Ferric Iron in the Upper Mantle and in Transition Zone Assemblages: Implications for Relative Oxygen Fugacities in the Mantle

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The $Fe^{3+}/\Sigma Fe$ ratio in least-depleted upper mantle spinel lherzolites is estimated to be $2.3 \pm 1\%$, from Mössbauer determinations of $Fe^{3+}/\Sigma Fe$ in each phase, multiplied by the total Fe determined by electron microprobe analysis, and the phase's modal abundance. This ratio is lower than previous direct determinations of $Fe^{3+}/\Sigma Fe$ in mantle samples by wet chemistry, but is compatible with $Fe^{3+}/\Sigma Fe$ measurements in primitive MORB glasses. This low $Fe^{3+}/\Sigma Fe$ leads to a relatively high oxygen fugacity in the spinel lherzolite upper mantle (i.e. $\Delta QFM = -1$ to $+0.5$ log-bar units) because the modally dominant phase in the upper mantle, olivine, almost completely excludes Fe^{3+}, and the next most abundant phase, orthopyroxene, accepts only limited amounts of Fe^{3+} into its structure. This concentrates Fe^{3+} in the modally minor phases, clinopyroxene and spinel. In contrast, experimental data show that the major phases in the mantle's transition zone, majorite garnet plus β-phase or silicate spinel, can all accommodate substantial amounts of Fe^{3+}, thus lowering the concentrations, and hence activities, of the Fe^{3+} components (i.e. Fe_3O_4 in spinel, $Fe^{2+}_3Fe^{3+}_2Si_3O_{12}$ in garnet). This will tend to result in lower relative fO_2's.

The minimum $Fe^{3+}/\Sigma Fe$ in either majorite garnet or silicate spinel occurs at any given T, P and $Mg/(Mg+Fe)$ ratio at its low fO_2 stability limit, when it is in equilibrium with excess SiO_2 and Fe. Mössbauer spectroscopy shows that majoritic garnet of composition $(Mg_{0.85}Fe_{0.15})SiO_3$ synthesized from Fe^{3+}-free orthopyroxene, in equilibrium with excess SiO_2 and Fe metal, at 18 GPa and 1900°C, contains $10 \pm 2\%$ $Fe^{3+}/\Sigma Fe$, while $(Mg_{0.85}Fe_{0.15})_2SiO_4$ spinel synthesised from the same starting material at 18 GPa and 1700°C, also with excess SiO_2 and Fe metal, contains approximately 3% $Fe^{3+}/\Sigma Fe$. This leads to a minimum whole rock $Fe^{3+}/\Sigma Fe$ for a pyrolite-like composition of 5%. Any material with upper mantle $Fe^{3+}/\Sigma Fe$ in the transition zone must produce the extra Fe^{3+} by disproportionation of Fe^{2+} to Fe^{3+} plus Fe^0, or by reduction of oxidized volatile components such as CO_2 and H_2O to CH_4; upper mantle material would thus probably be at an fO_2 close to metal saturation in the transition zone.

If in lower mantle assemblages $Fe^{3+}/\Sigma Fe$ is similar in coexisting perovskite and magnesiowüstite such that the magnesiowüstite has the same $Fe^{3+}/\Sigma Fe$ as that estimated for the upper mantle, the relative fO_2 in the lower mantle will be approximately similar to that of the upper mantle, well above metal saturation. In a mantle without major chemical stratification (including oxygen content), the transition zone will thus form a shell of reducing conditions between relatively oxidizing upper and lower mantle.

INTRODUCTION

The application of phase equilibrium methods to measure the oxygen fugacity at which upper mantle peridotites equilibrated (principally using the olivine-orthopyroxene-spinel assemblage, but also making use of other equilibria [Eggler, 1983; Haggerty and Tompkins, 1983; O'Neill and Wall, 1987; Wood and Virgo, 1989; Luth et al., 1990]) has led to a consensus that the upper mantle is nearly everywhere relatively oxidized, the majority of samples falling within -1.5 to +0.5 log-bar units of the quartz-fayalite-magnetite

oxygen buffer ($\Delta QFM = -1.5$ to $+0.5$). So far, the most reduced samples reliably documented are a few abyssal peridotites and some specimens from orogenic lherzolite massifs at $\Delta QFM = -2.5$ to -3 [Bryndzia and Wood, 1990; Woodland et al., 1992]. One consequence of this observation is that even the parts of the upper mantle at the lower end of the recorded range have oxygen fugacities >3 log-bar units more oxidized than that appropriate for chemical equilibrium with the Fe-rich metal now in the Earth's core. The oxidized nature of the upper mantle thus supports the evidence from the mantle's apparently anomalous overabundance of Ni and other siderophile elements [Ringwood, 1966] that the fundamental differentiation of the Earth into its metal core and silicate mantle could not have occurred by a simple one-stage metal segregation process, at least under upper mantle pressures. It has therefore often been argued that the

composition and oxidation state of the mantle is the net result of heterogenous accretion and more than one core-forming event [e.g. O'Neill, 1991a,b].

A major precept in this type of argument is that the metal-silicate equilibrium occurred at comparatively low pressures, within the upper mantle regime. Too little is known about how planets accrete to say if this precept is the only one likely. For instance, it has been argued that oxygen is the best candidate for the light element in the Earth's core [e.g. Ringwood, 1984]; if so, then this would require metal/silicate interactions at substantially higher pressures, as >16 GPa is needed to dissolve sufficient O in liquid Fe [Ringwood and Hibberson, 1990]. If metal segregation did occur at very high pressures, then the chemical constraints on core formation will have to take this into account. Several authors have pointed out that metal/silicate partition coefficients at higher pressures and temperatures tend to approach unity, thus to some extent diminishing the siderophile element anomaly [e.g. Urakawa et al., 1989; Ringwood et al., 1990; Ohtani et al., 1991; Rama Murthy, 1991; Urakawa, 1991]. This raises the question, what happens to the constraint on metal/silicate equilibria from the mantle's fO_2 at very high pressures? The purpose of this paper is to attempt to answer this question, by estimating the oxygen content of the upper mantle, and then, assuming constant chemical composition, using this to estimate the relative oxygen fugacity in the mantle's transition zone.

Knowledge of fO_2 in the deep mantle is also needed to predict fluid speciation in C-O-H volatiles, and its potential role in "redox melting" [e.g. Taylor and Green, 1988], which may occur where volatiles are locally concentrated. Briefly, the argument runs thus: below the topmost part of the mantle (i.e., below about 60 km), only fluids rich in CH_4 can exist, as CO_2-rich compositions would result in carbonation of mantle peridotite, while H_2O-rich compositions would result either in partial melting, or in phlogopite/amphibole production in the upper mantle [e.g. Eggler, 1983], or would be held in potentially hydrous phases such as the β-phase (and structurally related phases) in the transition zone [Smyth, 1987]. Large scale movement of volatiles in the mantle should thus be restricted to CH_4-rich fluids, but CH_4-rich fluids imply quite reducing conditions (roughly, below IW+1 in peridotite-C-O-H systems [Woermann and Rosenauer, 1985; Taylor and Foley, 1989]), such as are rarely if ever found in upper mantle samples. With a lower fO_2 in the transition zone, the existence of CH_4-rich fluid becomes a possibility. On passing to the higher fO_2 environment of the upper mantle, such fluid will be oxidized, triggering partial melting (e.g. $CH_{4(fluid)} + 4 Fe_2O_3 = CO_{2(melt)} + H_2O_{(melt)} + 8 FeO$). This kind of mechanism has been suggested for the origin of kimberlites.

The treatment of oxygen in the upper mantle has differed from that of most other elements in that it has largely been concerned with chemical potential (i.e. the oxygen fugacity), rather than actual amounts or concentrations of O. The amount of O in the mantle is most easily handled as $Fe^{3+}/\Sigma Fe$ ratios, as Fe is far more abundant than any other element with differing oxidation states, with the possible exceptions of the volatiles C, H, and S [Canil and O'Neill, in preparation]. Oxygen fugacity and $Fe^{3+}/\Sigma Fe$ are of course related, but in a complicated fashion, involving bulk composition, phase assemblage, temperature and pressure. The focus on fO_2 may be due to it being easier to measure with useful accuracy than $Fe^{3+}/\Sigma Fe$ ratios. Oxygen fugacity is also the useful quantity for constraining the nature of any inaccessible part of the original system, i.e. a C-O-H fluid phase, or for testing if the system could have been in equilibrium

with metal, and in situations when fO_2 behaves as an extrinsic variable, i.e. if oxidation state is controlled by oxygen exchange with a fluid reservoir (which may be the case for some types of mantle melting). In contrast, it seems likely that material circulating through the mantle will do so essentially isochemically, and in such situations oxygen fugacity will behave as an intrinsic variable, and it is oxygen content (as reflected in $Fe^{3+}/\Sigma Fe$, for example) which is the controlling quantity. The approach taken in this paper will be to assess the oxygen fugacity of the transition zone under the assumption that the entire mantle is essentially isochemical, i. e., that the transition zone has the same chemical composition as typical, least-depleted or "primitive" upper mantle [e.g. Jagoutz et al., 1979], including $Fe^{3+}/\Sigma Fe$. Note that for the purposes of this paper, we consider the mantle to be divided into three parts, namely the "upper mantle" down to 400 km depth with olivine as the dominant component, the "transition zone" from 400 to 670 km consisting mainly of β- or γ- phase plus majoritic garnet, and the "lower mantle" below the 670 km seismic discontinuity, consisting mainly of silicate perovskite plus magnesiowüstite. Since upper mantle $Fe^{3+}/\Sigma Fe$ is not at present well known, the first step in our argument is to provide an estimate for this ratio.

FE³⁺/ΣFE (OXYGEN CONTENT) OF THE UPPER MANTLE

For reasons that are discussed in Appendix 1, it seems that the determination of $Fe^{3+}/\Sigma Fe$ in upper mantle samples by traditional wet-chemical methods gives unreliable results, and that better estimates of $Fe^{3+}/\Sigma Fe$ in upper mantle samples may be made by using Mössbauer spectroscopy to determine $Fe^{3+}/\Sigma Fe$ in each phase individually, and then multiplying this ratio by total Fe, determined by electron microprobe analysis, and the modal abundance of the phase. Unfortunately, this restricts our data base to five spinel lherzolite xenoliths (four from the continental USA) analyzed by Dyar et al. [1989], for which approximate modes are available, eight spinel lherzolite xenoliths from British Columbia analyzed by Luth and Canil [1992], for which modes have to be estimated, and four high temperature garnet lherzolites hosted in Southern African kimberlites, for which reliable modes are available, but for which the $Fe^{3+}/\Sigma Fe$ Mössbauer determinations on the individual phases are incomplete.

The mineral chemistry of the spinel lherzolite xenoliths indicate that they are typical representatives of the continental spinel lherzolite suite, and nearly all of them appear to lie at the least depleted end of this suite. Importantly for our purpose, they have also all equilibrated at typical upper mantle oxygen fugacities (i.e. ~1 log unit below QFM [O'Neill, and Wall, 1987; Wood and Virgo, 1989]). We will first discuss the abundances of Fe^{3+} in the four phases of the upper mantle's spinel lherzolite facies (i.e. olivine, orthopyroxene, clinopyroxene and spinel), and then use this information to estimate $Fe^{3+}/\Sigma Fe$ for the primitive upper mantle.

Spinel

The need to determine $Fe^{3+}/\Sigma Fe$ in mantle spinels accurately, in order to calculate fO_2's from the olivine-orthopyroxene-spinel equilibrium, has led to a number of detailed Mössbauer studies [e.g. Wood and Virgo, 1989; Canil et al., 1990], which may be used to supplement the information from Dyar et al. [1989] and Luth and Canil [1992]. Taken together, these studies indicate that spinels from continental spinel lherzolite xenoliths have $Fe^{3+}/\Sigma Fe$ ranging from 0.15 to 0.35, varying mainly with fO_2. The mean of 70 samples is 0.24, and there is no obvious correlation of $Fe^{3+}/\Sigma Fe$ with the major

variable in mantle spinel chemistry, Cr/(Al+Cr). All samples studied by Dyar et al. [1989] and Luth and Canil [1992] fall within this range and thus appear typical. The Mössbauer determinations have been checked against synthetic spinels with known $Fe^{3+}/\Sigma Fe$ [Wood and Virgo, 1989], and have been shown to be free of systematic error.

Mantle spinel has the highest total iron (FeO* = 10-12%) of the four phases, so that with its high $Fe^{3+}/\Sigma Fe$, it contributes significantly to whole rock $Fe^{3+}/\Sigma Fe$, despite its low modal abundance of 1 to 2%. The corollary of this is that we need to know its mode quite precisely, and this is difficult to do by direct methods such as point counting [see, e.g. Dick et al., 1984]. Indeed, many xenoliths are simply too small for a reliable estimate to be made.

We avoid this problem by making use of the systematics of Cr_2O_3 in mantle peridotites. Cr is a compatible element, which during partial melting seems to partition about equally between melt and residue [e.g. Liang and Elthon, 1990a], and is not expected to be altered subsequently by metasomatism. Consequently, Cr shows an almost constant abundance in mantle peridotites, irrespective of the degree of depletion [e.g. Maaløe and Aoki, 1977; Frey et al, 1985]. From Maaløe and Aoki [1977] we take Cr_2O_3 = 0.42 wt% at 40% MgO as the mantle average, which agrees well with the estimate for the primitive mantle abundance for Cr of Jagoutz et al. [1979] (that is, 2870 vs. 3010 ppm). Since Cr is very heavily concentrated into spinel, it typically contains about 50% of the whole rock Cr content, despite its low modal abundance. The remaining Cr is held in orthopyroxene and clinopyroxene. The olivine of spinel peridotites usually contains <0.03 wt% Cr_2O_3 [e.g. Archbald, 1979; Stosch, 1981; Liang and Elthon, 1990b], low enough to be ignored. We then calculate the mode of spinel from a simple mass balance, as:

$$Z_{sp} = [0.42 - (Cr_2O_{3(opx)} \times Z_{opx} + Cr_2O_{3(cpx)} \times Z_{cpx})]/ Cr_2O_{3(sp)} \quad (1)$$

For typical peridotites, the uncertainty in the calculated modal percentage of spinel from this method is about ± 0.5% (absolute). If modes were to be estimated from whole rock analyses (information not available with the present data), it might also be preferable to use an idealized rather than the actually analyzed whole rock Cr_2O_3, because of the danger of the latter also suffering from spinel sampling errors. Probably some of the reported variation in Cr_2O_3 in mantle samples [e.g. as shown in Maaløe and Aoki, 1977] is caused by this [Liang and Elthon, 1990a]. In the present case, we note, for example, that the mode given by Dyar et al. [1989] for their otherwise fairly primitive-looking xenolith Ki-5-31 (10% clinopyroxene, 25% orthopyroxene, 5% spinel) implies whole rock Cr_2O_3 of 0.9 wt%, which is over twice

the estimated primitive upper mantle value, and larger than in any of the 302 whole rock analyses of continental spinel lherzolites treated by Maaløe and Aoki [1977], 300 of which have Cr_2O_3 < 0.65 wt%.

Clinopyroxene

Dyar et al. [1989] and Luth and Canil [1992] found that clinopyroxene has nearly as high $Fe^{3+}/\Sigma Fe$ as coexisting spinel, i.e. 0.12 to 0.23 (Dyar et al.) and 0.06 to 0.24 (Luth and Canil). Luth and Canil [1992] showed that such values are consistent with thermodynamic calculations (i.e. the activities of $CaFe^{3+}AlSiO_6$ and $NaFe^{3+}Si_2O_6$ components) at the T, P and fO₂ at which their samples equilibrated. Clinopyroxene is much more abundant than spinel in the least depleted lherzolites, but contains less total Fe (FeO* is typically only ~ 3%), so its net contribution to whole rock Fe_2O_3 is about the same (see Table 1).

Orthopyroxene

Both Dyar et al. [1989] and Luth and Canil [1992] found that their orthopyroxenes have $Fe^{3+}/\Sigma Fe$ = 0.03 to 0.06. Although this ratio is substantially less than in spinel or clinopyroxene, orthopyroxene typically has 6-7 wt% FeO*, and is present at about 25% in the mode; it thus holds a comparable portion of the whole rock's Fe_2O_3 to spinel or clinopyroxene (see Table 1).

Olivine

Olivine is the most abundant phase in the upper mantle (i.e. 55-60% in least depleted spinel lherzolites), and also contains the most FeO* (Fo_{89} has 10.7 wt % FeO , about equal to co-existing spinel). The combination of high FeO* and high abundance means that even quite small fractions of Fe^{3+} in olivine might contribute non-negligible amounts to whole rock $Fe^{3+}/\Sigma Fe$. For example, the limit of detection for $Fe^{3+}/\Sigma Fe$ by Mössbauer is commonly quoted as 0.02; if mantle olivine actually had 0.02 $Fe^{3+}/\Sigma Fe$, this would contribute 0.12 wt % Fe_2O_3 to the bulk rock, i.e. at about the same level as the contributions from the three other phases.

There are two lines of evidence which indicate that Fe^{3+} in mantle olivines is well below such a level. Firstly, the detailed thermogravimetric study of Nakamura and Schmalzried [1983] on synthetic Fe-Mg olivines shows that $Fe^{3+}/\Sigma Fe$ in fayalite (Fe_2SiO_4) remains very small (< 0.001) even at the maximum fO₂ for fayalite stability (i.e. QFM), and that substitution of Mg for Fe^{2+} causes $Fe^{3+}/\Sigma Fe$ to decrease exponentially. Since mantle olivines have generally equilibrated at fO₂ < QFM, and have $Fe^{2+}/(Fe^{2+}+Mg)$ = 0.1, this kind of intrinsic Fe^{3+} should be negligible.

TABLE 1. The contribution of each phase to whole rock Fe_2O_3 in spinel peridotite xenoliths.

Sample	Ba-2-3	Ep-1-13	Ki-5-31	Sc-1-1	H30-b2	SL32	SL47	SL125	LBR1	JL8	JL1	TKN15	RR222
Mode sp (%)	1.8	2.9	1.6	3.0	0.9	1.8	1.3	0.7	1.1	1.2	2.6	2.0	2.4
Fe_2O_3 fom sp (wt%)	0.05	0.08	0.06	0.08	0.04	0.07	0.06	0.02	0.07	0.03	0.06	0.04	0.05
Fe_2O_3 from cpx (wt%)	0.07	0.12	0.08	0.11	0.04	0.10	0.10	0.13	0.12	0.05	0.08	0.06	0.11
Fe_2O_3 from opx (wt%)	0.10	0.11	0.10	0.11	0.06	0.07	0.05	0.04	0.05	0.03	0.03	0.03	0.03
Whole rock Fe_2O_3 (wt%)	0.22	0.31	0.24	0.30	0.14	0.24	0.21	0.19	0.24	0.11	0.17	0.13	0.19
Whole rock $Fe^{3+}/\Sigma Fe$ (%)	2.5	3.4	3.0	3.4	3.0	2.0	1.9	2.0	2.2	1.4	2.1	1.5	2.3

All data from Dyar et al. [1989] and Luth and Canil [1992]. The amount of Fe_2O_3 contributed by each phase is given by $Fe^{3+}/\Sigma Fe$ determined from Mössbauer spectroscopy, multiplied by the total Fe from electron microprobe analysis and the phase's modal abundance. Idealized modes for orthopyroxene and clinopyroxene in least depleted spinel lherzolites of 25% and 15% are assumed, and the mode of spinel is calculated assuming Cr_2O_3 of 0.42% in the whole rock.

However, in chemically more complex environments heterogenous substitutions such as $Fe^{3+}_{(VI)} + Al_{(IV)} = Mg + Si$ (e.g. as in pyroxenes) become possible, and may enhance the solubility of Fe^{3+} in olivine. The maximum additional substitution by this mechanism (i.e. octahedral Fe^{3+} charge-balanced by tetrahedral Al), over that found in the Al-free system, should be given by $N_{Fe3+} = N_{Al} - N_{Cr}$, where the N's are the number of atoms per formula unit. Good quality microprobe analyses of olivine from typical spinel lherzolites show Al_2O_3 <0.05 wt%, which, allowing for 0.02wt% Cr_2O_3, suggests a maximum solubility for Fe_2O_3 of ~0.06 wt%. With an olivine mode of 60%, this sums to a contribution of < 0.04 wt % to the whole rock Fe_2O_3, which is small enough to be considered negligible.

Primitive upper mantle $Fe^{3+}/\Sigma Fe$

Since our goal is to calculate $Fe^{3+}/\Sigma Fe$ for primitive upper mantle (i.e. least depleted by extraction of partial melt; equivalent to pyrolite [Ringwood, 1975], or the model composition of Jagoutz et al. [1979]) we use idealized figures for pyroxene modal abundances, namely 25% for orthopyroxene and 15% for clinopyroxene. These abundances are similar to those reported by Takahashi [1986] for KLB1, and also to those from several other xenoliths with primitive major element chemistry, and which have equilibrated at similar P, T and fO_2 conditions to the samples in our data base [e.g. Stosch, 1981; Preß et al., 1986; Xue et al., 1990]. For spinel, we use the nominal mode computed by assuming whole rock Cr_2O_3 of 0.42 wt%, as explained above.

Our justification for this procedure is that, for the pyroxenes, we observe no correlation of $Fe^{3+}/\Sigma Fe$ with depletion, within the limited range of depletion covered by the available data. For spinel, while we expect Fe_2O_3 to increase with increasing depletion, as $Cr/(Cr+Al)$ increases [Reid and Woods, 1978], this tends to be cancelled by the concomitant decrease in calculated modal abundance.

The results are summarized in Table 1, and plotted in Figure 1. We find that calculated $Fe^{3+}/\Sigma Fe$ in the 13 spinel lherzolite samples of our data base is 0.023, with a statistical uncertainty of ±0.006. Additional systematic errors might accrue from systematic errors in the Mössbauer determination of $Fe^{3+}/\Sigma Fe$, or errors in our assumed modes. As for the former, we note that the Mössbauer determinations of $Fe^{3+}/\Sigma Fe$ in spinel have been checked against synthetic standards [Wood and Virgo, 1989], and have been shown to be accurate, while the $Fe^{3+}/\Sigma Fe$ in clinopyroxene accords well with that expected from thermodynamic calculation [Luth and Canil, 1992]. However, in orthopyroxene $Fe^{3+}/\Sigma Fe$ is near the Mössbauer limit of detection, and at these low levels peak areas often tend to be overestimated [Hawthorne and Waychunas, 1988]. For the modal abundances, any error for the assumed modal abundance of orthopyroxene is likely to be mostly compensated for by a change in the modal abundance of clinopyroxene, and vice versa: i.e. our estimate of 55 to 60% modal olivine in least-depleted spinel lherzolite is fairly robust. Taking all this into account, we estimate that primitive upper mantle $Fe^{3+}/\Sigma Fe$ must lie in the range 0.015 to 0.04. Taking the mean value of 0.023 $Fe^{3+}/\Sigma Fe$, and assuming a primitive mantle abundance for FeO* of 8 wt% [Maaløe and Aoki, 1977; Jagoutz et al., 1979], we obtain whole rock Fe_2O_3 of 0.20 wt%. This value is much lower than estimates from whole-rock wet chemical analyses of mantle peridotites, for reasons discussed in Appendix 1.

The relatively constant calculated $Fe^{3+}/\Sigma Fe$ in Figure 1 is of course partly an artefact of our assumption of particular pyroxene modal abundances, but it also reflects the fact that whole rock $Fe^{3+}/\Sigma Fe$ is a surprisingly insensitive function of fO_2 for peridotites with typical

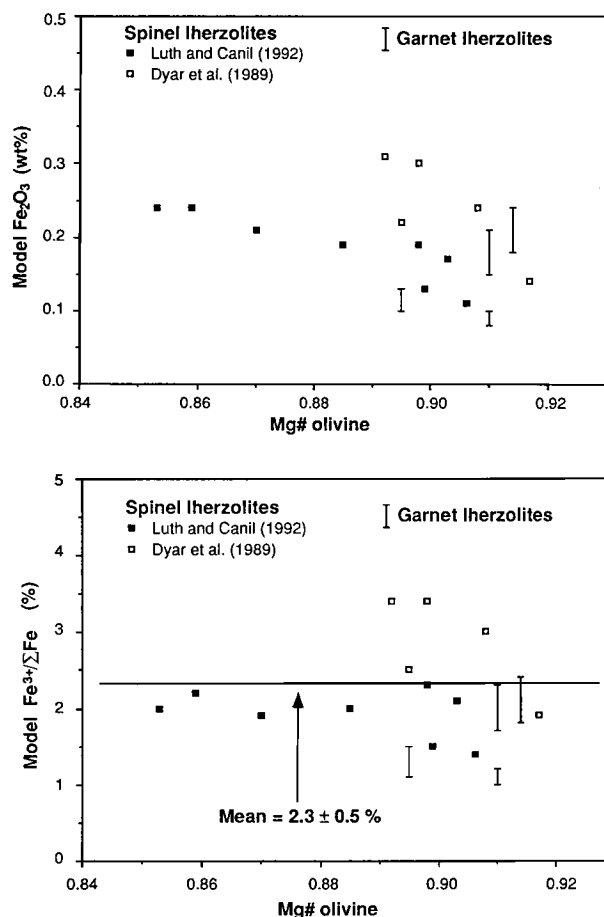Fig. 1. Fe^{3+} in the primitive (i.e. least depleted) upper mantle, estimated from Mössbauer determinations of $Fe^{3+}/\Sigma Fe$ in orthopyroxene, clinopyroxene and spinel, and ideal primitive mantle modes of 25% orthopyroxene, 15% clinopyroxene, and spinel as calculated from a mass balance for Cr_2O_3. a) Model Fe_2O_3 vs. $Mg/(Mg+Fe)$ in coexisting olivine, and b) Model $Fe^{3+}/\Sigma Fe$ vs. $Mg/(Mg+Fe)$ in coexisting olivine. The mean value ($Fe^{3+}/\Sigma Fe = 2.3\%$) is from the spinel lherzolites only. Primitive upper mantle olivine has $Mg/(Mg+Fe) = 0.89$.

upper mantle mineralogy. Conversely, fO_2 will vary greatly with small changes in $Fe^{3+}/\Sigma Fe$ - for example, metal saturation in the upper mantle occurs at fO_2's near the IW buffer, about 3 to 4 log-bar units below typical upper mantle values [O'Neill and Wall, 1987], yet this large change in fO_2 is only accompanied by a change in $Fe^{3+}/\Sigma Fe$ of ~0.023, if $Fe^{3+}/\Sigma Fe \cong 0$ at metal saturation.

We expect that increasing depletion will result in lower whole rock $Fe^{3+}/\Sigma Fe$ simply because of the large decrease in modal abundance of the pyroxenes with increasing depletion, and the consequent increase of modal olivine [e.g. Dick et al., 1984]. This holds regardless of whether the partial melting event which caused the depletion occurred with fO_2 extrinsically buffered (perhaps implying vapour saturation), or whether fO_2 varied intrinsically, or whether the depleted peridotite was then subsequently metasomatized - for example, if our argument that olivine contains virtually no Fe^{3+} is correct, then a residual dunite will have almost zero $Fe^{3+}/\Sigma Fe$. In other words, Fe_2O_3 behaves as an incompatible component during partial melting, whereas FeO is compatible.

If fO_2 is not controlled extrinsically, $Fe^{3+}/\Sigma Fe$ in primary magma will reflect the degree of partial melting, and high degree partial melts such as MORB will have relatively low $Fe^{3+}/\Sigma Fe$. For simple equilibrium batch melting of component M:

$$\frac{c_M^{liq}}{c_M^o} = \frac{1}{D_M^{sol/liq} + f(1 - D_M^{sol/liq})} \qquad (2)$$

where c denotes concentration, the superscript ^{o} the initial state, f the melt fraction, and D the average solid silicate/liquid silicate partition coefficient. We take $D_{FeO}^{sol/liq} = 1$, from the empirical observation that FeO* (≈FeO) remains nearly constant with increasing depletion [e.g. Maaløe and Aoki, 1977; Frey et al., 1985], hence for small $Fe^{3+}/\Sigma Fe$ ratios:

$$\left(\frac{Fe^{3+}}{\Sigma Fe}\right)_{liq} \cong \left(\frac{Fe^{3+}}{\Sigma Fe}\right)_o \left[\frac{1}{D_{Fe_2O_3}^{sol/liq} + f(1 - D_{Fe_2O_3}^{sol/liq})}\right] \qquad (3)$$

For high MgO MORB we take $f \approx 0.15$ [e.g. Hofmann, 1981]. We estimate $D_{Fe_2O_3}^{sol/liq} \cong 0.2$, suitable for a moderately incompatible component, and similar to the empirical partition coefficient for Ga [Goodman, 1972; Frey et al., 1985; O'Neill, 1991a], which is geochemically a close analogue for Fe^{3+}, and shows a similar distribution amongst the solid phases of mantle peridotite [McKay and Mitchell, 1988]. Hence $Fe^{3+}/\Sigma Fe$ for primary MORB should be about 0.07, in good agreement with the value measured by Christie et al. [1986] on MORB quench glass rims of 0.07 ± 0.03. The oxidation state of MORB is thus consistent with our estimate of low upper mantle $Fe^{3+}/\Sigma Fe$. At very low degrees of partial melting Equation (3) reduces to:

$$\left(\frac{Fe^{3+}}{\Sigma Fe}\right)_{liq} \cong \left(\frac{Fe^{3+}}{\Sigma Fe}\right)_o / D_{Fe_2O_3}^{sol/liq} \qquad (4)$$

that is, about 0.012 - so that using the relationship between fO_2 and $Fe^{3+}/\Sigma Fe$ of Kilinc et al. [1983], we estimate that, if fO_2 is an intrinsic variable during melting, primary low degree partial melts (alkali basalts?) should be ~1 log-bar unit more oxidized than MORBs - c.f. Carmichael and Ghiorso [1986]. Any primary melt with higher $Fe^{3+}/\Sigma Fe$ must reflect oxidizing metasomatism (e.g. many island arc basalts).

$Fe^{3+}/\Sigma Fe$ in garnet lherzolites

Modal data plus some $Fe^{3+}/\Sigma Fe$ analyses of individual phases exist for four high temperature garnet lherzolites hosted in Southern African kimberlites. These lherzolites are thought to represent samples of fertile asthenospheric mantle, originating from depths of ~200 km beneath the Kaapvaal craton [Boyd and Mertzman, 1987; Boyd, 1987]. Such "fertile" peridotites have similar bulk chemistry to least-depleted spinel lherzolite xenoliths [Boyd and Mertzman, 1987].

We present a preliminary estimate of $Fe^{3+}/\Sigma Fe$ in these fertile garnet lherzolites from the available data, summarized in Table 2. Luth et al. [1990] found that the garnets typically contain substantial amounts of ferric iron ($Fe^{3+}/\Sigma Fe = 0.1 - 0.13$). Of clinopyroxene from this facies only that from FRB1033 has been examined by Mössbauer spectroscopy: Luth and Canil [1992] found $Fe^{3+}/\Sigma Fe = 0.28$, which is at the high end of the range reported for clinopyroxenes from spinel lherzolites (see above). In the absence of further data, we use this value as typical for all garnet lherzolite facies clinopyroxene. There are no Mössbauer data for $Fe^{3+}/\Sigma Fe$ in orthopyroxene, so we assume that the

TABLE 2. Estimates of $Fe^{3+}/\Sigma Fe$ for four high temperature garnet lherzolite xenoliths

	FRB1033	BD2501	FRB76	PHN5267
Mg# olivine	0.895	0.910	0.910	0.914
Modes (%)				
garnet	4.9	5.1	9.0	7.7
clinopyroxene	3.5	2.6	4.0	7.6
orthopyroxene	7.5	6.0	15.0	20.0
wt% Fe_2O_3 in gt	0.94	0.86	0.89	0.83
wt% Fe_2O_3 in cpx[a]	1.03	(0.9)	(1.1)	(1.0)
wt% Fe_2O_3 in opx[b]	(0.2-0.6)	(0.2-0.5)	(0.2-0.6)	(0.2-0.5)
Whole Rock				
$Fe^{3+}/\Sigma Fe$ (%)	1.1-1.5	1.0-1.2	1.7-2.3	1.8-2.4
Fe_2O_3 (wt%)	0.10-0.13	0.08-0.10	0.15-0.21	0.18-0.24

The amount of Fe_2O_3 in each phase is given by $Fe^{3+}/\Sigma Fe$ determined from Mössbauer spectroscopy, multiplied by the total Fe from electron microprobe analysis. Modal data for BD2501 from Cox et al. [1987], others from F. R. Boyd (personal communication to D. Canil). $Fe^{3+}/\Sigma Fe$ in garnet from Luth et al. [1991] and in cpx from Luth and Canil [1992].
[a] Values in parentheses estimated using $Fe^{3+}/\Sigma Fe = 0.28$ from FRB1033.
[b] Estimated using $Fe^{3+}/\Sigma Fe = 0.03$ to 0.10, which is the range found for opx in spinel lherzolites (samples listed in Table 1).

range found for spinel lherzolite orthopyroxenes also holds (i.e. $Fe^{3+}/\Sigma Fe = 0.03$ to 0.10). Using these approximations, calculated whole rock $Fe^{3+}/\Sigma Fe$ for the four garnet lherzolites is given in Table 2, and plotted in Figure 1. These preliminary data suggest that there is no significant difference in $Fe^{3+}/\Sigma Fe$ between these garnet lherzolites, and the spinel lherzolites previously discussed.

THE REDOX STATE OF THE TRANSITION ZONE

The fundamental reason that the fO_2 of the upper mantle is quite high (i.e. near QFM), whereas its oxygen content is quite low ($Fe^{3+}/\Sigma Fe \cong 0.023$), is that Fe^{3+} is excluded for crystal-chemical reasons from entering the most abundant phase in the upper mantle assemblage, olivine, thereby forcing up its concentration in the minor phase, spinel. If, for the sake of argument, $Fe^{3+}/\Sigma Fe$ were the same in each phase of the upper mantle, so that $Fe^{3+}/\Sigma Fe$ in spinel were also 0.023 rather than ~0.24 (the average observed value), fO_2, as given by the olivine-orthopyroxene-spinel equilibrium:

$$3 Fe_2SiO_4 + O_2 = 2 Fe_3O_4 + 3 SiO_2 \qquad (5)$$
$$\text{olivine} \qquad\quad \text{spinel} \quad\ \text{ol/opx}$$
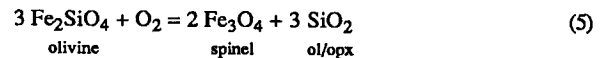
would decrease by approximately $(0.023/0.24)^4$, i.e. nearly 4 log units, since $a_{Fe_3O_4}^{sp} \propto (X_{Fe^{3+}}^{sp})^2$, and the small amount of Fe^{3+} means that its hypothetical redistribution will not affect the activities of the other participants in reaction (5). For most of the upper mantle, 4 log units more reducing would put the fO_2 near the level of metal saturation [e.g. O'Neill and Wall, 1987], and would also be in the regime where CH_4 would be the dominant gas species in C-O-H fluids at upper mantle pressures [e.g. Woermann and Rosenhauer, 1985].

Now, consider the distribution of Fe^{3+} in the next layer below the olivine rich upper mantle, the transition zone.

The transition zone in the mantle

Below 400 km in the mantle $(Mg,Fe)_2SiO_4$ olivine (with $Mg/(Mg+Fe)=0.9$) transforms over a narrow interval to a phase with a spinel-like structure, known as the β-phase, or wadsleyite. The β-phase in turn transforms to $(Mg,Fe)_2SiO_4$ with the spinel structure proper (the γ-phase) at 500-550 km, and this silicate spinel in turn disproportionates to $(Mg,Fe)SiO_3$ perovskite plus $(Mg,Fe)O$ magnesiowüstite at 670 km. The olivine/β-phase transformation coincides with the 400 km seismic discontinuity in the mantle, and the spinel/perovskite reaction with the 670 km discontinuity, leading to the view now held widely, albeit not unanimously, that the seismic structure of the mantle can be explained solely by these phase changes without recourse to major large-scale chemical layering [e.g. Weidner and Ito, 1987; Ringwood and Irifune, 1988; Bukowinski and Wolf, 1990]. The region in between the olivine/β-phase and spinel/perovskite phase changes is known as the transition zone (i.e. transition between the upper and lower mantles), and constitutes about 13% of the mantle by volume.

In a system with typical upper mantle bulk chemistry (i.e. similar to the pyrolite of Ringwood [1975]), as pressure increases above ~6 GPa, $(Ca,Mg,Fe)SiO_3$ pyroxenes become increasingly soluble in the garnet phase, e.g. as the majorite component $Mg_3(MgSi)Si_3O_{12}$. By pressures corresponding to the 400 km discontinuity, all or nearly all the pyroxene is reacted out [Irifune, 1987], so that the transition zone has an essentially bi-mineralic assemblage of β-phase plus majoritic garnet in its top half, and spinel plus majoritic garnet in the bottom half. Pyrolite composition consists of 57% β-phase or spinel, and 43% majoritic garnet [Ringwood, 1975]. In detail, a very small amount of a Ca-rich phase, pyroxene or Ca-silicate perovskite, may also be present [e.g. Ito and Takahashi, 1987], and, at slightly lower Mg# than pyrolite, perhaps also some stishovite.

If we assume that the transition zone has the same chemical composition as the upper mantle, including $Fe^{3+}/\Sigma Fe$, then the oxygen fugacity of the transition zone will depend on how well these phases can accommodate the small amounts of Fe^{3+}. We will now discuss the compatibility of Fe^{3+} in each of the major transition zone phases.

The crystal chemistry of Fe^{3+} in transition zone phases

γ-phase (silicate spinel). Fe_3O_4 of course also has the spinel structure, and there is complete solid solution of Fe_3O_4 with Fe_2SiO_4 at 9 GPa and 1100°C. At lower pressures (e.g. 7 GPa) the completeness of the solid solution is interrupted by the appearance of a spinelloid phase [Canil et. al., 1991; Ross et al., 1992], but there is no reason to suppose that the solution becomes intrinsically unstable. A summary of experimental results on the synthesis of spinel solid solutions along the Fe_3O_4 - Fe_2SiO_4 binary is given in Table 3, and the molar volumes are plotted as a function of composition in Figure 2. The linear dependence of the molar volume on composition reflects the fact that the Fe_3O_4 component retains the inverse cation arrangement across the solid solution [O'Neill and Navrotsky, 1984]. Karpinskaya et al. [1982] have also reported a spinel nearly halfway between Fe_3O_4 and Fe_2SiO_4 in composition at a temperature as low as 800°C at 10 GPa. The implication from the apparent lack of a solvus at such temperatures is that activity coefficients in Fe_3O_4-Fe_2SiO_4 spinel cannot be very large. Activity-composition relations have yet to be determined in any binary spinel system between a 4-2 normal spinel (like Fe_2SiO_4) and a 3-2 inverse spinel [O'Neill and Navrotsky, 1984], and therefore it is not yet possible to predict activity-composition relations in the Fe_3O_4 - Fe_2SiO_4 spinel system. However, the activity of magnetite ($a^{sp}_{Fe_3O_4}$) in silicate spinel in equililbrium with Fe metal at the fO_2 of the quartz-fayalite-iron buffer (the low fO_2 breakdown of Fe_2SiO_4 olivine at low pressure), is 0.007-0.015 at 1100-1500°C, implying Fe_3O_4 contents of around 1% if $a^{sp}_{Fe_3O_4} \approx X^{sp}_{Fe_3O_4}$, or 10% if $a^{sp}_{Fe_3O_4} \approx (X^{sp}_{Fe_3O_4})^2$. Thus even at the lowest oxygen fugacities at which "Fe_2SiO_4" spinel is stable, it is likely to contain Fe^{3+} at levels which are significant when compared to the low $Fe^{3+}/\Sigma Fe$ of the upper mantle. These levels also mostly fall within the range detectable by Mössbauer spectroscopy.

Figure 3 shows a Mössbauer spectrum of Fe_2SiO_4 spinel synthesized at 1000°C and 8 GPa in an Fe capsule. There was no detectable Fe^{3+} in the olivine starting material, but there is 0.07± 0.02 $Fe^{3+}/\Sigma Fe$ in the run product. The charge contained excess $FeSiO_3$ (mainly around the edge of the capsule), suggesting that fO_2 is buffered at the Fe_2SiO_4-$FeSiO_3$-Fe equilibrium.

TABLE 3. Synthesis data for Fe_2SiO_4 - Fe_3O_4 spinels*

Run#	Starting Material	P (GPa)	T (°C)	Run time (hours)	Products	Spinel lattice constant (Å)	mol% Fe_3O_4[§]
196	$Fa_{85}Mt_{15}$	7.0	950	15	sp,spd	8.2541(3)	16
195	$Fa_{85}Mt_{15}$	7.0	1075	12	sp,spd	8.2512(2)	18
195	$Fa_{40}Mt_{60}$	7.0	1075	12	sp,spd	8.3453(2)	74
205	$Fa_{85}Mt_{15}$	7.0	1150	12	sp,spd	8.2511(4)	18
205	$Fa_{40}Mt_{60}$	7.0	1150	12	sp,spd	8.3532(3)	72
269	$Fa_{90}Mt_{10}$	7.0	1175	11	sp,spd,cfs	8.2462(1)	10
219	Mt_{100}	7.0	1200	5	sp	8.3962(3)	100
155	$Fa_{85}Mt_{15}$	7.0	1200	5	sp,spd,cfs	8.2463(1)	10
321	$Fa_{25}Mt_{75}$	7.0	1200	5	sp	8.3541(2)	75
170**	Fa_{100}	8.0	1000	9	sp,cfs	n.d.	14
524	$Fa_{50}Mt_{50}$ + SiO_2	9.0	1100	12	sp,coes	8.315(2)	52

* lattice constants and phase relations for spinelloids will be presented elsewhere
** synthesized in Fe capsule, all other runs used Au capsules except #524 which used Ag
[§] from electron microprobe analysis
Fa = fayalite, Mt = magnetite, coes = coesite, sp = spinel, spd = spinelloid, cfs = clinoferrosilite, n.d. not determined
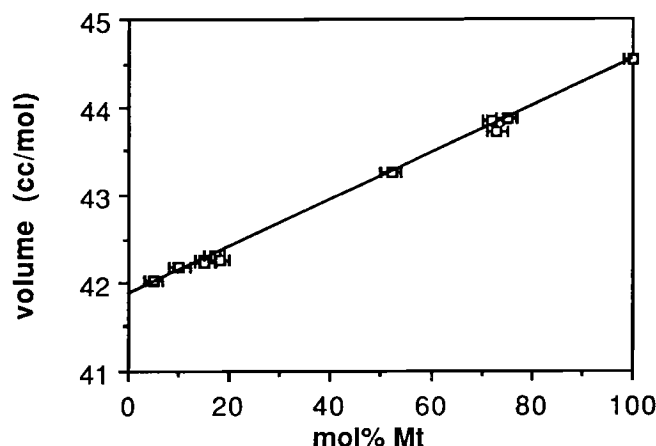
Fig. 2. Volume (in cm^3/mol) vs. composition for spinels synthesized at 7 to 9 GPa along the join Fe_2SiO_4 - Fe_3O_4. The linear trend extrapolates to 42.86 cm^3/mol at Fe_2SiO_4, which corresponds to a cell edge of 8.224 Å

The effect of adding Mg to the spinel system will be to raise the activity coefficient of Fe_3O_4, because the free energy of the reciprocal reaction:

$$1/2\ Fe_2SiO_4 + MgFe_2O_4 = 1/2\ Mg_2SiO_4 + Fe_3O_4 \qquad (6)$$

spinel   spinel   spinel   spinel
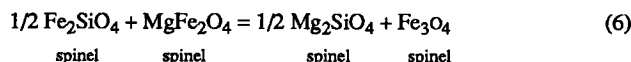
is strongly negative (~10 kJ/mol at 1000 K - thermo-dynamic data from Bina and Wood [1987] for the silicate spinels, and Robie et al. [1978] for the ferrite spinels). Adding Mg to the system also enlarges the stability field of spinel to lower fO_2's. Nevertheless, even Mg-rich silicate spinels contain sufficient Fe^{3+} to be detectable by the Mössbauer method (see below).

β-phase. The β-phase is a spinelloid polytype, and like spinel proper consists of an approximately cubic-close-packed oxygen lattice with 1/8 of the tetrahedral and 1/2 of the octahedral interstices occupied by cations, leading to an octahedral to tetrahedral cation site ratio (M:T) of 2:1. However, the spinelloids differ as to the degree of polymerization of the various sites, most importantly the polymerization of the T sites. In particular, β-phase has a single T site [Horiuchi and Sawamoto, 1981], polymerized to form T_2O_7 groups. The bridging oxygen, O2, is also bonded to M2, one of the three crystallographically distinct octahedral sites. Based on simple Pauling bond-strength sums, O3 and O4 (each coordinating one T and three M sites) are exactly charge balanced, whereas O1 (coordinating 5 M sites) is severely underbonded (1.67 v.u.) and O2 (the bridging oxygen) is severely overbonded (2.33 v.u.). Distortion of the structure, in particular the T site, causes some compensation, and based upon the bond-strength bond-length formulae of Brown and Altermatt [1985] the bonding to O1, O2, O3 and O4 is 2.07, 1.96, 1.91, and 2.01 v.u. respectively.

Although no systematic experiments investigating the compatibility of Fe^{3+} with the β-phase structure have been carried out, there are several lines of evidence that suggest that significant quantities of Fe^{3+} might easily be incorporated into this structure.

Hazen et al. [1990] have synthesized single crystals of β-phase with nominal compositions on the join Mg_2SiO_4 - Fe_2SiO_4 at 1800°C and 16 GPa. Mössbauer analysis of these samples revealed up to 0.08

$Fe^{3+}/\Sigma Fe$, indicating that at least under the conditions of synthesis (possible fO_2, in particular, is not reported) substantial amounts of ferric iron may be incorporated without difficulty. This substitution of Fe^{3+} had no clear effect on bulk modulus, linear compressibility, or unit cell dimensions.

Ohtani et al. [1986], Ito and Takahashi [1987] and Ohtani and Sawamoto [1987] have shown that β-phase in equilibrium with melt at 20 GPa contains up to 1.5 % Al_2O_3 and Cr_2O_3; thus there is no intrinsic difficulty in including trivalent cations larger than Si into the β-phase structure, although trivalent iron nominally requires larger M-O distances than either Al^{3+} or Cr^{3+} (1.865 Å vs. 1.757 Å or 1.803 Å for tetrahedral coordination, based on Brown and Altermatt [1985]).

A spinelloid phase has been recently described in the system Fe_3O_4 - Fe_2SiO_4 at 1200°C and 7 GPa [Canil et al., 1991; Ross et al, 1992], with $Fe^{3+}/\Sigma Fe \approx 0.46$. Although not isostructural with the β-phase, both are spinelloids and therefore have many structural similarities. In particular, the bridging oxygen (O2) in β-phase is topologically identical with O5 in this phase, but Pauling bond-sum charge-balance is improved by partial substitution of Fe^{3+} for Si in the tetrahedral sites; the reduced valence of the tetrahedrally-coordinated cation allows relaxation of the structure and regularization of the tetrahedral sites. Similarly, O1 in the β-phase shows severe underbonding based on Pauling bond-sums, although distortions in the adjoining octahedrally-coordinated cation sites result in good charge balance (based on Brown and Altermatt [1985]); this oxygen is topologically equivalent to O6
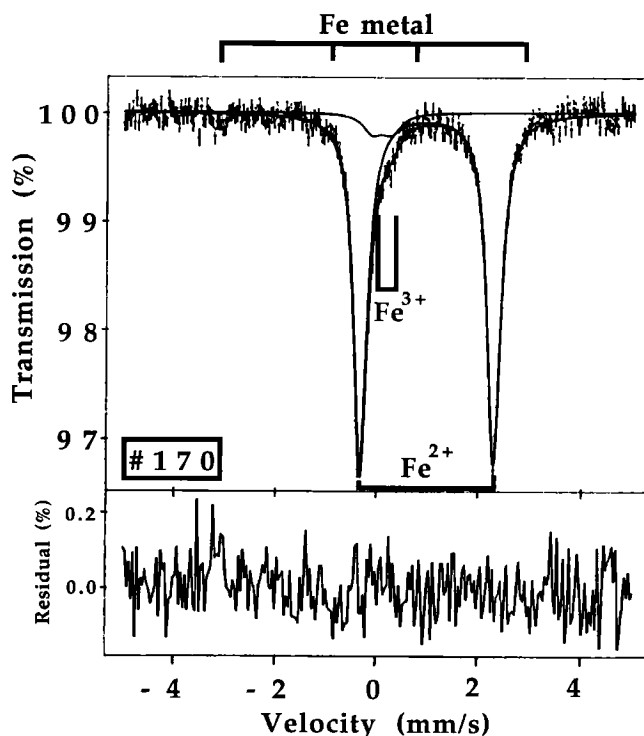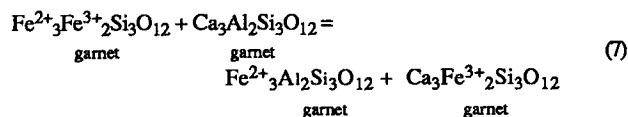

Fig. 3. ^{57}Fe Mössbauer spectrum (298 K) of "Fe_2SiO_4" spinel synthesized at 1000°C, 8GPa in an Fe capsule (run 170 in Table 3), fitted to two symmetrical Lorentzian doublets. A small amount of metallic iron (not fitted) is also visible. The residual gives the deviation of the observed spectrum from the calculated envelope, divided by the square-root of the background. Velocity scale relative to ^{57}Fe in Rh; for conversion relative to metallic iron, add 0.114 mm/s.

in the new phase, which also has a good Brown and Altermatt charge balance, but with considerably less distortion of the cation sites. As in spinel, half the Fe^{3+} must substitute on the T site (thus, incidentally, improving charge balance around O2). The octahedral substitution is less clear, but the smaller M-O distance for Fe^{3+} as compared to Mg or Fe^{2+} suggests that the M2 site might be preferred.

Smyth [1987] suggested that the β-phase might be a host for H_2O; the bonding pattern around O1 is such that occupation by hydroxyl might be energetically favorable. It was suggested that charge balance would be maintained by vacancy on M1. Another possible mechanism for maintaining charge balance in such a case would be substitution of Fe^{3+} for Si.

Majorite garnet. Many types of Fe^{3+}-bearing garnets are known, for example the magnetic REE ferrite garnets ($R_3Fe^{3+}{}_5O_{12}$), in which Fe^{3+} fills both the octahedral and the tetrahedral sites. Among silicate garnets Fe^{3+} is generally restricted to the octahedral site, although tetrahedral Fe^{3+} can occur under exceptional circumstances (e.g. Amthauer et al. [1976]). At low pressures, substantial fractions of Fe^{3+} only occur in Ca-garnets, i.e. as $Ca_3Fe^{3+}{}_2Si_3O_{12}$ (andradite). In the MgO-SiO_2-Fe-O system, Fe^{3+} can be considered in terms of a skiagite ($Fe^{2+}{}_3Fe^{3+}{}_2Si_3O_{12}$) or a khoharite ($Mg_3Fe^{3+}{}_2Si_3O_{12}$) component. These garnet end-members, which have not been found in nature, are expected to become more stable with increasing pressure [Schreyer and Baller, 1981]. This expectation has been borne out for skiagite in a series of synthesis experiments along the almandine ($Fe^{2+}{}_3Al_2Si_3O_{12}$) - skiagite join [Woodland and O'Neill, 1992]. The solubility of skiagite in almandine increases steadily with increasing pressure. At 1100°C, the skiagite component saturates at 12, 35, and 90 mole % at 2.7, 6.0, and 9.0 GPa respectively. The skiagite end-member itself becomes stable above ~9.5 GPa at 1100°C. Mössbauer spectra of these garnets indicate that all Fe^{3+} resides on the octahedral sites. The molar volume of end-member skiagite is 121.4 ± 0.1 cm^3, in agreement with the estimate from the systematics of garnet crystal chemistry of 121.2 cm^3 [Novak and Gibbs, 1971]. This implies that the molar $\Delta V_{(1,298)}$ for the reciprocal exchange reaction:

$$Fe^{2+}{}_3Fe^{3+}{}_2Si_3O_{12} + Ca_3Al_2Si_3O_{12} =$$

garnet   garnet

$$Fe^{2+}{}_3Al_2Si_3O_{12} + Ca_3Fe^{3+}{}_2Si_3O_{12} \qquad (7)$$

garnet   garnet

is positive, and is relatively large for a reciprocal reaction (~0.1 J/bar). This acts to lower the activity coefficient of $Fe^{2+}{}_3Fe^{3+}{}_2Si_3O_{12}$ at high pressures.

We have synthesized a number of majorite garnets in the MgO-SiO_2-Fe-O system, from starting material which contained no detectable Fe^{3+} ($Fe^{3+}/\Sigma Fe < 0.02$). Run conditions are summarized in Table 4, and experimental details are given in Appendix 2. Mössbauer spectroscopy shows that all these garnets contain substantial amounts of Fe^{3+}. A representative spectrum at 80 K for one sample, synthesized in a Re capsule, is shown in Figure 4. Visually, the spectum consists of a very intense outer doublet and two well-resolved, weaker inner peaks. The low-velocity peak of the latter two is much more intense than the high velocity peak, and therefore these two cannot belong to a single doublet. Rather, an additional doublet has to be fitted under the low-velocity peak and the minimum number of doublets in a fit must be three. Although structural considerations for these tetragonal garnets lead to a large number of possible doublets, in the absence of fine structure in the Mössbauer spectra the number of doublets was kept to the minimum of three. Based on the
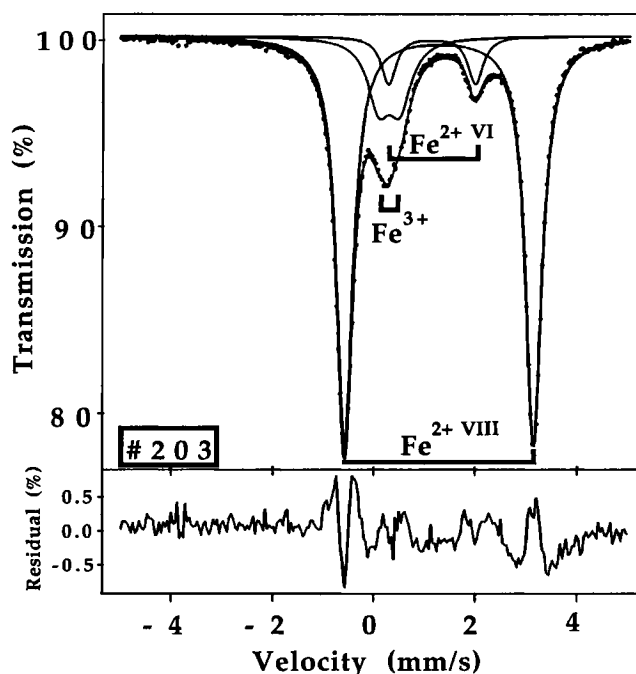

Fig. 4. ^{57}Fe Mössbauer spectrum (80 K) of majorite garnet (Mg/(Mg+Fe) = 0.9) synthesized at 1800°C, 18 GPa in a Re capsule (run 203 in Table 4), fitted to three symmetrical Lorentzian doublets that correspond to Fe^{2+} in the octahedral site, Fe^{2+} in the dodecahedral site, and Fe^{3+}. Residuals and velocity scale as in Figure 3.

resulting hyperfine parameters [Geiger et al., 1991], the intense outer doublet is due to Fe^{2+} in the dodecahedral site(s). Of the weaker inner doublets the one with the larger quadrupole splitting and isomer shift has to be assigned to Fe^{2+} in octahedral coordination, and the doublet with the smaller isomer shift and quadrupole splitting has to be assigned to Fe^{3+}. Although there is no certainty as to the site occupancy of Fe^{3+} in these garnets, the fractional area of the Fe^{3+} doublet and therefore the $Fe^{3+}/\Sigma Fe$ is well constrained, because it is determined by the intensity difference of the low-velocity and high velocity envelopes.

$Fe^{3+}/\Sigma Fe$ ratios for three garnet samples have been calculated from the Mössbauer data (collected both at 80 and 298 K) and structural formulae assigned under the assumption that Fe^{3+} occupies the octahedral site [Geiger et al., 1991]. $Fe^{3+}/\Sigma Fe$ ratios lie between 0.12 and 0.16 (Table 4), implying 3 to 5% of a $(Mg,Fe^{2+})_3Fe^{3+}{}_2Si_3O_{12}$ component. The $Fe^{3+}/\Sigma Fe$ ratios are derived from the 80 K spectra, to account for possibly different recoiless fractions of Fe^{3+} and Fe^{2+} [Amtauer et al., 1976]; however, the differences in $Fe^{3+}/\Sigma Fe$ between the 80 K and 298 K spectra were found to be less than 10% (relative), in agreement with results from synthetic $Fe^{2+}{}_3Al_2Si_3O_{12}$ - $Fe^{2+}{}_3Fe^{3+}{}_2Si_3O_{12}$ garnets [A. B. Woodland, unpublished data]. The two runs using Mo as the capsule material give slightly lower $Fe^{3+}/\Sigma Fe$ ratios than the run in the Re capsule. This may be significant if the Mo capsule exerts some buffering influence.

In summary: spinel, β-phase and high pressure majoritic garnet are all capable of containing substantial amounts of Fe^{3+} under transition zone conditions of temperature, pressure and likely Mg/(Mg+Fe) ratio. In fact, all syntheses of these phases seem to contain enough Fe^{3+} to

TABLE 4. $(Mg,Fe)SiO_3$ garnet and $(Mg,Fe)_2SiO_4$ spinel syntheses

Run#	Starting Material	Capsule	P(GPa)	T (°C)	Time (min)	Products	Lattice Constants (Å) §		$Fe^{3+}/\Sigma Fe$
(Mg,Fe)SiO₃ garnet							a	c	
203	Fs$_{10}$	Re	18.0	1800	30	gt (st)	11.5328(3)	11.4444(3)	0.16
307	Fs$_{20}$	Mo	18.0	1800	15	gt (st)	11.5291(10)	11.4458(10)	0.14
319	Fs$_{10}$	Mo	18.0	1800	15	gt (st)	11.5307(5)	11.4412(5)	0.12
526	Fs$_{15}$ + Fe + SiO$_2$	Fe	18.0	1900*	5	gt+st+Fe (sp)	11.5282(9)	11.4659(12)	0.10
(Mg,Fe)₂SiO₄ spinel									
519	Fs$_{15}$ + SiO$_2$	Fe	18.0	1700*	15	sp+st+Fe (gt)	8.101(2)		0.06**

Fs = ferrosilite, i.e. Fe/(Fe + Mg)
§ using stishovite as an internal standard, with a = 4.1790 Å, c = 2.6649 Å.
* Temperature estimated on power (± 100°C)
** probably a maximum value, from the fitting procedure - see discussion in text
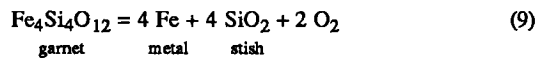gt = garnet, sp = spinel, st = stishovite, Fe = Fe metal, phases listed in brackets are in trace amounts

be detected by Mössbauer spectroscopy, even when these syntheses are accomplished using Fe^{3+}-free starting materials, and (supposedly) reducing Mo capsules. The importance of this observation for the transition zone fO_2 is that Fe^{3+} will not be concentrated into modally minor phases as in the upper mantle, but will be distributed throughout the major phases, lowering its chemical potential. This implies lower fO_2 (see Equations 10 and 11 below). In order to quantify this, we now report some experiments at the low fO_2 stability limits of spinel and majoritic garnet, under buffered conditions, to determine the minimum Fe^{3+} content of these phases.

Minimum $Fe^{3+}/\Sigma Fe$ in silicate spinel and majorite garnet in the system MgO-SiO_2-Fe-O

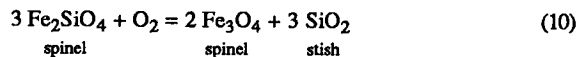The low fO_2 stability limit of $(Mg,Fe)_2SiO_4$ spinel is given by the reaction:

$$Fe_2SiO_4 = 2 Fe + SiO_2 + O_2 \qquad (8)$$
$$\text{spinel} \quad \text{metal} \quad \text{stish}$$
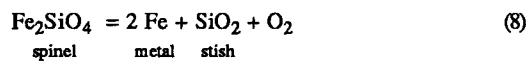
and that of $(Mg,Fe)_4Si_4O_{12}$ majorite garnet by:

$$Fe_4Si_4O_{12} = 4 Fe + 4 SiO_2 + 2 O_2 \qquad (9)$$
$$\text{garnet} \quad \text{metal} \quad \text{stish}$$

Both reactions show that in the presence of excess SiO_2 and Fe metal, fO_2 depends on the activities of Fe_2SiO_4 and $Fe_4Si_4O_{12}$, i.e. approximately on the $Fe^{2+}/(Mg+Fe)$ ratio in the simple MgO - SiO_2 - Fe - O system.

The amount of Fe^{3+} in each phase is controlled by the reactions:

$$3 Fe_2SiO_4 + O_2 = 2 Fe_3O_4 + 3 SiO_2 \qquad (10)$$
$$\text{spinel} \qquad \text{spinel} \quad \text{stish}$$

and:

$$5 Fe_4Si_4O_{12} + 2 O_2 = 4 Fe_3Fe_2Si_3O_{12} + 8 SiO_2 \qquad (11)$$
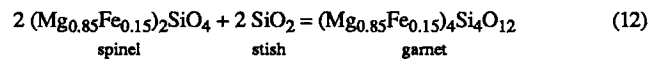$$\text{garnet} \qquad \text{garnet} \quad \text{stish}$$

The minimum amount of Fe^{3+} in either spinel or garnet at constant Mg/(Mg+Fe) occurs at the low fO_2 stability limits as given by reactions (8) and (9) - that is, buffered by excess Fe metal and SiO_2.

In order to determine these mimimum Fe^{3+} contents, we synthesized spinel+stishovite+Fe metal and garnet+stishovite+Fe metal, both from a composition of $(Mg_{0.85}Fe_{0.15})SiO_3$ plus excess Fe and SiO_2. The spinel was synthesized at 18 GPa and 1700°C, the garnet at 18 GPa and 1900°C, the higher temperature being to the right hand side of the divariant reaction:

$$2 (Mg_{0.85}Fe_{0.15})_2SiO_4 + 2 SiO_2 = (Mg_{0.85}Fe_{0.15})_4Si_4O_{12} \qquad (12)$$
$$\text{spinel} \qquad \text{stish} \qquad \text{garnet}$$

c.f. Ohtani and Kagawa [1989]. Both experiments were done using Fe capsules. Experimental details are described in Appendix 2, and the results summarized in Table 4.

The Mössbauer spectrum for the garnet is shown in Figure 5. The spectrum is similar to that found for other majorite garnets (e.g. Figure 4), but with one extra peak between the high velocity Fe^{2+}(VIII) and Fe^{2+}(VI) peaks. Fitting an extra doublet to this peak results in hyperfine parameters essentially identical to those found for spinel (Figure 3), and this interpretation is consistent with the small amount of spinel identified in the run product by powder XRD. The $Fe^{3+}/\Sigma Fe$ ratio is found to be 0.10 ± 0.02, which is only slightly less than that found for the garnets synthesized in Mo or Re, implying that the fO_2 in these other runs was not anomalously high. This is obviously an amount of some consequence when compared to the estimated upper mantle whole rock $Fe^{3+}/\Sigma Fe$ of 0.023.

The Mössbauer spectrum from the spinel run (Figure 6) is similar to that described earlier for Fe_2SiO_4 spinel (Figure 3), but contains a small high-velocity peak consistent with <5% majorite, a small amount of which was also identified by XRD. There is a small but distinct shoulder at 0.3 mm/s, which we assign to Fe^{3+}, as in other silicate spinel spectra (e.g. Figure 3). The amount of Fe^{3+} is difficult to estimate because the shoulder is not resolved, and fitted areas in these regions tend to overestimate the actual area [Hawthorne and Waychunas, 1988]. The fit gives 0.06 $Fe^{3+}/\Sigma Fe$, but the uncertainty is such that ratios as low as 0.03 are not excluded.

DISCUSSION

We apply these experimental results to the problem of the oxidation state of the transition zone bearing in mind differences in
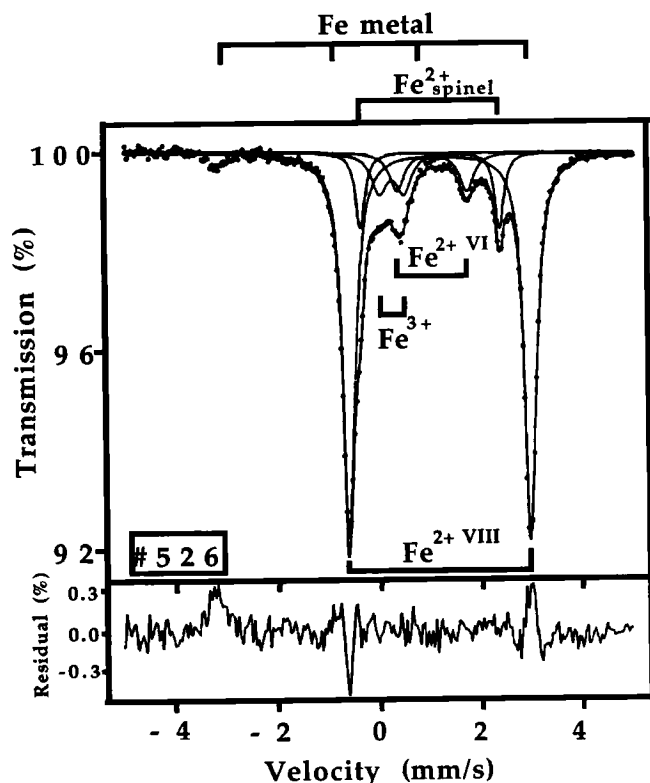
Fe metal

Fe$^{2+}_{spinel}$

Fe^{2+} VI

Fe^{3+}

Fe^{2+} VIII

#526

Velocity (mm/s)

Fig. 5. ^{57}Fe Mössbauer spectrum (298 K) of majorite garnet (Mg/(Mg+Fe) = 0.85) synthesized at 1900°C, 18 GPa in an iron capsule, coexisting with metallic iron, stishovite and a trace of silicate spinel (run 526 in Table 4). The Mössbauer spectra of the contaminant spinel (cf. Figure 3) and the Fe metal (not fitted) are displayed, in the form of bar diagrams, at the top of the figure. Residuals and velocity scale as in Figure 3.

temperature (the mantle probably has a temperature of about 1600°C at our experimental pressure of 18 GPa - e.g. Ito and Katsura [1989]), and in composition, for example the presence of substantial Al$_2$O$_3$ in garnet (~10wt% in the garnet phase for a primitive upper mantle composition, e.g. Takahashi and Ito [1987]), and a slight difference in Mg# (0.88 versus 0.85). The pyrolite composition in the transition zone is also undersaturated in SiO$_2$ (no stishovite present), allowing higher fO$_2$'s and Fe^{3+} contents in equilibrium with Fe metal (see Equations 8 to 11 above). Nevertheless, all these differences are of a second order nature, and should have a relatively minor influence on our main point, which is that Fe^{3+} is so compatible in the major transition zone phases that the oxygen fugacity of a system with primitive upper mantle composition will be very low, probably near the level of metal saturation. This conclusion and some of its implications will now be discussed in more detail.

The exact pressure-temperature co-ordinates of the olivine/β-phase transition, and the spinel-to-perovskite+magnesiowüstite reaction, and the widths of the associated divariant fields, are important clues to the temperature distribution in the mantle, and as to whether the mantle might be compositionally layered [e.g. Bina and Wood, 1987; Ito and Takahashi, 1989; Wood, 1990]. A major aim of high pressure experimental petrology is to match the results from the experimentally determined phase equilibria to the seismic observations. The strong preference of Fe^{3+} for the transition zone phases may influence the

experimentally determined phase boundaries at a level which is significant compared to the desired precision. For example, in experiments on the olivine/β-phase transition in which fO$_2$ is not buffered, and Fe^{3+} not determined, the β-phase will be additionally stabilized to an unknown extent, perhaps resulting in an erroneous impression of the width of the olivine/β-phase (pseudo-) divariant field. There are also obvious implications for interpreting physical property measurements, e.g. the jump in electrical conductivity at the olivine/spinel transition [Omura, 1989].

In order to estimate the minimum possible bulk Fe^{3+}/ΣFe for a primitive upper mantle composition in the transition zone, we take the compositions of co-existing spinel and garnet experimentally determined by Takahashi and Ito [1987] at 1600°C and 20 GPa, assume that each phase has Fe^{3+}/ΣFe as in our experiments (0.10 for majoritic garnet, and a conservatively estimated 0.03 for silicate spinel), and assume 60% spinel, 40% garnet (ignoring the small amount of Ca-perovskite phase in their experiment). We find Fe^{3+}/ΣFe = 0.05, with uncertainties suggesting a possible range of 0.03 to 0.08. At 8.0 wt% FeO*, this implies 0.44 wt % Fe$_2$O$_3$. This minimum Fe^{3+}/ΣFe occurs at saturation with Fe metal, and is calculated for equilibrium in the simple MgO-SiO$_2$-Fe-O system with excess SiO$_2$; silica undersaturated conditions will raise Fe^{3+}/ΣFe (Equations 8 to 11 above).

We have estimated that primitive upper mantle has 0.2 wt % Fe$_2$O$_3$, i.e. lower than this estimate for the transition zone minimum. In the absence of the oxidized volatile components H$_2$O and CO$_2$,
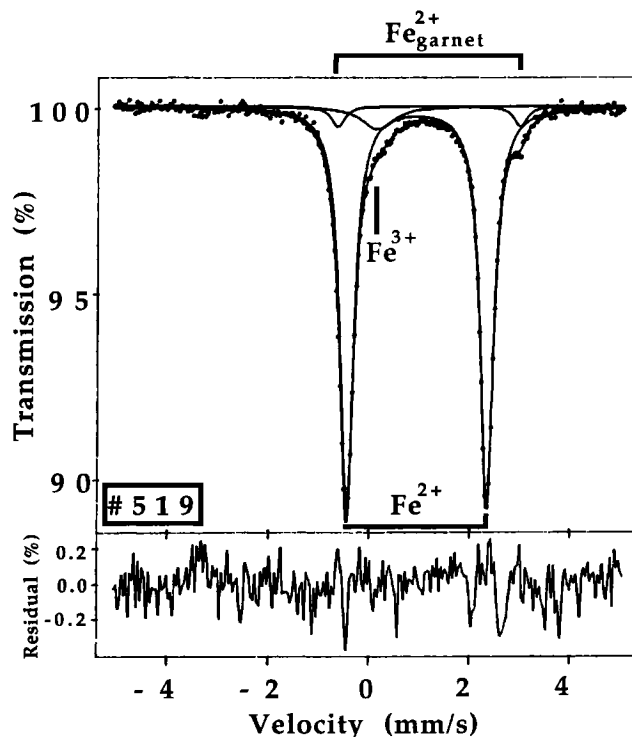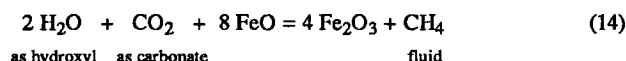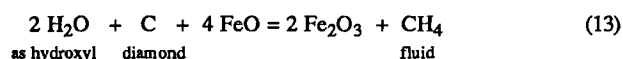
Fe$^{2+}_{garnet}$

Fe^{3+}

#519

Fe^{2+}

Velocity (mm/s)

Fig. 6. ^{57}Fe Mössbauer spectrum (298 K) of (Mg$_{0.85}$Fe$_{0.15}$)$_2$SiO$_4$ spinel (run 519 in Table 4) synthesized at 1700°C, 18 GPa in coexistence with metallic iron, stishovite and a trace of majorite garnet (indicated by the bar diagram on top of the figure). For Fe^{3+} in spinel, only a broadened singlet instead of the required doublet could be fitted. Residuals and velocity scale as in Figure 3.

adjustment of the $Fe^{3+}/\Sigma Fe$ ratio might procede through partitioning of Fe (actually, mostly Ni at first) into the mantle sulfide phase, i.e. $3\,Fe^{2+}_{(silicate)} = Fe^{0}_{(sulfide)} + 2\,Fe^{3+}_{(silicate)}$ (there is ~200 ppm S in the primitive upper mantle, e.g. O'Neill [1991b, Appendix 1]. The implication is that in the absence of any buffering effect from volatiles, the present $Fe^{3+}/\Sigma Fe$ of the upper mantle is more or less consistent with metal saturation under transition zone conditions. The metal would be an Fe-Ni-S alloy.

Extrapolation of fluid equilibria in the H-O and C-H-O systems to transition zone pressures is uncertain because of lack of high pressure data, but the trends calculated for upper mantle pressures indicate that at the low fO_2 of metal saturation, CH_4 is the dominant species in a fluid phase [e.g. Woermann and Rosenhauer, 1985]. Therefore, provided that the amounts of C and H components do not exceed the oxygen buffering capacity of the Fe^{3+}/Fe^{2+} equilibrium, CH_4 may be produced in transition zone assemblages by reduction of the hydroxyl component in the silicates in the presence of carbon, together with any carbonate, i.e., according to the reactions:

$$2\,H_2O\ +\ C\ +\ 4\,FeO = 2\,Fe_2O_3\ +\ CH_4 \tag{13}$$
as hydroxyl   diamond   fluid

$$2\,H_2O\ +\ CO_2\ +\ 8\,FeO = 4\,Fe_2O_3 + CH_4 \tag{14}$$
as hydroxyl   as carbonate   fluid

Increasing Fe_2O_3 from 0.2 wt % to 0.44 wt % could, according to reaction (13), reduce 270 ppm H_2O if sufficient elemental C is present; alternatively, the required increase in Fe_2O_3 according to reaction (14) could reduce 130 ppm H_2O plus 330 ppm CO_2. These amounts are comparable to the estimated primitive mantle abundances of H_2O and CO_2.

So far as is presently known, CH_4, unlike H_2O and CO_2, does not dissolve into, or react with, mantle silicates at deep mantle temperatures and pressures, and may therefore co-exist with mantle peridotite as a discrete fluid phase. If this low density, low viscosity fluid phase can separate from its silicate matrix and migrate upwards, then the transition zone would form a barrier against re-circulation of C-H volatiles from the upper mantle (and crust) into the lower mantle. This effect may also apply to subducted oceanic crust, the basaltic part of which transforms to >90% majoritic garnet (plus stishovite) at transition zone pressures [Irifune and Ringwood, 1987]. Transfer of material between upper and lower mantles (the extent of which is, at present, under debate) would be a one way process for C, H and any other component which partitions into a CH_4-rich fluid, concentrating them relative to silicate-compatible components in the upper mantle over geological time.

CH_4-rich fluids upwelling from the transition zone, perhaps from subducted basaltic material, are expected to undergo the reverse of reactions (13) and (14) on encountering the higher fO_2's of the olivine upper mantle, triggering redox melting [e.g. Taylor and Green, 1987].

The lower mantle

A lower mantle of pyrolite composition would consist of 65 to 75% silicate perovskite with $Mg/(Mg+Fe) = 0.96$, 16 to 18% magnesiowüstite with $Mg/(Mg+Fe) = 0.8$, plus some Ca-silicate perovskite and perhaps an Al-rich phase [Ringwood, 1989; Ito et al., 1984; Ito and Takahashi, 1989]. Since Mg-Fe silicate perovskite is manifestly very poor in total Fe, it may be assumed that perovskite holds only a fairly small proportion of the whole rock's total Fe^{3+}, the major part of which would therefore be concentrated into the

coexisting magnesiowüstite. From the estimate of the lower mantle mineralogy given above, magnesiowüstite would contain about 75% of the whole rock FeO* in a pyrolitic mantle. Assuming equal $Fe^{3+}/\Sigma Fe$ in perovskite and magnesiowüstite, the latter would have the estimated mantle $Fe^{3+}/\Sigma Fe$ of about 0.023, i.e. a composition near $(Mg_{0.8}Fe^{2+}_{0.195}Fe^{3+}_{0.005})_{0.998}O$. At atmospheric pressure and 1500°C, such a magnesiowüstite would exist at log $fO_2 = -7.4$ [Valet et al., 1975, their eqns. 21 and 27], which is about half way between the (extrapolated) QFM and IW buffers - in other words, unless pressure has a large effect on the thermochemistry of Fe^{3+} in magnesiowüstite, and preliminary data indicate that it does not [Kato et al., 1989], the lower mantle has a roughly similar relative oxygen fugacity to that of the upper mantle, and, like the upper mantle, is far removed in fO_2 from metal saturation (by ~2.5 log-bar units according to the above calculation). It seems that at least this postulated level of $Fe^{3+}/\Sigma Fe$ in magnesiowüstite is needed to explain the high electrical conductivity of the lower mantle [Peyronneau and Poirier, 1989; Wood and Nell, 1991]. It would also be difficult to obtain the necessary high electrical conductivity if the lower mantle had a non-pyrolitic, more silica-rich bulk composition, and consequently less magnesiowüstite [Wood and Nell, 1991].

The transition zone therefore forms a shell of reduced conditions sandwiched between relatively oxidized upper mantle and lower mantle. The further implications of this for core formation in the early Earth must depend largely on the ability of metal to separate from a silicate matrix. It has been argued that metal cannot segregate unless it is molten, and unless either the silicate is also partially molten, or the high surface potential of the metal is somehow lowered sufficiently for it to wet the silicate [Stevenson, 1990]. Certainly, the empirical evidence is that small amounts of sulfide have existed in the upper mantle since core formation was completed [O'Neill, 1991b], which, from Pb isotopic evidence, is constrained to be shortly after accretion [Patterson, 1956]. We do not think, therefore, that the putative presence of Fe-Ni-S metal in the transition zone in the present Earth need imply continuing loss of metal to the core.

Metal saturation in the transition zone might seem to resurrect the possibility that core formation took place in the early Earth by a one step segregation of metal from this region, for example, from the bottom of a terrestrial magma ocean. Whether or not this did happen needs to be tested by comparing the mantle abundances of the siderophile elements with their appropriate high pressure metal/silicate partition coefficients. Estimates from mineral/melt partitioning at high pressure coupled with the existing low pressure melt/metal data suggest that this scenario cannot satisfactorily explain either the overabundance of the moderately siderophile elements, e.g. Ni and Co, or the depletion relative to chondritic of the least siderophile of the potential siderophiles, Cr and V [Ohtani et al., 1991]: a two-stage model [e.g. O'Neill, 1991b] is still required.

APPENDIX 1

Comparison of $Fe^{3+}/\Sigma Fe$ from Mössbauer spectroscopy with wet chemical analyses

Our estimate of $Fe^{3+}/\Sigma Fe$ is so much lower than published wet chemical analyses of mantle peridotites as to require further comment. We will first compare the Mössbauer determinations of $Fe^{3+}/\Sigma Fe$ for the individual phases with the available wet chemical data.

For Cr-spinels of mantle-like compositions, Osborne et al. [1981] found wet chemical analyses to be in good agreement with Mössbauer determinations of $Fe^{3+}/\Sigma Fe$, whereas Lucas et al. [1989] found that

wet chemistry gave inflated Fe^{3+} values. This illustrates a well-known problem with the wet-chemical data, that results differ markedly from one laboratory to another, so that it is always difficult to be sure of the reliability of the data. For pyroxenes, we are aware of only one set of $Fe^{3+}/\Sigma Fe$ wet chemical analyses from mantle peridotites which is accompanied by full major element analyses of co-existing phases, namely that published by Frey and Green [1974] on six spinel lherzolite xenoliths from Victoria, Australia (analyst E. Kiss). The chemistry of these samples indicates that they are more depleted than the ones in the Mössbauer studies of Dyar et al. [1989] and Luth and Canil [1992], but have equilibrated at comparable P, T, and fO_2; the two analytical methods should give similar results. By and large, this they do, but the wet chemical analyses show greater dispersion than the Mössbauer determinations. For the wet chemical analyses, $Fe^{3+}/\Sigma Fe$ in orthopyroxene ranges from 0.03 to 0.10 (cf. 0.03 to 0.06 by Mössbauer), and in clinopyroxene from 0.18 to 0.36 (cf. 0.06 to 0.24). There is no correlation of $Fe^{3+}/\Sigma Fe$ in orthopyroxene with that in clinopyroxene, nor any correlation of either orthopyroxene or clinopyroxene with $Fe^{3+}/\Sigma Fe$ in spinel, or with calculated fO_2. We believe that the most straightforward interpretation of these data is that they support the Mössbauer results, but are less precise, and tend to be skewed towards higher Fe_2O_3, by oxidation during the analytical process. This latter point probably accounts for the generally higher $Fe^{3+}/\Sigma Fe$ in comparable pyroxenes from various laboratories listed by Deer et al. [1978].

There are many more whole rock determinations of $Fe^{3+}/\Sigma Fe$ in mantle samples - a compilation is given in Table 5. We have not included samples with obvious alteration (e.g. high H_2O or CO_2 contents, which includes most garnet peridotites).

We believe that certainly the higher of these $Fe^{3+}/\Sigma Fe$ estimates, and probably even the lower ones, are an inflated measure of the true oxidation state of the upper mantle, as an inversion of the modal abundance/Fe_2O_3-content argument will show. Consider a typical mantle peridotite with $FeO^* = 8.0$ wt%, and consisting of 60% modal

olivine, composition $Mg/(Mg+\Sigma Fe) = 0.90$. For reasons given above, we assume that olivine contains no Fe_2O_3, so that all the nominal 9.8% FeO in olivine of this composition is indeed FeO; the olivine therefore contributes 5.9% FeO to the whole rock total. If all the remaining Fe in the pyroxenes, spinel or garnet were Fe^{3+}, the net $Fe^{3+}/\Sigma Fe$ would be 0.26. Clearly, not all the Fe in these phases can possibly be Fe^{3+}, particularly in orthopyroxene, the next most abundant phase after olivine. Fe-Mg partitioning experiments between olivine and Fe^{3+}-free orthopyroxene in the simple system MgO-FeO-SiO_2 show that $K_{D\,ol\text{-}opx}^{Fe^{2+}\text{-}Mg}$ is ~1 at mantle temperatures for $Mg/(Mg+Fe)$ ~0.90 [e.g. von Seckendorff and O'Neill, 1992]. Since in mantle peridotites $K_{D\,ol\text{-}opx}^{\Sigma Fe\text{-}Mg}$ is invariably near unity (actually, usually slightly greater than unity due to the effects of other components), very little of the Fe in orthopyroxene can be Fe^{3+}, in agreement with the Mössbauer data. Orthopyroxene in mantle peridotite contains ~6% "FeO"; if we take $Fe^{3+}/\Sigma Fe = 0.20$ in orthopyroxene to be an upper limit, with 25% orthopyroxene in the mode, this contributes a further 1.2 wt% FeO to the whole rock, leaving a maximum whole rock $Fe^{3+}/\Sigma Fe$ of 0.12. Furthermore, if half the remaining Fe in clinopyroxene, spinel and garnet is Fe^{2+} (again an obvious underestimate, as may similarly be deduced from olivine-clinopyroxene or olivine-garnet Fe-Mg partitioning relations), the maximum possible $Fe^{3+}/\Sigma Fe$ is reduced to ~0.06. This we regard to be a maximum realistic limit for $Fe^{3+}/\Sigma Fe$ in any peridotite of upper mantle mineralogy, even for the most oxidized samples (i.e. QFM+1); higher $Fe^{3+}/\Sigma Fe$ would have to be reflected in lower olivine modal abundance and high modal abundance of Fe_3O_4-rich spinel. Only the analyses reported by Frey and Green [1974] and Preß et al. [1986] fall near this maximum limit. Even in these cases, we argue that our lower, Mössbauer-based estimate is a more realistic determination of upper mantle $Fe^{3+}/\Sigma Fe$, since these wet-chemical whole rock Fe_2O_3 analyses seem to vary erratically with either fO_2, as calculated from the olivine-orthopyroxene-spinel equilibrium, or with degree of depletion, as indicated by wt% MgO. In the case of the data of Frey

TABLE 5. A compilation of Fe_2O_3 and $Fe^{3+}/\Sigma Fe$ determinations on mantle peridotites by wet chemistry.

Locality	No. of samples	Fe_2O_3 range (wt%)	$Fe^{3+}/\Sigma Fe$ range (%)	$Fe^{3+}/\Sigma Fe$ mean (%)	Reference
Spinel lherzolites and harzburgites					
Itinome-gata, Japan	11	0.83 - 2.20	10 - 21	17	Kuno and Aoki [1970]
Dreiser Weiher, Germany	12	1.06 - 2.07	13 - 21	17	"
Victoria, Australia	6	0.38 - 1.50	4.6 - 18	6.3[a]	Frey and Green [1974]
Puy Beaunit, France	27	0.56 - 2.09	-	15	Hutchison et al. ([975]
Volcan de Zanière, FR	18	1.08 - 2.13	-	17	"
Montboissier, FR	41	1.33 - 2.60	-	23	"
Monistrol d'Allier, FR	16	0.63 - 1.92	-	15	"
Tarreyres, FR	40	0.80 - 2.29	-	16	"
Mongolia	11	0.17 - 0.75	2.0 - 8.3	5.5	Preß et al. [1986]
Victoria, Australia[b]	12	0.42 - 0.99	4.5 - 11	7.7	Stolz and Davies [1988]
Garnet lherzolites and associated harzburgites					
Lashaine, Tanzania[c]	8	0.71 - 1.30	9.2 - 19	12	Rhodes and Dawson [1975]
"	8	0.72 - 1.39	8.7 - 21	15	"

Only samples with 6 to 9.5% FeO^* and $MgO > 36\%$ are included.

[a] not including an outlier with 18% $Fe^{3+}/\Sigma Fe$.

[b] 8 of these contain amphibole (mode 3 to 17%); there is no correlation of $Fe^{3+}/\Sigma Fe$ with modal amphibole.

[c] described as "remarkably fresh", but analyses report ~0.3% H_2O^+. The first 8 xenoliths contain 4 - 8% modal garnet and 63 - 79% olivine; the second 8 are more depleted and contain no garnet but >80% ol.

and Green [1974], the separate determinations of Fe_2O_3 in the spinels and pyroxenes, when multiplied by the modes for these phases, are also inconsistent with whole rock Fe_2O_3. The Mongolian peridotite suite analyzed by Preß et al. [1986] shows particularly good trends for all other moderately incompatible elements versus MgO, but almost random scatter for Fe_2O_3.

In some cases, some part of the high $Fe^{3+}/\Sigma Fe$ may be due to alteration, e.g. serpentinisation or in the kelyphitic rims of garnet. An example of this is presented in Figure 7, which shows a plot of whole rock Fe_2O_3/FeO versus H_2O^+, obtained by Frey et al. [1985] on a suite of variably serpentinized high temperature peridotites from the Ronda Massif. This suite shows very well defined major element and trace element depletion trends vs. MgO, indicating that the serpentinisation has not significantly affected most of the whole rock chemistry. This does not apply to the oxidation state of the samples. There is a good correlation between Fe_2O_3/FeO and H_2O^+ (R=0.98), and the effect is clearly going to be strong enough to destroy more subtle effects, such as a correlation with MgO (i.e. degree of depletion). The trend extrapolates to $Fe_2O_3/FeO = 0.14$ (equivalent to $Fe^{3+}/\Sigma Fe = 0.11$) at the $H_2O^+ = 0$ intercept, which is still somewhat high.

The data summarized in Table 5, though, are for spinel peridotites xenoliths which are often very fresh, containing virtually no low temperature, hydrous alteration, and yet are still reported to have unrealistically high $Fe^{3+}/\Sigma Fe$. It is not possible to state categorically that this is always due to analytical error, but we suspect that this may be the case. An initial difficulty is caused simply by the low $Fe^{3+}/\Sigma Fe$ of mantle samples, so that any oxidation during the analytical process is magnified in its effects. Thus an error of, say, ±0.05 in $Fe^{3+}/\Sigma Fe$ which would have little consequence at $Fe^{3+}/\Sigma Fe = 0.5$, has larger implications at $Fe^{3+}/\Sigma Fe = 0.05$. Secondly, about one third of the Fe^{3+} in a mantle peridotite is held in spinel, which is notoriously difficult to dissolve prior to wet chemical analysis. It is conceivable

that the severe level of acid attack needed to dissolve spinel may result in extra oxidation of easily soluble olivine in the whole rock powder.

APPENDIX 2

Experimental details

The Mg-Fe majorite garnets and silicate spinels synthesized in this study were made from three separate starting compositions. Two compositions on the $MgSiO_3$-$FeSiO_3$ join at $Mg/(Mg+Fe) = 0.8$ and 0.9 were prepared from mixtures of MgO, SiO_2 and [57]Fe-enriched Fe_2O_3. The mixtures were heated at 900°C for several hours in a CO-CO_2 atmosphere at $fO_2 < QFM$ to reduce Fe_2O_3 to FeO. The mixes were then sealed in iron capsules with a small amount of H_2O and run in a conventional piston cylinder apparatus at 900°C and 1.5 GPa for 24 hours. From optical, X-ray and Mössbauer investigations, the products consisted of >99% orthopyroxene containing no detectable Fe^{3+} ($Fe^{3+}/\Sigma Fe < 0.02$).

A third composition corresponding to $(Mg_{0.85}Fe_{0.15})SiO_3$ plus 20% excess SiO_2 and 20% excess Fe metal was prepared from MgO, SiO_2, [57]Fe-enriched Fe_2O_3 and isotopically normal Fe metal. This mixture was first crystallized to orthopyroxene + quartz + Fe metal in a piston-cylinder apparatus at 1000°C and 1.9 GPa for 6.5 hours, using a silver capsule with a tight fitting lid. The run product was examined optically, and by Mössbauer spectroscopy, which revealed a spectrum characteristic of $(Mg,Fe)SiO_3$ orthopyroxene, with no discernible trace of Fe^{3+}. There is little if any isotopic equilibration between the [57]Fe-enriched Fe_2O_3 and the isotopically normal Fe metal, which experimentally has the very convenient consequence that the excess metal in this material (and in the high pressure syntheses) is barely visible in the Mössbauer spectra, and does not interfere with the silicate spectra.

High pressure syntheses were done in a 1200 ton uniaxial split-sphere multianvil apparatus. Toshiba F grade tungsten carbide anvils with a 5 mm truncation edge length were used with 10 mm MgO octahedral sample assemblies containing a $LaCrO_3$ heater. Pressure was calibrated at room temperature using transitions in Bi, ZnS and GaAs, and at 1200°C and 1600°C using the olivine/β-phase and β-phase/spinel transitions in Mg_2SiO_4 [Akaogi et al., 1989]. Temperatures were monitored using a W3%Re/W25%Re thermocouple. In each experiment, ~3 mg of sample was contained in a capsule made from pure Re, Mo or Fe foil. Ceramic components of the sample assembly were fired at 1000°C and prior to each high-pressure experiment the complete sample assembly was dried at 230°C in a vacuum for at least 12 hours. Rubie et al. [1992] have demonstrated that this procedure results in effectively anhydrous conditions during high temperature, high pressure multianvil experiments. A summary of the experimental conditions for each run is given in Table 4.

The experiments with excess Fe metal were performed in Fe capsules, and in addition contained finely divided Fe metal powder in the starting mixture. This Fe metal was found to have remained evenly dispersed throughout the capsule at the end of the run, suggesting that all parts of the experimental charge were in equilibrium with Fe metal. Clinopyroxene synthesized from the $(Mg_{0.85}Fe_{0.15})SiO_3 + SiO_2 + Fe$ starting material at 15 GPa and a nominal temperature of 1600°C, using the same experimental procedures and sample assembly as for the majorite and silicate spinel syntheses, was found to contain no discernible Fe^{3+} by Mössbauer spectroscopy.

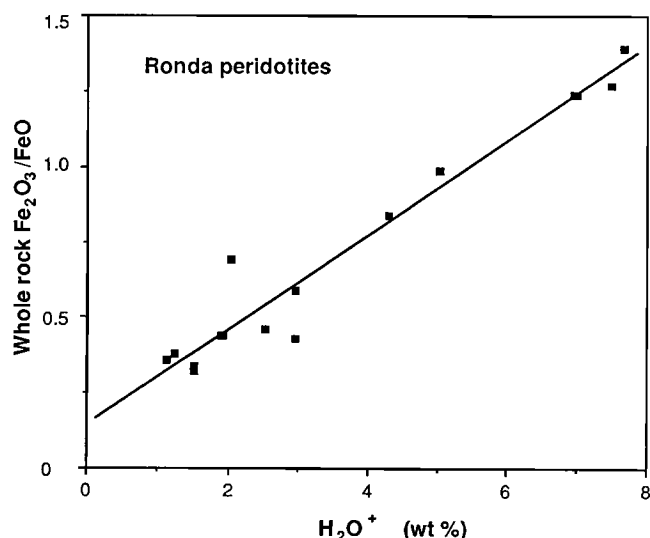Silicate spinels along the join Fe_2SiO_4 - Fe_3O_4 were synthesized at 7 to 9 GPa also using a multianvil apparatus (Table 3). Pressure

Fig. 7. Possible influence of hydrous low temperature alteration of mantle peridotites on whole rock Fe_2O_3/FeO, analyzed by wet chemistry. Data from Frey et al. [1985].

assemblies and calibrations employed in these experiments are identical to those described in Canil [1991] except that Pt/Pt10%Rh instead of W3%Re/W25%Re thermocouples were used to measure temperature. Starting materials were mixtures of pure fayalite synthesized in an evacuated silica tube from a stoichiometric mix of Fe, Fe_2O_3 and SiO_2, and puratronic grade magnetite (Johnson Matthey).

Mössbauer spectra were collected using a variable temperature Mössbauer spectrometer with a ^{57}Co in Rh source of 50 mCi nominal activity in the constant acceleration mode. Left-hand and right-hand sides of the spectra were recorded independently. Fe metal foil served for calibration of the velocity scale, and isomer shifts were determined relative to metallic Fe at room temperature. Symmetrical doublets with Lorentzian lineshapes have been fitted to the folded data.

REFERENCES

Akaogi, M., E. Ito, and A. Navrotsky, Olivine-modified spinel-spinel transitions in the system Mg_2SiO_4-Fe_2SiO_4: Calorimetric measurements, thermo-chemical calculation , and geophysical application, *J. Geophys. Res., 94*, 15,671-15,685, 1989.

Amthauer, G., H. Annersten, and S. S. Hafner, The Mössbauer spectrum of ^{57}Fe in silicate garnets, *Zeit. Kristal., 143*, 14-55, 1976.

Archbald, P. N., Abundances and dispersions of some compatible volatile and siderophile elements in the mantle, *Unpublished M. Sc. Thesis*, Australian National University, 1979.

Bina, C.R., and B. J. Wood, Olivine-spinel transitions: Experimental and thermodynamic constraints and implications for the nature of the 400-km seismic discontinuity, *J. Geophys. Res., 92*, 4853-4866, 1987.

Boyd, F.R., High - and low-tmperature garnet peridotite xenoliths and their possible relation to the asthenosphere-lithosphere boundary beneath Souther Africa, in *Mantle Xenoliths*, edited by P. H. Nixon, 403-412, John Wiley, New York, 1987.

Boyd, F. R. and S. A. Mertzman, Composition and structure of the Kaapvaal lithosphere, Southern Africa, in *Magmatic Processes: Physiochemical Principles*, edited by B. O. Mysen, The Geochemical Society Spec. Publ. No.1, Pennsylvania, U.S.A., 13-24, 1987.

Brown, I. D., and D. Altermatt, Bond-valence parameters obtained from a systematic analysis of the Inorganic Crystal Structure Database, *Acta Cryst., B41*, 244-247, 1985.

Bryndzia, L. T., and B. J. Wood, Oxygen thermobarometry of abyssal spinel peridotites: The redox state and C-O-H volatile composition of the Earth's sub-oceanic mantle, *Amer. J. Sci., 290*, 1093-1116, 1990.

Bukowinski, M. S., and G. H. Wolf, Thermodynamically consistent decompression: Implications for lower mantle composition, *J. Geophys. Res., 95*, 12,583-12,593, 1990.

Canil, D., Experimental evidence for the exsolution of cratonic peridotite from high-temperature harzburgite, *Earth Planet. Sci. Lett., 106*, 64-72, 1991.

Canil, D., H. O'Neill, and C. R. Ross II, A preliminary look at phase relations in the system Fe_3O_4 - γ-Fe_2SiO_4 at 7 GPa, *Terra Abstr., 3*, 65, 1991.

Canil, D., D. Virgo, and C. M. Scarfe, Oxidation state of mantle xenoliths from British Columbia, Canada, *Contrib. Mineral. Petrol., 104*, 453-462, 1990.

Carmichael, I. S. E., and M. S. Ghiorso, Oxidation-reduction relations in basic magma: A case for homogeneous equilibria, *Earth Planet. Sci. Lett., 78*, 200-210, 1986.

Christie, D. M., I. S. E. Carmichael, and C. H. Langmuir, Oxidation states of mid-ocean ridge basalt glasses, *Earth Planet. Sci. Lett., 79*, 397-411, 1986.

Cox, K. G., M. R. Smith, and S. Beswetherick, Textural studies of garnet lherzolites: Evidence of probable exsolution origin from high temperature harzburgite, in *Mantle Xenoliths*, edited by P. H. Nixon, 537-550 John Wiley, New York, 1987.

Deer, W. A., R. A. Howie, and J. Zussman, *Rock Forming Minerals, Volume 2A: Single Chain Silicates*, 668pp., Longman, London, second edition, 1978.

Dick, H. J. B., R. L. Fisher, and W. B. Bryan, Mineralogic variability of the uppermost mantle along mid-ocean ridges, *Earth Planet. Sci. Lett., 69*, 88-106, 1984.

Dyar, M. D., A. V. McGuire, and R. D. Ziegler, Redox equilibria and crystal

chemistry of coexisting minerals from spinel lherzolite mantle xenoliths, *Amer. Mineral., 74.*, 969-980, 1989.

Eggler, D. H., Upper mantle oxidation state: Evidence from olivine-ortho-pyroxene-ilmenite assemblages, *Geophys. Res. Lett., 10*, 365-368, 1983.

Frey, F. A., and D. H. Green, The mineralogy, geochemistry and origin of lherzolite inclusions in Victorian basanites, *Geochim. Cosmochim. Acta, 38*, 1023-1059, 1974.

Frey, F. A., C. J. Suen, and H. W. Stockman, The Ronda high temperature peridotite: Geochemistry and petrogenesis, *Geochim. Cosmochim. Acta, 49*, 2469-2491, 1985.

Geiger, C., D. C. Rubie, C. R. Ross II, and F. Seifert, Synthesis and ^{57}Fe Mössbauer study of (Mg,Fe)SiO_3 garnet, *EOS, Trans. Amer. Geophys. Union, 72*, 564, 1991.

Goodman, R. J., The distribution of Ga and Rb in coexisting groundmass and phenocryst phases of some basic volcanic rocks, *Geochim. Cosmochim. Acta, 36*, 303-317, 1972.

Haggerty, S. E., and L. A. Tompkins, Redox state of the Earth's upper mantle from kimberlitic xenoliths, *Nature, 303*, 295-300, 1983.

Hawthorne, F. C., and G. A. Waychunas, Spectrum-fitting methods, in *Reviews in Mineralogy Volume 8*, edited by F. C. Hawthorne, Mineralogical Society of America, Washington D.C., 63-98, 1988.

Hazen, R. M., J. Zhang, and J. Ko, Effects of Fe/Mg on the compressibility of synthetic wadsleyite: β-(Mg$_{1-x}$Fe$_x$)$_2$SiO$_4$ (x≤0.25), *Phys. Chem. Min., 17*, 416-419, 1990.

Hofmann, A. W., Chemical differentiation of the Earth: the relationship between mantle, continental crust, and oceanic crust, *Earth Planet. Sci. Lett., 90*, 297-314, 1988.

Horiuchi, H. and H. Sawamoto, β-Mg_2SiO_4: Single-crystal X-ray diffraction study, *Amer. Mineral., 66*, 568-575, 1981.

Hutchison, R., A. L. Chambers, D.K. Paul, and P. Harris, Chemical variation among French ultramafic xenoliths - evidence for a heterogeneous mantle, *Mineralog. Mag.*, 40, 153-170, 1975.

Irifune, T., An experimental investigation of the pyroxene-garnet transformation in a pyrolite composition and its bearing on the constitution of the mantle, *Phys. Earth Planet. Interiors, 45*, 324-336, 1987.

Irifune, T. and Ringwood, A. E., Phase Transformations in primitive MORB and pyrolite compositions to 25 GPa and some geophysical implications, in *High Pressure Research in Mineral Physics*, edited by M. H. Manghnani and Y. Syono, Terra Pub/Amer. Geophys. Union, Tokyo/Washington D. C., 231-242, 1987.

Ito, E., and T. Katsura, A temperature profile of the mantle transition zone, *Geophys. Res. Lett., 16*, 425-428, 1989.

Ito, E., and E. Takahashi, Melting of peridotite at uppermost mantle conditions, *Nature, 328*, 514-517, 1987.

Ito, E., and E. Takahashi, Postspinel transformations in the system Mg_2SiO_4-Fe_2SiO_4 and some geophysical implications, *J. Geophys. Res., 94*, 10,637-10,646, 1989.

Ito, E., E. Takahashi, and Y. Matsui, The mineralogy and chemistry of the lower mantle: An implication of the ultrahigh-pressure phase relations in the system MgO-FeO-SiO_2, *Earth Planet. Sci. Lett., 67*, 238-248, 1984.

Jagoutz, E., H. Palme, H. Baddenhausen, K. Blum, M. Cendales, G. Dreibus, B. Spettel, V. Lorenz, and H. Wänke, The abundances of major, minor, and trace elements in the Earth's mantle as derived from ultramafic nodules, *Proc. 10th Lunar Planet. Sci. Conf.*, 2031-2050, 1979.

Kato, M., S. Urakawa, and M. Kumazawa, Stability fields of nonstoichiometric wüstite and magnesiowüstite at high pressure, *Abstract of DELP 1989 Misasa International Symposium*, 80-82, 1989.

Karpinskaya, T. B., I. A. Ostrovsky, and T. L. Yevstigneeva, Synthetic pure iron skiagite garnet, *Izvestia AN SSSR (Moscow), ser. geol., no. 9*, 128-129, 1982, [in Russian].

Kilinc, A., I. S. E. Carmichael, M. L. Rivers, and R. O. Sack, The ferric-ferrous ratio of natural silicate liquids equilibrated in air, *Contrib. Mineral. Petrol., 83*, 136-140, 1983.

Kuno, H., and K. Aoki, Chemistry of ultramafic nodules and their bearing on the origin of basaltic magmas, *Phys. Earth Planet. Interiors, 3*, 273-301,1970.

Liang, Y., and D. Elthon, Evidence from chromium in mantle rocks for extraction of picrite and komatiite melts, *Nature, 343*, 551-553, 1990a.

Liang, Y., and D. Elthon, Geochemistry and petrology of spinel lherzolite xenoliths from Xalapasco de La Joya, San Luis Potosi, Mexico: Partial melting and mantle metasomatism, *J. Geophys Res., 95*, B10, 15,859-15,877, 1990b.

Lucas, H., M. T. Muggeridge, and D. M. McConchie, Iron in kimberlitic ilmenites and chromian spinels: A survey of analytical techniques, in *Kimberlites and Related Rocks volume 2*, edited by J. Ross, Geol. Soc. Australia Spec. Publ. 14, Blackwell, Australia, 311-319, 1989.

Luth, R. W., and D. Canil, Ferric iron in mantle-derived pyroxenes and a new oxybarometer for the mantle, *Contrib. Mineral. Petrol.*, in press.

Luth, R. W., D. Virgo, F. R. Boyd, and B. J. Wood, Ferric iron in mantle-derived garnets, implications for thermobarometry and for the oxidation state of the mantle, *Contrib. Mineral. Petrol., 104*, 56-72, 1990.

Maaløe, S., and K. Aoki, The major element composition of the upper mantle estimated from the composition of lherzolites, *Contrib. Mineral. Petrol., 63*, 161-173, 1977.

McKay, D. B., and R. H. Mitchell, Abundance and distribution of gallium in some spinel and garnet lherzolites, *Geochim. Cosmochim. Acta, 52*, 2867-2870, 1988.

Nakamura, A., and H. Schmalzried, On the stoichiometry and point defects of olivine, *Phys. Chem. Mineral., 10*, 27-37, 1983.

Novak, G. A., and G. V. Gibbs, The crystal chemistry of the silicate garnets, *Amer. Mineral., 56*, 791-825, 1971.

Ohtani, E., and N. Kagawa, Stability of tetragonal garnet (Mg,Fe)SiO$_3$ and hydrous mineral phase B at high pressure and temperature, *Abstract of DELP 1989 Misasa International Symposium*, 87-89, 1989.

Ohtani, E., T. Kato, and E. Ito, Transition metal partitioning between lower mantle and core materials at 27 GPa, *Geophys. Res. Lett., 18*, 85-88, 1991.

Ohtani, E., T. Kato, and H. Sawamoto, Melting of a model chondritic mantle to 20 GPa, *Nature, 322*, 352-353, 1986.

Ohtani, E., and H. Sawamoto, Melting experiment on a model chondritic mantle at 25 GPa, *Geophys. Res. Lett., 14*, 733-736, 1987.

Omura, K., Change of electrical conductivity of olivine associated with the olivine-spinel transition, *Abstract of DELP 1989 Misasa International Symposium*, 23-24, 1989.

O'Neill, H. St.C., The origin of the Moon and the early history of the Earth - a chemical model. part 1: The Moon, *Geochim. Cosmochim. Acta, 55*, 1135-1157, 1991a.

O'Neill, H. St.C., The origin of the Moon and the early history of the Earth - a chemical model. part 2: The Earth, *Geochim. Cosmochim. Acta, 55*, 1159-1172, 1991b.

O'Neill, H. St.C., and A. Navrotsky, Cation distributions and thermodynamic properties of binary spinel solid solutions, *Amer. Mineral., 69*, 733-753, 1984.

O'Neill, H. St.C., and V. J. Wall. The olivine-orthopyroxene-spinel oxygen geobarometer, the nickel precipitation curve, and the oxygen fugacity of the Earth's upper mantle, *J. Petrol., 28*, 1169-1191, 1987.

Osborne, M. D., M. E. Fleet, and G. M. Bancroft, Fe^{2+}-Fe^{3+} ordering in chromite and Cr-bearing spinels, *Contrib. Mineral. Petrol., 77*, 251-255, 1981.

Patterson, C. C., Age of meteorites and the Earth, *Geochim. Cosmochim. Acta, 10*, 230, 1956.

Peyronneau, J., and J. P. Poirier, Electrical conductivity of the Earth's lower mantle, *Nature, 342*, 537-539, 1989.

Preß, S., G. Witt, H. A. Seck, D. Eonov, and V. I. Kovalenko, Spinel peridotite xenoliths from the Tariat Depression, Mongolia II: Geochemistry and Nd and Sr isotopic composition and their implications for the evolution of the subcontinental lithosphere, *Geochim. Cosmochim. Acta, 50*, 2601-2614, 1986.

Rama Murthy, V., Early differentiation of the Earth and the problem of siderophile elements: A new approach, *Science, 253*, 303-306, 1991.

Reid, J. B., and G. A. Woods, Oceanic mantle beneath the Rio Grande Rift, *Earth Planet. Sci. Lett., 41*, 303-316, 1978.

Rhodes, J. M., and J. B. Dawson, Major and trace element chemistry of peridotite inclusions from the Lashaine volcano, Tanzania, *Phys. Chem. Earth, 9*, 545-557, 1975.

Ringwood, A. E., Chemical evolution of the terrestrial planets, *Geochim. Cosmochim. Acta, 30*, 41-104, 1966.

Ringwood, A. E., *Composition and Petrology of the Earth's Mantle*, McGraw-Hill, 1975.

Ringwood, A. E., The Earth's core: Its composition, formation, and bearing upon the origin of the Earth, *Proc. Royal Soc. London, A395*, 1-46, 1984.

Ringwood, A. E., Constitution and evolution of the mantle, in *Kimberlites and Related Rocks volume 2*, edited by J. Ross, Geol. Soc. Australia Spec. Publ. 14, Blackwell, Australia, 457-485, 1989.

Ringwood, A. E., and W. Hibberson, The system Fe-FeO revisited, *Phys. Chem. Mineral., 17*, 313-319, 1990.

Ringwood, A. E., and T. Irifune, Nature of the 650-km seismic discontinuity: implications for mantle dynamics and differentiation, *Nature, 331*, 131-136, 1988.

Ringwood, A. E., T. Kato, W. Hibberson, and N. Ware, High pressure geochemistry of Cr, V, and Mn and implications for the origin of the Moon, *Nature, 347*, 174-176, 1990.

Robie, R. A., B. S. Hemingway, and J. R. Fisher, Thermodynamic properties of minerals and related substances at 298.15K and 1 bar (10^5 Pa) pressure and at higher temperature, *U. S. Geol. Surv. Bull. 1452*, Washington D.C., 456pp, 1978.

Ross II, C. R., T. Armbruster, and D. Canil, Crystal structure refinement of a spinelloid in the system Fe$_3$O$_4$ - Fe$_2$SiO$_4$, *Amer. Mineral.*, in press, 1992.

Rubie, D. C., S. Karato, H. Yan, and H. St. C. O'Neill, Low differential stress and controlled chemical environment in multi-anvil high-pressure experiments, *J. Geophys. Res.*, submitted.

Schreyer, W., and Th. Baller, Calderite, Mn$^{+2}_3$Fe$^{+3}_2$Si$_3$O$_{12}$, a high-pressure garnet, *Proc. XII M. A. Meeting Novosibirsk 1978* (publ. Nauka), *Experimental Mineralogy*, 68-77, 1981.

Seckendorff, V. von, and H. St. C. O'Neill, An experimental study of Fe-Mg partitioning between olivine and orthopyroxene at 1173, 1273, and 1423 K and 1.6 GPa, *Contrib. Mineral.Petrol.*, in press.

Smyth, J. R., b-Mg$_2$SiO$_4$: A potential host for water in the mantle?, *Amer. Mineral., 72*, 1051-1055, 1987.

Stevenson, D. J., Fluid dynamics and core formation, in *Origin of the Earth*, edited by H. E. Newsom and J. H. Jones, Oxford University Press, New York, 231, 1990.

Stolz, A. J., and G. R. Davies, Chemical and isotopic evidence from spinel lherzolite xenoliths for episodic metasomatism of the upper mantle beneath southeatern Australia, in *Oceanic and Continental Lithosphere: Similarities and Differences*, edited by M. A. Menzies and K. G. Kox, 303-330, Oxford University Press, Oxford, 1988.

Stosch, H.-G., Sc, Cr, Co, and Ni partitioning between minerals from spinel peridotite xenoliths, *Contrib. Mineral. Petrol., 78*, 166-174, 1981.

Takahashi, E., Melting of a dry peridotite KLB-1 up to 14 GPa: Implications on the origin of peridotitic upper mantle, *J. Geophys Res., 91*, 9367-9382, 1986.

Takahashi, E., and E. Ito, Mineralogy of mantle peridotite along a model geotherm up to 700 km depth, in *High Pressure Research in Mineral Physics*, edited by M. H. Manghnani and Y. Syono, Terra Pub/Amer. Geophys. Union, Tokyo/Washington D. C., 427-438, 1987.

Taylor, W. R. and S. F. Foley, Improved oxygen buffering techniques for C-O-H fluid-saturated experiments at high pressure, *J. Geophys. Res., 94*, 4146-4158, 1989.

Taylor, W. R., and D. H. Green, Measurement of reduced peridotite-C-O-H solidus and implications for redox melting of the mantle, *Nature, 332*, 349-52, 1988.

Urakawa, S., Partitioning of Ni between magnesiowüstite and metal at high pressure: Implications for core-mantle equilibrium, *Earth Planet. Sci. Lett., 105*, 293-313, 1991.

Urakawa, S., M. Kato, and M. Kumazawa, An experimental approach to core formation process of the earth, *Abstract of DELP 1989 Misasa International Symposium*, 114-115, 1989.

Vallet, P-M., W. Pluschkell, and H-J. Engell, Gleichgewichte von MgO-FeO-Fe$_2$O$_3$ Mischkristallen mit Sauerstoff, *Arch. Eisenhüttenwes., 46*, 383-388, 1975.

Weidner, D. J., and E. Ito, Mineral physics constraints on a uniform mantle composition, in *High Pressure Research in Mineral Physics*, edited by M. H. Manghnani and Y. Syono, Terra Pub/Amer. Geophys. Union, Tokyo/Washington D. C., 439-446, 1987.

Woermann, E., and M. Rosenhauer, Fluid phases and the redox state of the Earth's mantle, *Fortschr. Mineral., 83*, 263-349, 1985.

Wood, B. J., Postspinel transformations and the width of the 670-km discontinuity: A comment on "Postspinel transformations in the system Mg$_2$SiO$_4$-Fe$_2$SiO$_4$ and some geophysical implications", *J. Geophys. Res., 95*, 12,681-12,685, 1990.

Wood, B. J., and J. Nell, High-temperature electrical conductivity of the lower mantle phase (Mg,Fe)O, *Nature, 351*, 309-311, 1991.

Wood, B. J., and D. Virgo, Upper mantle oxidation state: Ferric iron contents of lherzolite spinels by ^{57}Fe Mössbauer spectroscopy and resultant oxygen fugacities, *Geochim. Cosmochim. Acta, 53*, 1277-1291, 1989.

Woodland, A. B., J. Kornprobst, and B. J. Wood, Oxygen thermobarometry of orogenic lherzolite massifs, *J. Petrol.*, 33, 203-230, 1992.

Woodland, A. B., and H. St. C. O'Neill, Synthesis of skiagite ($Fe^{+2}_3Fe^{+3}_2Si_3O_{12}$) and phase relations with almandine ($Fe^{+2}_3Al_2Si_3O_{12}$) - skiagite solid solutions (abstract), *Terra Abstr.*, 4, 47, 1992.

Xue, X., H. Baadsgaard, A. J. Irving, and C. M. Scarfe, Geochemical and isotopic characteristics of lithospheric mantle beneath West Kettle River, British Columbia: Evidence from ultramafic xenoliths, *J. Geophys. Res.*, 95, B10, 15,879-15,891, 1990.

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