine or orthopyroxene in the system MgO-FeO-SiO_2, at anything more than trace (ppm) levels, (2) olivine and orthopyroxene can coexist with BaO-B_2O_3 over the whole compositional range of Mg/Fe ratios, (3) stability of the flux over a wide range of fO_2 (4) low melting temperatures of the flux in the system BaO-B_2O_3-MgO-FeO-SiO_2 for the chosen ratio BaO : B_2O_3 (1073–1173 K for BaO-B_2O_3-SiO_2; Levin et al. 1964), compared with basalt, for example, and (5) the flux is not volatile and can therefore also be used for experiments at atmospheric pressure, in a gas mixing furnace. The starting mixtures were pressed to pellets before inserting them into the graphite capsules. The experiments were done using the "piston-in" method. The runs were pressurized to 0.7 GPa, heated to the final temperature while pressurizing to the final pressure of 1.6 GPa (2 GPa nominal). Temperature was measured and controlled with a $Pt/Pt_{90}Rh_{10}$ thermocouple. No corrections have been made for pressure effects on the thermocouple emf, but apart from this, the accuracy of temperature measurement is reckoned to be ± 5 K. Pressure was calibrated using the equilibria albite-jadeite-quartz (Holland 1980), ferrosilite-fayalite-quartz (Bohlen et al. 1980), and the polymorphic transitions in $CaGeO_3$ and Mg_2GeO_4 (Ross et al. 1986; Ross and Navrotsky 1987). We obtained a friction correction of $-20 \pm 2\%$ of applied nominal pressure for piston-in conditions.

The products of both synthesis runs and final reversal experiments were mounted in epoxy, polished and analyzed for Mg, Si, Fe, Ba on a CAMECA SX50 electron microprobe in the wavelength dispersive (WDS) method using synthetic forsterite, Fe metal, andradite and $BaSO_4$ as standards. The use of Fe metal as a standard was checked by analyzing synthetic fayalite, with satisfactory results. We also checked each run for Ca, Ti, Mn and Al in case of contamination. Except for some initial runs (identified in Table 2) which contained small amounts of Al_2O_3 in the orthopyroxene (from our use, at first, of 99.5% SiO_2), these elements were below the level of detection. Points for analysis were selected using a back-scattered electron image. Beam conditions were 15 kV and 15 nA. Counting times were 20 s on the peak and 10 s on each side of the background. For each run, 15 points on both olivine and orthopyroxene rims were analyzed if possible, and additionally 3 points for the flux. The analyses totalled between 97 and 100 wt.%. For each analysis the molar ratio N_{Mg}/N_{Fe} was calculated, and these were used to obtain the mean and standard deviation of composition for each phase.

The starting materials were homogenous with standard deviations of 0.1 to 1.2 mol-% for olivines and 0.5 to 2.8 mol-% for orthopyroxenes. Mössbauer spectroscopy of some representative orthopyroxene starting materials showed Fe^{3+}-contents to be less than the detection limit (i.e. $Fe^{3+}/(Fe^{3+} + Fe^{2+}) < 0.02$).

Run products consisted of euhedral to subhedral, approximately equidimensional grains of olivine plus orthopyroxene, set in a matrix of BaO-B_2O_3-MgO-FeO-SiO_2 glass. The crystal sizes at the end of the runs (typically 68 h at 1173 K, 48 h at 1273 K, 22 h at 1423 K) varied between 10 and 50 μm. The crystals consist of a small core of the starting composition (5 to 20 μm) and of growth rims of the equilibrium compositions (5 to 30 μm). Mg-rich compositions tend to show smaller crystal sizes and less well defined crystal outlines, and consequently tended to have smaller growth rims. This probably reflects slower growth rate and homogenization of the Mg-rich solid solutions, consistent with the decrease in Mg-Fe interdiffusion coefficients with increasing Mg content shown by both olivine and orthopyroxene (Morioka and Nagasawa 1991; Wilson 1982). Medaris (1969) also observed more sluggish kinetics for the Mg-rich compositions. We attempted to improve accuracy in two Mg-rich runs (13/2 and 1/5) by re-grinding and re-running the product of the first stage, but found that this had only a minor effect on the standard deviations of the final product.

The compositions of the analyzed growth rims of olivine and orthopyroxene are generally very homogenous: the means of all standard deviations are 0.25 mol% at 1423 K, 0.35 mol% at 1273 K and 0.41 mol% at 1173 K. Compositions of coexisting olivine and orthopyroxene are presented in Table 2 and Fig. 1.

Table 2. Run conditions and microprobe analyses of starting materials and run products. Numbers in parentheses are 1σ standard deviations for the average of the given N measurements

| 1173 K, 1.6 GPa | | starting | | final | | | | | | | |
Run	Time [h]	X_{Fe}^{ol}	X_{Fe}^{opx}	X_{Fe}^{ol}	N^{ol}	X_{Fe}^{opx}	N^{opx}	K_D	1σ	$\ln K_D$	1σ
41	65	0.000	0.109	0.053 (2)	15	0.051 (3)	15	1.0563	0.0764	0.0548	0.0723
42	98	0.198	0.000	0.071 (5)	15	0.062 (4)	15	1.1612	0.1167	0.1495	0.1005
46	67	0.099	0.215	0.169 (3)	15	0.146 (4)	15	1.1834	0.0416	0.1684	0.0352
44	68	0.198	0.308	0.287 (3)	15	0.230 (4)	15	1.3482	0.0367	0.2987	0.0272
45	67.4	0.605	0.308	0.500 (4)	15	0.377 (6)	15	1.6499	0.0483	0.5007	0.0293
39[4]	69	0.605	0.610	0.612 (5)	15	0.480 (4)	15	1.7046	0.0425	0.5333	0.0250
43[4]	56	0.903	0.608	0.787 (4)	15	0.641 (8)	4	2.0660	0.0803	0.7256	0.0389
40	72	0.903	0.898	0.908 (3)	15	0.814 (4)	15	2.2589	0.0979	0.8149	0.0434
48/1	0.5	1.000	0.901	0.945 (7)	15	0.896 (3)	15	2.0034	0.2733	0.6949	0.1364
48/2	72	1.000	0.950	0.979 (0)	15	0.950 (3)	15	2.4419	0.1417	0.8928	0.0580

| 1273 K, 1.6 GPa | | starting | | final | | | | | | | |
Run	Time [h]	X_{Fe}^{ol}	X_{Fe}^{opx}	X_{Fe}^{ol}	N^{ol}	X_{Fe}^{opx}	N^{opx}	K_D	1σ	$\ln K_D$	1σ
13/1	44	0.000	0.109	0.028 (4)	10	0.032 (2)	16	0.8957	0.1376	-0.1101	0.1536
13/2	50.5+98	0.000	0.109	0.036 (5)	15	0.036 (1)	15	1.0005	0.1441	0.0005	0.1441
1/1[1]	77	0.099	0.000	0.040 (3)	5	0.037 (3)	13	1.1035	0.1187	0.0985	0.1075
1/5	70.5+42.2	0.099	0.000	0.043 (2)	15	0.037 (3)	16	1.1648	0.1165	0.1526	0.1001
15	32	0.198	0.000	0.072 (4)	18	0.070 (2)	16	1.0313	0.0674	0.0308	0.0653
3/3	26	0.099	0.221	0.129 (3)	15	0.110 (2)	15	1.1892	0.0383	0.1733	0.0322
16	41.6	0.198	0.109	0.141 (7)	15	0.124 (7)	15	1.1623	0.0952	0.1504	0.0819
20	45.8	0.307	0.206	0.248 (4)	15	0.201 (6)	15	1.3128	0.0530	0.2722	0.0404
17/2	41.6	0.198	0.308	0.271 (2)	15	0.221 (3)	16	1.3123	0.0274	0.2718	0.0209
8	41	0.406	0.221	0.281 (6)	15	0.230 (4)	15	1.3066	0.0473	0.2675	0.0362
23	40	0.307	0.298	0.291 (9)	15	0.240 (5)	18	1.3001	0.0625	0.2624	0.0481
25[2]	47	0.406	0.409	0.392 (5)	15	0.308 (3)	15	1.4519	0.0369	0.3729	0.0254
7[2]	36	0.605	0.308	0.490 (3)	16	0.375 (4)	17	1.6022	0.0323	0.4713	0.0201
18/2	34	0.501	0.509	0.498 (3)	15	0.387 (3)	15	1.5686	0.0271	0.4502	0.0173
14	30	0.705	0.409	0.573 (5)	15	0.448 (8)	14	1.6511	0.0605	0.5015	0.0366
5	48	0.605	0.597	0.592 (2)	7	0.464 (2)	7	1.6775	0.0182	0.5173	0.0109
21	44	0.705	0.705	0.700 (2)	15	0.568 (5)	15	1.7745	0.0353	0.5735	0.0199
4	41	0.903	0.597	0.777 (2)	6	0.647 (5)	5	1.9011	0.0411	0.6425	0.0216
22	40.5	0.903	0.705	0.821 (2)	15	0.700 (3)	15	1.9606	0.0370	0.6733	0.0188
11	48.4	0.903	0.898	0.888 (1)	15	0.797 (3)	15	2.0118	0.0408	0.6990	0.0203
6	43	1.000	0.791	0.917 (1)	16	0.839 (3)	16	2.1121	0.0539	0.7477	0.0255
12	44	1.000	0.898	0.960 (1)	15	0.917 (2)	15	2.1703	0.0804	0.7748	0.0371
27	50.5	1.000	0.950	0.977 (1)	15	0.952 (2)	15	2.1134	0.0920	0.7483	0.0435

| 1423 K, 1.6 GPa | | starting | | final | | | | | | | |
Run	Time [h]	X_{Fe}^{ol}	X_{Fe}^{opx}	X_{Fe}^{ol}	N^{ol}	X_{Fe}^{opx}	N^{opx}	K_D	1σ	$\ln K_D$	1σ
33[3]	20.5	0.099	0.000	0.040 (2)	15	0.032 (2)	16	1.2455	0.0966	0.2196	0.0776
38[3]	22	0.000	0.109	0.050 (2)	7	0.046 (1)	15	1.1047	0.0598	0.0996	0.0541
34	23	0.198	0.000	0.081 (6)	15	0.060 (4)	15	1.4008	0.1468	0.3371	0.1048
37	24	0.198	0.109	0.138 (3)	15	0.113 (2)	15	1.2535	0.0413	0.2260	0.0329
30/3	22.5	0.099	0.215	0.159 (3)	15	0.134 (3)	15	1.2216	0.0387	0.2002	0.0317
36	21.5	0.198	0.308	0.262 (2)	15	0.213 (3)	15	1.3097	0.0277	0.2698	0.0211
32/2	22.5	0.605	0.308	0.426 (2)	15	0.337 (3)	15	1.4599	0.0201	0.3783	0.0138
31/2[2]	21.5	0.605	0.597	0.548 (1)	15	0.439 (3)	15	1.5508	0.0216	0.4388	0.0139
31/1[2]	32	0.605	0.597	0.570 (2)	15	0.450 (3)	15	1.6162	0.0234	0.4801	0.0145
35	24	0.903	0.597	0.702 (3)	15	0.582 (4)	15	1.6905	0.0365	0.5250	0.0216
47	22	0.903	0.901	0.907 (1)	15	0.839 (3)	15	1.8737	0.0416	0.6279	0.0222
28/3[2]	24	1.000	0.901	0.952 (1)	15	0.914 (2)	15	1.8546	0.0533	0.6177	0.0287
28/1[2]	77	1.000	0.898	0.961 (1)	15	0.928 (3)	15	1.8894	0.0737	0.6363	0.0390

[1] Olivine present only in small amounts
[2] Run slightly contaminated by Al_2O_3. The reported orthopyroxene analyses contained < 0.1 wt% Al_2O_3
[3] Small grain size of olivines
[4] Small grain size of orthopyroxenes

Results

All the data in Table 2 were fitted simultaneously to the expression:

$$0 = \Delta H^{\circ}_{(T*,16)} - T \cdot \Delta S^{\circ}_{(T*,16)} + (1 - 2 \cdot X_{Mg}^{ol}) \cdot W_{G_{Mg-Fe}^{ol}}$$
$$- (1 - 2 \cdot X_{Mg}^{opx}) \cdot W_{G_{Mg-Fe}^{opx}} \qquad (9)$$

using non-linear least squares multiple regression (Seifert and O'Neill 1987). $T*$ refers to an average temperature for the data, which is a formalism allowing us to assume that $\Delta H_{(T*,16)}$ and $\Delta S_{(T*,16)}$ are constants. X_{Mg}^{ol} and X_{Mg}^{opx} were weighted according to their observed standard deviations, as reported in Table 2, and T was weighted assuming a standard deviation of ± 5 K (which is almost negligible). The regression gave $\Delta H_{(T*,16)} = 2381 \pm 625$ J/mol, $\Delta S_{(T*,16)} = -1.516 \pm 0.457$ J/K · mol, $W_{G_{Mg-Fe}^{ol}} = 5625 \pm 574$ J/mol (implying 5450 J/mol at 1 bar) and $W_{G_{Mg-Fe}^{opx}} = 2145 \pm 614$ J/mol. The reduced χ^2 (i.e. $\chi_v^2 = \chi^2/(N - n - 1)$, where N means number of data, and
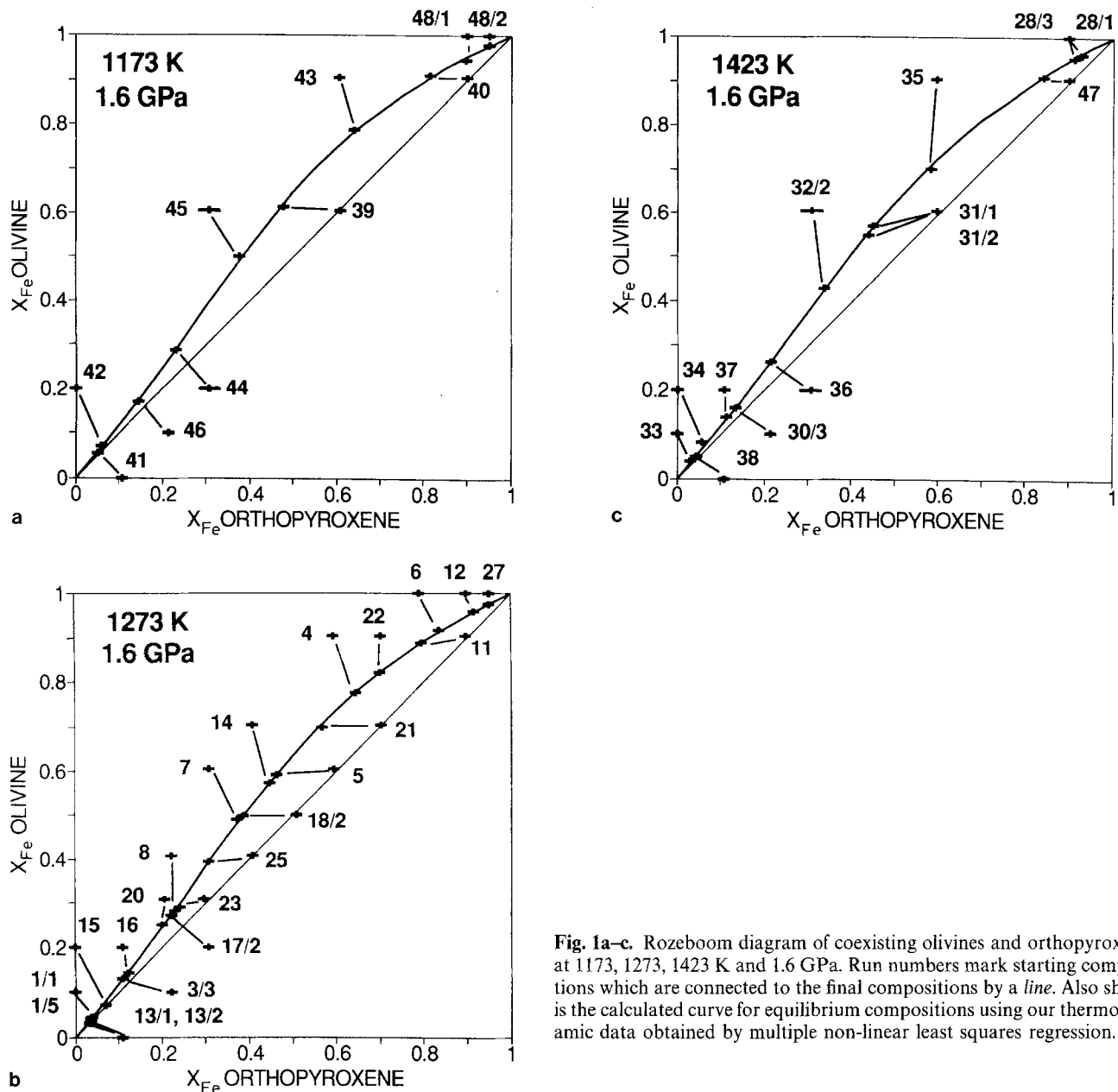
Fig. 1a–c. Rozeboom diagram of coexisting olivines and orthopyroxenes at 1173, 1273, 1423 K and 1.6 GPa. Run numbers mark starting compositions which are connected to the final compositions by a *line*. Also shown is the calculated curve for equilibrium compositions using our thermodynamic data obtained by multiple non-linear least squares regression.

n the number of parameters) for the regression was 0.84, which is satisfactorily close to unity. It is notorious, however, that for partitioning data of this type, it is the difference in the W_G parameters which is best constrained by the data (Matsui and Nishizawa 1974; O'Neill and Wood 1979; Seifert and O'Neill 1987). This is because of a very high degree of correlation between the two W_G parameters in Eq. (9). To illustrate this, and the extent of other correlations with $\Delta H_{(T*,16)}$ and $\Delta S_{(T*,16)}$, we repeated the regression analysis using fixed values of $W_{G^{ol}_{Mg-Fe}}$ from -1000 to 12000 J/mol. Results are summarized in Fig. 2. Note that the difference $(W_{G^{ol}_{Mg-Fe}} - W_{G^{ol}_{Mg-Fe}})$ is virtually independent of the assumed $W_{G^{ol}_{Mg-Fe}}$.

The χ^2 for these regressions are plotted against $W_{G^{ol}_{Mg-Fe}}$ in Fig. 3. The probability of a result exceeding the minimum χ^2_ν is given by an F test, where F is the ratio of the observed χ^2_ν to the minimum χ^2_ν (e.g. Bevington

1969, pp. 196–197). At the 5% probability level, Table C6 in Bevington (1969) shows that $F \cong 1.75$ for 40 by 40 degrees of freedom, indicating that χ^2_ν in Fig. 3 should not exceed about 1.5 for this level of probability. This corresponds to $W_{G^{ol}_{Mg-Fe}}$ from 2000 to 8000 J/mol.

The variation of $\Delta H^\circ_{(T*,16)}$ and $\Delta S^\circ_{(T*,16)}$ with assumed $W_{G^{ol}_{Mg-Fe}}$ shown in Fig. 2b demonstrates that these quantities might provide valuable additional constraints if they are known independently with the required accuracy. We therefore calculated $\Delta G^\circ_{(T,16)}$ at 1073 to 1473 K from the "internally consistent" thermodynamic datasets of Berman (1988) and of Holland and Powell (1990), and in Fig. 4 these calculated values are compared to our refined values, for assumed values of $W_{G^{ol}_{Mg-Fe}}$ of 2000, 5625 and 8000 J/mol. The literature data suggest a somewhat larger free energy than that implied by our 95% confidence limits for $W_{G^{ol}_{Mg-Fe}}$, but clearly favour lower values of the latter.
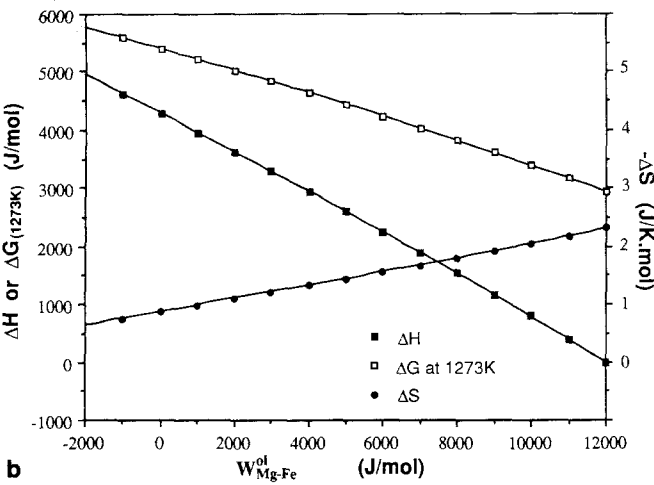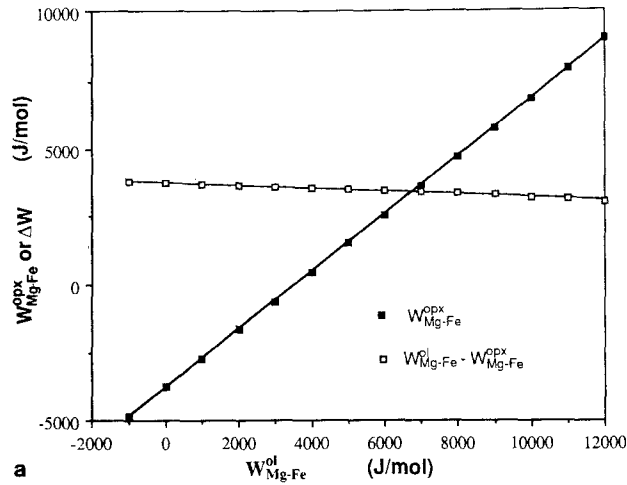
Fig. 2. a Values of a $W_{G^{opx}_{Mg-Fe}}$ and $(W_{G^{ol}_{Mg-Fe}} - W_{G^{opx}_{Mg-Fe}})$, and b $\Delta H^{\circ}_{(T*,16)}$, $\Delta S^{\circ}_{(T*16)}$ and $\Delta G^{\circ}_{(1273K,16)}$, obtained from non-linear least squares analysis of the data in Table 2, assuming different input values for $W_{G^{ol}_{Mg-Fe}}$

Fig. 3. χ^2_v assuming different input values for $W_{G^{ol}_{Mg-Fe}}$. At 95% confidence limits, the ratio of χ^2_v to the minimum χ^2_v is $\sim$ 1.75. The values for $W_{G^{ol}_{Mg-Fe}}$ of Wiser and Wood (1991) and of Koch – Müller et al. (1992) fall within these limits and therefore may be considered compatible with our results, but that of Sack and Ghiorso does not

Fig. 4. $\Delta G^{\circ}_{(T,16)}$ obtained from regression of the olivine-ortho-pyroxene partitioning data for $W_{G^{ol}_{Mg-Fe}}$ = 2000, 5625 and 8000 J/mol, compared to $\Delta G^{\circ}_{(T,16)}$ calculated from the datasets of Berman (1988) and Holland and Powell (1990). The partitioning data suggest a smaller $\Delta G^{\circ}_{(T,16)}$ with less of a temperature dependence. Best agreement is at low values of $W_{G^{ol}_{Mg-Fe}}$

The "internally consistent" thermochemical data has a greater temperature dependence of $\Delta G^{\circ}_{(T,16)}$ (i.e. larger $\Delta S_{(T*,16)}$) than that found from our regression, and also shows some curvature. To see if these factors would affect the refined W parameters, we fitted Holland and Powell's $\Delta G^{\circ}_{(T,16)}$ to an expression of the type $A + BT + CT\ln T$, and included this expression in the regression equation to produce:

$$0 = [\Delta G^{\circ}_{(T*,16)}]_{H\&P} + \Delta A + (1 - 2 \cdot X^{ol}_{Mg}) \cdot W_{G^{ol}_{Mg-Fe}}$$

$$- (1 - 2 \cdot X^{opx}_{Mg}) \cdot W_{G^{opx}_{Mg-Fe}} \qquad (10)$$

The term ΔA is a constant independent of temperature, introduced in recognition of the probability of the standard state enthalpy of the reaction being subject to more uncertainty than the other thermodynamic quantities. We obtained: $\Delta A = -1386 \pm 118$ J/mol, $W_{G^{ol}_{Mg-Fe}} = 5953 \pm 563$ J/mol and $W_{G^{opx}_{Mg-Fe}} = 2480 \pm 603$ J/mol, $\chi^2_v = 1.24$. Without the ΔA term (i.e. fixing at the exact values from Holland and Powell) gives $\chi^2_v = 3.2$, i.e. a relatively poor
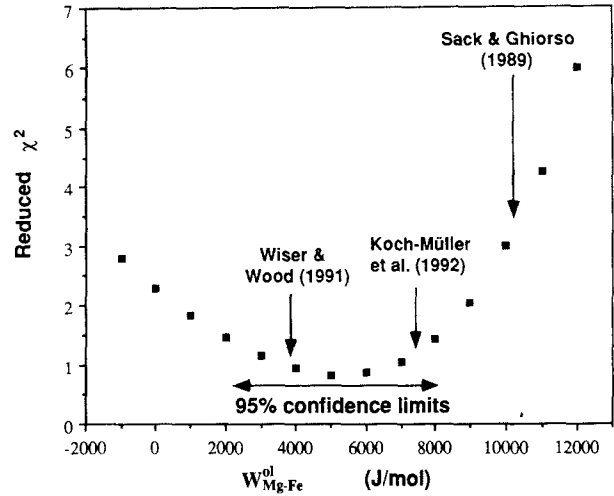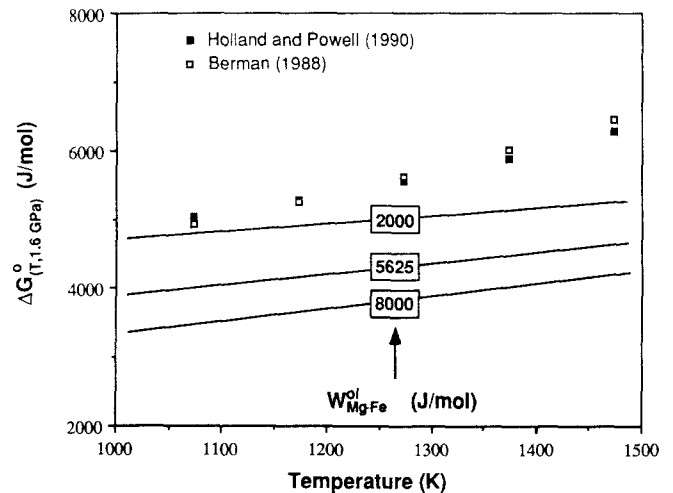
fit to the data. This indicates some need to adjust the "internally consistent" values slightly.

The agreement between the two "internally consistent" datasets is very good, although in detail there are some dissimilarities due to the use of different heat capacity and P-V-T functions. In particular, the C_p function used by Berman (from Berman and Brown 1985) is designed to flatten out at high temperatures, and is therefore ill suited to deal with the pre-melting increase in C_p shown by fayalite (from the heat content measurements of Orr 1953). At 1400 K, the C_p for fayalite used by Berman is 6% lower than that given by a traditional extended

Maier-Kelley function, such as that used by Holland and Powell (1990). It seems to be by coincidence that the difference in $\Delta G^{\circ}_{(T, 16)}$ which this should cause, relative to the values of Holland and Powell (1990), is cancelled out at 1.6 GPa and 1073–1473 K by an opposite difference in the $\int_{1}^{P} \Delta V^{\circ}_{(T, P)} \cdot dP$ term resulting from the different treatments of the P-V-T data.

Since the cation order/disorder in orthopyroxene might produce an anomalous temperature dependence to the activity coefficients, we repeated the regression analysis with $W_{G^{opx}_{Mg-Fe}} = W_{H^{opx}_{Mg-Fe}} - T \cdot W_{S^{opx}_{Mg-Fe}}$. We obtained $\Delta H_{(T*, 16)} = 3168 \pm 677$ J/mol, $\Delta S_{(T*, 16)} = -0.963 \pm 0.493$ J/K·mol, $W_{G^{ol}_{Mg-Fe}} = 5290 \pm 590$ J/mol, $W_{H^{opx}_{Mg-Fe}} = -2988 \pm 1712$ J/mol and $W_{S^{opx}_{Mg-Fe}} = -3.651 \pm 1.134$ J/K·mol, $\chi^2_v = 0.59$. The fit is improved slightly, and the magnitude of $W_{S^{opx}_{Mg-Fe}}$ is consistent with ordering, but $\Delta G^{\circ}_{(T, 16)}$ is no nearer the database values, and the negative value for $W_{H^{opx}_{Mg-Fe}}$ is inconsistent with the calorimetric study of Chatillon-Collinet et al. (1983) (see later). Finally, allowing either olivine or orthopyroxene to behave as a subregular (asymmetric) solution produced no improvement in the fit. However, it is conceivable that both solutions show similar asymmetries, a situation which our data would not be expected to resolve.

Comparison with previous olivine-orthopyroxene Mg – Fe partitioning studies

The results of previous experimental studies on the partitioning of Mg and Fe between olivine and orthopyroxene (or other pyroxene polymorph, as indicated), at temperatures from 973 to 1623 K and various pressures, are compared in detail with our present results in Fig. 5, by plotting $\ln K_D$ versus X^{ol}_{Fe} or X^{opx}_{Fe}. Our data is represented by curves calculated from the best fit thermodynamic parameters obtained above, extrapolated where necessary outside the actual temperature range of our measurements. To facilitate the comparisons, we have also drawn confidence limits corresponding to the uncertainty in $\ln K_D$ which would be caused by a simultaneous uncertainty in both X^{ol}_{Fe} and X^{opx}_{Fe} of ± 0.01, this level of uncertainty being typical of the standard deviations quoted in most previous studies (e.g. Fonarev 1987; Koch-Müller et al. 1992; the lower standard deviations given by Matsui and Nishizawa 1974, are not consistent with the internal scatter of their data).

We have adjusted all the previous data to 1.6 GPa using the molar volume, compressibility and thermal expansion data of Holland and Powell (1990), and the approximation $\Delta(\ln K_D) = \int_{16}^{P} \Delta V^{\circ}_{(T, P)} \cdot dP$. The compressibility data are for room temperature and generally low pressure conditions, so that this correction may be expected to become increasingly unreliable with increasing pressure and temperature.

In general the agreement between all the previous studies and our results is good, as is also the agreement between the previous work at $T < 1173$ K or $T > 1423$ K and the extrapolation of our results. Such differences as there are tend not to be systematic, except for a tendency in some studies for lower K_D at the Mg-rich end of the system (i.e. $\ln K_D$ near zero or even slightly negative, im-

plying olivine more magnesian than co-existing pyroxene), which we will discuss more fully later.

The results of Koch-Müller et al. (1992; their Table 8) at 1173 K, 1.0 GPa and 1273 K, 1.3 GPa for $0 < X^{ol}_{Fe} < 0.7$ agree with our results, except the most Mg-rich runs (see later). At the Fe-rich part of the system the data of Koch-Müller et al. (1992; their Table 2), which include both synthesis and reversal experiments, show a wider scatter, generally tending to be at higher K_D than our data. This behaviour does not depend on whether the experiment was of the synthesis or reversal kind, but except for two synthesis runs at 1273 K, these differences are in any case within two standard deviations of our results. Note that the values of $\ln K_D$ tabulated by Koch-Müller et al. in their Table 11 and plotted in their Fig. 6 are smoothed data.

The Fe-rich part of the system was previously covered by Bohlen and Boettcher (1981) at the same temperatures as Koch-Müller et al. (1992), and at similar pressures. Bohlen and Boettcher's (1981) reversed exchange experiments all bracket exactly our calculated curve at 1173 K and 1273 K (Fig. 5b, c). This bracketing behaviour indicates that their experiments approached rather than achieved equilibrium. At 1073 K their results include one anomalous datum, which plots at lower K_D, i.e., in the opposite direction to the tendency towards higher K_D shown by the data of Koch-Müller et al. in this region of composition. Our run times are two to three times longer than both these previous studies at the same temperature, which should have helped to promote a closer approach to equilibrium in our experiments.

Matsui and Nishizawa (1974) performed both synthesis experiments (starting from mixtures of olivine plus amorphous silica) and unreversed exchange experiments at 1273 K, 0.1 MPa and 3 GPa, but the actual starting compositions are not given. In Fig. 5c their pressure-corrected 0.1 MPa results agree well with our calculated curve, but their 3 GPa experiments seem to plot at systematically lower K_D, outside our confidence band. This could be an artefact of our pressure correction, since, as noted above, this correction is based on the available P-V-T data (Holland and Powell 1990) and is expected to become less efficaceous with increasing pressure. We remark that if their 3 GPa data were not corrected for pressure, they would fit very well with our 1.6 GPa model curve.

The tendency for lower $\ln K_D$ at the Mg-rich end of the system is summarized in Fig. 6, where we have plotted the difference in $\ln K_D$ between our results and the previous data for $0 < X^{ol}_{Fe} < 0.2$ against temperature. We believe that this tendency is an artefact for the following reasons: (1) we also found low $\ln K_D$ for run 13/1, but a repeat run with the same starting materials, but with longer total run time and intermittent grinding (run 13/2) gave a higher $\ln K_D$ (see Table 2); (2) Fig. 6 shows no systematic dependence of this discrepancy with temperature; and (3) the vast majority of naturally occurring coexisting olivine and orthopyroxene pairs at high Mg (e.g. peridotite xenoliths from the mantle, with two-pyroxene equilibration temperatures from 850 to 1300 K) have positive $\ln K_D$ (note that the effect of erroneously counting Fe^{3+} as Fe^{2+} in the natural orthopyroxenes would be
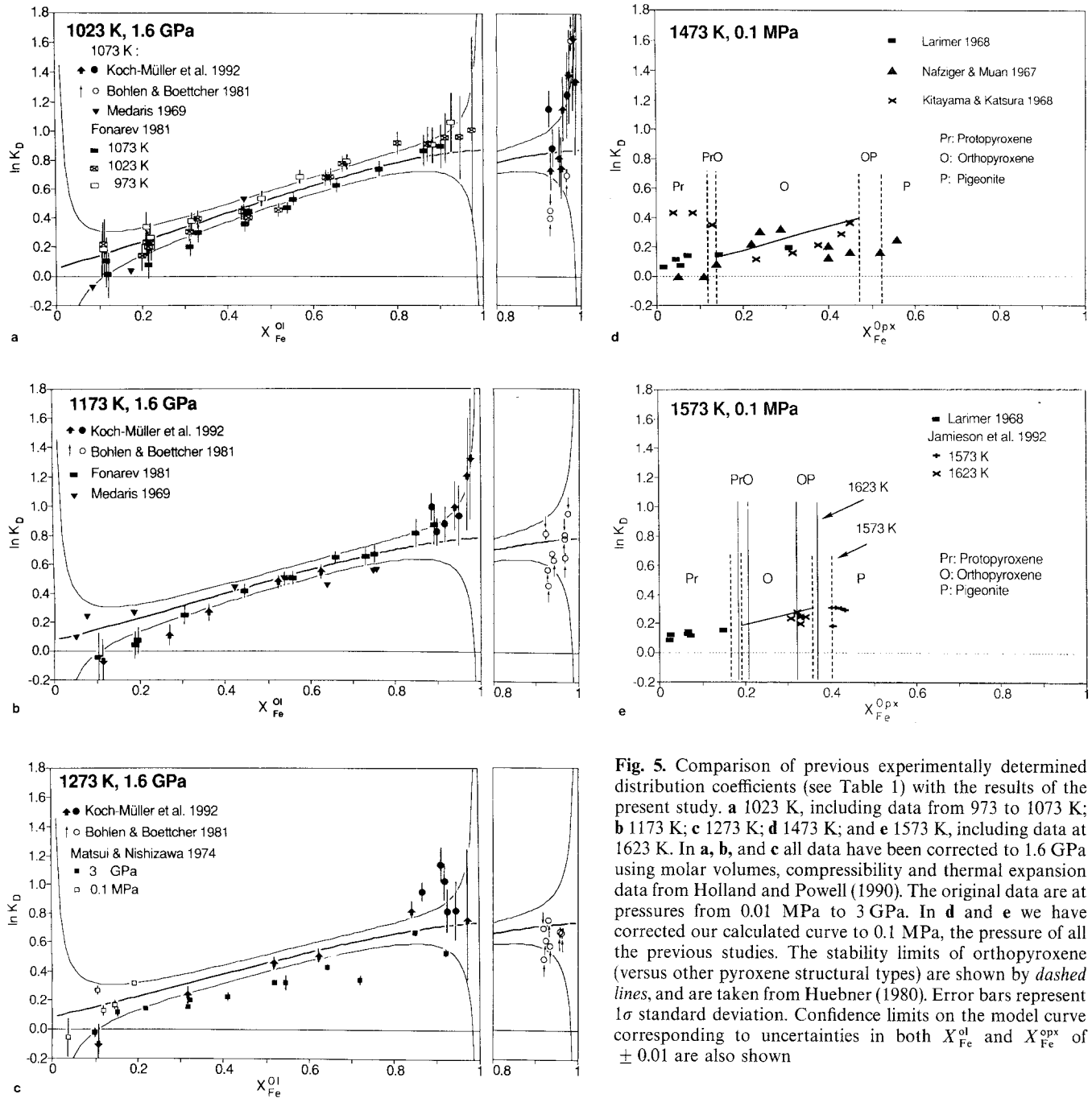
1023 K, 1.6 GPa
1073 K :
✦ ● Koch-Müller et al. 1992
↑ ○ Bohlen & Boettcher 1981
▼ Medaris 1969
Fonarev 1981
■ 1073 K
▩ 1023 K
□ 973 K

$\ln K_D$ vs X_{Fe}^{ol} (a)

1473 K, 0.1 MPa
■ Larimer 1968
▲ Nafziger & Muan 1967
✕ Kitayama & Katsura 1968

Pr: Protopyroxene
O: Orthopyroxene
P: Pigeonite

$\ln K_D$ vs X_{Fe}^{Opx} (d)

1173 K, 1.6 GPa
✦ ● Koch-Müller et al. 1992
↑ ○ Bohlen & Boettcher 1981
■ Fonarev 1981
▼ Medaris 1969

$\ln K_D$ vs X_{Fe}^{ol} (b)

1573 K, 0.1 MPa
■ Larimer 1968
Jamieson et al. 1992
✦ 1573 K
✕ 1623 K

Pr: Protopyroxene
O: Orthopyroxene
P: Pigeonite

$\ln K_D$ vs X_{Fe}^{Opx} (e)

1273 K, 1.6 GPa
✦● Koch-Müller et al. 1992
↑ ○ Bohlen & Boettcher 1981
Matsui & Nishizawa 1974
■ 3 GPa
□ 0.1 MPa

$\ln K_D$ vs X_{Fe}^{ol} (c)

Fig. 5. Comparison of previous experimentally determined distribution coefficients (see Table 1) with the results of the present study. **a** 1023 K, including data from 973 to 1073 K; **b** 1173 K; **c** 1273 K; **d** 1473 K; and **e** 1573 K, including data at 1623 K. In **a**, **b**, and **c** all data have been corrected to 1.6 GPa using molar volumes, compressibility and thermal expansion data from Holland and Powell (1990). The original data are at pressures from 0.01 MPa to 3 GPa. In **d** and **e** we have corrected our calculated curve to 0.1 MPa, the pressure of all the previous studies. The stability limits of orthopyroxene (versus other pyroxene structural types) are shown by *dashed lines*, and are taken from Huebner (1980). Error bars represent 1σ standard deviation. Confidence limits on the model curve corresponding to uncertainties in both X_{Fe}^{ol} and X_{Fe}^{opx} of ± 0.01 are also shown

to lower $\ln K_D$). The reason for this effect may be a result of the sluggish reaction kinetics at Mg-rich compositions.

In contemplating Fig. 5, two points should be borne in mind: (a) the slope of $\ln K_D$ versus X_{Fe}^{ol} is mostly due to the difference in the deviations from ideality of the two solutions, i.e. ($W_{G_{Mg-Fe}^{ol}} - W_{G_{Mg-Fe}^{opx}}$) for the simple solution model; while (b) curvature on this slope reflects increasing magnitudes of $W_{G_{Mg-Fe}^{ol}}$ and $W_{G_{Mg-Fe}^{opx}}$. The slope would be strictly linear for $W_{G_{Mg-Fe}^{opx}} = 0$ (ideality), provided the olivine solution behaves symmetrically, but, alternatively, curvature could also reflect asymmetry in either solution. The systematic tendency towards erroneously low $\ln K_D$ at the Mg-rich end of the system will therefore both increase the slope of the data, thus increas-

ing ($W_{G_{Mg-Fe}^{ol}} - W_{G_{Mg-Fe}^{opx}}$), and increase the curvature, thereby making $W_{G_{Mg-Fe}^{ol}}$ and $W_{G_{Mg-Fe}^{opx}}$ seem higher. This is the reason for the higher values of $W_{G_{Mg-Fe}^{ol}}$ and $W_{G_{Mg-Fe}^{opx}}$ reported by Koch-Müller et al. (1992).

Some of the early data (Nafziger and Muan 1967; Kitayama and Katsura 1968; Larimer 1968) were obtained at conditions under which the $(Mg,Fe)_2Si_2O_6$ compound should crystallize in the protopyroxene structure (see the phase diagram in Huebner 1980, his Fig. 8). This is indicated in Fig. 5d–e. However, the effect of this on K_D seems to be too small to be noticeable.

The results of this study do not agree with the recent assessment of Sack and Ghiorso (1989), who recommended the unacceptably high value of 10170 ± 250 J/mol for
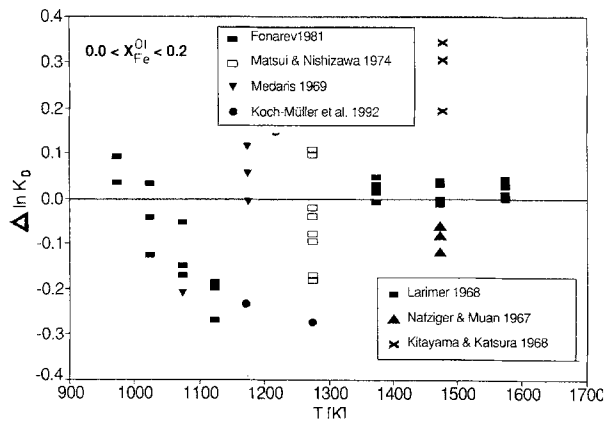
Fig. 6. Deviations of previous determinations of $\ln K_D$ from our model (corrected for pressure) for $X_{Fe}^{ol} = 0$ to 0.2, as a function of temperature. Certain studies show a tendency towards low K_D at these magnesian compositions, but there appears to be no systematic trend of this with temperature
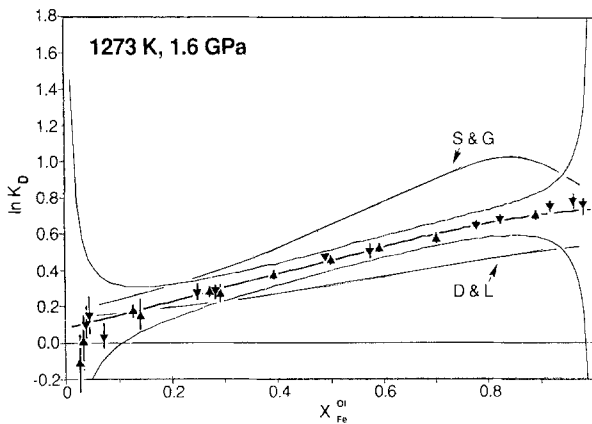

Fig. 7. Comparison of different models for $\ln K_D$ versus composition of olivine at 1273 K, 1.6 GPa. Our data (Table 2) are shown with symbols with 1σ error bars together with our calculated model curve. For comparison, the curves for 1273 K and 1.5 GPa presented by Sack and Ghiorso (1989) are shown, using their own model ($S\&G$) and the model of Davidson and Lindsley (1989; $D\&L$)

$W_{G_{Mg-Fe}^{ol}}$. This is shown in Fig. 7. One contributing reason for this discrepancy may be Sack and Ghiorso's choice of partitioning data. Sack and Ghiorso list in their appendix (their Table A1) a large number of olivine-orthopyroxene pairs from rocks thought to have equilibrated in the range 848 to 1223 K, plus the experimental partitioning data of Larimer (1968) at 1373, 1473 and 1573 K and 0.1 MPa, Matsui and Nishizawa (1974) at 1273 K, and 0.1 MPa or 3.0 GPa, Bohlen and Boettcher (1981) at 1173 and 1273 K and various pressures, and one datum from Davidson and Lindsley (1989) at 1073 K and 0.2 GPa. The other partitioning studies listed in our Table 1 were either not available to Sack and Ghiorso, or were not considered by them. Of the listed data, Sack and Ghiorso then selected some 28 olivine-orthopyroxene pairs which they considered as preferred data. Their constraints for the selection were orthopyroxene compositions most close

to the binary Mg–Fe solid solution, and representative of naturally occurring material. These 28 pairs included 26 from rocks, plus the datum of Davidson and Lindsley, and one out of the 17 data of Matsui and Nishizawa (1974). The reason for rejecting the other 16 data of Matsui and Nishizawa was not given, as neither were the reasons for the rejection of the rest of the experimental data (listed or otherwise). Of the 28 preferred data, only six have $X_{Fe}^{ol} < 0.8$, i.e. Sack and Ghiorso's preferred data are almost entirely concentrated at the Fe-rich end of the system. This must inevitably result in loss of accuracy, since the extraction of activity-composition relations from partitioning data is based directly on the variation of K_D with composition, and thus requires as large a composition range as possible. Whether this was a significant factor is uncertain, for Sack and Ghiorso's assessed values provide but a poor fit their preferred data anyway (see Sack and Ghiorso's Fig. 15).

The use of partitioning data from naturally occurring mineral pairs, particularly from slowly cooled metamorphic rocks, is fraught with the danger of one phase continuing to maintain equilibrium with a third phase, or with a fluid reservoir, during cooling. This is a particular hazard for olivine, given the relatively rapid rate of Mg – Fe interdiffusion in olivine (e.g. Morioka and Nagasawa 1991). Such a process could lead either to erroneouly higher or lower K_D, depending on the nature of the reservoir.

Sack and Ghiorso also took into account the standard state thermochemical data of Berman (1988). However, when applied to our partitioning data, Berman's data seem to imply lower values of $W_{G_{Mg-Fe}^{ol}}$ (see Fig. 4).

Comparison with other data on the thermodynamics of Mg – Fe olivine and orthopyroxene solutions

Olivine

The heats of mixing in Mg_2SiO_4-Fe_2SiO_4 olivines were measured by Wood and Kleppa (1981) using oxide melt solution calorimetry at 970 K. Re-analysis of their data (O'Neill and Wall 1987) showed that the excess enthalpies could be modelled by a symmetric regular solution with $W_{H_{Mg-Fe}^{ol}} = 7080 \pm 1800$ J/mol, with a rather large χ_v^2 of 2.92. This is mostly due to an apparently anomalous datum at $X_{Fe}^{ol} = 0.6$; ignoring this datum gives $W_{H_{Mg-Fe}^{ol}} = 4565 \pm 2000$ J/mol, with $\chi_v^2 = 0.13$. Either way, the agreement of the calorimetric $W_{H_{Mg-Fe}^{ol}}$ with $W_{G_{Mg-Fe}^{ol}}$ from our data (or with $W_{G_{Mg-Fe}^{ol}}$ from Wiser and Wood 1991, or Koch-Müller et al. 1992) indicates that any excess entropy in Mg_2SiO_4-Fe_2SiO_4 olivines is small (i.e. $W_{S_{Mg-Fe}^{ol}} <$ about 2 J/K·mol).

Orthopyroxene

Heats of mixing have also been measured on $Mg_2Si_2O_6$-$Fe_2Si_2O_6$ orthopyroxenes by Chatillon-Collinet et al. (1983), at 1023 K on samples synthesized at 1393 K. The state of order of their samples is not known (i.e. whether the order corresponds to the synthesis temperature, or the temperature of the calorimeter, or somewhere in between).

A least squares fit to their results gives $W_{G_{Mg-Fe}^{ol}} = 4750 \pm 2500$ J/mol, with a low χ_v^2 of 0.07 (data weighted according to the reported standard deviations). This $W_{H_{Mg-Fe}^{opx}}$ is rather larger than $W_{G_{Mg-Fe}^{opx}}$ obtained from our measurements, but is compatible within the precision of the calorimetric data. $W_{H_{Mg-Fe}^{opx}} > W_{G_{Mg-Fe}^{opx}}$ is contrary to what we expect from our neglect of the effect of order-disorder on the configurational entropy of the orthopyroxene solution.

Sharma et al. (1987) measured activity-composition relations in $Mg_2Si_2O_6$-$Fe_2Si_2O_6$ orthopyroxenes using the displacement in $T - \mu O_2$ space of the reaction:

$$Fe_2Si_2O_6 = 2SiO_2 + 2Fe + O_2 \tag{12}$$

They used an electrochemical method with calcia-stabilized zirconia electrolytes, and a reference electrode of Fe + "FeO" (iron-wüstite). Results were reported only at 1000 K. Compositions with Mg/(Mg + Fe) up to 0.1 were investigated. The authors report that they synthesized pyroxenes from oxide starting mixtures for all the investigated compositions at atmospheric pressure and 1173 to 1473 K, although the compositions with Mg/(Mg + Fe) < 0.4 fall outside the accepted stability field of pyroxene (and into that of olivine plus silica) under these conditions (Huebner 1980).

The cell arrangement used by Sharma et al. (1987) was that of a simple electrode/electrolyte sandwich, in which both the sample and the reference electrodes were exposed to the same flowing stream of inert gas; this design is similar to that used in the pioneering experiments of Kiukkola and Wagner (1957). Such an arrangement can give surprisingly good results with highly reactive electrodes such as simple metal-metal oxide mixtures (e.g. Kiukkola and Wagner 1957), but is usually considered inadequate for the study of kinetically sluggish silicate equilibria, or for non-reversible electrodes involving solid solutions (e.g. Seetharaman and Abraham 1980). Sharma et al. (1987) found larger positive deviations from ideality than those implied by this work; fitted to a regular solution model, their measurements give $W_{G_{Mg-Fe}^{opx}} = 8200$ J/mol. However, their measurements imply ΔG_f^0 for $Fe_2Si_2O_6$ (i.e. from reaction 12) which is 7 ± 2 kJ/mol less negative than that calculated from assessed thermodynamic data (Berman 1988; or Powell and Holland 1990), which in turn comes largely from combining well-founded data from the two much studied reactions:

$$Fe_2SiO_4 = SiO_2 + 2Fe + O_2 \tag{13}$$

(O'Neill 1987 and earlier references therein; Jacob et al. 1989), and:

$$Fe_2SiO_4 + SiO_2 = Fe_2Si_2O_6 \tag{14}$$

(Bohlen et al. 1980; Koch-Müller et al. 1992). The free energies for both of these reactions are known to within ± 0.5 kJ/mol. An explanation for this discrepancy is that the open cell design could not prevent some oxidation and consequent polarization of the $(Fe,Mg)_2Si_2O_6 + SiO_2$ + Fe sample electrodes, causing measured emfs to be erroneously low (e.g. the observed emf may be a combination of the equilibrium emf plus the emf for the Fe + "FeO" equilibrium). Such effects are particularly

likely at the unusually low temperature (1000 K) used by Sharma et al. (1987) for this type of electrochemical experiment. A further indication that polarization may have been a problem comes from the observation of Sharma et al. (1987) that their cell emfs rapidly returned to the original value on application of an external emf. Since the cell reaction is divariant, application of an external emf (i.e. titration of oxygen into or out of the cell) ought to have resulted in a displacement of the equilibrium. Finally, there is no certainty that the measured emfs in cells with Mg/(Mg + Fe) < 0.4 correspond to the metastable pyroxene-quartz-Fe equilibrium rather than the stable olivine-quartz-Fe equilibrium.

Conclusions

The high degree of correlation between $W_{G_{Mg-Fe}^{ol}}$, $W_{G_{Mg-Fe}^{opx}}$ and the standard free energy of the exchange reaction means that it would be inappropriate simply to recommend our "best fit" value for $W_{G_{Mg-Fe}^{ol}}$. Instead, we emphasize that our partitioning data agree well with $W_{G_{Mg-Fe}^{ol}} = 3700 \pm 800$ J/mol recently determined from the olivine-magnesiowüstite-iron equilibrium by Wiser and Wood (1991), using the activity-composition relations for magnesiowüstite in equilibrium with iron of Srečeč et al. (1987). With this value of $W_{G_{Mg-Fe}^{ol}}$, corrected to 1.6 GPa using $W_{V_{Mg-Fe}^{ol}} = 108$ J/GPa we obtain $W_{G_{Mg-Fe}^{opx}} = 280 \pm 900$ J/mol (the uncertainty includes that in $W_{G_{Mg-Fe}^{ol}}$, as will subsequently quoted uncertainties).

This value for $W_{G_{Mg-Fe}^{ol}}$ also agrees with that originally proposed by O'Neill and Wood (1979) from their study of olivine garnet $Mg - Fe^{2+}$ partitioning equilibria, namely $W_{G_{Mg-Fe}^{ol}} = 4140 \pm 870$ J/mol at 3.0 GPa, (i.e. 3820 J/mol at 1 bar). However, O'Neill and Wood (1979) used a simple linear regression analysis, which results in inappropriate weighting of the data. Re-analysis of their data using non-linear least squares with appropriate weighting, and assuming $W_{G_{Mg-Fe}^{ol}} = 3700 + 108$ P J/mol, gives $W_{G_{Mg-Fe}^{gt}} = 280 \pm 960$ J/mol. This value is based on 93 experimental runs at 1173 to 1773 K and 3.0 GPa, covering Mg/(Mg + Fe) = 0.2 to 0.9 and $X_{Ca}^{gt} = 0$ to 0.3. The more recent olivine-garnet $Mg - Fe^{2+}$ experimental data of Hackler and Wood (1989) at 1273 K and 0.9 GPa give an almost identical result: with $W_{G_{Mg-Fe}^{ol}} = 3700 + 108$ P J/mol, and assuming uncertainties in X_{Mg}^{ol} and X_{Mg}^{gt} of ± 0.005 (1 σ), we obtain $W_{G_{Mg-Fe}^{gt}} = 1130 \pm 960$ J/mol. Allowing garnet to behave as a subregular solution resulted in no decrease of χ^2, and in agreement with Hackler and Wood (1989) we emphasize that any asymmetry in $Mg - Fe^{2+}$ garnet solutions is minor.

Similarly, re-analysis of the data on activity coefficients in binary $Mg - Fe^{2+}$ ferrite, chromite and aluminate spinels from olivine-spinel $Mg - Fe^{2+}$ partitioning (reviewed in O'Neill and Wall 1987) shows that these solutions are also close to ideal, with $W_{G_{Mg-Fe}^{sp}} = 700 \pm 1000$ J/mol. The olivine - ilmenite $Mg - Fe^{2+}$ partitioning data of Anderson and Lindsley (1979) at 1 bar give $W_{G_{Mg-Fe}^{ilm}} = 6200 \pm 1500$ J/mol.

Davies and Navrotsky (1983) demonstrated that there is a good empirical relationship between the magnitude of the regular solution parameter (W) and the relative differ-
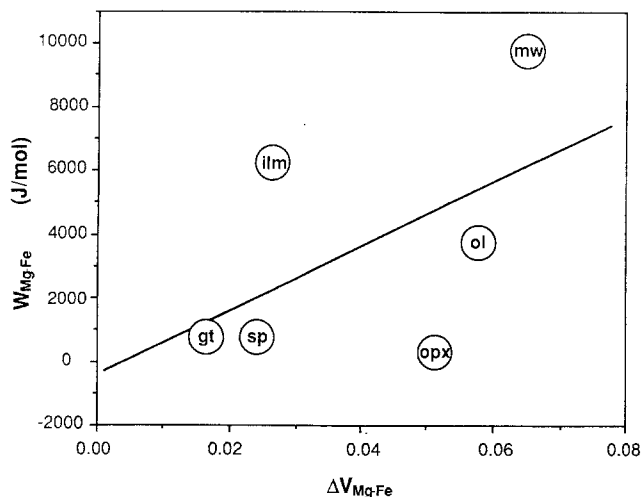
Fig. 8. W_{Mg-Fe} versus size mismatch ΔV_{Mg-Fe} (Eq. 16 in text) for some ferromagnesian solid solutions. The *line* is the correlation for divalent solid solutions from Davies and Navrotsky (1983). The datum for magnesiowüstite (*mw*) is not corrected for the change in (Mg + Fe)/O stoichiometry across the solution

ence in the molar volumes of the end-members, implying that positive deviations from ideality in simple solid solutions are largely a result of the lattice strain from the mixing of cations of different sizes. For the mixing of divalent cations in a variety of structures, Davies and Navrotsky (1983) found:

$$W_{1-2} = 100.8\Delta V_{1-2} - 0.4 \text{ (kJ/mol)} \tag{15}$$

where

$$\Delta V_{1-2} = \frac{V_2 - V_1}{0.5(V_2 - V_1)} \tag{16}$$

In Fig. 8 this relationship is tested against the internally consistent set of W_{Mg-Fe} parameters (all based on partitioning with olivine solid solution) described already. There is much scatter around the correlation recommended by Davies and Navrotsky (1983). This is perhaps not unexpected: the difference between the ionic radii of Mg and Fe^{2+} is small, and at such levels other contributions to the free energy of mixing may become significant, for example, the change across the solid solution in the crystal field stabilization energy of Fe^{2+} with the size and shape of the co-ordination polyhedra (Burns 1985), or order/disorder, as in orthopyroxene.

References

Andersen DJ, Lindsley DH (1979) The olivine–ilmenite thermometer. Proc Lunar Planet Sci Conf 10th: 493–507

Berman RG (1988) Internally consistent thermodynamic data for minerals in the system $Na_2O-K_2O-CaO-MgO-FeO-Fe_2O_3-$

$Al_2O_3-SiO_2-TiO_2-H_2O-CO_2$. J Petrol 29:445–552

Berman RG, Brown TH (1985) The heat capacity of minerals in the system $K_2O-Na_2O-CaO-MgO-FeO-Fe_2O_3-Al_2O_3-SiO_2-TiO_2-H_2O-CO_2$: representation, estimation, and high temperature extrapolation. Contrib Mineral Petrol 89:168–183

Bevington PRC (1969) Data reduction and error analysis for the physical sciences. McGraw-Hill, New York, pp 336

Bohlen SR, Boettcher AL (1981) Experimental investigations and geological applications of orthopyroxene geobarometry. Am Mineral 66:951–964

Bohlen SR, Essene EJ, Boettcher AL (1980) Reinvestigation and application of olivine–quartz–orthopyroxene barometry. Earth Planetary Sci Lett 47:1–10

Boyd FR, England JL (1960) Apparatus for phase-equilibrium measurements at pressures up to 50 kilobars and temperatures up to 1750°C. J. Geophys Res 65:741–748

Burns RG (1985) Thermodynamic data from crystal field spectra. In: Kieffer SW, Navrotsky A (eds) Reviews in Mineralogy, vol 14: Microscopic to macroscopic: 277–316

Chatillon-Collinet C, Newton RC, Perkins D III, Kleppa OJ (1983) Thermochemistry of $(Fe^{2+}, Mg)SiO_3$ orthopyroxene. Geochim Cosmochim Acta 47:1597–1603

Davidson PM, Lindsley DH (1989) Thermodynamic analysis of pyroxene-olivine-quartz equilibria in the system $CaO-MgO-FeO-SiO_2$. Am Mineral 74:18–30

Davies PK, Navrotsky A (1983) Quantitative correlations of deviations from ideality in binary and pseudo-binary solid solutions. J Solid State Chem 46:1–22

Fonarev VI (1981) Thermodynamic functions of olivine and orthopyroxene solid solutions. Geochem Int 18:142–157

Hackler RT, Wood BT (1989) Experimental determination of Fe and Mg exchange between garnet and olivine and estimation of Fe – Mg mixing properties in garnet. Am Mineral 74:994–999

Hauptmann Z, Wanklyn BM, Smith SH (1973) Flux growth of Fe_2TiO_4 from $BaO-B_2O_3$ in an iron crucible. J Mat Sci 8:1695–1698

Holland TJB (1980) The reaction albite = jadeite + quartz determined experimentally in the range 600–1200°C. Am Miner 65:129–134

Holland TJB, Powell R (1990) An enlarged and updated internally consistent thermodynamic dataset with uncertainties and correlations: the system $K_2O-Na_2O-CaO-MgO-MnO-FeO-Fe_2O_3-Al_2O_3-TiO_2-SiO_2-C-H_2-O_2$. J Metam Geol 8:89–124

Huebner JS (1980) Pyroxene phase equilibria at low pressure. In: Prewitt CT (ed) Pyroxenes. Reviews in Mineralogy, vol 7. Mineralogical Society of America, Washington DC, pp 213–288

Jacob KT, Kale GM, Iyengar GNK (1989) Chemical potentials of oxygen for fayalite-quartz-iron and fayalite-quartz-magnetite equilibria. Metallurg Trans B 20B:679–685

Jamieson HE, Roeder PL, Grant AH (1992) Olivine–orthopyroxene-Pt-Fe alloy as an oxygen geobarometer. J Geol 100:138–145

Kitayama K, Katsura T (1968) Activity measurements in orthosilicate and metasilicate solid solutions. I. $Mg_2Si_4-Fe_2SiO_4$ and $MgSiO_3-FeSiO_3$ at 1204°C. Bull Chem Soc Japan 41:1146–1151

Kiukkola K, Wagner C (1957) Measurements on galvanic cells involving solid electrolytes. J Elektrochem Soc 104:379–387

Koch-Müller M, Cemic L, Langer K (1992) Experimental and thermodynamic study of Fe – Mg exchange between olivine and orthopyroxene in the system $MgO-FeO-SiO_2$. Eur J Mineral 4:115–135

Kushiro I (1976) Changes in viscosity and structure of melt of $NaAlSi_2O_6$ composition at high pressures. J Geophys Res 81:6347–6350

Larimer JW (1968) Experimental studies on the system $Fe-MgO-SiO_2-O_2$ and their bearing on the petrology of chondritic meteorites. Geochim Cosmochim Acta 32:1187–1207

Levin EM, Robbins CR, McMurdie HF (1964) Phase diagrams for ceramists. Volume I (Figures 1–2066). The American Ceramic Society, Columbus

Linares RC (1962) Growth of yttrium-iron garnet from molten barium borate. J Amer Ceram Soc 45:307–310

Matsui Y, Nishizawa O (1974) Iron(II)-magnesium exchange equilibrium between olivine and calcium-free pyroxene over a temperature range 800°C to 1300°C. Bull Soc Fr Mineral Cristallogr 97:122–130

Medaris LG Jr (1969) Partitioning of Fe^{++} and Mg^{++} between coexisting synthetic olivine and orthopyroxene. Am J Sci 267:945–968

Morioka M, Nagasawa H (1991) Ionic diffusion in olivine. In: Ganguly J (ed) Diffusion, atomic ordering, and mass transport. Springer, New York Berlin Heidelberg London Paris Tokyo Hong Kong Barcelona, pp 176–196

Nafziger RH, Muan A (1967) Equilibrium phase compositions and thermodynamic properties of olivines and pyroxenes in the system MgO–"FeO"–SiO_2. Am Mineral 52:1364–1384

O'Neill HStC (1987) The quartz-fayalite-iron and quartz-fayalite-magnetite equilibria and the free energies of formation of fayalite (Fe_2SiO_4) and magnetite (Fe_3O_4). Am Mineral 72:67–75

O'Neill HStC, Wall VJ (1987) The olivine-orthopyroxene-spinel oxygen geobarometer, the nickel precipitation curve, and the oxygen fugacity of the Earth's upper mantle. J Petrol 28:1169–1191

O'Neill HStC, Wood BJ (1979) An experimental study of Fe–Mg partitioning between garnet and olivine and its calibration as a geothermometer. Contrib Mineral Petrol 70:59–70

Orr RL (1953) High temperature heat contents of magnesium orthosilicate and ferrous orthosilicate. J Am Chem Soc 75:528–529

Ottonello G, Princivalle F, Della Giusta A (1990) Temperature, composition, and fO_2 effects on intersite distribution of Mg and Fe^{2+} in olivines: experimental evidence and theoretical interpretation. Phys Chem Mineral 17:301–312

Ramberg H, De Vore G (1951) The distribution of Fe^{++} and Mg^{++} in coexisting olivines and pyroxenes. J Geol 59:193–210

Ross NL, Navrotsky A (1987) The Mg_2GeO_4 olivine-spinel phase transition. Phys Chem Mineral 14:473–481

Ross NL, Akaogi M, Navrotsky A, Susaki J–I, McMillan P (1986) Phase transitions among the $CaGeO_3$ polymorphs (wollastonite, garnet, and perovskite structures): studies by high-pressure synthesis, high-temperature calorimetry, and vibrational spectroscopy and calculation. J Geophys Res 91(B5):4685–4696

Sack RO, Ghiorso MS (1989) Importance of considerations of mixing properties in establishing an internally consistent thermodynamic database: thermochemistry of minerals in the system Mg_2SiO_4–Fe_2SiO_4–SiO_2. Contrib Mineral Petrol 102:41–68

Schwab RG, Küstner D (1977) Präzisionsgitterkonstantenbestimmung zur Festlegung röntgenographischer Bestimmungskurven für synthetischen Olivin der Mischkristallreihe Forsterit–Fayalit. N Jahrb Mineral Monatsh 1977:205–215

Seetharaman S, Abraham KP (1980) Thermodynamic properties of oxide systems. In: Subbarao EC (ed) Solid electrolytes and their applications. Plenum, New York London, pp 127–163

Seifert F (1989) Recent advances in the mineralogical applications of the 57Fe Mösbauer effect. In: Salje EKH (ed) Physical properties and thermodynamic behaviour of minerals. Reidel, Dordrecht Boston Lancaster Tokyo, pp 687–703

Seifert S, O'Neill HStC (1987) Experimental determination of activity–composition relations in Ni_2SiO–Mg_2SiO_4 and Co_2SiO_4–Mg_2SiO_4 olivine solid solutions at 1200 K and 0.1 MPa and 1573 K and 0.5 GPa. Geochim Cosmochim Acta 51:97–104

Sharma KC, Agrawal RD, Kapoor ML (1987) Determination of thermodynamic properties of (Fe, Mg)-pyroxenes at 1000 K by the emf method. Earth Planet Sci Lett 85:302–310

Srečeč I, Ender A, Woermann E, Gans W, Jacobsson E, Eriksson G, Rosen E (1987) Activity–composition relations of the magnesiowustite solid solution series in equilibrium with metallic iron in the temperature range 1050–1400 K. Phys Chem Mineral 14:492–498

Thompson JB Jr (1967) Thermodynamic properties of simple solutions. In: Abelson PH (ed) Researches in geochemistry, vol 2. Wiley, New York, pp 340–361

Turnock AC, Lindsley DH, Grover JE (1973) Synthesis and unit cell parameters of Ca–Mg–Fe pyroxenes. Am Mineral 58:50–59

Virgo D, Hafner SS (1969) Fe^{2+}, Mg order-disorder in heated orthopyroxenes. Mineral Soc Am Spec Pap 2:67–81

Wiser NM, Wood BJ (1991) Experimental determination of activities in Fe-Mg olivine at 1400 K. Contrib Mineral Petrol 108:146–153

Wilson AH (1982) The geology of the Great 'Dyke', Zimbabwe: the ultramafic rocks. J Petrol 23:240–292

Wood BJ, Kleppa OJ (1981) Thermochemistry of forsterite–fayalite olivine solutions. Geochim Cosmochim Acta 45:569–581