

The Olivine–Orthopyroxene–Spinel Oxygen Geobarometer, the Nickel Precipitation Curve, and the Oxygen Fugacity of the Earth's Upper Mantle

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ABSTRACT

The common upper mantle assemblage olivine–orthopyroxene–spinel may be used to calculate the oxygen fugacity at which mantle-derived peridotites have equilibrated. The equilibrium has been calibrated using the large amount of existing data on the thermodynamic properties of each phase in this assemblage. A by-product of this procedure is a new calibration of the olivine–spinel Mg–Fe²⁺ exchange geothermometer. Application of the equilibrium to a variety of peridotite xenoliths indicates that the oxygen fugacity of the upper mantle lies between the quartz–fayalite–magnetite (QFM) and wüstite–magnetite (WM) oxygen buffers; the few apparent exceptions to this rule may be due to analytical error, particularly in the Fe³⁺ content of the spinel phase. In fact, the determination of Fe³⁺ in spinel is at present the limiting factor in the accurate application of the method: within this limitation, the presently available evidence suggests that the oxygen fugacity of the mantle may be laterally homogeneous over wide regions, but may also show small differences between these regions. The fluid species in the system C–H–O at such oxygen fugacities are predominantly CO₂ and/or H₂O, and not CH₄/H₂.

The minimum possible oxygen fugacity of the mantle is given by the nickel content of olivine in equilibrium with orthopyroxene; for typical mantle compositions this minimum curve is virtually coincident with the iron–wüstite (IW) oxygen buffer.

INTRODUCTION

The redox state of the Earth's upper mantle remains one of the most important yet least known constraints on models for the origin and subsequent evolution of the Earth. For example, it is of interest to know whether the mantle, or at least some parts of it, preserves the oxygen fugacity appropriate to the segregation of the iron-rich metal which forms the Earth's core. Such knowledge is fundamental to any hypothesis regarding the early history of the Earth (e.g., Arculus & Delano, 1981; Brett, 1984; Jones & Drake, 1986).

Secondly, the oxygen fugacity either controls or reflects the composition of any volatile phase in the C–O–H system which may be present in the upper mantle. In equilibrium with elemental carbon (graphite or diamond) the species in such a fluid change from predominantly CO₂ + H₂O at relatively high oxygen fugacities (e.g., around the quartz–fayalite–magnetite (QFM) oxygen buffer) to CH₄ + H₂ under reducing conditions (e.g., below the iron–wüstite (IW) oxygen buffer) (Ryabchikov *et al.*, 1981; Eggler & Baker, 1982; Woermann & Rosenhauer, 1985; Taylor & Green, 1986). This has obvious implications for volatile-induced partial melting in the mantle, mantle metasomatism by such fluids, and

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even as to whether there might be an almost inexhaustible source of natural gas deep within the Earth (Gold, 1986).

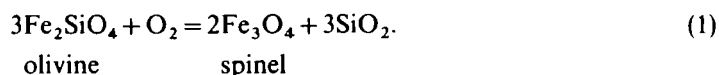
Previous estimates of mantle redox conditions have been made from 'intrinsic' oxygen fugacity measurements on upper mantle derived peridotite and megacryst assemblages (Ulmer *et al.*, 1976, 1987; Arculus & Delano, 1981; Arculus *et al.*, 1984). These results indicated that the redox state of the mantle was considerably heterogeneous, with, most remarkably, the commonest (that is, the 'chrome-diopside' type of Wilshire & Shervais (1975), Group I of Frey & Prinz (1978) or the type A of other authors) spinel lherzolites recording 'intrinsic' oxygen fugacities near or even more reduced than the IW buffer, where CH_4 would be the dominant species in a C-O-H fluid in equilibrium with graphite or diamond.

In contrast, the inferred redox state of mantle-derived basalts is universally some 4 to 5 log units more oxidized than this, and falls near the QFM buffer (Haggerty, 1978). It is therefore desirable to check the results of the 'intrinsic' oxygen fugacity measurements through some independent method. Equilibria involving assemblages containing phases of variable Fe^{2+} to Fe^{3+} ratios potentially provide such methods. For example, the assemblages olivine-orthopyroxene-ilmenite and ilmenite-spinel have both been used (Eggler, 1983; Haggerty & Tompkins, 1983) to obtain estimates of the equilibrium oxygen fugacity of mantle-derived xenoliths and megacrysts. The results indicate fairly oxidized conditions, at or just below QFM, which is in good agreement with the results of the intrinsic measurements on ilmenite-bearing assemblages. However, ilmenite is not a common constituent of the upper mantle: it occurs only in Fe-enriched environments, and therefore these observations have limited relevance to the question of the typical redox state of the mantle as recorded by the far more abundant type A spinel lherzolites.

Equilibrium oxygen fugacities may also be calculated from the almost ubiquitous upper mantle paragenesis olivine-orthopyroxene-spinel (O'Neill *et al.*, 1982) which is present in both type A and B ('Al-augite' or Group II) spinel-lherzolites, spinel-harzburgerites, and those garnet-lherzolite and harzburgite xenoliths which contain accessory magnesiochromite. This olivine-orthopyroxene-spinel oxygen barometer is thus applicable to virtually the whole range of upper mantle peridotitic assemblages not covered by the ilmenite equilibria. In addition to this, an independent estimate of the *minimum* oxygen fugacity of the mantle may be made from the Ni-content of olivine in equilibrium with orthopyroxene. It is the purpose of this paper to present experimentally based calibrations of both these equilibria, to apply them to a range of mantle-derived xenoliths, and to discuss briefly the results and some of the implications.

THE OLIVINE-ORTHOPYROXENE-SPINEL OXYGEN GEOBAROMETER

The reaction which is the basis of the olivine-orthopyroxene-spinel oxygen geobarometer is the familiar QFM equilibrium:



At equilibrium:

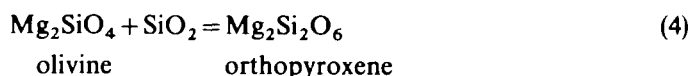
$$\log f_{\text{O}_2} = \frac{\Delta G^\circ(1)T}{2 \cdot 303 RT} + 2 \log a_{\text{Fe}_3\text{O}_4}^{\text{sp}} + 3 \log a_{\text{SiO}_2} - 3 \log a_{\text{Fe}_2\text{SiO}_4}^{\text{ol}}. \quad (2)$$

Since most solid oxygen fugacity buffers have slopes in P - T space that are sub-parallel to

each other, it is convenient to report results relative to the QFM buffer. Hence:

$$\Delta \log f_{\text{O}_2} = 2 \log a_{\text{Fe}_3\text{O}_4}^{\text{P}} + 3 \log a_{\text{SiO}_2} - 3 \log a_{\text{Fe}_2\text{SiO}_4}^{\text{ol}} \quad (3)$$

The activity of SiO_2 in olivine–orthopyroxene assemblages may be calculated using the reaction:



$$\log a_{\text{SiO}_2} = \frac{\Delta G^\circ(4)}{2 \cdot 303 RT} + \log a_{\text{Mg}_2\text{Si}_2\text{O}_6}^{\text{opx}} - \log a_{\text{Mg}_2\text{SiO}_4}^{\text{ol}} \quad (5)$$

In mantle assemblages the components Fe_2SiO_4 and, particularly, Fe_3O_4 , are present only in dilute amounts in olivine and spinel. Hence a reliable calibration of the geobarometer is only possible if the activity–composition relations in the respective crystalline solutions are known within reasonable limits. We believe that this is now the case. For the calculation of $\log a_{\text{Fe}_2\text{SiO}_4}^{\text{ol}}$, mantle olivines may be considered as essentially binary solid solutions between Mg_2SiO_4 and Fe_2SiO_4 , and there have been a large number of studies on the thermodynamic properties of this system. These are briefly reviewed and best values selected below. For $\log a_{\text{Fe}_3\text{O}_4}^{\text{P}}$, the situation is not quite so clear. The composition of natural spinels, such as those occurring in peridotites, lie almost wholly within the fairly complex multicomponent system $\text{MgO}–\text{FeO}–\text{Fe}_2\text{O}_3–\text{Al}_2\text{O}_3–\text{Cr}_2\text{O}_3–\text{TiO}_2$. Additional complexity is introduced by the fact that the spinel structure contains two crystallographically distinct sites, one tetrahedrally coordinated by oxygen, the other octahedrally, and that many cations (e.g., Mg, Fe^{2+} , Fe^{3+} , Al) are capable of substituting into both sites. The task of evaluating the activity of one component (e.g., Fe_3O_4) in such a compositionally and structurally complex phase might therefore appear somewhat daunting; however, we believe that it is amenable to rationalization. The model used, and the fitting of the model to the available experimental data, are described below in some detail.

For the calculation of $\log a_{\text{SiO}_2}$ from equation (5), the problem of activity–composition relations does not arise, as both Mg_2SiO_4 , and $\text{Mg}_2\text{Si}_2\text{O}_6$ are the major components in mantle olivines and orthopyroxenes, and therefore activity coefficients are constrained to be close to unity. Thus the accuracy of the calculation depends only on the accuracy of $\Delta G^\circ(4)$. The available data on this quantity will be assessed below.

CALIBRATION OF THE GEOBAROMETER

Activity–composition relations in $\text{Mg}_2\text{SiO}_4–\text{Fe}_2\text{SiO}_4$ olivine solutions

Most of the experimental work on the activity–composition relations in $\text{Mg}_2\text{SiO}_4–\text{Fe}_2\text{SiO}_4$ olivine solutions has concentrated on the partitioning of Mg and Fe^{2+} between olivine and some other coexisting ferromagnesian phase. While in theory, if some mixing model such as the regular solution model is assumed, it is possible to extract mixing parameters for both phases from such experiments, in practice it is always found that the correlation between the mixing parameters is so great that only the difference between them is accurately constrained (e.g., Matsui & Nishizawa, 1974; O'Neill & Wood, 1979). It is also apparent that the accuracy of such studies cannot justify the selection of anything but the simplest possible model to describe the excess mixing properties of olivine solutions, that of the strictly regular solution, which gives:

$$RT \ln a_{\text{Mg}_2\text{SiO}_4}^{\text{ol}} = 2RT \ln X_{\text{Mg}}^{\text{ol}} + 2 W_{\text{Mg}–\text{Fe}}^{\text{ol}} (1 - X_{\text{Mg}}^{\text{ol}})^2 \quad (6)$$

$$RT \ln a_{\text{Fe}_2\text{SiO}_4}^{\text{ol}} = 2RT \ln X_{\text{Fe}}^{\text{ol}} + 2 W_{\text{Mg}–\text{Fe}}^{\text{ol}} (X_{\text{Mg}}^{\text{ol}})^2 \quad (7)$$

with the W parameter being a constant independent of temperature. There is no other data of any kind of sufficient accuracy to negate this conclusion (see below).

Within these limitations, the partitioning data clearly show that ferromagnesian olivine solutions exhibit larger positive deviations from ideality than co-existing ferromagnesian orthopyroxene (Matsui & Nishizawa, 1974; Kawasaki & Matsui, 1983), garnet (O'Neill & Wood, 1979; Kawasaki & Matsui, 1983), ilmenite (Anderson & Lindsley, 1979), or spinel (Engi, 1983; Jamieson & Roeder, 1984). Recently, Kawasaki & Matsui, (1983) have carried out an extensive and internally consistent statistical analysis of the experimentally determined phase equilibria involving olivine, orthopyroxene, and garnet in the systems MgO-FeO-SiO_2 , $\text{MgO-FeO-Al}_2\text{O}_3\text{-SiO}_2$, and $\text{CaO-MgO-FeO-Al}_2\text{O}_3\text{-SiO}_2$. They deduced that $W_{\text{Mg-Fe}}^{\text{ol}} = (6570 + 6.7 P) (\pm 335) \text{ J g-atom}^{-1}$ (P in kb). Unfortunately, equation A8 in Kawasaki & Matsui (1983) contains some algebraic errors and it is not known how these might have affected the results. Kawasaki & Matsui (1978, 1983), however, have clearly shown that the appropriate method of statistical analysis for this type of problem is a *non-linear* least squares one (e.g., Deming, 1943). This prompted us to re-examine the partitioning data of O'Neill & Wood (1979) on olivine-garnet. Linear regression had earlier given $W_{\text{Mg-Fe}}^{\text{ol}} = 4140 \pm 900 \text{ J g-atom}^{-1}$ at $P = 30 \text{ kb}$. Non-linear regression gives $W_{\text{Mg-Fe}}^{\text{ol}} = 2200 \pm 1240 \text{ J g-atom}^{-1}$, with, however, an apparently negative $W_{\text{Mg-Fe}}^{\text{il}} = (-1230 \pm 1280) \text{ J g-atom}^{-1}$. The reduced χ^2 ($\sigma(\text{ext})^2$ in the nomenclature of Deming (1943)) for this regression is 0.67, which, since this statistic is substantially less than unity, indicates that the accuracy of the data does not constrain the magnitude of the parameters too well. Therefore, a further analysis was attempted, constraining $W_{\text{Mg-Fe}}^{\text{il}}$ to be ideal. This procedure gave $W_{\text{Mg-Fe}}^{\text{ol}} = (3380 \pm 150) \text{ J g-atom}^{-1}$, with a reduced χ^2 of 0.73 (i.e. only marginally increased, and still substantially less than unity). This emphasizes the very high correlation of $W_{\text{Mg-Fe}}^{\text{ol}}$ with $W_{\text{Mg-Fe}}^{\text{il}}$. It is apparent, however, that the correct non-linear least squares procedure does not increase the magnitude of the $W_{\text{Mg-Fe}}^{\text{ol}}$ parameter to the high value reported by Kawasaki & Matsui (1983), at least for this extensive and relatively quite precise set of data. Furthermore, constraining $W_{\text{Mg-Fe}}^{\text{ol}}$ to $6770 \text{ J g-atom}^{-1}$ at 30 kb (i.e. the value proposed by Kawasaki & Matsui (1983)) gives a reduced χ^2 for the regression of 1.09, greater than unity. Therefore this value is near the top end of the range allowed by these data. We thus tentatively conclude that $W_{\text{Mg-Fe}}^{\text{ol}}$ lies in the range $3380\text{--}6770 \text{ J g-atom}^{-1}$ at 30 kb .

The partitioning of Mg and Fe^{2+} between olivine and aluminous spinel is considered in more detail later. Again it is found that there is a very high correlation between $W_{\text{Mg-Fe}}^{\text{ol}}$ and $W_{\text{Mg-Fe}}^{\text{sp}}$. A best fit to the highly precise data of Jamieson & Roeder (1984) is obtained with $W_{\text{Mg-Fe}}^{\text{ol}}$ near 5000 J g-atom , and this value, being in the middle of the range deduced above, has therefore been adopted, with a probable uncertainty estimated to be approximately $\pm 2000 \text{ J g-atom}$. The remaining ferromagnesian partitioning data are not as precise as these studies, and, while they in no way contradict this conclusion, add nothing of any consequence to it. We have not considered the data of Schullien *et al.* (1970) on the partitioning of Mg and Fe^{2+} between olivine and aqueous chloride solution because of the unknown properties of the latter at low temperatures.

Heats of mixing along the $\text{Mg}_2\text{SiO}_4\text{-Fe}_2\text{SiO}_4$ olivine binary have been measured by Wood & Kleppa (1981) using oxide melt solution calorimetry at 970 K . These authors concluded that the heats of mixing showed an asymmetric deviation from ideality, but this conclusion arises solely from the fact that the fit to the data appears to have been constrained to pass directly through the mid points of the heat of solution brackets at the end-member compositions, $X_{\text{Mg}} = 0$ and $X_{\text{Mg}} = 1$ (see also Cohen (1986) for a similar comment on the treatment of other heat of mixing data from the same laboratory). We have therefore re-analysed the data reported in Wood & Kleppa (1981) using linear regression with the data weighted, in the usual way, according to the inverse of the observed variance. The fit to the regular solution model (a quadratic polynomial in $X_{\text{Mg}}^{\text{ol}}$) gave $W_{\text{H Mg-Fe}}^{\text{ol}} = 7080 \pm 1800 \text{ J g-atom}$, with a rather large reduced χ^2 of 2.92. As noted by Wood & Kleppa, this largely due to an apparently anomalous measurement at $X_{\text{Mg}}^{\text{ol}} = 0.4$. However, for the fit to the subregular solution model (a cubic polynomial in $X_{\text{Mg}}^{\text{ol}}$) we found that: (a) the extra cubic term was effectively zero, the other terms remaining unchanged; and (b) the reduced χ^2 increased to 4.38. Thus, the data emphatically do not suggest an asymmetric model. Incidentally, if the datum at $X_{\text{Mg}}^{\text{ol}} = 0.4$ is eliminated, for which there is admittedly no justification except for its anomalous value, $W_{\text{H Mg-Fe}}^{\text{ol}} = 4565 \pm 2000 \text{ J g-atom}^{-1}$, with a reduced χ^2 of 0.13. In any event, $W_{\text{H Mg-Fe}}^{\text{ol}}$ measured at 970 K is in good agreement with $W_{\text{Mg-Fe}}^{\text{ol}}$ selected above from measurements at temperatures of $1173\text{--}1773 \text{ K}$, and therefore there is no evidence for any excess entropy of mixing.

This value of $W_{\text{Mg-Fe}}^{\text{ol}}$ is furthermore in good agreement with the earlier gas mixing studies of Nafziger & Muan (1967) and Kitayama & Katsura (1968).

The estimated uncertainty of $\pm 2000 \text{ J g-atom}^{-1}$ is propagated through equation (2) (the ol-opx-sp oxygen geobarometer) by multiplying by a factor of approximately 4, not, as might seem at first sight, by a factor of 6, as this selected value was used to obtain $W_{\text{Mg-Fe}}^{\text{ol}}$, which appears multiplied by 2 in equation (2). Hence at 1200 K and $X_{\text{Mg}}^{\text{ol}} = 0.9$, this uncertainty will produce an uncertainty in $\Delta \log f_{\text{O}_2}$ of ± 0.3 .

Excess volumes of mixing in $\text{Mg}_2\text{SiO}_4\text{-Fe}_2\text{SiO}_4$ olivines have been measured by Akimoto & Fujisawa (1968), Fisher & Medaris (1969), and Schwab & Küstner (1977). The latter study is the most extensive, and also gives a result in between the other two, and has therefore been adopted. Hence $W_{\text{V Mg-Fe}}^{\text{ol}} = 10.8 \text{ J kb}^{-1}$, and $W_{\text{Mg-Fe}}^{\text{ol}} = (5000 + 10.8 P) \text{ J g-atom}^{-1}$.

The activity of Fe_3O_4 in multicomponent spinel solid solutions

The procedure for calculating the activity of Fe_3O_4 in the natural, multicomponent spinels of interest to this study is based on the model of O'Neill & Navrotsky (1984) for binary spinel solutions. The fairly abundant experimental data on the thermodynamic properties of the binary solutions are used to calibrate the model, which then provides a means for extrapolating into the multicomponent system. The procedure follows three distinct and successive steps:

1. The site occupancy of each cation, and hence the contribution of the cation distribution to the free energy of the solid solution, is calculated using the model of O'Neill & Navrotsky (1984). The free energy of mixing at this stage is termed $\Delta G^\circ(\text{ICD})$, where ICD stands for ideal cation distribution.

2. The excess free energy of mixing which results from the mixing of cations of different sizes (called SM for size mismatch) is then calculated. This procedure is also described in O'Neill & Navrotsky (1984) for binary solutions. It is found that the asymmetry and irregular temperature dependence which is often observed for the macroscopic mixing properties of these binary solutions is largely accounted for by the ICD component of the mixing; consequently only the simplest possible model for the size mismatch effect, that of a strictly regular solution, suffices to obtain a good fit to the binary solution data.

3. The effect of the simultaneous and potentially independent substitution of Mg and Fe^{2+} (hereafter called M type cations) on one hand, and Al, Cr, Fe^{3+} , and M + Ti (the Y type of cations) on the other, is calculated using the reciprocal solution formalism (e.g., Wood & Nicholls, 1978). The excess free energy of mixing from this stage is termed $\Delta G^\circ \text{REC}$.

It is emphasized that at all stages this approach is based on the fitting of the model to experimental observation. Thus the regular solution parameters in stage 2 (size mismatch) are obtained by fitting activities calculated from the ideal cation distribution to experimentally determined activity-composition relations, and miscibility gaps, on the relevant binary joins. Hence any errors introduced in the first stage through the use of inappropriate site preference energies, or indeed through inadequacies in the model, are compensated for in the next stage.

These three stages, and the data used to obtain the necessary parameters, will now be described in more detail.

Ideal cation distribution

In order to simplify not only this step, but also some of those described below, the approximation has been made that the site preference energies of Fe^{2+} and Mg are equal. This is not likely to be correct in detail; however, the site preference energies of these two cations as derived in O'Neill & Navrotsky (1984) from the observed cation distributions in simple end-member spinels are sufficiently similar (the values given are actually equal at 700 K) for this approximation to have but a trivial effect on the subsequently calculated activity-composition relations. With this assumption, the site occupancies in

the spinel may be defined as (c.f. O'Neill & Navrotsky, 1984):

Cation	Tet. site	Oct. site	Sum
M (Fe ²⁺ + Mg)	1 - x - y	N _{Ti} + x + y	1 + N _{Ti}
Fe ³⁺	x	N _{Fe³⁺} - x	N _{Fe³⁺}
Al	y	N _{Al} - y	N _{Al}
Cr	—	N _{Cr}	N _{Cr}
Ti	—	N _{Ti}	N _{Ti}
Total	1	2	3

N_{Al}, etc. are the number of Al cations, etc. to 4 oxygens. Hence for mole fractions, $X_{Al} = N_{Al}/2$, but $X_{Ti} = N_{Ti}$. Note that Cr and Ti are assumed to reside only on the octahedral site.

The equilibrium cation distribution may then be calculated from the two equations:

$$RT \ln \left| \frac{x(N_{Ti} + x + y)}{(N_{Fe^{3+}} - x)(1 - x - y)} \right| + \alpha_{M-Fe^{3+}} + 2\beta(x + y) = 0 \quad (8)$$

$$RT \ln \left| \frac{y(N_{Ti} + x + y)}{(N_{Al} - y)(1 - x - y)} \right| + \alpha_{M-Al} + 2\beta(x + y) = 0 \quad (9)$$

where α and β are the disordering energies (given in Table 1).

The change in the free energy of the spinel solution from cation disordering, relative to an idealized standard state of complete order, is:

$$\Delta G^\circ(\text{disorder}) = RT \sum X_i \ln X_i + \alpha_{M-Fe^{3+}} \cdot x + \alpha_{M-Al} \cdot y + \beta(x + y)^2 \quad (10)$$

where X_i is the fraction of i type cations on each site, so that the first term on the right hand side is the configurational entropy of the solution multiplied by temperature. The free energy of mixing of the

TABLE 1

Summary of the parameters used in this model for the thermodynamic mixing properties of multicomponent spinel solid solutions. References to the original experimental data are given in the text, as is a description of the parameters. All parameters are assumed to be independent of temperature

Parameter	Value (kJ mol ⁻¹)
<i>Cation distribution</i>	
α_{M-Al}^*	56
$\alpha_{M-Fe^{3+}}^*$	20
β	-20
<i>Size mismatch</i>	
$W_{Al-Fe^{3+}}$	18.25
$W_{Cr-Fe^{3+}}$	6.25
W_{Al-Cr}	12.37
$W_{Ti-Fe^{3+}}$	4.60
W_{Ti-Al}^\dagger	26.0
W_{Ti-Cr}^\dagger	10.0
$W_{Mg-Fe^{3+}}$	1.96
<i>Reciprocal solution</i>	
ΔG° (REC 1)	25.15
ΔG° (REC 2)	6.54
ΔG° (REC 3)	0

* Taken for M = Mg.

† Mean of Mg/Ti and Fe²⁺/Ti

‡ Estimated from the correlation in fig. 14 of O'Neill & Navrotsky (1984).

solution relative to the end-member component spinels is then:

$$\Delta G^\circ(\text{ICD}) = \Delta G^\circ(\text{disorder}) - X_{\text{Fe}^{3+}} \Delta G^\circ(\text{disorder})(\text{MFe}_2\text{O}_4) - X_{\text{Al}} \Delta G^\circ(\text{disorder})(\text{MAl}_2\text{O}_4) - X_{\text{Ti}} \cdot 2RT \ln 2. \quad (11)$$

The activity of MFe_2O_4 may be calculated from the above by using numerical differentiation and the definition of activity:

$$RT \ln a_{\text{MFe}_2\text{O}_4} = \Delta G^\circ(\text{ICD}) + (1 - X_{\text{Fe}^{3+}}) \frac{d \Delta G^\circ(\text{ICD})}{d X_{\text{Fe}^{3+}}}. \quad (12)$$

Since we have assumed the equivalence of Mg and Fe^{2+} with regard to the cation distribution, the appropriate correction necessary to calculate the ICD activity of Fe_3O_4 is simply given by statistical thermodynamics (e.g., Kerrick & Darken, 1975) as:

$$\ln a_{\text{Fe}_3\text{O}_4} = \ln a_{\text{MFe}_2\text{O}_4} + (1 + N_{\text{Ti}}) \ln X_{\text{Fe}^{2+}} \quad (13)$$

(the $(1 + N_{\text{Ti}})$ term occurs because this is the number of atoms of Mg and Fe^{2+} per formula unit).

Size mismatch

The model of O'Neill & Navrotsky (1984) assumes that the regular solution interaction parameters (the W terms, below) are constants independent of both the composition and degree of inversion of the spinels. This is to some extent tested in what follows, although the necessary data are somewhat sparse. This assumption, together with that of the equivalence in site preference of Mg and Fe^{2+} , leads to a simple and straightforward extrapolation of the properties of the binary spinel solutions, for which data are available, into the complex multicomponent system. The regular solution model gives (neglecting, as is usual, any possible ternary and quarternary terms):

$$\Delta G^\circ(\text{SM}) = \sum_{\text{M}, \text{Y}} \sum_{i, j} n W_{i-j} X_i X_j \quad (14)$$

and hence

$$RT \ln \gamma_i(\text{SM}) = \sum_{\text{M}, \text{Y}} \left(\sum_j n W_{i-j} X_j + \sum_k n (W_{i-j} + W_{i-k} - W_{j-k}) X_j X_k \right) \quad (15)$$

where n is the number of sites per formula unit on which mixing takes place.

For example, for Fe_3O_4 :

$$\begin{aligned} RT \ln \gamma_{\text{Fe}_3\text{O}_4}(\text{SM}) = & (1 + X_{\text{Ti}}) W_{\text{Mg}-\text{Fe}^{2+}} X_{\text{Mg}}^2 + 2[W_{\text{Al}-\text{Fe}^{3+}} X_{\text{Al}}^2 + \\ & W_{\text{Cr}-\text{Fe}^{3+}} X_{\text{Cr}}^2 + W_{\text{Ti}-\text{Fe}^{3+}} X_{\text{Ti}}^2 + (W_{\text{Al}-\text{Fe}^{3+}} + W_{\text{Cr}-\text{Fe}^{3+}} - W_{\text{Al}-\text{Cr}}) \\ & X_{\text{Al}} X_{\text{Cr}} + (W_{\text{Ti}-\text{Fe}^{3+}} + W_{\text{Al}-\text{Fe}^{3+}} - W_{\text{Al}-\text{Ti}}) X_{\text{Ti}} X_{\text{Al}} \\ & + (W_{\text{Ti}-\text{Fe}^{3+}} + W_{\text{Cr}-\text{Fe}^{3+}} - W_{\text{Ti}-\text{Cr}}) X_{\text{Ti}} X_{\text{Cr}}]. \end{aligned} \quad (16)$$

Note that any interaction terms between the M and Y types of cations are already implicitly taken care of in the calculation of the cation disorder, and therefore do not appear in the above equation.

Values for the W terms are mostly taken from O'Neill and Navrotsky (1984), and are summarized in Table 1. The Ti-contents of spinels from peridotites are generally so low as to be almost negligible, and therefore for the present application of the model only the terms $W_{\text{Al}-\text{Fe}^{3+}}$, $W_{\text{Cr}-\text{Fe}^{3+}}$ and $W_{\text{Al}-\text{Cr}}$ are quantitatively important. $W_{\text{Al}-\text{Fe}^{3+}}$ was obtained from the solvus in the system FeAl_2O_4 – Fe_3O_4 (Turnock & Eugster, 1962), the top of which is at 1133 K. Activities so obtained are in fair agreement with the activity-composition data of Petric *et al.* (1981) at 1573 K, although the method used by the latter (equilibration with Pt–Fe alloys) is apparently not very accurate, as may be judged from two of the calibration experiments, which produced virtually identical alloy compositions in equilibrium with Fe_3O_4 0.01 log f_{O_2} units apart (see Petric *et al.*, 1981). $W_{\text{Cr}-\text{Fe}^{3+}}$ was obtained from the data of Snethlage & Schröke (1976), 1273–1473 K, Katsura *et al.* (1975), 1500 K, and Petric & Jacob (1982a), 1673 K. These results are only in moderate agreement with each other, and therefore the uncertainty in $W_{\text{Cr}-\text{Fe}^{3+}}$ is estimated to be about $\pm 3000 \text{ J g-atom}^{-1}$. This would propagate through equation (2) to produce an uncertainty in log f_{O_2} of ± 0.4 for an alumina-free spinel with $X_{\text{Fe}^{3+}} = 0.1$ at 1200 K.

Activity-composition relations have been measured in both the systems MgAl_2O_4 – MgCr_2O_4 (1066–1523 K, 25 kb) (Oka *et al.*, 1984) and FeAl_2O_4 – FeCr_2O_4 (1373 K, 1 b) (Petric & Jacob, 1982b), by

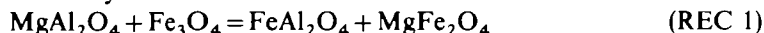
equilibration with $\text{Al}_2\text{O}_3\text{--Cr}_2\text{O}_3$ solid solutions. This allows us to test two of the assumptions made above, namely that the excess mixing properties of the Y type cations are independent of the M type cations, and also that the W terms are independent of temperature.

Activities from the ideal cation distribution model were calculated for the mixing of $\text{MAl}_2\text{O}_4\text{--MCr}_2\text{O}_4$ at each temperature. The logarithms of the ratios of these activities were then fitted to an empirical polynomial in composition (X_{Cr}). These were used, together with the activity–composition relations for $\text{Al}_2\text{O}_3\text{--Cr}_2\text{O}_3$ solutions given in Chatterjee *et al.* (1982), to extract $W_{\text{Al--Cr}}$ for each series of partitioning experiments. The appropriate corrections for pressure were applied to the data of Oka *et al.* (1984), using the molar volumes and excess volumes of mixing given in that reference. Non-linear regression analyses were used, with the data weighted according to the standard deviations quoted in Oka *et al.* (1984). For the data of Petric & Jacob (1982b), no uncertainties are given and, therefore, the standard deviations were assumed to be ± 0.002 and ± 0.005 for $X_{\text{FeCr}_2\text{O}_4}$ and $X_{\text{Cr}_2\text{O}_3}$ respectively. The results of these regression analyses are summarized in Table 2. It may be seen that $W_{\text{Al--Cr}}$ is indeed the same for all four series of experiments, within experimental error. The mean value is $12370 \pm 244 \text{ J g-atom}^{-1}$. It may also be noted that the asymmetry present in the mixing properties of $\text{MAl}_2\text{O}_4\text{--MCr}_2\text{O}_4$ solutions is satisfactorily accounted for by the ideal cation distribution model.

$W_{\text{Mg--Fe}^{2+}}^{\text{sp}}$ was obtained from the available experimental data on the partitioning of Mg and Fe^{2+} between olivine and spinel. This is described below.

The reciprocal solution effect

There are three independent reciprocal exchange reactions in the multicomponent spinel solutions of interest to this study:



The reciprocal solution model is described in detail by Wood & Nicholls (1978). The model gives, for example:

$$RT \ln \gamma_{\text{Fe}_3\text{O}_4}(\text{REC}) = X_{\text{Mg}} X_{\text{Al}} \Delta G^\circ(\text{REC } 1) + X_{\text{Mg}} X_{\text{Cr}} \Delta G^\circ(\text{REC } 2) \\ + X_{\text{Mg}} X_{\text{Ti}} \Delta G^\circ(\text{REC } 3) \quad (18)$$

TABLE 2

Summary of the results of non-linear regression analyses of the experimental partitioning of Al and Cr between $\text{MAl}_2\text{O}_4\text{--MCr}_2\text{O}_4$ and $\text{Al}_2\text{O}_3\text{--Cr}_2\text{O}_3$ solid solutions. All parameters are recalculated to a pressure of 1b

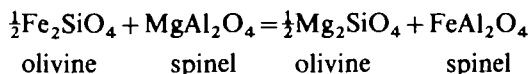
System and reference	T (K)	$\Delta G^\circ(\text{exchange})$ (J g-atom ⁻¹)	$\sigma(\Delta G^\circ)$ (J g-atom ⁻¹)	$W_{\text{Al--Cr}}^{\text{sp}}$ (J g-atom ⁻¹)	$\sigma(W_{\text{Al--Cr}}^{\text{sp}})$ (J g-atom ⁻¹)	Reduced χ^2	Estimated $\sigma(W_{\text{Al--Cr}}^{\text{sp}})$ † (J g-atom ⁻¹)
Mg*	1523	–506	38	12 563	163	5.03	366
"	1323	–1089	161	12 085	897	0.61	698
"	1069	–1221	344	12 035	1696	0.18	714
Fe^{2+} ‡	1373	–10 601	237	12 333	388	1.26	436
Mean	—	—	—	12 370	244	0.22	—

* Oka *et al.* (1984).

† Petric & Jacob (1982b).

‡ The reduced χ^2 for the regressions of the Mg-system data show considerable differences from the expected value, which should be near unity if the number of data is large. This seems to be due not to a failure of the model, but rather to the estimates of the standard deviations of the experimentally observed compositions in Oka *et al.* (1984). Hence, for the purpose of calculating a mean value of $W_{\text{Al--Cr}}^{\text{sp}}$, the reduced χ^2 has been adjusted to be equal to unity, and thus σ^2 (estimated) = σ^2 (observed) \times reduced χ^2 (observed).

Attempts to calibrate the free energies of the reciprocal reactions from the thermodynamic properties of the component spinels have not proved very successful due to the rather large experimental uncertainties in these properties (see e.g., Roeder *et al.*, 1979). However, the considerable interest shown in the partitioning of Mg and Fe^{2+} between olivine and spinel for use as a geothermometer has resulted in a number of experimental studies from which $\Delta G^\circ(\text{REC } 1)$, etc. may be obtained. This reaction may be written:



and therefore, at equilibrium:

$$\begin{aligned} RT \ln K_D = & -\Delta G^\circ(\text{ol-al}) + X_{\text{Cr}}(\Delta G^\circ(\text{REC } 2) - \Delta G^\circ(\text{REC } 1)) \\ & + X_{\text{Fe}^{3+}} \Delta G^\circ(\text{REC } 1) + X_{\text{Ti}}(\Delta G^\circ(\text{REC } 3) - \Delta G^\circ(\text{REC } 1)) \\ & + W_{\text{Mg-Fe}}^{\text{ol}} (1 - 2 X_{\text{Mg}}^{\text{ol}}) - W_{\text{Mg-Fe}^{2+}}^{\text{sp}} + (1 + N_{\text{Ti}}) (1 - 2 X_{\text{Mg}}^{\text{sp}}). \end{aligned} \quad (19)$$

Note that in the model for spinel solutions adopted in this study, the effect of the cation distribution on $a_{\text{MgAl}_2\text{O}_4}$ and $a_{\text{FeAl}_2\text{O}_4}$ cancels out in equation (19), as do the Y type cation size mismatch terms ($W_{\text{Al-Cr}}$, etc).

The parameters in equation (19) were obtained from various experimental studies as follows:

1. Using the value of $W_{\text{Mg-Fe}}^{\text{ol}}$ adopted above (i.e. $5000 \text{ J g-atom}^{-1}$) the highly precise data of Jamieson & Roeder (1984) in the partitioning of Mg and Fe^{2+} between olivine and both Al- and Fe^{3+} -spinel at 1573 K were simultaneously fitted to equation (19) (without the X_{Cr} and X_{Ti} terms) by non-linear regression, with the data weighted according to the observed standard deviations. The two runs done in an atmosphere of air were eliminated as the spinels probably show considerable deviations from the ideal stoichiometry (Jamieson & Roeder, 1984). Since Jamieson & Roeder also report that the concentration of $X_{\text{Fe}^{3+}}$ in the aluminate spinels increases with increasing Fe^{2+} content up to a level of 0.06, but do not give exact values, $X_{\text{Fe}^{3+}}$ was estimated from a preliminary version of this model (O'Neill *et al.*, 1982) for spinel in equilibrium with metallic iron. The maximum value of $X_{\text{Fe}^{3+}}$ so calculated is 0.042, with an assumed uncertainty of ± 20 per cent.

The regression gives $\Delta G^\circ(\text{ol-al}) = 870 \pm 150$, $W_{\text{Mg-Fe}^{2+}}^{\text{sp}} = 1960 \pm 270$ and $\Delta G^\circ(\text{REC } 1) = 25150 \pm 280$ (all in J mol^{-1}), with a reduced χ^2 of 1.70, which indicates a reasonably good fit to the model. This also confirms that the same $W_{\text{Mg-Fe}^{2+}}^{\text{sp}}$ is appropriate for both aluminate and ferrite spinels.

Recently Lehmann & Roux (1986) have presented experimental results for the partitioning of Mg and Fe^{2+} between spinel and aqueous chloride solutions at 800°C and 4 kb. They deduced that the spinel solution showed considerably larger positive deviations from ideality than those obtained here. It is apparent, however, from the description of their experimental method that the fugacity of water ($f_{\text{H}_2\text{O}}$) in their experiments must have varied considerably from run to run, either from dilution with CO_2 (they added oxalic acid or ascorbic acid to some runs), or from H_2 (for example $f_{\text{H}_2} > f_{\text{H}_2\text{O}}$ at $P = 4$ kb and 800°C at the IW oxygen buffer (Eugster & Skippen, 1967). Therefore the molality of the chloride solution must have also varied from run to run, and consequently the interpretation of the Mg- Fe^{2+} spinel-chloride exchange data is not at all obvious.

Activity-composition relations along the join $\text{MgFe}_2\text{O}_4\text{-Fe}_3\text{O}_4$ have been measured several times (e.g., Berthet & Perrot, 1970; Trinel-Dufour & Perrot, 1977; Shishkov *et al.*, 1980) by equilibration with MgO-FeO solutions. The reported results cover a sufficiently large range that it would be difficult not to find one to agree with one's own prejudices: we therefore merely note that the results of Shishkov *et al.* (1980) are in excellent agreement with the present work.

The value of $W_{\text{Mg-Fe}^{2+}}^{\text{sp}}$ obtained above at 1573 K was assumed to be independent of temperature, and was used in all the subsequent steps of this analysis.

2. Although we have reservations about the interpretation of the spinel-chloride partitioning data of Lehmann & Roux (1986), these authors also present valuable compositional data for seven pairs of co-existing Al-rich and Fe^{3+} -rich spinels in the system $\text{MgO-FeO-Al}_2\text{O}_3\text{-Fe}_2\text{O}_3$. These may be used to achieve a direct estimate of $\Delta G^\circ(\text{REC } 1)$ at 1073 K. Non-linear regression gives $\Delta G^\circ(\text{REC } 1) = 23110$

$\pm 1670 \text{ J mol}^{-1}$, with a reduced χ^2 of 0.15. This is almost the same value as obtained at 1573 K. We have therefore assumed that $\Delta G^\circ(\text{REC } 1)$ is independent of temperature (see also below); thus the change in entropy across the reciprocal reaction (REC 1) is zero. This is not unexpected: analogous hypothetical exchange reactions have been proposed as a means of estimating the entropy of a phase precisely by assuming zero entropy of reaction (e.g., Helgeson *et al.*, 1978).

3. $\Delta G^\circ(\text{REC } 2) - \Delta G^\circ(\text{REC } 1)$ may be obtained at 1373 K from the difference of the free energies of the exchange reactions $\text{Mg}(\text{Al, Cr})_2\text{O}_4 - (\text{Al, Cr})_2\text{O}_3$ and $\text{Fe}(\text{Al, Cr})_2\text{O}_4 - (\text{Al, Cr})_2\text{O}_3$ (see Table 2). The result is $18\,620 \text{ J mol}^{-1}$.

4. The above values were applied to the extensive and meticulous data of Engi (1983), on the partitioning of Mg and Fe^{2+} between olivine and Al, Cr spinels at 923–1173 K, in order to obtain the temperature dependences of $\Delta G^\circ(\text{ol-al})$ and $(\Delta G^\circ(\text{REC } 23) - \Delta G^\circ(\text{REC } 1))$ (i.e. $\Delta S^\circ(\text{ol-al})$, etc.). Of the 46 runs reported by Engi which contain olivine plus spinel, 9 were discarded as obviously not having achieved equilibrium (nos 146, 142, 136, 140, 137, 133, 104, 135, and 138). These runs are all at $X_{\text{Fe}}^{\text{ol}} \sim 1$, at temperatures of 1073 K or below, and are interpreted by the author in a likewise fashion (see figs. 2–4 in Engi, 1983). The remaining 37 runs gave, from the non-linear regression, $\Delta S^\circ(\text{ol-al}) = 4.705 \pm 0.170 \text{ J K}^{-1} \text{ mol}^{-1}$ and $(\Delta S^\circ(\text{REC } 2) - \Delta S^\circ(\text{REC } 1))$ effectively zero, with a reduced χ^2 of 1.88. Thus the entropy of reaction REC 2 is also zero, and the value of $(\Delta G^\circ(\text{REC } 2) - \Delta G^\circ(\text{REC } 1))$, obtained completely independently of olivine-spinel exchange equilibria, provides a very good fit to such equilibria.

5. Rawson & Irvine (1979–80) have measured the exchange of Mg and Fe^{2+} between olivine and ferrite-titanate spinels at 1340 and 1440 K. $X_{\text{Mg}}^{\text{ol}}$ and $X_{\text{Fe}}^{\text{sp}}$ are given to the nearest 0.01, but $X_{\text{Mg}}^{\text{sp}}$ had to be read from graphs. Also no uncertainties are reported, so we assumed that all compositions had the same uncertainty. Regression gave $\Delta G^\circ(\text{REC } 1) = 24\,570$ at 1340 K, and $25\,370$ at 1440 K (J mol^{-1}), with $\Delta G^\circ(\text{REC } 3)$ being effectively zero in both cases. These values of $\Delta G^\circ(\text{REC } 1)$ confirm the assumption of the negligible temperature dependence of this quantity.

A by-product of the fitting procedure is that, with the parameters derived above, equation (19) may be inverted to be explicit in temperature, thus yielding a new calibration of the olivine-spinel Mg- Fe^{2+} exchange geothermometer:

$$T(\text{K}) = \frac{6530 + 28P + (5000 + 10.8P)(X_{\text{Mg}}^{\text{ol}} - X_{\text{Fe}}^{\text{ol}}) - 1960(1 + X_{\text{Ti}}^{\text{sp}})(X_{\text{Mg}}^{\text{sp}} - X_{\text{Fe}}^{\text{sp}}) + 18\,620X_{\text{Cr}}^{\text{sp}} + 25\,150(X_{\text{Fe}}^{\text{sp}} + X_{\text{Ti}}^{\text{sp}})}{R \ln K_D + 4.705} \quad (20)$$

where R is $8.31441 \text{ (J K}^{-1} \text{ mol}^{-1})$ and P is the pressure in kilobars. The pressure dependence of the geothermometer is from O'Neill (1981). Note that this is the first formulation of the olivine-spinel geothermometer which specifically takes into account the effect of Ti.

Combining the results of all three stages in the procedure for calculating the activity of Fe_3O_4 in multicomponent spinel solutions gives:

$$\ln a_{\text{Fe}_3\text{O}_4} = \ln a_{\text{Fe}_3\text{O}_4}(\text{ICD}) + \ln \gamma_{\text{Fe}_3\text{O}_4}(\text{SM}) + \ln \gamma_{\text{Fe}_3\text{O}_4}(\text{REC}). \quad (21)$$

Molar volumes of spinel solutions reflect the cation distribution in the solutions (O'Neill & Navrotsky, 1984), and are thus expected to vary substantially with temperature. For Fe_3O_4 -containing spinels, it is doubtful if the equilibrium cation distribution at high temperature can be quenched, and therefore it would not be appropriate to use the rather large excess volumes of mixing observed in e.g., $\text{FeCr}_2\text{O}_4 - \text{Fe}_3\text{O}_4$, for evaluating the effect of pressure on the activity of Fe_3O_4 at high temperature (O'Neill & Navrotsky, 1984). For this reason we have made the assumption that pressure has negligible effect on $a_{\text{Fe}_3\text{O}_4}$.

The activity of SiO_2 defined by olivine + orthopyroxene

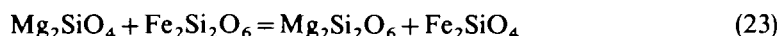
The free energy of reaction (4), $\Delta G^\circ(4)$, may be obtained from the enthalpy of reaction measured by oxide melt solution calorimetry at 1073 K (Brousse *et al.*, 1984) and the entropy

and heat capacity of SiO_2 (Richet *et al.*, 1982), Mg_2SiO_4 (Robie *et al.*, 1982), and $\text{Mg}_2\text{Si}_2\text{O}_6$ (opx) (Krupka *et al.*, 1985a, b). These data give (in J mol^{-1}):

$$\Delta G^\circ(4) = 6710 + 0.31 T(900\text{--}1600 \text{ K}). \quad (22)$$

The heat capacity of $\text{Mg}_2\text{Si}_2\text{O}_6$ (opx) has only been measured up to 1000 K (Krupka *et al.*, 1985b) and therefore the 3-term Maier–Kelley equation for C_p° was used for extrapolating above this temperature. Unfortunately, it appears that this equation gives a $\Delta G^\circ(4)$ some 2900 J mol^{-1} less negative at 1000 K than the alternative 5-term polynomial for C_p° ($\text{Mg}_2\text{Si}_2\text{O}_6$) which is also offered by Krupka *et al.* In addition to this, the uncertainty in the enthalpy of reaction is itself quite large, $\pm 2860 \text{ J mol}^{-1}$ (Brousse *et al.*, 1984).

An alternative, potentially more precise, route to $\Delta G^\circ(4)$ is through the following two reactions:



$$\Delta G^\circ(4) = \Delta G^\circ(23) - \Delta G^\circ(24). \quad (25)$$

$\Delta G^\circ(23)$ may be obtained from the experimental data on the partitioning of Mg and Fe^{2+} between olivine and orthopyroxene (Matsui & Nishizawa, 1974; O'Neill, 1981) (its value is not very sensitive to the solution model chosen for either phase, within reasonable limits), and $\Delta G^\circ(24)$ is very tightly constrained by the highly precise, reversed phase equilibrium study of Bohlen *et al.* (1980). However, $\Delta G^\circ(4)$ calculated in this way is some 4000 J mol^{-1} less negative than that given by equation (22), and this is beyond any acceptable uncertainty in the calorimetric data. The reason for this discrepancy remains unresolved. For the purposes of this study, we have used equation (22). An uncertainty of $\pm 4000 \text{ J mol}^{-1}$ for $\Delta G^\circ(4)$ propagates through equations (5) and (2) to give an uncertainty in $\log f_{\text{O}_2}$ of ± 0.5 at 1200 K.

To correct for pressure we have ignored the effects of compressibility and thermal expansion, both here and throughout this paper, so that:

$$\Delta G^\circ(P, T) = \Delta G^\circ(1, T) + \Delta V^\circ_{298} P \quad (26)$$

Any errors introduced by this approximation are expected to be small (e.g., Helgeson *et al.*, 1978). $\Delta V^\circ_{298}(4)$ has been taken to be -3.75 cm^3 (data from Robie *et al.*, 1978 and Kawasaki & Matsui, 1983). Note that any phase changes in SiO_2 (i.e. $\beta \rightarrow \alpha$ quartz, quartz to coesite) effectively cancel out between reactions (2) and (4).

In view of the uncertainty in $\Delta G^\circ(4)$, no accuracy is lost by making the simplest possible assumption with regard to calculating the activity of $\text{Mg}_2\text{Si}_2\text{O}_6$ in orthopyroxene, namely ideal two-site mixing, such that:

$$a_{\text{Mg}_2\text{Si}_2\text{O}_6} = X_{\text{Mg}}^{\text{M1}} \cdot X_{\text{Mg}}^{\text{M2}} \quad (27)$$

where
$$X_{\text{Mg}}^{\text{M1}} = \frac{N_{\text{Mg}}}{N_{\text{Mg}} + N_{\text{Fe}}} \left(1 - \frac{1}{2}(N_{\text{Al}} + N_{\text{Cr}}) - N_{\text{Ti}}\right) \quad (28)$$

$$X_{\text{Mg}}^{\text{M2}} = \frac{N_{\text{Mg}}}{N_{\text{Mg}} + N_{\text{Fe}}} (1 - N_{\text{Ca}} - N_{\text{Na}} - N_{\text{Mn}}). \quad (29)$$

where the N 's are the number of cations to 6 oxygens in the formula unit.

This completes the evaluation of the thermodynamic basis of the olivine–orthopyroxene–spinel geobarometer. A computer program to perform all the above calculations, written in BASIC, is available from either author on request.

THE ACCURACY, LIKELY PRECISION, AND SOME TESTS OF THE EQUILIBRIUM

The accuracy of the present calibration may be estimated by propagating the likely uncertainties in each of the component parts through equation (2): we find, for typical peridotitic compositions, that the likely accuracy is approximately ± 0.8 in $\Delta \log f_{O_2}$. The precision of the method depends on uncertainties in temperature, pressure and the compositions of the constituent phases, olivine, orthopyroxene, and spinel. For typical peridotite compositions and temperatures, an error of $\pm 100^\circ\text{C}$ in assumed temperature produces an error of less than ± 0.2 in $\Delta \log f_{O_2}$; ± 10 kb in assumed pressure corresponds to $\pm 0.5 \log f_{O_2}$ at 1200 K. The largest contribution to the precision of the method is the determination of Fe^{3+} in spinel. Since most analyses are performed by electron microprobe, which cannot distinguish Fe^{2+} and Fe^{3+} , the latter must be calculated from assumed ideal stoichiometry, by subtraction. Where alternative analytical methods have been used, such as Mossbauer spectroscopy and wet chemistry, these determinations have been shown to be reasonably accurate (Osborne *et al.*, 1981; Lucas *et al.*, 1986). However, if Fe^{3+} is in any case low, this may still lead to quite substantial errors in the calculated $\Delta \log f_{O_2}$; indeed, some spinel analyses apparently give a zero Fe^{3+} content, which would imply almost infinitely low oxygen fugacities. Fortunately, in most of the upper mantle sample, $X_{\text{Fe}^{3+}}^{\text{sp}}$ is sufficiently large for the likely error in its determination to yield an error of less than ± 1 log units in the calculated $\Delta \log f_{O_2}$.

Determination of Fe^{3+} by stoichiometry presupposes that the spinels are in fact stoichiometric. Significant deviations from stoichiometry in upper mantle spinels would not be expected because of: (a) low activities of Al_2O_3 and Fe_2O_3 ; (b) reasonably low temperatures (< 1500 K); and (c) high pressures (defect spinels have large molar volumes). If the analysis of a spinel neglects minor components, such as Si, V, Mn, Ni, etc. then the calculated $X_{\text{Fe}^{3+}}$ will be too low, and hence the calculated $\Delta \log f_{O_2}$ too reducing.

The model may be tested in a number of ways. First, $\log a_{\text{Fe}_3\text{O}_4}$ may be calculated for both the low- Fe^{3+} and high- Fe^{3+} co-existing spinels, produced by Lehmann & Roux (1986) on either side of the miscibility gap in the $\text{MgO-FeO-Al}_2\text{O}_3\text{-Fe}_2\text{O}_3$ system at 1073 K. This is a very sensitive test, as $a_{\text{Fe}_3\text{O}_4}$ varies rapidly with composition and temperature near the region of the miscibility gap. We find that the difference in $\log a_{\text{Fe}_3\text{O}_4}$ calculated for each pair ranges from zero (perfect agreement) to 0.47, with a mean of 0.27. This implies a slightly wider miscibility gap in this system than predicted. However, the experimental uncertainty in the observed spinel compositions is such that agreement may be said to be reasonable.

Secondly, in order to test an earlier calibration of the olivine-spinel geothermometer, Roeder *et al.* (1979) heated some natural peridotites for long periods at 1200°C , at the oxygen fugacity of the QFM buffer. It is not stated whether orthopyroxene was present in these experiments, but if so, its composition may be estimated, and $\Delta \log f_{O_2}$ calculated. The results of this exercise are given in Table 3, from where it may be seen that the agreement between calculated and experimental oxygen fugacities is very good. A similar test is possible using the experimental data, obtained over a wide range of oxygen fugacities, recently presented by Barnes (1986); this time the compositions of the olivines were not reported, and were therefore also estimated. For all 20 experiments the mean $\Delta \log f_{O_2}$ (observed-calculated) is 0.7 ± 1.2 .

Finally, D. H. Green & N. Orteiz (pers. comm.) have equilibrated olivine + orthopyroxene + spinel assemblages in the system $\text{MgO-FeO-Fe}_2\text{O}_3\text{-Cr}_2\text{O}_3\text{-SiO}_2$ at a number of oxygen fugacities from IW to $\text{Fe}_3\text{O}_4\text{-Fe}_2\text{O}_3$ at 30 kb and 1373 K. They used a piston-cylinder apparatus, with the double capsule technique. Again calculated and experimentally observed oxygen fugacities are in reasonably good agreement, except for those experiments on the IW

TABLE 3

Comparison of observed and calculated $\log f_{O_2}$ for some experimental run products with olivine + orthopyroxene + spinel

Sample No.	T(K)	T(K) calculated†	$\log f_{O_2}$ observed	$\log f_{O_2}$ calculated	Difference
B. H. (rim)*	1473	1461	-8.41	-8.4	0
R. 2882 (rim)*	1473	1387	-8.41	-8.2	+0.2
B.O.I. 7271(rim)*	1473	1466	-8.41	-8.2	+0.2
J.O.A. (rim)*	1473	1479	-8.41	-9.5	-1.1
J.O.O. (rim)*	1473	1430	-8.41	-9.0	-0.6
B/24†	1469	—	-7.60	-8.8	-1.2
B/27†	1430	—	-8.11	-9.4	-1.3
A/4†	1567	—	-7.45	-8.0	-0.5
A/7†	1524	—	-8.21	-9.4	-1.2
B/21†	1582	—	-8.68	-10.7	-2.0
B/26†	1538	—	-9.35	-10.2	-1.8
B/28†	1432	—	-10.67	-8.8	+1.9
B/13†	1594	—	-10.07	-12.5	-2.4
A/9†	1524	—	-10.81	-11.6	-0.8
B/11†	1475	—	-11.55	-9.6	+2.0
B/14†	1596	—	-10.44	-11.8	-1.4
B/16†	1573	—	-10.64	-13.7	-3.0
B/6†	1479	—	-11.74	-12.4	-0.7
B/18†	1452	—	-12.22	-11.1	+1.1
A/26†	1439	—	-12.51	-12.1	+0.4

* Roeder *et al.* (1979): orthopyroxene assumed present, and its composition estimated.

† Barnes (1986): olivine composition estimated from ol-opx Mg-Fe²⁺ exchange.

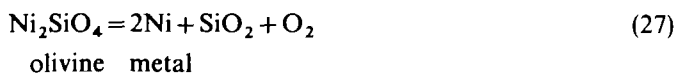
‡ From equation (20).

buffer, where Fe loss to the capsule and buffer exhaustion may have contributed to experimental problems (D. H. Green, pers. comm.).

The olivine-orthopyroxene-spinel oxygen geobarometer may thus be applied with some confidence to upper mantle assemblages. However, before this is done, the minimum possible oxygen fugacity of the upper mantle, as obtained from the Ni-content of olivine in equilibrium with orthopyroxene, will be calculated.

THE NICKEL PRECIPITATION CURVE

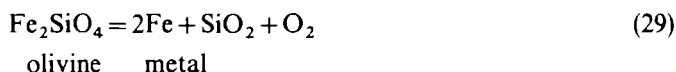
Ringwood (1966) pointed out that the abundance of Ni in the upper mantle was far too high to have been in equilibrium with the iron-rich metal that formed the Earth's core, at least at the present temperatures and pressures of the upper mantle. The corollary of this is that, on reducing an upper mantle lherzolite or harzburgite assemblage, Ni-rich metal will eventually precipitate. This has recently been experimentally observed by Boland & Duba (1986). The nickel precipitation reaction may be written:



and therefore the oxygen fugacity at which this occurs is:

$$\log f_{O_2} = \frac{-\Delta G(27)}{2.303 RT} + \log a_{\text{Ni}_2\text{SiO}_4}^{\text{ol}} - \log a_{\text{SiO}_2} - 2 \log a_{\text{Ni}}^{\text{met}}. \quad (28)$$

Activity–composition relations in the system $\text{Mg}_2\text{SiO}_4\text{--Ni}_2\text{SiO}_4$ have been measured using two independent methods (Campbell & Roeder, 1968; Seifert & O'Neill, 1987). The results are in excellent agreement, and show that mixing in this binary is effectively ideal on a two-site basis (i.e. $a_{\text{Ni}_2\text{SiO}_4}^{\text{ol}} = (X_{\text{Ni}}^{\text{ol}})^2$). The relatively small amounts of Fe_2SiO_4 in the mantle olivines of interest should not significantly alter this conclusion (Seifert & O'Neill, 1987). ΔG° (27) is taken from O'Neill (1987*b*) $\log a_{\text{SiO}_2}$ may be calculated as above, and $\log a_{\text{Ni}}^{\text{met}}$, and thus the composition of the nickel-rich metal, may be calculated with the additional reaction:



using the data of O'Neill (1987*a*) and activity–composition relations for Fe–Ni metal from Fraser & Rammensee (1982). The result of such a calculation, for typical mantle olivine with $X_{\text{Ni}}^{\text{ol}} = 0.0035$ and $X_{\text{Fe}}^{\text{ol}} = 0.1$, in equilibrium with orthopyroxene, at a pressure of 1 b, is shown in Fig. 1, relative to QFM (O'Neill, 1987*a*). It may be noted that the position of the nickel precipitation curve is almost coincident with the IW buffer; this relationship is maintained at higher pressures (see Figs. 2 and 5).

Since Ni-rich metal is not observed in most (if any) peridotite assemblages, the oxygen fugacity of the upper mantle is constrained to lie at least on, but probably somewhere above this curve. This is a constraint of the utmost importance, as the nickel content of upper mantle olivines is remarkably uniform, in the range 2500–3500 p.p.m. (corresponding to $X_{\text{Ni}}^{\text{ol}}$

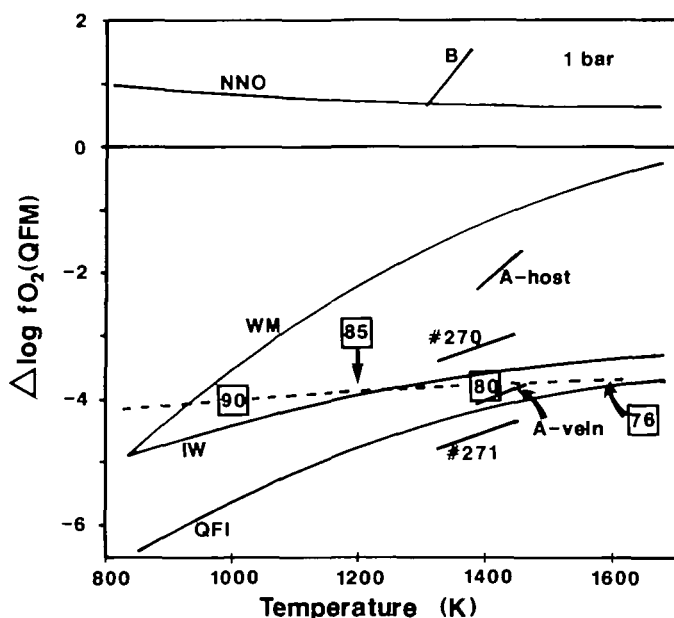


FIG. 1. The nickel precipitation curve (dashed line) for a typical mantle olivine + orthopyroxene assemblage with $X_{\text{Ni}}^{\text{ol}} = 0.0035$ and $X_{\text{Fe}}^{\text{ol}} = 0.1$, plotted relative to the quartz–fayalite–magnetite (QFM) oxygen buffer at a pressure of 1 b. The composition of the first metal (in mol per cent Ni) to precipitate from olivine on this curve is given at several temperatures. Also shown are the positions relative to QFM of the common oxygen buffers QFI (quartz–fayalite–iron), IW (iron–wüstite), WM (wüstite–magnetite) and NNO (nickel–nickel oxide), taken from O'Neill (1987*a, b*), and O'Neill (in prep.). The results of 'intrinsic' oxygen fugacity measurements for two spinel separates from Cr-diopside (type A) spinel lherzolite (nos. 270 and 271) (Arculus & Delano, 1981), and for whole rock type A (i.e. Cr-diopside) (host and vein) and type B (i.e. Al-augite) xenoliths (Arculus *et al.*, 1984) are also given.

= 0.0035–0.0045). Note that progressive reduction of olivine under equilibrium conditions below the nickel precipitation curve will deplete the olivine in both nickel and iron, and the composition of the metal will become progressively more Fe-rich. Ultimately, when the olivine is effectively reduced to nearly pure Mg_2SiO_4 , the composition of this metal should have the Fe: Ni ratio of the bulk peridotite, or about 25:1 (Jagoutz *et al.*, 1979). This means that the almost nickel-free iron metal observed as inclusions in diamond by Sobolev *et al.* (1981) cannot have come from an equilibrium upper mantle peridotite assemblage, and therefore is unlikely to have any bearing on the typical redox state of the mantle.

Also shown in Fig. 1 are the results of some 'intrinsic' oxygen fugacity measurements on a variety of peridotitic material of upper mantle origin (Arculus & Delano, 1981; Arculus *et al.*, 1984). The range of these results covers some 6 orders of magnitude in oxygen fugacity, from below the quartz–fayalite–iron buffer to above the nickel–nickel oxide. The most reduced sample (a spinel separated from a typical Cr-diopside xenolith, no. 271, from Mt. Porndon, Victoria (Archbald, 1979)) plots well below the nickel precipitation curve, and would thus seem to be an unlikely representation of typical mantle redox states.

RESULTS FROM THE OLIVINE–ORTHOPYROXENE–SPINEL OXYGEN GEOBAROMETER

Figure 2 shows the calculated $\Delta \log f_{\text{O}_2}$ s for a number of upper mantle-derived peridotite xenoliths from several localities in Western Europe (Berger, 1978; Donaldson, 1978;

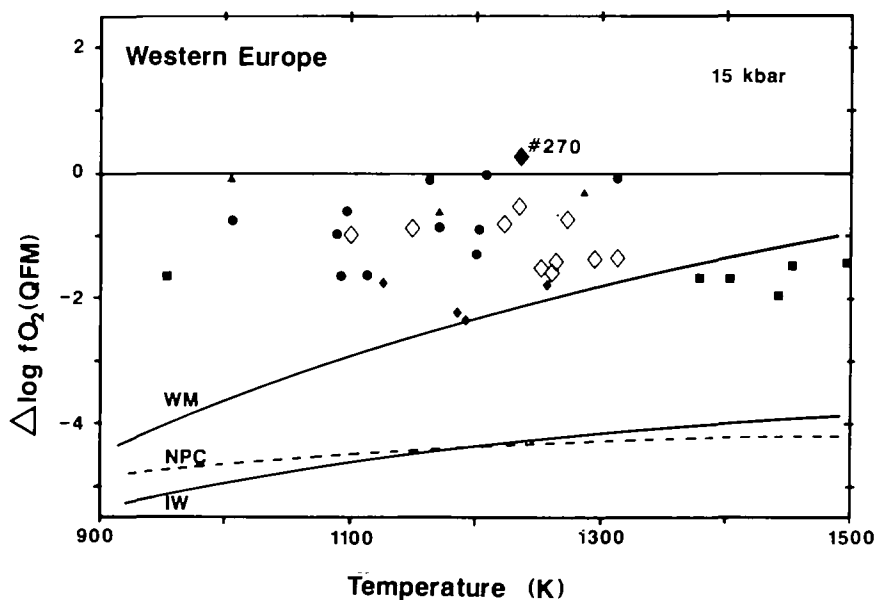


FIG. 2. Western Europe: oxygen fugacities recorded by some Cr-diopside spinel lherzolite xenoliths, calculated from the olivine–orthopyroxene–spinel oxygen 'geobarometer', relative to the QFM buffer, and plotted against temperature of equilibration as calculated from the olivine–spinel geothermometer (equation 20 in the text). A pressure of 15 kb was assumed for all xenoliths and buffer curves. Also shown is the position of the nickel precipitation curve (NPC) at this pressure, and some common oxygen buffers. Analytical data for the xenoliths were taken from: Archbald (1979), Massif Central, France (triangles) and Dreiser Weiber, West Germany (large solid diamond, no. 270); Brown *et al.* (1980), Massif Central, dots; Berger (1978), Massif Central, squares; Sachtleben & Seck (1981), Westeifel, large open diamonds; and Donaldson (1978), Calton Hill, Derbyshire, England, small solid diamonds, in an alkali basalt of Lower Carboniferous age. All others are in lavas of late Tertiary to Recent age.

Archbald, 1979; Brown *et al.*, 1980; Sachtleben & Seck, 1981). Temperatures of equilibration were obtained from equation (20), and are in reasonable agreement with other methods of geothermometry, such as the two-pyroxene equilibrium, although in detail some differences between the various geothermometric methods might be anticipated, due to different rates of response to pressure/temperature changes during the history of the xenolith. Since there is at present no method available with which to calculate pressures of equilibration of spinel lherzolite assemblages from routine microprobe analyses, a uniform pressure of 15 kb has been assumed for all xenoliths.

These xenoliths cover a large range of equilibration temperatures, a variety of different textures, and a range of bulk chemical compositions (within that usual for Cr-diopside peridotites), and were analysed by different workers in different laboratories; yet all record a consistently more oxidized $\Delta \log f_{O_2}$ than is inferred from the 'intrinsic' oxygen fugacity measurements on this type of peridotite. Of especial interest is the calculated $\Delta \log f_{O_2}$ for nodule no. 270, from Dreiser Weiher, West Germany, as the 'intrinsic' oxygen fugacity of the spinel phase from this xenolith was measured by Arculus & Delano (1981) (shown in Fig. 1). There is a discrepancy of four orders of magnitude in f_{O_2} between the calculated and the 'intrinsic' methods. In fact, no. 270 shows the highest calculated $\log f_{O_2}$ of any xenoliths considered in this paper, which reflects the relatively very high Fe_2O_3 content of its spinel, 4.74 wt. per cent (Archbald, 1979).

Linear regression of $\Delta \log f_{O_2}$ against T for the twenty-six Cr-diopside xenoliths shown in Fig. 2 from late Tertiary to Recent localities in the Massif Central, France, and Westeifel, West Germany, reveals that $\Delta \log f_{O_2}$ is apparently independent of the temperature of equilibration, and has a mean value of 0.89 ± 0.58 . (The high temperature xenoliths reported by Berger (1978) which are also plotted in Fig. 2, were omitted from this analysis because of their presumed origin as high pressure tholeiitic cumulates.) The standard deviation of this mean, 0.58, is close to that which is expected from the present precision of the method, considering likely errors in calculated temperature of equilibration, assumed pressure, and composition of the phases (most importantly, $X_{Fe^{Sp}}^{Sp}$), and therefore the possibility exists that the uppermost mantle beneath Western Europe is homogeneous in oxygen fugacity. It is interesting to note that the limited sample of European xenoliths from Palaeozoic localities (Donaldson, 1978; see also Griffin, 1973) appears to record a slightly more reducing $\Delta \log f_{O_2}$.

A similar story is told by an extensive suite of Cr-diopside xenoliths from Eastern Australia (Fig. 3). These xenoliths come from a variety of localities in the mid-Tertiary to Recent volcanic province which extends some 3000 km down the eastern margin of the Australian continent, from North Queensland to Tasmania. They were collected over a period of years by several different workers, although all analyses are from Archbald (1979). Again, a large range of textural types, equilibration temperatures and bulk chemistries are represented, and again nearly all nodules show calculated $\Delta \log f_{O_2}$ s which fall between the QFM and WM oxygen buffers at 15 kb. The mean $\Delta \log f_{O_2}$ is also apparently independent of temperature, and is 1.78 ± 0.66 . The mean $\Delta \log f_{O_2}$ for Eastern Australia thus appears to be statistically significantly different from that of Western Europe (*t*-test at the 99 per cent level of confidence). This could be dismissed as an artefact caused by systematic interlaboratory differences in the electron microprobe analyses (most probably in the analyses of the spinel phase from which the Fe^{3+} content must be obtained by difference), were it not for the fact that all four xenoliths from Western Europe which were also analysed by Archbald (1979) plot at higher $\Delta \log f_{O_2}$ than any of the 42 xenoliths from Eastern Australia. Thus the intriguing possibility is raised that not only may the oxygen fugacity of the upper mantle be homogeneous over wide geographical regions, but also that small differences in the oxygen fugacity may exist between these regions.

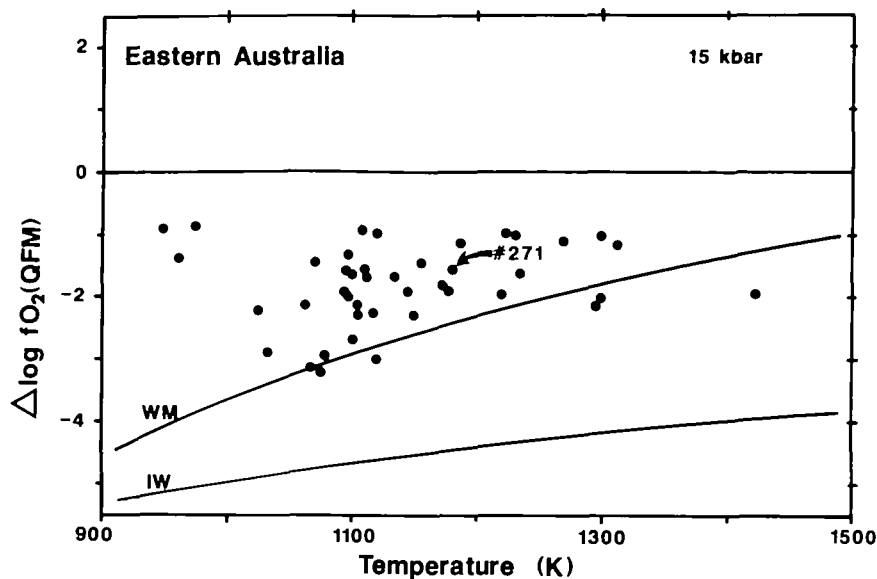


FIG. 3. Eastern Australia. All analytical data from Archbald (1979). The 'intrinsic' oxygen fugacity of a spinel separate from no. 271 (Arculus & Delano, 1981) is shown in Fig. 1.

Such conclusions must be regarded as preliminary, as the mineral analyses used for the calculations have been taken from a literature that has not, in the past, been too concerned with the accurate determination of the Fe^{3+} content of spinels. Thus a rather different picture emerges from a consideration of the peridotitic nodules from San Carlos, Arizona (Frey & Prinz, 1978) shown in Fig. 4. Of the spinel analyses of the Cr-diopside xenoliths reported by these authors, four out of thirteen are given as having zero Fe^{3+} , and have therefore been represented in Fig. 4 as having unknown but very low $\Delta\log f_{\text{O}_2}$ s (for Cr-bearing spinels in equilibrium with olivine and orthopyroxene, zero, or even apparently 'negative', calculated $X_{\text{Fe}^{3+}}$ would be possible at finite f_{O_2} because of the electron exchange reaction $\text{Fe}^{2+} + \text{Cr}^{3+} = \text{Fe}^{3+} + \text{Cr}^{2+}$ (e.g., Katsura *et al.*, 1975). Another nodule has spinel with such a low Fe^{3+} -content that it plots well below the IW buffer, and hence also the nickel precipitation curve. These zero or very low Fe^{3+} -contents are obviously incompatible with the nickel content of the peridotites, which in the whole-rock analyses fall within the usual range, although the olivine analyses reported by Frey & Prinz do show some with apparently zero $X_{\text{Ni}}^{\text{ol}}$; these, however, do not necessarily come from the same nodules as the spinels with zero $X_{\text{Fe}^{3+}}^{\text{sp}}$. It would therefore appear that the zero or low Fe^{3+} -contents may well be a result of analytical error, and before definite evidence of a reducing region in the mantle is admitted, such seemingly anomalous determinations should be checked by some independent, more accurate analytical technique, such as Mössbauer spectroscopy. It is also worth noting that analyses of spinels from other San Carlos xenoliths from other laboratories (e.g., Archbald, 1979; Arculus *et al.*, 1984; R. J. Arculus, pers. comm.) do not report unusually low Fe^{3+} -contents.

Calculated $\Delta\log f_{\text{O}_2}$ s for some Al-augite (Fe-rich, low Cr spinel) peridotite xenoliths from San Carlos are also shown in Fig. 4. These generally appear similar to the Cr-diopside xenoliths, although again one xenolith described by Frey & Prinz (1978) has apparently zero $X_{\text{Fe}^{3+}}^{\text{sp}}$. The calculated $\Delta\log f_{\text{O}_2}$ s of Cr-diopside and Al-augite xenoliths (type A and type B), the 'intrinsic' oxygen fugacity of which were measured by Arculus *et al.* (1984), are very

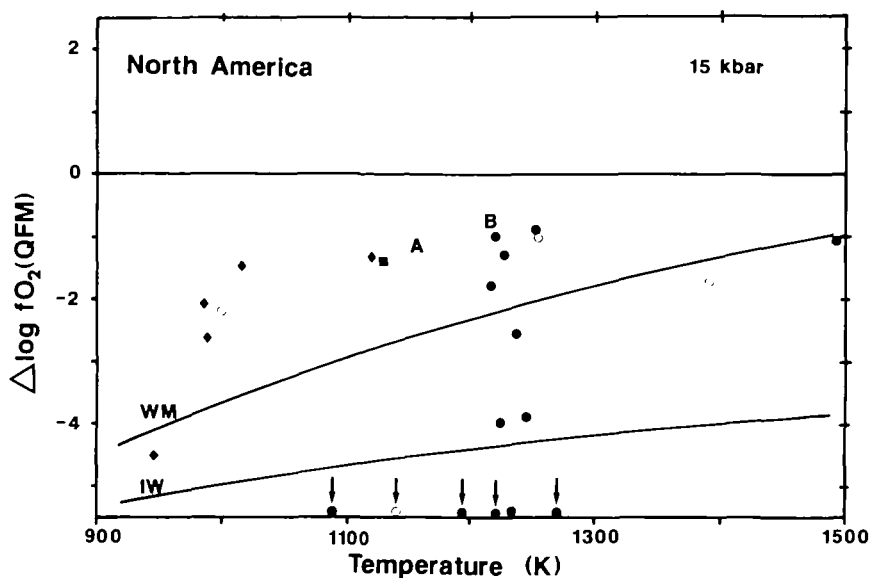


FIG. 4. North America. Data from: Frey & Prinz (1978), San Carlos, Arizona, Cr-diopside (type A) spinel lherzolites, dots, Al-augite (type B) open circles; Archbald (1979), San Carlos, square, Kyser *et al.* (1981), Baja California, diamonds. 'A' and 'B' mark the calculated oxygen fugacities of the type A and type B xenoliths which were used for 'intrinsic' oxygen fugacity measurements by Arculus *et al.* (1984), shown in Fig. 1.

similar to each other, and plot in the region of $\log f_{O_2} - T$ space found for the Western European and Eastern Australian xenoliths.

Garnet-peridotite xenoliths from kimberlites originate at a deeper level in the upper mantle than the spinel-peridotite xenoliths considered so far. Some of these contain accessory Cr-rich spinel, and hence may be used to calculate f_{O_2} s. The results for some xenoliths from Lesotho kimberlites are shown in Fig. 5, calculated at an assumed pressure of 30 kb. The $\Delta \log f_{O_2}$ s so found cover virtually the same region as for the Cr-diopside spinel-lherzolites, i.e. between the QFM and WM buffers, although there are again a couple of xenoliths which show unusually low $\Delta \log f_{O_2}$ (one with zero $X_{Fe^{3+}}$). Also shown in Fig. 5 are the $\Delta \log f_{O_2}$ s calculated for a diamond-bearing xenolith from Siberia (Pokhilenko *et al.*, 1976) and for an olivine-orthopyroxene-chromite inclusion in a diamond from Ghana (Meyer & Boyd, 1970).

The literature on upper mantle peridotitic xenoliths with olivine-orthopyroxene-spinel assemblages is very extensive, and in addition to the xenoliths considered above and illustrated in Figs. 2-5, we have also calculated $\Delta \log f_{O_2}$ s for xenoliths from as wide a range of geographical regions, tectonic provinces and host-rock types as we could find the analytical data for. Included were xenoliths from alkali basalts erupted as oceanic islands such as Hawaii (Kyser *et al.*, 1981) and Tahiti (Tracy, 1980), from Ichinomegata, Japan (Takahashi, 1980), as well as xenoliths from the ocean floor (Hamlyn & Bonatti, 1980) and from highly alkaline magmas (Griffin, 1973; Suwa *et al.*, 1975). In total, the oxygen fugacities from over 200 xenoliths were calculated; with the exception of one additional report of a spinel with zero $X_{Fe^{3+}}$ (Girod *et al.*, 1981), all show $\Delta \log f_{O_2}$ s similar to those in Figs. 2-5 (i.e. predominantly between the QFM and WM oxygen buffers). Thus the consistent picture emerges of an upper mantle which probably does not show large variations in oxygen fugacity, and is not particularly reducing.

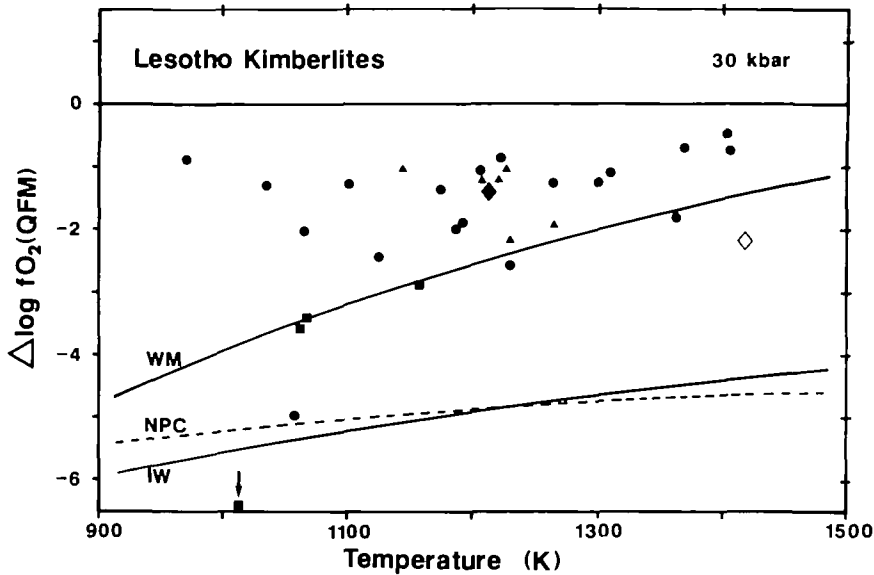


FIG. 5. Lesotho (from kimberlites). Data from: Carswell *et al.* (1979), dots; Nixon & Boyd (1973), triangles; Mon (1976), squares. Also shown are calculated $\Delta \log f_{O_2}$ s for a diamond bearing xenolith from Udachnaya, Siberia (Pokhilenko *et al.*, 1976), closed diamond; and an inclusion in a diamond from Ghana (Meyer & Boyd, 1970), open diamond.

CONCLUSIONS

The minimum oxygen fugacity possible in nearly all parts of the Earth's upper mantle is constrained by the precipitation of nickel-rich metal to lie on or above the IW oxygen buffer. The actual oxygen fugacity of the lithospheric upper mantle, as calculated from olivine–orthopyroxene–spinel assemblages in a wide variety of peridotitic xenoliths of high pressure origin, is rather more oxidized than this, generally lying in the field bounded by the QFM and WM buffers. This conclusion is in agreement with oxygen fugacities calculated from ilmenite-bearing assemblages (Eggler, 1983; and Haggerty & Tompkins, 1983); the few exceptions (i.e. those xenoliths with reportedly zero Fe^{3+} in spinel) are most probably artefacts caused by analytical error.

This range of oxygen fugacities is close to, but nevertheless somewhat more reducing, than that inferred for most erupted basalts (Haggerty, 1978). However, a recent study on primitive MORB glasses (Christie *et al.*, 1986) has shown that the quenched rims of these glasses have oxygen fugacities 1–2 log units below the QFM buffer, in excellent agreement with the present results.

Apart from the dubious exceptions mentioned above, there is no support for earlier contentions, based on 'intrinsic' oxygen fugacity measurements of mantle-derived samples, that significant portions of the mantle are relatively reduced (i.e. close to, or even below, the IW buffer). It is not the purpose of this paper to speculate on the reasons for the 'intrinsic' results, but it may be noted that, at least in some cases, the ubiquitous presence of a reducing film of organic origin on all exposed surfaces in the Earth's biosphere (Mattey *et al.*, 1986; Mathez *et al.*, 1986) may be responsible for the near instantaneous reduction of any sample of low buffering capacity in the 'intrinsic' oxygen fugacity apparatus. This reduction might be expected to proceed until the nearest self-buffering equilibrium is reached; this, for a Ni-containing phase, may be the appropriate nickel precipitation curve for that phase. Thus

plots of 'intrinsic' f_{O_2} vs. T for different phases from the same peridotite might be expected (ignoring the effect of pressure) to intersect at the temperature of equilibration, where their activities of nickel would be equal, but would still not record meaningful f_{O_2} s. Fe_2O_3 -containing ilmenites, on the other hand, would exsolve titanomagnetite of appropriate composition on reduction, and would therefore be expected to be much more capable of maintaining f_{O_2} s somewhere near to that under which they formed. This might explain the relatively good agreement between the 'intrinsic' f_{O_2} measurements and the f_{O_2} s calculated from phase equilibria for ilmenite samples from the mantle (Arculus *et al.*, 1984).

It seems quite probable that the oxygen fugacity of the upper mantle was 'set' at the nickel precipitation curve early in the Earth's history, perhaps by fractionation of a small amount of nickel-rich metal to the core as the last stage of the core-forming process (O'Neill, in preparation). If so, then the oxygen fugacity of the mantle must have evolved through time to the more oxidizing conditions seen today, presumably by the circulation of material through the oceanic crust (i.e. plate tectonics). This hypothesis might be testable by attempting a correlation of the oxygen fugacity of a peridotite with its degree of primitiveness, as judged by trace element and isotope data. It may also be noted that whilst the majority of the xenoliths we have considered come from the lithospheric part of the upper mantle, the available evidence from samples that might be derived from the asthenosphere, such as ocean floor ultramafics (Hamlyn & Bonatti, 1980), and primitive MORB glasses (Christie *et al.*, 1986), show no significant differences in calculated f_{O_2} .

The major species in a C-O-H fluid at upper mantle temperatures and pressures, at all oxygen fugacities on or above the WM buffer, will be almost entirely CO_2 and/or H_2O (which of these also depends on pressure, temperature, the buffering effect of the coexisting solid phases and the presence or absence of elemental carbon), and *not* CH_4 or H_2 (Ryabchikov *et al.*, 1981; Eggler & Baker, 1982; Woermann & Rosenhauer, 1985; Taylor & Green, 1986). However, such reduced species cannot at present be completely ruled out, if significant pockets of 'primitive' mantle with a redox state near the nickel precipitation curve still persist, and also contain volatiles. Most fluid inclusions in upper-mantle derived samples are in fact composed of nearly pure CO_2 (Roedder, 1984).

Finally, the present evidence indicates that large regions of the lithospheric upper mantle may be homogeneous in oxygen fugacity (e.g., beneath Western Europe or Eastern Australia), with there being, however, small but significant differences between these regions. This conclusion is put forward tentatively, and needs to be checked with more accurate analytical data for Fe^{3+} in mantle spinels.

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