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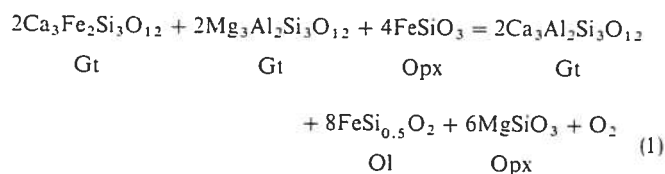
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G. Gudmundsson · B. J. Wood

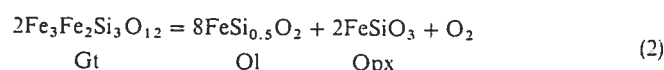
**Experimental tests of garnet peridotite oxygen barometry**

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**Abstract** We have performed experiments aimed at testing the calibration of oxygen barometers for the garnet peridotite [garnet (Gt)-olivine (Ol)-orthopyroxene (Opx)] phase assemblage. These involved equilibrating a thin layer of garnet sandwiched between layers of olivine and orthopyroxene at 1300°C and 25–35 kbar for 1–7 days. Oxygen fugacity was controlled (but not buffered) by using inner capsules of Fe–Pt alloy or graphite or molybdenum sealed in welded Pt outer capsules. Post-experiment measurement of  $f_{O_2}$  was made by determining the compositions of Pt–Fe alloy sensors at the interface between garnet and olivine + orthopyroxene layers. The composition of alloy in equilibrium with olivine + orthopyroxene was approached from Fe-oversaturated and Fe-undersaturated conditions in the same experiment with, in general, excellent convergence. Product phase compositions were determined by electron microprobe and a piece of the garnet layer saved for  $^{57}\text{Fe}$  Mössbauer spectroscopy. The latter gave the  $\text{Fe}^{3+}$  content of the garnet at the measured  $P$ - $T$ - $f_{O_2}$  conditions. Approach to equilibrium was checked by observed shifts in  $\text{Fe}^{3+}$  content and by the approach of garnet-olivine Fe–Mg partitioning to the expected value. The compositions of the phases were combined with mixing properties and thermodynamic data to calculate an apparent  $f_{O_2}$  from two possible garnet oxybarometers:-



and



Comparison of calculated  $f_{O_2}$ s with those measured by the Pt–Fe sensors demonstrated that either barometer gives the correct answer within the expected uncertainty. Data from the first (Luth et al. 1990) has an uncertainty of about 1.6 log  $f_{O_2}$  units, however, while that from equilibrium (2) (Woodland and O'Neill 1993) has an error of  $+/-$  0.6 log units, comparable to that of the spinel peridotite oxybarometer. We therefore conclude that equilibrium (2) may be used to calculate the  $f_{O_2}$  recorded by garnet peridotites with an uncertainty of about  $+/-$  0.6 log units, providing the potential to probe the oxidation environment of the deep continental lithosphere. Preliminary application based on data from Luth et al. (1990) indicates that garnet peridotite xenoliths from Southern Africa record oxygen fugacities about 3.0 log units below the FMQ (fayalite-magnetite-quartz) buffer. These are substantially more reducing conditions than those recorded by continental spinel lherzolites which typically give oxygen fugacities close to FMQ (Wood et al. 1990).

**Introduction**

The oxidation state and oxygen fugacity of the Earth's upper mantle is a subject which has evoked considerable debate in recent years. This interest stems in part from a consideration of the dynamical processes of early Earth differentiation, in which a metallic core separated, and from the anticipated effects of mantle degassing, through volcanism, and of fluid recycling through subduction. A simple model would be that the upper mantle was initially reduced, through equilibration with an Fe-rich alloy, and is undergoing secular oxidation via the subduction of  $\text{H}_2\text{O}$  and  $\text{CO}_2$ . Interest

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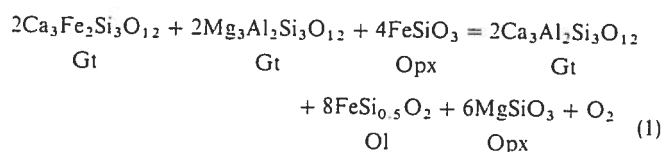
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in this subject has led to a number of studies of the oxidation states of minerals from spinel lherzolite xenoliths in continental basalts (Wood and Virgo 1989; Dyar et al. 1989; Canil et al. 1990), from oceanic abyssal spinel peridotites (Bryndzia and Wood 1990) and from orogenic spinel peridotite massifs (Woodland et al. 1992). When combined with experimental and thermochemical data on the olivine-orthopyroxene-spinel equilibrium (O'Neill and Wall 1987; Ballhaus et al. 1991; Bryndzia and Wood 1990) the data demonstrate that the uppermost part of the upper mantle is relatively oxidised with the majority of samples falling within  $-1.5$  to  $+0.5 \log f_{O_2}$  units of the fayalite-magnetite-quartz (FMQ) oxygen buffer. This applies to samples of Cenozoic age. Small systematic differences exist between the mantle in different tectonic environments, however. Results to date indicate that lherzolites from continental rift localities are relatively reduced, while those from subduction zone environments have the highest  $f_{O_2}$ s (above the FMQ buffer) and frequently contain hydrous minerals (Wood et al., 1990; Ballhaus et al. 1991; Ionov and Wood 1992). In the case of abyssal spinel peridotites, which are commonly thought to represent the residua from partial melting (Dick et al. 1984) the results are in very good agreement with independent data on the oxygen fugacities recorded by mid-ocean ridge basalt glasses (Christie et al. 1986).

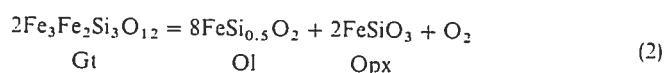
These studies of spinel lherzolites provide information on the oxidation state of the uppermost upper mantle in recent geological times. They show that partial melting occurs under moderately reducing conditions ( $-1.0 \log$  units relative to FMQ) and that primary melts have  $Fe^{3+}/(Fe^{3+} + Fe^{2+})$  of approximately 0.1 (Christie et al. 1986). They also demonstrate that any fluid attending melting or metasomatism is relatively oxidised. In the C-O-H system such fluids must be dominantly  $CO_2$  and  $H_2O$  with negligible contents of  $CH_4$  and  $H_2$  (Wood et al. 1990).

From the standpoint of Earth evolution the possibility that upper mantle oxidation state exhibits secular variation is of considerable interest. In order to investigate the suggestion further requires study of samples of Proterozoic and Archaean age from, for, example the deep interiors of cratons. One possibility is measurement of the oxidation states of diamond inclusions, some of which show Archaean ages (Richardson et al. 1984). Another, perhaps more representative sampling is provided by the garnet lherzolite xenoliths found in cratonic kimberlite eruptions. Although many such eruptions are of relatively recent age the xenoliths they contain show chemical evidence of Archaean differentiation (Boyd 1989). Since such xenoliths do not, in general contain spinel, the olivine-orthopyroxene-spinel oxybarometer cannot be applied and it is necessary to use other equilibria to estimate the  $f_{O_2}$  which they record. In a study of ferric iron in garnets from peridotites and eclogites, Luth et al. (1990) suggested

several equilibria involving garnet components which might be used to calculate  $f_{O_2}$ . Given, for example, coexistence of olivine, orthopyroxene and garnet one might use:



or



Addition of clinopyroxene to the system leads to several other possibilities (Luth et al. 1990), all of which require determination of the ferric iron content of the garnet in order for  $f_{O_2}$  to be calculated. Luth et al. demonstrated that the garnets from these xenoliths contain moderate amounts of  $Fe^{3+}$  ( $Fe^{3+}/\Sigma Fe$  of up to 0.16) concentrations which are, in principle, measurable by  $^{57}Fe$  Mössbauer spectroscopy with reasonable accuracy. The major difficulty in applying equilibria such as (1) and (2) lies in the availability of thermochemical data for the ferric garnet components (particularly  $Fe_5Si_3O_{12}$  "skiaegite") and in the solid solution assumptions which must be made for this phase. The ferric components are low in concentration and the garnet is a complex multisite phase, with the implication that activity coefficients for the ferric components depend strongly on composition. Luth et al. (1990) appreciated these problems of calibration and therefore calculated  $f_{O_2}$  using three different equilibria with different sets of assumptions about the thermodynamic properties of garnet. They obtained results indicating that  $f_{O_2}$  in the garnet facies lies between  $-2$  and  $+2 \log$  units relative to FMQ with little dependence on apparent pressure of crystallisation. The results imply, therefore, that the deeper parts of the continental lithosphere have similar  $f_{O_2}$  to the shallower lithosphere and asthenosphere and that there is no evidence that cratonic areas are more reduced.

In view of the widespread occurrence of garnet lherzolites and the relative inaccuracy of the oxybarometers used by Luth et al. (1990), an experimental calibration or test is necessary. In this paper we describe experimental results on the oxidation states of garnets equilibrated with olivine and orthopyroxene at high pressures at known (measured) oxygen fugacity. This provides the means to test and refine oxygen barometers for garnet peridotites.

## Experimental

The experimental arrangement is illustrated in Fig. 1. A layer of natural garnet 1–1.5 mm thick is sandwiched between layers of a mixture of natural olivine and orthopyroxene. The sandwich is contained in an inner capsule of graphite or platinum-iron alloy or

molybdenum. Platinum oxygen fugacity sensors are placed at the boundary between garnet and olivine-orthopyroxene layers and the entire assembly is sealed in a 5 mm outside diameter Pt capsule. In these experiments the capsule was placed at the centre of an 0.5" outside diameter pressure cell made of BaCO<sub>3</sub> and run in a conventional piston-cylinder apparatus at 1300°C and at between 25 and 35 kbar for 1–7 days. (Table 2) Quoted experimental pressures have been corrected downwards by 10% to take account of friction losses. The pressure correction is based on calibration of the albite = jadeite + quartz reaction at 1200°C and 32 kbar (Holland 1980). Temperature measurement and control was via a W<sub>3</sub>/W<sub>25</sub> thermocouple placed on top of the capsule and control was within ± 1°C. We estimate a temperature uncertainty of 5–10°C in the temperatures on top of the capsule and a temperature at the mid point of the garnet layer 20–30° higher than at the thermocouple. The latter estimate is based on measurements of the diopside-enstatite miscibility gap at high pressures and temperatures along the length of the capsule.

Compositions of the starting materials are given in Table 1. All of the natural minerals were separates which had been acid-washed in concentrated HCl and hand-picked to ensure minimal contamination. The separates were then ground to < 10 µm size before mixing and placing in the capsules. In general the "sandwich" was moistened slightly before sealing the outer capsule in the expectation that small amounts of H<sub>2</sub> and H<sub>2</sub>O would aid equilibration. The oxygen fugacity of the experiment was measured with Pt-Fe alloy

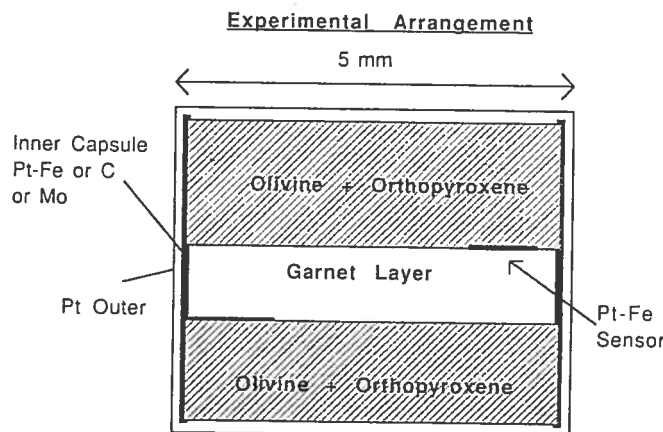


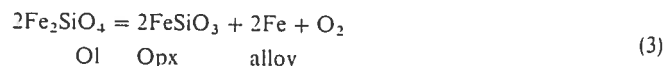
Fig. 1 The experimental arrangement employed in this study. The garnet layer is 1–1.5 mm thick and the outer Pt capsule about 4 mm in length

Table 1 Compositions of starting materials

	Vi313-5 Garnet	Vi313-6 Garnet	PHN3982 Garnet	RAJBG1 Garnet	SC O1 Olivine	SC Opx Opx
SiO <sub>2</sub>	43.7	42.30	42.1	42.8	40.77	57.0
Al <sub>2</sub> O <sub>3</sub>	23.1	23.33	23.2	21.4	0.01	2.37
TiO <sub>2</sub>	0.16	0.08	0.57	ND	ND	0.02
Cr <sub>2</sub> O <sub>3</sub>	1.28	1.30	0.35	4.34	0.04	0.62
FeO <sup>a</sup>	7.59	7.41	10.55	6.36	8.64	5.30
MnO	0.31	0.30	0.19	0.24	0.12	0.12
MgO	20.3	20.34	19.4	23.1	49.13	33.40
CaO	4.74	4.91	4.63	2.52	0.08	0.94
Na <sub>2</sub> O	0.04	0.03	0.06	0.02	0.02	0.05
NiO	0.03	ND	ND	ND	0.41	0.08
Total	101.2	100.0	101.0	100.8	99.2	99.9
Fe <sup>3+</sup> /ΣFe	0.074	0.083	0.123	0.088		

<sup>a</sup>Total Fe as FeO

sensors rather than buffered, although in the case of graphite capsules the measured  $f_{O_2}$  is very close to that calculated from C-CO<sub>2</sub>-CO equilibrium (see below). The  $f_{O_2}$  measurement comes from use of the equilibrium:



The assemblage olivine-orthopyroxene-Pt(Fe) alloy has been calibrated as an oxygen sensor at 1 atm to 20 kbar by Gudmundsson and Holloway (1993) and at oxygen fugacities between air and 2.6 log units below the FMQ buffer. The pressure effect on  $f_{O_2}$  is weak and may be calculated from the measured partial molar volume of Fe in the Fe-Pt alloy (Gudmundsson and Holloway 1993). We applied this sensor by measuring the compositions of Pt-Fe alloy, olivine and orthopyroxene after the experiment. We ensured that one of the two sensors depicted in Fig. 1 was richer in Fe than the equilibrium value while the other was pure Pt. This provided us with an in-situ reversal from low  $f_{O_2}$  (Fe-rich sensor) and from high  $f_{O_2}$  (pure Pt sensor) simultaneously. In general there was extremely good convergence of the two sensor compositions (Table 3) indicating that  $f_{O_2}$  was constant across the garnet layer.

After the experiment the capsule was mounted in epoxy cement and sliced longitudinally to reveal a cross-section through the sandwich. Approximately half was saved for microprobe analysis while in the other half the garnet was removed for Mössbauer spectroscopy (see below).

Starting materials and experimental products were analysed (Tables 1, 3 and 4) using the JEOL 8600 microprobe in the Department of Geology at the University of Bristol. A range of silicate standards were used for the silicate minerals and the microprobe was operated in wavelength-dispersive mode at 15 kV accelerating voltage and 15 nA beam current. Full ZAF corrections were applied. The Pt-Fe redox sensors were analysed under the same conditions using pure Pt and pure Fe metals as standards. In general the silicate phases exhibited modest changes in bulk composition while the garnets showed appreciable changes in ferric iron content (see discussion). We performed several experiments in which severe and substantial Fe-loss to the Pt-Fe capsule liner was observed. These experiments were discarded. All data discussed below refer to experiments in which the Fe/Mg ratios of the products are essentially homogeneous throughout the charge. The product Pt-Fe alloys were always essentially homogeneous and we noted excellent convergence of Fe-poor and Fe-rich compositions. The one exception to this general observation was experiment GR17, performed in an Mo inner capsule, in which Fe-rich and Fe-poor sensors did not converge in composition to within analytical error (Table 3). Some experiments produced spinels among the products (Table 4b) and these were analysed on the microprobe using spinel standards whose

**Table 2** Experimental conditions and starting material. (*Vi*), (*phn*) and (*raj*) refer to garnets Vi313-6, PHN3982 and RAJBG1 respectively. In experiment GR25 an olivine of composition  $Fa_{50}$  was used

Experiment	$T$ °C	$P$ kbar	Time (h)	Starting	Capsule
GR1	1300	25	22	Ol, opx, gt(Vi)	Fe-Pt alloy
GR10	1300	35	96	Ol, opx, gt(Vi)	Fe-Pt alloy
GR11	1300	35	69	Ol, opx, gt(phn)	Fe-Pt alloy
GR13	1300	35	25	Ol, opx, gt(phn)	Fe-Pt alloy
GR16	1300	35	76	Ol, opx, gt(phn)	Graphite
GR17	1300	35	74	Ol, opx, gt(phn)	Mo
GR24	1300	30	167	Ol, opx, gt(phn)	Graphite
GR25	1300	30	147	$Fa_{50}$ , opx, gt(phn)	Mo
GR29	1300	30	147	Ol, opx, gt(raj)	Graphite
GR31	1300	35	147	Ol, opx, gt(raj)	Mo
GR32	1300	35	168	Ol, opx, gt(raj)	Graphite

**Table 3** Compositions of Fe-Pt alloys and calculated oxygen fugacities. Figures in brackets refer to  $f_{O_2}$  uncertainties arising from differences in compositions between initially Fe rich (Fe-Pt) and initially Fe free (Pt) alloys

Experiment	$X_{Fe}(Fe-Pt)$	$X_{Fe}(Pt)$	$f_{O_2}$ (alloy)	$f_{O_2}$ (CCO) <sup>b</sup>	$f_{O_2}$ (ol-opx-sp)
GR1	0.3495	0.3075	- 6.51 (0.4)	—	- 6.36
GR10	0.2456	0.2196	- 5.64 (0.2)	—	—
GR11	0.2075	0.1695	- 5.43 (0.4)	—	—
GR13	0.4500	0.3900	- 7.94 (0.4)	—	—
GR16	0.298	0.290	- 6.06 (0.1)	- 5.73; - 6.46	—
GR17	0.37	0.2144	- 5.60 <sup>a</sup>	—	—
GR24	0.340	0.336	- 7.30 (0.1)	- 6.27; - 6.77	—
GR25	0.4527	0.4007	- 7.33 (0.4)	—	—
GR29	0.289	0.281	- 6.61 (0.1)	- 6.27; - 6.77	- 6.42
GR31	0.265	0.240	- 5.86 (0.2)	—	—
GR32	0.245	0.221	- 5.57 (0.2)	- 5.73; - 6.46	—

<sup>a</sup>Fe-rich alloys strongly zoned;  $f_{O_2}$  based on Pt alloy only

<sup>b</sup>First figures based on Jakobsson and Oskarsson (1994), second on Ulmer and Luth (1991)

$Fe^{3+}$  contents had been determined by  $^{57}Fe$  Mössbauer spectroscopy. This enabled us to estimate the  $Fe^{3+}$  contents of the product spinels from stoichiometry in the manner described in detail by Wood and Virgo (1989).

Ferric iron contents of starting and product garnets were determined by  $^{57}Fe$  Mössbauer spectroscopy. As discussed above, garnet was removed from one half of the sandwich and ground to a fine powder in order to make a bulk analysis of  $Fe^{3+}/\Sigma Fe$  using the Mössbauer technique. The powders were spread on aluminium foil and  $^{57}Fe$  spectra at 298 and 77 K taken using a 40 mCi Co/Pd source. Sample thicknesses were controlled so that the absorber density was less than 5 mgm Fe/cm<sup>2</sup> to avoid saturation effects (Bancroft 1973). Mirror image spectra were recorded over 512 channels using a multichannel analyser. A velocity range of approximately + 4 to - 4 mm/s was used and the velocity was calibrated using Fe foil with values of  $g_0$  of 3.9156 mm/s and  $g_1$  of 2.2363 mm/s (Stevens and Stevens 1972). Spectra at 77 K were taken to check on the possibility that the ratios of recoil-free fractions in dodecahedral and octahedral sites are temperature dependent (Amthauer et al. 1976).

The spectra (Fig. 2a, b) were folded and fitted using various assumptions. In general, spectra of natural garnets are fitted using one asymmetric doublet for dodecahedral  $Fe^{2+}$  and one symmetric doublet for octahedral  $Fe^{3+}$  (Amthauer et al. 1976; Luth et al. 1990). We used the same approach. The widths and areas of the two halves of the  $Fe^{2+}$  doublet were left unconstrained while both halves of the  $Fe^{3+}$  doublet were fixed at the same width and area. Line shape was assumed to be Lorentzian. Two computer programmes were used for fitting the spectra, MOSSFITA (after Davidson 1959, modified at the Geophysical Laboratory) and PCMOSS supplied by CMTE Elektronik, 8012 Riemerling, Germany. No significant differences in  $Fe^{3+}/\Sigma Fe$  were observed.

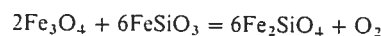
## Results

### Oxygen fugacity accuracy

The method which we used to determine oxygen fugacity (Gudmundsson and Holloway 1993) is based on equilibrium (3) involving components of olivine, orthopyroxene and Pt-Fe alloy. Based on experimental tests relative to CO-CO<sub>2</sub> gas mixtures at 1 atm pressure the barometer is estimated by Gudmundsson and Holloway to be accurate to within  $+/- 0.2 \log f_{O_2}$  units in the range of our experiments. Additional uncertainties accrue from compositional variations in the sensor phases and at high pressure from the uncertainty in the partial molar volume of Fe in the sensor (Gudmundsson and Holloway 1993) In Table 3 we give uncertainties arising purely from phase compositions while in Figs. 3, 6 and 7 we have added this to the 0.2 log units' uncertainty in the barometer. Several of our experiments yielded assemblages which enable us to test the applicability of this equilibrium. Firstly, experiments GR1 and GR29 yielded small amounts of spinel close to the interface between garnet and olivine-orthopyroxene layers. This spinel (Sp) enables  $f_{O_2}$  to be calculated from the equilibrium:

Table 4a Compositions of product garnets

	GR1 [1]	GR10 [12]	GR11 [21]	GR13 [42]	GR16 [31]	GR17 [19]	GR24 [39]	GR25 [21]	GR29 [42]	GR31 [69]	GR32 [49]
SiO <sub>2</sub>	41.43	42.23(32)	43.36(1.0)	41.4(70)	41.72(42)	41.85(30)	42.75(73)	41.85(46)	42.95(38)	42.63(1.6)	42.54(2.0)
Al <sub>2</sub> O <sub>3</sub>	22.64	22.20(27)	24.70(51)	22.2(1.0)	22.96(35)	22.72(28)	23.43(70)	22.91(27)	21.32(84)	20.69(1.8)	20.59(2.6)
TiO <sub>2</sub>	0.21	0.16(07)	0.34(12)	0.57(18)	0.42(15)	0.60(13)	0.41(09)	0.48(11)	0.04(08)	0.01(01)	0.01(01)
Cr <sub>2</sub> O <sub>3</sub>	1.46	1.28(08)	0.36(16)	0.24(04)	0.30(12)	0.30(07)	0.33(08)	0.31(07)	3.45(1.0)	3.96(49)	3.91(52)
FeO <sup>a</sup>	7.13	6.94(29)	6.25(2.5)	10.2(1.1)	9.25(76)	9.21(93)	7.90(76)	13.63(1.7)	5.89(46)	6.04(24)	6.01(20)
MnO	0.34	0.26(04)	0.30(04)	0.25(04)	0.26(04)	0.28(05)	0.31(04)	0.22(04)	0.31(04)	0.32(04)	0.31(05)
MgO	20.24	21.28(63)	23.38(2.5)	19.25(1.6)	19.89(75)	19.90(67)	20.83(82)	17.73(1.1)	23.35(56)	23.57(1.1)	23.21(1.5)
CuO	4.98	4.22(62)	3.07(101)	4.61(64)	4.40(42)	4.45(34)	4.25(45)	4.04(63)	2.46(40)	2.33(34)	2.33(28)
Total	98.4	98.6	101.8	98.7	99.2	99.3	100.2	101.2	99.8	99.5	98.9
Fe <sup>3+</sup> /ΣFe	ND	0.216(i)	0.147(i)	0.080(d)	0.168(i)	0.25(i)	0.099(d)	0.117(nc)	0.130(i)	0.194(i)	0.195(i)
X <sub>Fe(ol)</sub>	0.16	0.08(1)	0.05(1)	0.094(8)	0.140(7)	0.12(3)	0.120(3)	0.31(1)	0.075(2)	0.087(2)	0.086(2)
<i>a</i> <sub>Fe<sup>3+</sup>(sp)}</sub>	0.195	0.106	0.065	0.119	0.172	0.150	0.150	0.355	0.096	0.110	0.109
K <sub>d</sub> <sup>b</sup>	-	1.65(i)	2.43(i)	2.62(i)	1.33(d)	1.43(d)	1.41(d)	0.89(i)	1.52(i)	1.22(d)	1.24(d)

<sup>a</sup>Total Fe as FeO<sup>b</sup>Ferric iron content of garnet subtracted (i), (d) and (nc) refer to increase, decrease and no change respectively. Figures in parentheses [ ] refer to total number of analyses; numbers in parentheses ( ) refer to 1 standard deviation

Sp            Opx            Ol

(4)

provided the ferric iron content of spinel and hence the activity of Fe<sub>3</sub>O<sub>4</sub> in this phase may be determined. We calculated Fe<sup>3+</sup> contents from the microprobe analyses as discussed above and then calculated *f*<sub>O<sub>2</sub></sub> from the oxybarometer calibration given by Wood et al. (1990) and Bryndzia and Wood (1990). As can be seen from Table 3 and Fig. 3 there is excellent agreement between the spinel oxybarometer and the Pt-Fe version.

A second test is provided by experiments performed in graphite capsules. Although we do not know the composition of any fluid phase present in the capsule it must, under oxidising conditions, be a mixture of CO<sub>2</sub> and H<sub>2</sub>O with a small amount of CO. If we make the simplest assumption of a pure CO<sub>2</sub>-CO fluid, then we can calculate the oxygen fugacity from equilibrium between graphite and CO<sub>2</sub>. Results shown in Table 3 and Fig. 3 are based on two independent calibrations of the *f*<sub>O<sub>2</sub></sub> of the C-CO<sub>2</sub>-CO buffer, those of Ulmer and Luth (1991) and Jakobsson and Oskarsson (1994). The latter calibrations differ from one another slightly in the pressure range of interest because we have been forced to extrapolate them linearly outside the pressure range in which they strictly apply. In general, however, they agree with equilibrium (3) within 0.5 log units, which is the approximate uncertainty in the Pt-Fe alloy method. The comparison with C-CO<sub>2</sub>-CO requires several assumptions, of course, but these are perhaps better than one would think at first sight. Firstly, any fluid in the capsule is dominated by the presence of large amounts of graphite, so would be expected to be mostly CO<sub>2</sub>. Secondly, even if the fluid were only 50% CO<sub>2</sub>, the error in *f*<sub>O<sub>2</sub></sub> would only be about 0.3 log units, well within the uncertainty in the method. The agreement with C-CO<sub>2</sub>-CO contradicts earlier suggestions (e.g. Thompson and Kushiro 1972) that graphite capsules buffer *f*<sub>O<sub>2</sub></sub> conditions close to the iron-wüstite equilibrium. The results shown in Fig. 3 demonstrate that we can be confident in the accuracy of *f*<sub>O<sub>2</sub></sub> determinations with equilibrium (3) and of their comparability with the olivine-orthopyroxene-spinel oxybarometer.

#### Ferric iron contents of garnet

The procedure which we used for fitting the Mössbauer spectra of the garnets is described above. Results, in terms of Fe<sup>3+</sup>/(Fe<sup>3+</sup> + Fe<sup>2+</sup>), and of hyperfine parameters for the garnet spectra are given in Table 5. For our spectra collected at 298 K we observe good agreement of hyperfine parameters and line widths with those given for garnets of similar composition by Luth et al. (1990). Luth et al. (1990) observed, however, substantial differences between the Fe<sup>3+</sup>/ΣFe ratios

Table 4b Chemical compositions of product spinels and orthopyroxenes. Parentheses [ ] and ( ) have same meaning as in Table 4a

	GR1 [18]	GR29 [10]	GRI [02]	GR10 [18]	GR11 [26]	GR13 [7]	GR16 [10]
SiO <sub>2</sub>	0.80(52)	0.37(05)	55.39(04)	57.96(47)	58.28(66)	55.50(67)	55.19(49)
Al <sub>2</sub> O <sub>3</sub>	46.70(75)	34.4(2.4)	2.40(03)	3.50(57)	4.0(1.4)	2.00(20)	2.74(21)
TiO <sub>2</sub>	0.50(03)	0.13(02)	—	0.09(04)	0.13(10)	0.02(03)	0.14(06)
Cr <sub>2</sub> O <sub>3</sub>	5.50(63)	34.0(2.8)	0.58(03)	0.38(09)	0.30(24)	0.53(07)	0.26(19)
FeO <sup>a</sup>	33.91(86)	9.60(28)	4.97(60)	6.07(67)	3.69(98)	5.26(11)	7.43(73)
MnO	0.13(04)	0.22(03)	0.13(02)	0.20(04)	0.16(03)	0.07(06)	0.11(06)
MgO	9.85(40)	18.5(47)	33.36(28)	33.18(71)	34.04(67)	33.64(51)	31.42(53)
CaO	0.06(04)	0.06(01)	0.95(04)	1.06(26)	0.70(19)	0.95(05)	1.23(15)
Na <sub>2</sub> O	—	0.04(02)	0.05(01)	0.03(02)	0.08(02)	0.03(03)	0.08(03)
Total	97.5	97.3	98.4	102.5	101.4	98.0	98.6
Fe <sup>3+</sup> /ΣFe	0.28	0.21	—	—	—	—	—
<sup>4</sup> FeSiO <sub>3</sub>	—	—	0.073	0.086	0.053	0.077	0.110
<sup>4</sup> MgSiO <sub>3</sub>	—	—	0.875	0.841	0.868	0.879	0.828
	GR17 [3]	GR24 [10]	GR25 [13]	GR29 [11]	GR31 [20]	GR32 [20]	
SiO <sub>2</sub>	56.23(46)	56.15(30)	53.69(68)	56.39(93)	57.27(122)	56.94(73)	
Al <sub>2</sub> O <sub>3</sub>	2.62(30)	4.43(21)	3.15(25)	4.17(28)	3.58(49)	3.03(29)	
TiO <sub>2</sub>	0.17(13)	0.19(05)	0.18(05)	0.04(02)	0.00(01)	0.00(01)	
Cr <sub>2</sub> O <sub>3</sub>	0.35(24)	0.13(05)	0.09(02)	0.78(14)	1.13(26)	1.02(28)	
FeO <sup>a</sup>	6.40(1.2)	6.47(37)	15.84(68)	4.39(10)	4.98(13)	4.93(18)	
MnO	0.13(03)	0.17(04)	0.10(05)	0.13(05)	0.16(03)	0.13(04)	
MgO	31.71(1.1)	31.8(40)	25.61(86)	33.00(34)	32.17(62)	32.81(82)	
CaO	1.20(25)	1.34(47)	1.24(43)	0.66(06)	0.75(14)	0.63(09)	
Na <sub>2</sub> O	0.12(05)	0.10(01)	0.15(05)	0.06(03)	0.17(07)	0.11(13)	
Total	98.9	100.8	100.0	99.6	100.2	99.6	
<sup>4</sup> FeSiO <sub>3</sub>	0.095	0.094	0.240	0.064	0.073	0.072	
<sup>4</sup> MgSiO <sub>3</sub>	0.835	0.820	0.690	0.870	0.838	0.855	

<sup>a</sup>Total Fe as FeO

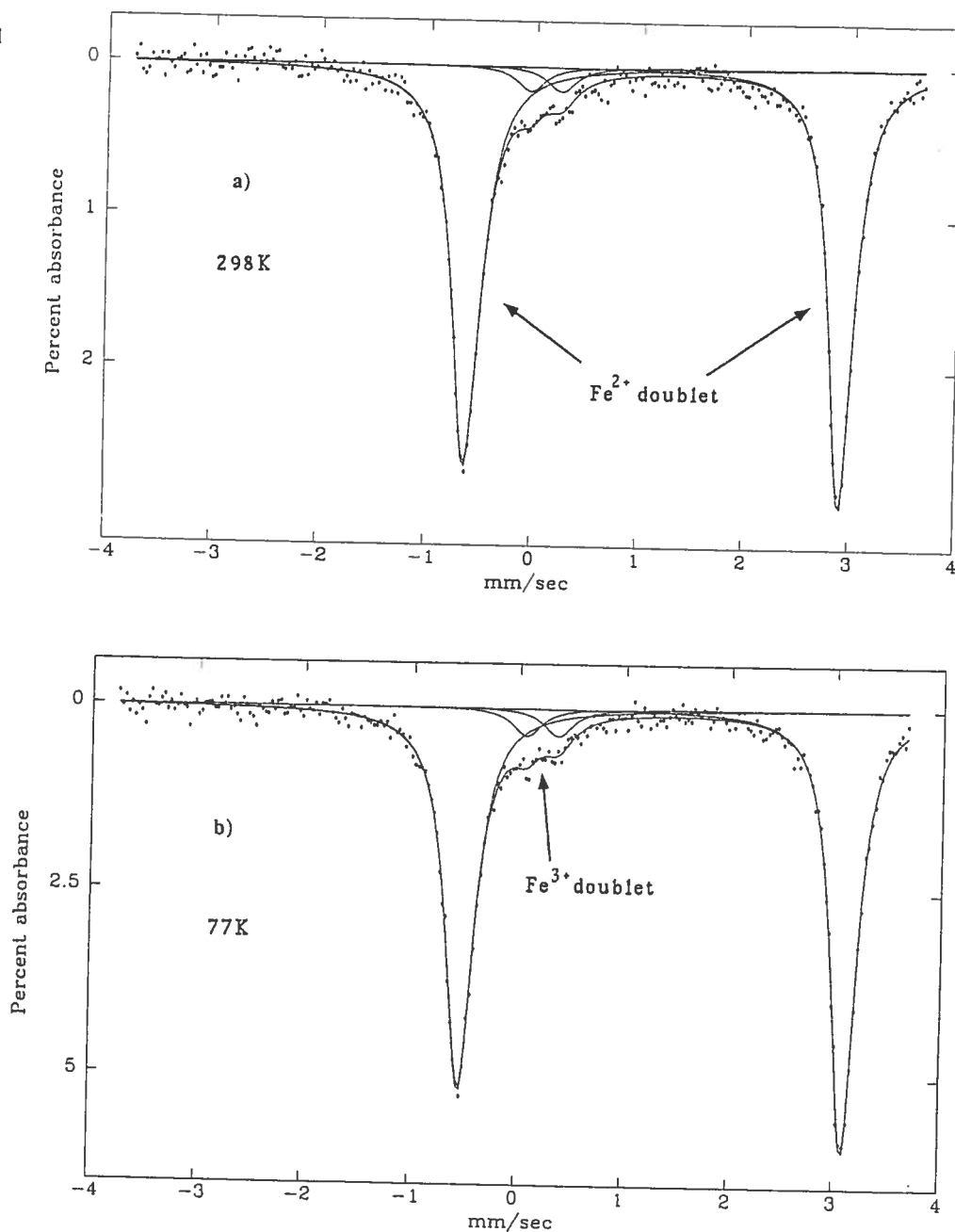
determined from spectra obtained at 77 K and those determined at 298 K. They found an apparent diminution of Fe<sup>3+</sup> content with decreasing temperature of the measurement, due to changing recoil-free fraction, in general accord with the results of Amthauer et al. (1976). In some cases, however, Luth et al. (1990) obtained much larger differences between 298 K and 77 K than those anticipated. At low values of Fe<sup>3+</sup>/ΣFe ( $\leq 0.05$ ) they found only about one half to one third the peak area for ferric iron at 77 K as at 298 K, in contrast to Amthauer et al. (1976) who found the relative change in area between 298 and 77 K to be only of the order of 10%. The observations of Luth et al. (1990) may have been an artefact of fitting spectra with broadened peaks, since they also found, at 77 K, considerable broadening of the ferrous doublet. For example in garnet FRB 76, line widths of 0.324 mm/s (low velocity peak) and 0.266 mm/s (high velocity peak) obtained at 298 K, broadened to 0.547 mm/s and 0.466 mm/s respectively at 77 K. This observation is counter to those of Amthauer et al. (1976) who found almost no difference in line width between 298 and 77 K spectra and suggests to us that Luth et al. (1990) had some unsuspected experimental problem such as vibration of the sample or crystallisation of ice on the windows of the cryostat. Our results indicate little change in relative areas of ferric and ferrous doublets

between 77 and 298 K (Table 5), 2 samples showing a slight decrease at 77 K and the third an increase. Line widths (full width at half-height) are also unchanged between 77 and 298 K, in agreement with the results of Amthauer et al. (1976) (see Fig. 2). The temperature dependencies of the hyperfine parameters are also in good agreement with Amthauer et al.'s data, the Isomer Shift for Fe<sup>2+</sup>, for example, decreasing from 1.42 to 1.29 mm/s in exact agreement with their observations for pyropic garnet. In view of the small differences between apparent ferric iron contents obtained at 77 and 298 K, and the agreement of our results with those of Amthauer et al. (1976) we opted to neglect the temperature dependence of the recoil-free fraction and to use apparent Fe<sup>3+</sup> contents derived from 298 K data for our thermobarometric calculations. If the Fe<sup>3+</sup> contents are, based on the 298 K data, actually overestimated by 10% (Amthauer et al. 1976; A. Woodland and H. O'Neill, personal communication) then the error in calculated  $f_{O_2}$  is only +0.2 log units.

#### Approach to equilibrium

The changes in compositions of the garnets, olivines and orthopyroxenes during our experiments are shown in Tables 4a, b and in Fig. 4, a plot of oxidation state as

Fig. 2 Mössbauer spectra of garnet Vi313-5 at 298 K (a) and 77 K (b). Note that line widths and the relative areas of  $\text{Fe}^{3+}$  (0.07) and  $\text{Fe}^{2+}$  (0.93) doublets are insensitive to absorber temperature (see text)



a function of  $f_{\text{O}_2}$  relative to the FMQ buffer. For this figure we took FMQ at 1 atm from O'Neill (1987a) and corrected to high pressure using the mineral volumes given by Robie et al. (1978). It can be seen that substantial changes in ferric iron content (as  $\text{Fe}^{3+}/\Sigma\text{Fe}$ ) occurred during many of the experiments and that the final oxidation states correlate with oxygen fugacity. Although we were able both to reduce and to oxidise the garnet starting materials, it appears, from Fig. 4 that, in general, oxidation progresses more easily than reduction in our experimental arrangement.

Figure 5 shows that the olivine-garnet Fe-Mg partition coefficient  $K_d$  also changed appreciably during

most experiments. We define  $K_d$  as:

$$K_d = \frac{X_{\text{Mg}}^{\text{ol}} \cdot X_{\text{Fe}}^{\text{gt}}}{X_{\text{Mg}}^{\text{gt}} \cdot X_{\text{Fe}}^{\text{ol}}} \quad (5)$$

and, in Fig. 5, compare it with the values, derived from O'Neill and Wood (1979) which would be expected at equilibrium. The range shown takes account of uncertainty in the calibration of O'Neill and Wood and the effects of variable Ca content of the garnet, increasing Ca acting to increase  $K_d$  (O'Neill and Wood 1979). Figure 5 shows that, while most experiments approached the equilibrium values, there is still



a correlation between initial and final  $K_d$  values implying disequilibrium in the high and low  $K_d$  experiments. This conclusion applies irrespective of whether or not one corrects the garnet Fe/Mg ratio for  $Fe^{3+}$  content i.e. subtracts  $Fe^{3+}$  from the Fe content in order to calculate a charge-balanced  $K_d$  with Mg and  $Fe^{2+}$ . O'Neill and Wood did not correct their  $K_d$  values for  $Fe^{3+}$  content of garnet since they were unable to measure the latter, but we believe that their  $Fe^{3+}$  contents should have been towards the low end of our spectrum of values. We therefore present  $Fe^{3+}$ -corrected

$K_d$  values in Fig. 5 and anticipate, as observed, that most values should be towards the low end of the values of O'Neill and Wood (1979) because their values are inflated by any  $Fe^{3+}$  present in their product garnets.

The observed incomplete Fe-Mg equilibration between olivine and garnet phases in three experiments is unsurprising in view of their physical separation in the starting assemblage (Fig. 1) and the known refractory nature of garnet. What is encouraging, however, is that almost all experiments showed substantial shifts in  $K_d$  and in garnet oxidation state towards the equilibrium values. When we consider the three experiments which are clearly not in Fe-Mg exchange equilibrium, GR11,

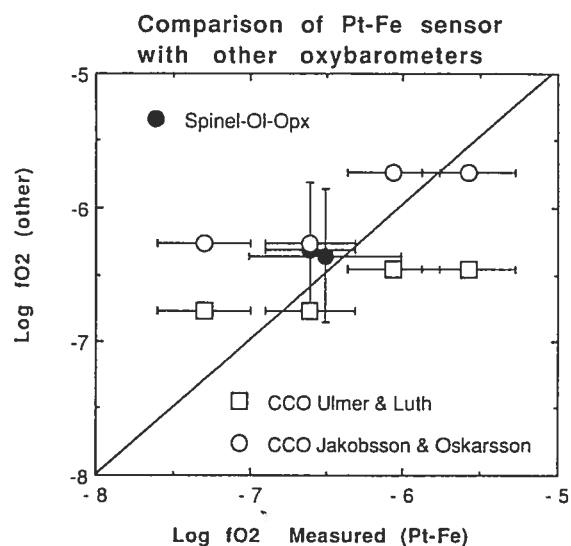


Fig. 3 Figure showing comparison between  $f_{O_2}$  measured with the Pt-Fe sensor and values derived from the spinel-olivine-orthopyroxene barometer (experiments GR1, GR29) and from the calculated equilibrium between graphite, CO and  $CO_2$  (CCO) (experiments GR16, GR24, GR29 and GR32). In the latter case the calibrations of Ulmer and Luth (1991) and of Jakobsson and Oskarsson (1994) are shown for comparison

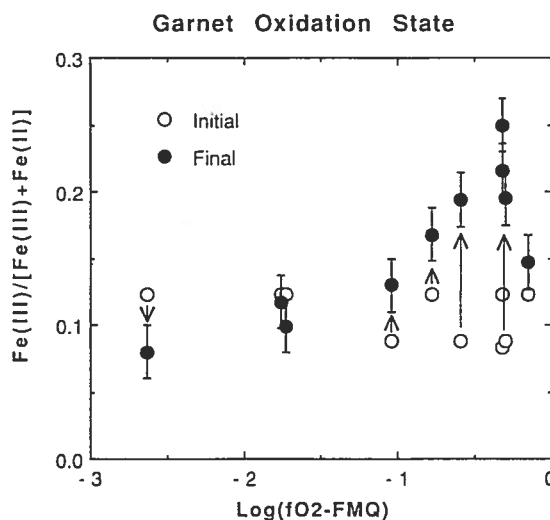


Fig. 4 The observed shifts in ferric iron contents of garnet during the experiments. Note that many experiments produced dramatic shifts in oxidation state and that there is a correlation between oxidation state and measured  $f_{O_2}$ .

Table 5 Mössbauer data for garnet starting materials and products.  $\chi^2$  is given on a per channel basis for folded spectra of 512 channels (*I.S.* Isomer Shift, *Q.S.* Quadrupole Splitting and Width are in mm/s; *LV* and *HV* refer to low and high velocity peaks of the ferrous doublet)

Sample	I.S. $Fe^{2+}$	Q.S.	Width (LV)	Width (HV)	Area (LV/HV)	I.S. $Fe^{3+}$	Q.S.	Width	Area ( $Fe^{3+}$ )	$\chi^2$
Vi313-5	1.290	3.561	0.323	0.281	1.035	0.232	0.319	0.472	0.074	1.232
Vi77K	1.423	3.651	0.326	0.281	0.991	0.359	0.298	0.348	0.072	0.982
PHN3982	1.291	3.560	0.296	0.252	1.03	0.308	0.285	0.396	0.123	1.188
PHN77K	1.424	3.652	0.296	0.279	0.97	0.393	0.239	0.346	0.114	1.017
RAJBG1	1.290	3.563	0.337	0.266	0.991	0.175	0.317	0.434	0.088	1.319
RAJB77K	1.424	3.651	0.363	0.295	0.973	0.300	0.331	0.330	0.110	1.236
Vi313-6	1.290	3.562	0.293	0.248	0.989	0.204	0.342	0.355	0.083	1.243
GR10	1.294	3.546	0.279	0.250	0.977	0.201	0.350	0.325	0.216	0.990
GR11	1.290	3.560	0.267	0.236	1.012	0.206	0.322	0.286	0.147	1.097
GR13	1.295	3.548	0.313	0.259	1.108	0.275	0.270	0.305	0.080	1.376
GR16	1.289	3.545	0.285	0.243	1.024	0.228	0.329	0.328	0.168	1.161
GR17	1.288	3.540	0.279	0.251	0.968	0.244	0.294	0.326	0.250	0.871
GR24	1.288	3.554	0.275	0.242	0.970	0.180	0.411	0.331	0.099	1.001
GR25	1.287	3.552	0.273	0.235	0.933	0.204	0.334	0.309	0.117	1.228
GR29	1.293	3.546	0.343	0.264	1.013	0.180	0.396	0.312	0.130	1.033
GR31	1.292	3.557	0.321	0.254	1.000	0.210	0.316	0.338	0.194	1.036
GR32	1.288	3.571	0.311	0.262	0.954	0.220	0.372	0.357	0.195	1.012

GR13 and GR25, the first two of which were of relatively short duration (Table 2), it is clear that any errors in Fe content of the two phases will propagate into errors in calculated  $f_{O_2}$  because equilibria (1) and (2) use  $Fe^{2+}$  contents of garnet and olivine as well as the  $Fe^{3+}$  content of garnet. When propagated into  $f_{O_2}$  calculations, equilibria (1) and (2) should yield high values for GR11 and GR13 and low values for GR25.

#### Comparison of Pt-Fe sensor and garnet oxybarometers

Equilibria (1) and (2) were used to calculate the oxygen fugacities recorded by the garnet-olivine-orthopyroxene assemblage in our experimental products. In the case of equilibrium (1) we calculated activities of  $FeSiO_3$  and  $MgSiO_3$  components in orthopyroxene using cation site assignments suggested by Wood and Banno (1973) and assumed ideal mixing on M1 and M2 sites. Mössbauer data (Dyar et al. 1989; Wood, unpublished) show that the  $Fe^{3+}/\Sigma Fe$  of orthopyroxenes of upper mantle composition is only about 0.05, an amount which can be neglected in the calculation of

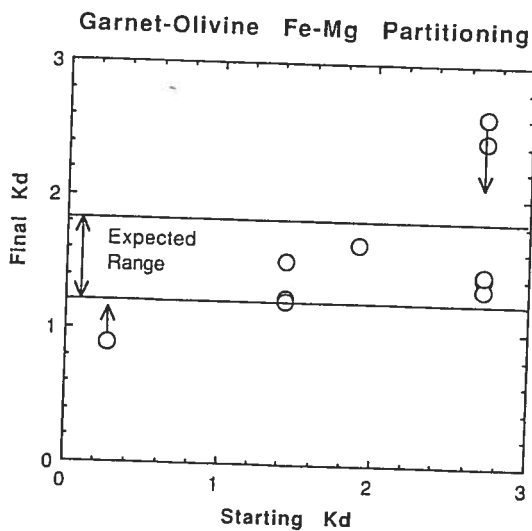


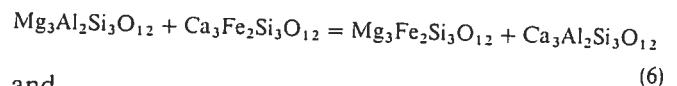
Fig. 5 Measured garnet-olivine Fe-Mg partitioning in the products shown as  $Kd = X_{Mg}^{ol} \cdot X_{Fe}^{gr} / X_{Mg}^{gr} \cdot X_{Fe}^{ol}$ . Note that many experiments approached Fe-Mg exchange equilibrium but that three (GR11, GR13 and GR25) are outside the likely range of equilibrium values (O'Neill and Wood 1979). Arrow indicates observed direction of change

Table 6 Activity coefficient expressions for garnet components (after Wood and Nicholls, 1978). In each expression  $X_i$  refers to the atomic fraction of  $i$  on either cubic or octahedral sites. Ca, Mg and  $Fe^{2+}$  were assumed to reside on the cubic sites and  $Fe^{3+}$ , Al and Cr on octahedral sites.  $X_{Fe}$  refers to  $Fe^{2+}$  and  $X_{Fe(3)}$  to  $Fe^{3+}$

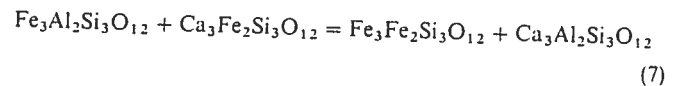
Component	$RT \ln \gamma$
$Ca_3Al_2Si_3O_{12}$	$-X_{Mg}X_{Fe(3)}\Delta G_6^0 - X_{Fe}X_{Fe(3)}\Delta G_7^0 - X_{Mg}X_{Cr}\Delta G_8^0 - X_{Fe}X_{Cr}\Delta G_9^0$
$Ca_3Fe_2Si_3O_{12}$	$X_{Mg}(1-X_{Fe(3)})\Delta G_6^0 + X_{Fe}(1-X_{Fe(3)})\Delta G_7^0 - X_{Mg}X_{Cr}\Delta G_8^0 - X_{Fe}X_{Cr}\Delta G_9^0$
$Mg_3Al_2Si_3O_{12}$	$(1-X_{Mg})X_{Fe(3)}\Delta G_6^0 - X_{Fe}X_{Fe(3)}\Delta G_7^0 + (1-X_{Mg})(1-X_{Fe(3)})\Delta G_8^0 - X_{Fe}X_{Cr}\Delta G_9^0$
$Fe_3Fe_2Si_3O_{12}$	$X_{Mg}(1-X_{Fe(3)})\Delta G_6^0 - (X_{Mg} + X_{Ca})(1-X_{Fe(3)})\Delta G_7^0 - X_{Mg}X_{Cr}\Delta G_8^0 - X_{Fe}X_{Cr}\Delta G_9^0$

$FeSiO_3$  activity. The activity of  $FeSi_{0.5}O_2$  component in olivine was calculated from the olivine composition using the regular solution parameter of 3700 J/mol for Mg-Fe mixing measured by Wiser and Wood (1991). Results for orthopyroxene and olivine are given in Tables 4b and 4a respectively. By combining the results of Hackler and Wood (1989) on garnet-olivine Fe-Mg partitioning with the olivine nonideality measured by Wiser and Wood (1991),  $Fe^{2+}$ -Mg mixing on the cubic garnet site is found, within error, to be ideal. We therefore assumed ideal 3-site mixing for  $Fe^{2+}$ -Mg and, for lack of good constraint, ideal  $Fe^{3+}$ -Al-Cr mixing on the octahedral garnet site too. (Available data on the latter properties, discussed by Luth et al. 1990, suggest that deviations from ideality on the octahedral site are small and they are certainly swamped by the reciprocal term discussed below). The standard state free energy change for reaction (1) at the pressures and temperatures of the experiments was calculated, following Luth et al. (1990), from the internally consistent data base of Moecher et al. (1988). This gives a value of  $\log_{10} K$  for reaction (1) of  $-3.807$  at 35 kbar 1300°C and  $-3.783$ , at 30 kb/1300°C.

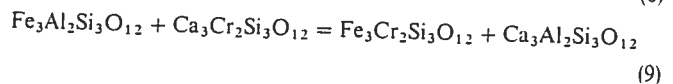
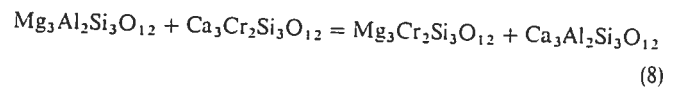
The major nonideality in the garnet phase is that due to the reciprocal reactions:-



and



Using the model of Wood and Nicholls (1978), the standard state free energy changes of these reactions and the analogous reactions below for chromium components add activity coefficients to the garnet components in equilibria (1) and (2) as shown in Table 6. In the Table,  $\Delta G_6^0$  refers to the standard state (pure phase at the  $P$  and  $T$  of interest) free energy change for reaction (6) and so on. The relevant equilibria involving Cr components are:-

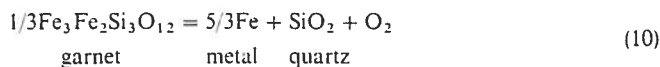


Luth et al. (1990) assumed that the free energy changes for (6) and (7) are the same, independent of pressure and temperature and between 25 and 50 kJ. The standard free energy changes for (8) and (9) are, from the correlation between Ca and Cr in Iherzolite garnets, believed to be about 50 kJ (Wood and Nicholls 1978).

The activity coefficient terms due to the reciprocal reactions are much larger for equilibrium (1) than for (2) so, because of the uncertainties in their magnitude, the corresponding uncertainties in calculated  $f_{O_2}$  are much larger for the first equilibrium. Using values of  $\Delta G^0$  for (6) and (7) of 25 kJ we obtain the oxygen fugacities shown in Fig. 6. Given that the reciprocal terms in the  $f_{O_2}$  calculation are equivalent to about 1.5 log  $f_{O_2}$  units, the uncertainty in the results is at least this large. Uncertainties arising from uncertainties in activity-composition relations for olivine and orthopyroxene are 0.2–0.3 log units (Wiser and Wood 1991) while the uncertainty in  $Fe^{3+}$  content of garnet leads to 0.3–0.4 log units in  $f_{O_2}$  uncertainty. Combining errors in the normal way gives a combined uncertainty of 1.6 log units in  $f_{O_2}$ , excluding any error in the logK of the reaction. It can be seen from Fig. 6 that the barometer proposed by Luth et al. (1990) agrees with the Pt-Fe barometer within this large uncertainty, but that oxygen fugacities appear to be overestimated, in general by about 0.5 log units.

Woodland and O'Neill (1993) have determined the free energy of formation of  $Fe_3Fe_2Si_3O_{12}$  ("skiaigite") garnet at 1100°C from the partitioning of  $Fe^{3+}$  and Al

between coexisting  $Fe_3Fe_2Si_3O_{12}$ - $Fe_3Al_2Si_3O_{12}$  garnet and  $FeAl_2O_4$ - $Fe_3O_4$  spinel solid solutions over the pressure range 15 to 100 kbar. From their data they obtain a logK value of -12.06 at 1373 K for the reaction:-



Combining this with the free energies of the quartz-iron-fayalite (O'Neill 1987b) and quartz-fayalite-ferrosilite (Wood 1987) reactions we obtain logK<sub>2</sub> (for reaction 2) of -5.07 at 1373 K and 1 bar pressure. Extrapolation to the conditions of our experiments requires an estimate of the entropy change of reaction (2) and data for the volumes of the solid phases. The latter were taken from Woodland and O'Neill (1993) for garnet and from Wood (1987) for the other phases. Since almost all solid  $f_{O_2}$  buffers have very similar slopes on logK versus 1/T diagrams, it is possible to extrapolate the Woodland and O'Neill data to 1300°C with considerable confidence. We estimated the entropy of  $Fe_3Fe_2Si_3O_{12}$  garnet at high temperature from the values for  $Ca_3Fe_2Si_3O_{12}$ ,  $Fe_3Al_2Si_3O_{12}$  and  $Ca_3Al_2Si_3O_{12}$  garnets tabulated by Moecher et al. (1988) (i.e.  $S_{ski} = S_{andr} + S_{alm} - S_{gros}$ ). We then used the Moecher et al. results for the other solid phases in reaction (2) and took the values for  $O_2$  from Robie et al. (1978). This yields a temperature dependence for the free energy of reaction (2) which, as anticipated, is similar to that for fayalite-magnetite-quartz (O'Neill 1987b) and nickel-nickel oxide (O'Neill 1987a). We obtain logK<sub>2</sub> as:-

$$\text{LogK}_2 = 9.79 - 20400/T - 0.045P/T \quad (11)$$

From equilibrium (2) we also calculate oxygen fugacities in very good agreement with those observed (Fig. 7) and in this case the uncertainties are smaller than for equilibrium (1) because the activity coefficient terms for the garnet are very much smaller (Table 6). Uncertainty in the free energy of formation of  $Fe_3Fe_2Si_3O_{12}$  garnet, quoted by Woodland and O'Neill, gives an uncertainty of 0.2 log units in  $f_{O_2}$ . The reciprocal terms in the  $f_{O_2}$  calculation are typically on the order of 0.3 log units if we use the values of  $\Delta G_6^0$  and  $\Delta G_7^0$  given by Woodland and O'Neill:

$$\Delta G_6^0 = \Delta G_7^0 = 40200 - 70P(\text{kbar})J$$

So that the largest uncertainties arise from the  $Fe^{3+}$  contents of the garnets rather than, as with equilibrium (1), the mixing properties. Propagating uncertainties from activity-composition relations in olivine and pyroxene yields uncertainties in calculated  $f_{O_2}$ , for equilibrium (2) of about 0.6 log units, of similar order to those obtained for spinel oxygen barometry. As can be seen from Fig. 7, oxygen fugacities calculated from equilibrium (2) are in excellent agreement with oxygen

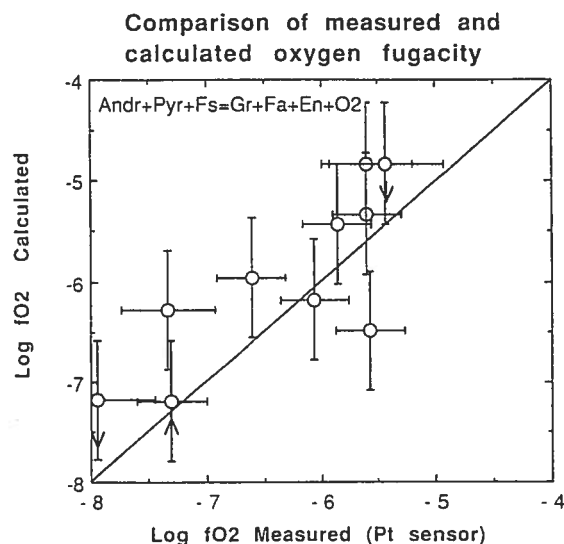


Fig. 6 Comparison of  $f_{O_2}$  measured with the Pt-Fe sensor with  $f_{O_2}$  calculated from equilibrium (1). Error bars shown for calculated  $f_{O_2}$  are  $\pm 0.6$  log units and, for clarity, smaller than the nominal uncertainty (see text). They give an indication of the real apparent error in the barometer of about 0.5 log  $f_{O_2}$  units, however. Arrows indicate the direction of "true"  $f_{O_2}$  equilibrium for those experiments in which olivine and garnet did not reach Fe-Mg exchange equilibrium.

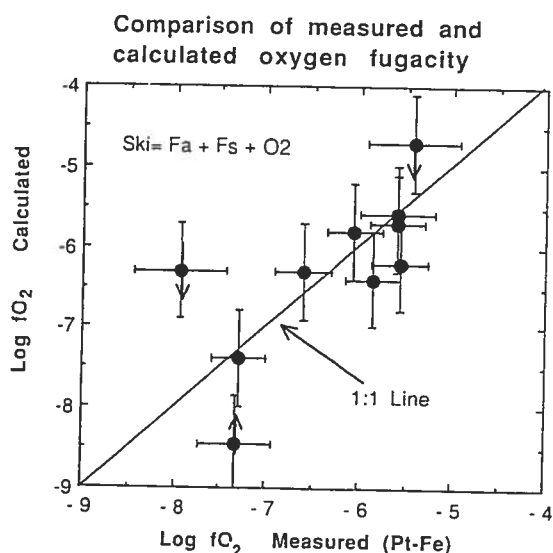


Fig. 7 Comparison of measured  $f_{O_2}$  with values calculated from equilibrium (2). Error bars in both cases are about  $0.6 \log f_{O_2}$  units and agreement is extremely good (see text). Arrows have same significance as in Fig. 6

fugacities measured with the Pt-Fe sensors. The only data which lie outside the quoted uncertainties are from those experiments, discussed above, in which garnet and olivine were not in exchange equilibrium. We conclude, therefore, that equilibrium (2), with free energy expressed by Eq (11) and with the activity terms discussed above should, in general, yield oxygen fugacity to within 0.6 log units.

## Conclusions

We have developed a method for re-equilibrating olivine orthopyroxene and garnet in which oxygen fugacity is measured by two Pt-Fe sensors at the interface between a layer of garnet and a mixed olivine-orthopyroxene layer. A comparison of  $f_{O_2}$  determined from the sensor and that recorded by olivine-orthopyroxene-spinel equilibrium indicates that the former is accurate to within the estimated uncertainty of  $\pm 0.5 \log f_{O_2}$  units.

Despite the separation of olivine and garnet, the two phases approached Fe-Mg exchange equilibrium in experiments of 3–7 days duration at  $1300^\circ\text{C}$  and 30–35 kbar pressure. Ferric iron contents of product garnets removed from the garnet layer were determined by  $^{57}\text{Fe}$  Mössbauer spectroscopy at 298 K. Comparison of spectra obtained at 298 K with results at 77 K indicates that the temperature dependencies of the recoil-free fractions on cubic and octahedral sites are similar and that the apparent  $\text{Fe}^{3+}$  content changes little between 298 and 77 K.

Use of our data to test potential garnet peridotite oxygen barometers shows that the equilibria discussed

by Luth et al. (1990) are suitable and reasonably well calibrated for oxygen thermobarometry. Uncertainties are large, however, because of the large and uncertain nonideality terms for the garnet components. A more precise barometer is provided by the recent determination of the free energy of formation of "Skiagite" garnet,  $\text{Fe}_3\text{Fe}_2\text{Si}_3\text{O}_{12}$  by Woodland and O'Neill (1993). When oxygen fugacity is calculated from equilibrium (2) using the properties of this component, the effects of nonideality are small (order 0.3 log units in  $f_{O_2}$ ) and hence uncertainties are much smaller than for equilibrium (1) where the nonideality terms are on the order of 1.5  $\log f_{O_2}$  units. Comparison of  $f_{O_2}$  values calculated from equilibrium (2) with those obtained from the Pt-Fe sensor indicates that the former yields  $f_{O_2}$  values which are accurate to within  $\pm 0.6 \log f_{O_2}$  units i.e. with comparable uncertainty to the spinel-olivine-orthopyroxene oxybarometer.

Our data on the  $f_{O_2}$  dependence of the oxidation state of Fe in mantle garnets demonstrate that oxygen barometry may be applied quantitatively to garnet peridotites, extending the potential of this technique to deep samples of the continental lithosphere. Preliminary application to the xenoliths from Southern Africa described by Luth et al. (1990) yields oxygen fugacities close to 3.0 log units below the FMQ buffer. This contrasts with continental spinel lherzolite xenoliths which generally lie within 1.0 log units of FMQ (Wood et al. 1990). The explanation for the more reduced nature of the garnet peridotite facies is probably crystallochemical rather than geochemical. As pointed out by Wood et al. (1990) and O'Neill et al. (1993), production of a relatively large volume of dense  $\text{Fe}^{3+}$ -containing garnet at the expense of a smaller volume of spinel means that, even at constant bulk  $\text{Fe}_2\text{O}_3$  content of peridotite, the oxygen fugacity should go down relative to FMQ. Thus the garnet peridotite facies may be inherently more reduced, with the implication that any fluids interacting with such rocks should be correspondingly richer in species such as  $\text{CH}_4$  and poorer in  $\text{CO}_2$  than at shallower levels.

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## References

- Amthauer GH, Annerstan H, Hafner SS (1976) The Mössbauer spectrum of  $^{57}\text{Fe}$  in silicate garnets. *Z Kristallogr* 143:14–55
- Ballhaus C, Berry RF, Green DH (1991) High pressure experimental calibration of the olivine-orthopyroxene-spinel oxygen geobarometer: implications for the oxidation state of the upper mantle. *Contrib Mineral Petrol* 107:27–40
- Bancroft GM (1973) Mössbauer spectroscopy: an introduction for inorganic chemists and geochemists. Wiley, New York
- Boyd FR (1989) Compositional distinction between oceanic and cratonic lithosphere. *Earth Planet Sci Lett* 96:15–26

- Bryndzia LT, Wood BJ (1990) Oxygen thermobarometry of abyssal spinel peridotites: the redox state and C-O-H volatile composition of the Earth's suboceanic mantle. *Am J Sci* 290:1093-1116
- Canil D, Virgo D, Scarfe CM (1990) Oxidation state of mantle xenoliths from British Columbia, Canada. *Contrib Mineral Petrol* 104:453-462
- Christie DM, Carmichael ISE, Langmuir CH (1986) Oxidation states of mid-ocean ridge basalt glasses. *Earth Planet Sci Lett* 79:397-411
- Davidson WC (1959) Variable metric method for minimization. Argonne Nat Lab Doc ANL-5990
- Dick HJB, Fisher RL, Bryan WB (1984) Mineralogic variability of the uppermost mantle along mid-ocean ridges. *Earth Planet Sci Lett* 69:88-106
- Dyar MD, McGuire AV, Ziegler RD (1989) Redox equilibria and crystal chemistry of coexisting minerals from spinel lherzolite mantle xenoliths. *Am Mineral* 74:969-980
- Gudmundsson G, Holloway JR (1993) Activity-composition relationships in the system Fe-Pt at 1300 and 1400°C and at 1 atm and 20 kbar. *Am Mineral* 78:178-186
- Hackler RT, Wood BJ (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
- Holland TJB (1980) The reaction albite = jadeite + quartz determined experimentally in the range 600-1200°C. *Am Mineral* 65:129-134
- Ionov DA, Wood BJ (1992) The oxidation state of subcontinental mantle: oxygen thermobarometry of mantle xenoliths from central Asia. *Contrib Mineral Petrol* 111:179-193
- Jakobsson S, Oskarsson N (1994) The system C-O in equilibrium with graphite at high pressure and temperature: an experimental study. *Geochim Cosmochim Acta* 58:9-18
- Luth RW, Virgo D, Boyd FR, Wood BJ (1990) Ferric iron in mantle-derived garnets: implications for thermobarometry and for the oxidation state of the mantle. *Contrib Mineral Petrol* 104:56-72
- Moecher DP, Essene EJ, Anovitz LM (1988) Calculation and application of clinopyroxene-garnet-plagioclase-quartz geobarometers. *Contrib Mineral Petrol* 100:92-106
- O'Neill HStC (1987a) Quartz-fayalite-iron and quartz-fayalite-magnetite equilibria and the free energy of formation of fayalite ( $\text{Fe}_2\text{SiO}_4$ ) and magnetite ( $\text{Fe}_3\text{O}_4$ ). *Am Mineral* 72:67-75
- O'Neill HStC (1987b) Free energies of formation of  $\text{NiO}$ ,  $\text{CoO}$ ,  $\text{Ni}_2\text{SiO}_4$  and  $\text{Co}_2\text{SiO}_4$ . *Am Mineral* 72:280-291
- O'Neill HStC, Wall VJ (1987) The olivine-spinel oxygen geobarometer, the nickel precipitation curve and the oxygen fugacity of the upper mantle. *J Petrol* 28:1169-1192
- 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
- O'Neill HStC, Rubie DC, Canil D, Geiger CA, Ross CRII, Seifert F, Woodland AB (1993) Ferric iron in the upper mantle and in transition zone assemblages: implications for relative oxygen fugacities in the mantle. *Am Geophys Union Geophys Monogr* 74:73-88
- Richardson SH, Gurney JJ, Erlank AJ, Harris JW (1984) Origin of diamonds in old enriched mantle. *Nature* 310:198-202
- Robie RA, Hemingway BS, Fisher JR (1978) Thermodynamic properties of minerals and related substances at 298.15 K and 1 bar ( $10^5$  Pa) pressure and at higher temperature. *US Geol Surv Bull* 1452
- Stevens IG, Stevens VE (1972) Mössbauer effect data index, covering the 1970 literature. IFI/Plenum Data Corporation, New York
- Thompson RN, Kushiro I (1972) The oxygen fugacity within graphite capsules in piston-cylinder apparatus at high pressures. *Yearbook Carnegie Inst Wash* 71:615-616
- Ulmer P, Luth RW (1991) The graphite-COH equilibrium in  $P$ - $T$ - $f_{\text{O}_2}$  space: an experimental determination to 30 kbar and 1600°C. *Contrib Mineral Petrol* 106:265-272
- Wiser N, Wood BJ (1991) Experimental determination of activities in Fe-Mg olivine at 1400 K. *Contrib Mineral Petrol* 108:146-163
- Wood BJ (1987) Thermodynamics of multicomponent systems containing several solid solutions. (Reviews in mineralogy 17) *Mineral Soc Am, Washington, DC*, pp 71-94
- Wood BJ, Banno S (1973) Garnet-orthopyroxene and orthopyroxene-clinopyroxene relationships in simple and complex systems. *Contrib Mineral Petrol* 42:109-124
- Wood BJ, Nicholls J (1978) The thermodynamical properties of reciprocal solid solutions. *Contrib Mineral Petrol* 66:389-400
- Wood BJ, Virgo D (1989) Upper mantle oxidation state: ferric iron contents of lherzolite spinels by  $^{57}\text{Fe}$  Mossbauer spectroscopy and resultant oxygen fugacities. *Geochim Cosmochim Acta* 53:1277-1291
- Wood BJ, Bryndzia LT, Johnson KE (1990) Mantle oxidation state and its relationship to tectonic environment and fluid speciation. *Science* 248:337-345
- Woodland AJ, Kornprobst J, Wood BJ (1992) Oxygen thermobarometry of orogenic lherzolite massifs. *J Petrol* 33:203-230
- Woodland AB, O'Neill HStC (1993) Synthesis and stability of  $\text{Fe}_3^{2+}\text{Fe}_3^{3+}\text{Si}_3\text{O}_{12}$  garnet and phase relations with  $\text{Fe}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ - $\text{Fe}_3^{2+}\text{Fe}_2^{3+}\text{Si}_3\text{O}_{12}$  solutions. *Am Mineral* 78:1002-1015