Water and Carbon in the Earth's Mantle

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The concentrations of H_2O and C in mid-ocean ridge basalts indicate that the upper, degassed, part of the mantle contains approximately 200 ppm H_2O and 80 ppm C. Estimates for the bulk silicate earth are less precise, but, from geochemical and cosmochemical arguments, values of 550–1900 ppm for H_2O and 900–3700 ppm for C are plausible. The implication is that the (undegassed) lower mantle is enriched relative to the upper mantle in these volatile components, but concentrations there are only of the order of 2000 ppm.

No known hydrate is stable in the normal asthenosphere. In the absence of hydrates, water must reside in nominally anhydrous phases such as olivine and β-$(Mg,Fe)_2SiO_4$. The latter has recently been found to dissolve greater than 1.5 wt% H_2O and partitioning of H_2O between β-$(Mg,Fe)_2SiO_4$ and olivine is greater than 10:1.

The strong preference of H_2O for β-$(Mg,Fe)_2SiO_4$ means that mantle water content influences the width of the seismic discontinuity at 410 km, given that the latter corresponds to the olivine to β-$(Mg,Fe)_2SiO_4$ transformation. The seismically observed width of the discontinuity (less than 10 km) constrains the water content of upper mantle olivine to be 0–500 ppm. A similar type of constraint can probably be applied to the γ-spinel to perovskite plus magnesiowüstite transformation. Thus, arbitrary amounts of water cannot be assigned to the deeper parts of the mantle without considering the seismological implications.

In contrast to hydrates, carbonates in peridotite are extremely refractory; they are likely to survive subduction and are stable over a wide range of mantle P–T conditions. Storage of carbon depends on redox relationships with Fe, however, and recent experimental results indicate that the deeper parts of the upper mantle and transition zone are relatively reduced. Subducted carbonate should therefore be reduced by Fe to diamond and stored in this form. Reoxidation to CO_2 or carbonate occurs in the shallower parts of the asthenosphere or in the lithosphere. The reduction of subducted carbonate to C is a hypothesis consistent with the 'eclogitic suite' of diamond inclusions, minerals included within diamond which could reasonably be the remnants of subducted basaltic crust.

1. Introduction

The abundances of water and carbon dioxide in the mantle have important effects on its viscosity, the nature of convection and on related geological processes such as partial melting and volcanic degassing. The concentrations of these species in the uppermost mantle can be approximated from corresponding abundances in mid-ocean ridge basalt (MORB) glasses, while those in the whole mantle may be estimated

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from geochemical arguments based on, for example, assumptions about the manner in which the Earth accreted (Wänke & Dreibus 1988, 1994), or the K/H ratio of the exosphere (Jambon & Zimmermann 1990) or the C/^{4}He ratios of MORBs, ultramafic xenoliths and hotspot basalts (Trull *et al.* 1993).

Phase equilibrium and trace element data (Presnall *et al.* 1979) indicate that MORB are the products of approximately 10% partial melting of an upper mantle which is depleted, relative to the bulk silicate earth, in lithophile elements such as Rb, U and the light rare-earth elements (Allègre *et al.* 1983). Given that H_2O and CO_2 enter melts preferentially, the MORB concentrations of about 0.2% H_2O and 0.3% CO_2 lead to concentrations in this depleted upper mantle of approximately 200 and 300 ppm by weight, respectively. The figure for CO_2 corresponds to 80 ppm of carbon. Jambon & Zimmermann (1990) argue that the bulk silicate earth water content (including crust and exosphere) is in the range 550–1900 ppm, with the lower bound corresponding to the oceans plus the water concentration in the MORB source and the upper bound coming from the assumption that the K_2O/H_2O ratio of the exosphere (0.14) applies to the bulk silicate earth. In the former case, current water concentrations in the whole mantle would be similar to those for the MORB source region (200 ppm) and would correspond reasonably well to those derived from cosmochemical arguments (Wänke & Dreibus 1988, 1994). In the latter case, the mantle would currently contain about 1500 ppm water and if this were distributed between a degassed upper mantle containing 200 ppm and a lower undegassed mantle, the latter would currently contain about 2000 ppm H_2O.

From the observed correlation between C and ^{36}Ar in chondritic meteorites one can estimate that the Earth contains between 3 and 12×10^{23} moles of C, depending on the assumption about the extent to which ^{36}Ar has been outgassed (Jambon 1994). If we subtract the 8×10^{21} moles in the external reservoirs and crust, then the average mantle concentration should be 900–3700 ppm if the core is C-free. If we assume that the MORB source concentration of 80 ppm applies to all of the upper mantle then we obtain an estimate for the lower mantle of 1200–5000 ppm C by weight. This is similar to the range derived by Trull *et al.* (1993) from their two-reservoir model of C/^{4}He and C/^{3}He systematics. In practice, some of the Earth's carbon must be present in the core (Wood 1993), but this simple analysis does not provide any constraint on core concentration.

These geochemical arguments indicate that the concentrations of H_2O and C in both upper and lower mantles are much less than 1%, so that they are unlikely to affect the elastic properties or density of the mantle except where conditions are close to the solidus. Therefore, direct constraints on concentration are difficult to derive, although, as we show below, the widths of seismic discontinuities provide a possible means of placing upper limits on water content.

2. H_2O storage

Given that the upper mantle is dominantly peridotitic in composition, then the most important mineralogical transformations between 100 and 700 km depth are the reactions of $(Mg,Fe)_2SiO_4$ olivine to β-$(Mg,Fe)_2SiO_4$ at about 14 GPa and the breakdown of γ-$(Mg,Fe)_2SiO_4$ spinel to $(Mg,Fe)SiO_3$ perovskite plus (Mg,Fe)O magnesiowüstite at about 24 GPa. These transformations correlate in pressure with the seismic discontinuities at 410 and 660 km depth, respectively.

Addition of water to anhydrous peridotite produces stability fields of hydrated

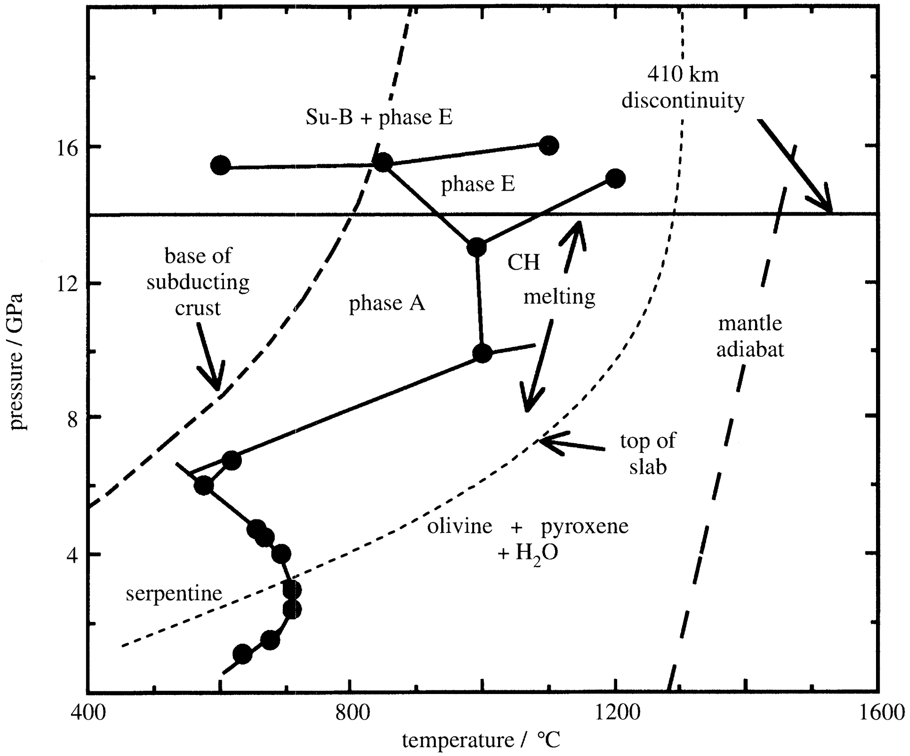

Figure 1. Stabilities of hydrates (CH refers to clinohumite) in peridotitic composition compared to a typical mantle adiabat and to temperatures in a rapidly subducting (10 cm a^{-1}) oceanic lithosphere (range of values after Peacock 1991). (N.B. Phase diagram is simplified by the exclusion of all but the most important reactions.)

magnesium silicates as shown in figure 1, redrawn and simplified from the experimental data of Yamamoto & Akimoto (1977), Gasparik (1993) and Luth (1996). No known hydrous phase is stable under 'normal' mantle pressure–temperature conditions (mantle adiabat of figure 1) and, given the form of the water-release curve, hydrated magnesium silicates only remain stable under conditions such as those found in cold subduction zones. Of even greater importance to water and subduction zones is the high-pressure behaviour of the hydrated basalt of the uppermost oceanic crust (Ito *et al.* 1983). Apart from the fact that amphibole dehydrates above 3 GPa (Hill & Boettcher 1970) however, only qualitative deductions may be made for lack of data. The most important observation (Pawley 1994) is that lawsonite is stable at least to 12 GPa under the thermal regime of subducting oceanic crust, providing a mechanism for deep recycling of some of the water tied-up in the oceanic lithosphere. Although the water cycle is poorly understood, estimates by Ito *et al.* (1983) indicate that the mass released by mid-ocean ridge and island-arc volcanism is only about 25% of the amount being subducted in hydrated lithosphere (about 9×10^{14} g a^{-1}), which suggests that long-term recycling into the deep mantle is very significant. Although the recycled amount cannot be as large as implied by these figures (the oceans would empty in 2 Ga), the water content of the mantle below 150 km would appear to be stable or perhaps slowly increasing.

The requirement that depleted mantle must contain some water and the lack of any major stable hydrous phase means that most mantle water must reside in one of the nominally anhydrous phases; olivine, pyroxene or garnet. These are all capable of dissolving several hundred ppm by weight of water (Bell & Rossman 1992). Recent experiments (Kohlstedt *et al.* 1994) show that, at pressures close to the 410 km discontinuity, olivine contains about 1600 ppm. Furthermore, H_2O partitions at least 10:1 in favour of β-(Mg,Fe)$_2$SiO$_4$ relative to olivine (Young *et al.* 1993; Kohlstedt *et al.* 1994; Inoue 1994), with the implication that the latter could contain at least 1.5 wt% H_2O in the transition zone (Kohlstedt *et al.* 1994; Inoue 1994; Inoue *et al.* 1995). This large solubility means that β-(Mg,Fe)$_2$SiO$_4$ is a potential host for recycled water in the transition zone (Smyth 1987, 1994) and that H_2O must affect the olivine to β-(Mg,Fe)$_2$SiO$_4$ transformation and the 410 km seismic discontinuity (Wood 1995).

3. Water and the 410 km discontinuity

Potentially, one of the most important constraints on the water contents of the transition zone and lower mantle are the observed depth intervals over which phase transformations occur. Recent seismological studies using high-frequency reflected waves indicate that both 410 and 660 km discontinuities are very sharp and that the changes in physical properties associated with them occur over very small depth intervals. For the 660 km discontinuity, a width of 4–5 km is consistent with the seismic data (Paulssen 1988; Benz & Vidale 1993; Yamazaki & Hirahara 1994). Most authors favour a slightly broader 410 km discontinuity, about 10 km wide (Paulssen 1988), but a recent study of precursors to P′P′ (Benz & Vidale 1993) implies that this too is locally extremely sharp, there being of the order of 4 km between upper and lower boundaries in some areas. The implications for mantle phase transitions are considerable. The chemical system of the mantle is multicomponent and simple phase relations show that the transformation from olivine to β-phase must occur in a divariant loop (figure 2), giving a somewhat smeared-out transition interval. In order to explain the reflections observed by Benz & Vidale (1993), a maximum interval of about 8 km (0.3 GPa) is required (Helffrich & Wood 1994). Although experimental data on the olivine to β-(Mg,Fe)$_2$SiO$_4$ reaction are not inconsistent with transformation intervals of 8 km or less (Helffrich & Wood 1994), their analysis is predicated on the assumption that the chemical system of the Earth is MgO–FeO–SiO$_2$ and that other components such as CaO, Al$_2$O$_3$ and Fe$_2$O$_3$ have no effect on the positions and widths of the phase transformations. Although not tested in all cases, this simplification is likely to be particularly in error in the case of H_2O, which has the potential to broaden transformation intervals, particularly those involving β-(Mg,Fe)$_2$SiO$_4$ (Wood 1995).

In order to calculate the effect of water on the transformation of olivine to β-(Mg,Fe)$_2$SiO$_4$, it is necessary to develop models for the free energy of solution of H_2O in the two phases. We adopted a solution model based on Smyth's (1987) calculations which suggest that the O(1) sites in β-Mg$_2$SiO$_4$ are readily protonated. Given charge balance by vacancies on Mg sites, this yields a hydrated end-member containing 3.3 wt % H_2O of formula Mg$_7$Si$_4$O$_{14}$(OH)$_2$. A recent crystal structure analysis of synthetic end-member Mg$_7$Si$_4$O$_{14}$(OH)$_2$ by Kudoh *et al.* (1994) confirms that the O(1) atoms are protonated and that there is no long-range ordering of M-site vacancies. In a mantle saturated with (Mg,Fe)$_2$SiO$_4$ and the (Mg,Fe)SiO$_3$ component

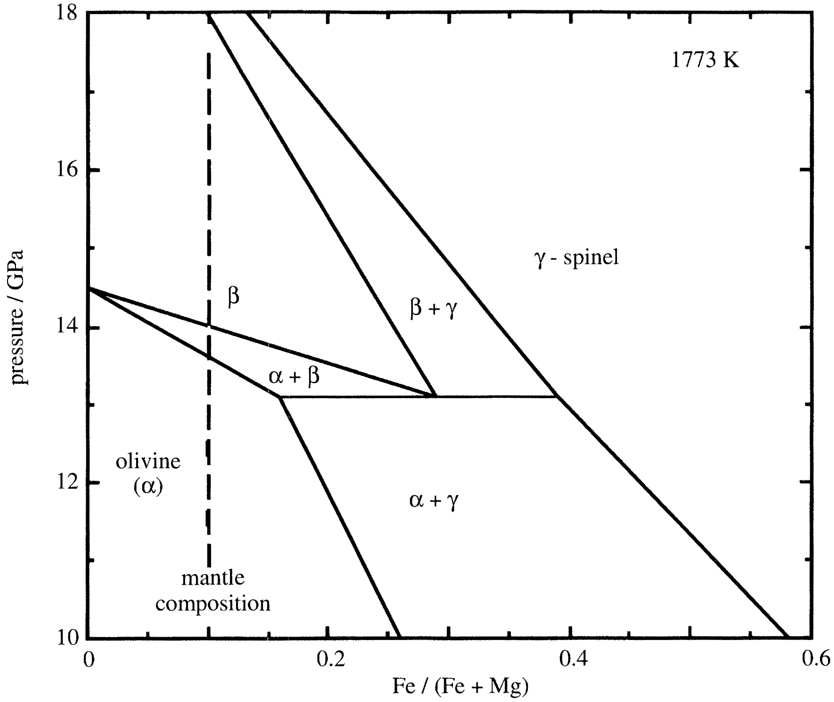

Figure 2. Phase diagram (after Katsura & Ito 1989) for Mg_2SiO_4–Fe_2SiO_4 at high pressures. Note that the transformations of olivine to β-$(Mg,Fe)_2SiO_4$, β to γ and so on are divariant and occur over a range of pressures at any given temperature. Peridotitic mantle has Fe/Fe + Mg of about 0.1.

of pyroxene, the formation of the end-member may be represented by the equilibrium

$$\underset{\beta}{3\mathrm{Mg_2SiO_4}} + \underset{\text{pyroxene}}{\mathrm{MgSiO_3}} + \mathrm{H_2O} = \underset{\beta}{\mathrm{Mg_7Si_4O_{14}(OH)_2}}\,. \tag{3.1}$$

In order to calculate the effect of water on the two-phase loop, it is necessary to obtain the partial molar free energies of Mg_2SiO_4 and Fe_2SiO_4 components in the hydrated β-$(Mg,Fe)_2SiO_4$ solid solution. At low concentrations of OH, the solution of this component will be in the Henry's law region where its only effect on the major components is entropic. In that case the chemical potentials of Mg_2SiO_4 and Fe_2SiO_4 components are given by

$$\left.\begin{aligned} \mu^{\beta}_{\mathrm{Mg_2SiO_4}} &= \mu^{0}_{\mathrm{Mg_2SiO_4}} + RT\ln\{X^2_{\mathrm{Mg}}\gamma_{\mathrm{Mg}}\cdot(1-X_{\mathrm{OH}})^{0.5}\}, \\ \mu^{\beta}_{\mathrm{Fe_2SiO_4}} &= \mu^{0}_{\mathrm{Fe_2SiO_4}} + RT\ln\{X^2_{\mathrm{Fe}}\gamma_{\mathrm{Fe}}\cdot(1-X_{\mathrm{OH}})^{0.5}\}. \end{aligned}\right\} \tag{3.2}$$

In equation (3.2), X_{Mg} and X_{Fe} refer to atomic fractions of magnesium and iron, respectively, on the large cation positions, while X_{OH} is the fraction of O(1) sites which are hydroxyl positions. The standard state chemical potentials $\mu^0_{Mg_2SiO_4}$ and $\mu^0_{Fe_2SiO_4}$ refer to the free energies of the pure end-member β-phases at the pressure and temperature of interest. The activity coefficients for the Mg–Fe sites, γ_{Mg} and γ_{Fe} refer to non-ideal Mg–Fe mixing, combined with (nominally) ideal mixing of vacancies, which have a concentration

$$V^{\mathrm{ll}}_{\mathrm{Mg}} = 0.125X_{\mathrm{OH}}. \tag{3.3}$$

Equations (3.2) and (3.3) enable calculation of the effect of water on the two major components, given the assumptions of random mixing of OH groups with O(1) and of vacancies with Mg and Fe. The non-ideal part of Mg–Fe mixing was obtained by assuming a symmetric interaction parameter W_{MgFe} of 4.0 kJ per gram atom (Akaogi *et al.* 1989).

For olivine, Bai & Kohlstedt (1993) found H-solubility data to be consistent with formation of complexes between H and interstitial O atoms. In Kröger–Vink notation this may be represented in simplified form as

$$\mathrm{O}_{\mathrm{i}}^{\prime\prime} + \mathrm{H_2O} = 2\mathrm{OH}_{\mathrm{i}}^{\prime} \tag{3.4}$$

Calculation of the chemical potentials of $\mathrm{Mg_2SiO_4}$ and $\mathrm{Fe_2SiO_4}$ components in the partially hydrated olivine, relative to water-free olivine under the same conditions of intensive variables, are obtained from

$$\mu_{\mathrm{Mg}}^{\alpha} = \mu_{\mathrm{Mg_2SiO_4}}^{0} + RT\ln\{X_{\mathrm{Mg}}^{2} \cdot \gamma_{\mathrm{Mg}} \cdot (1 - X_{\mathrm{OH}})^4/(1 - 0.5X_{\mathrm{OH}})^4\}, \tag{3.5}$$

with a similar form for the $\mathrm{Fe_2SiO_4}$ component. In equation (3.5), we have taken explicit account of the fact that creation of OH defects destroys half as many pre-existing oxygen interstitials (denominator on the right-hand side) and the standard state values μ^0 refer to hypothetical olivine free of oxygen interstitials. Activity coefficients, γ_{Mg}, γ_{Fe} were calculated from the symmetric solution model using the experimentally measured interaction parameter of Wiser & Wood (1991), adjusted to 14 GPa from the excess volumes on the forsterite–fayalite join (Wood 1987), giving a value of +5.0 kJ per gram atom.

The combined effect of water and iron on the olivine–β transition may be calculated by fixing the bulk Fe/(Fe + Mg) and water content of mantle olivine at a point just above the depth where β-(Mg,Fe)$_2$SiO$_4$ appears and then calculating the shift in equilibrium pressure relative to the value for pure anhydrous $\mathrm{Mg_2SiO_4}$.

Proportions of phases through the two-phase region were calculated as follows: the Fe/(Fe + Mg) ratio of the olivine was set at the value above the transition zone. The Fe/(Fe + Mg) ratio of coexisting β-(Mg,Fe)$_2$SiO$_4$ was then obtained from the partitioning data of Katsura & Ito (1989). Phase proportions were obtained from the bulk Fe/(Fe + Mg) using the lever rule. Given proportions of β-(Mg,Fe)$_2$SiO$_4$ and olivine, the concentrations of water in the two phases were calculated from the approximate partition coefficient of 10:1 (Kohlstedt *et al.* 1994) and the fixed water content of olivine above the transition zone. The equilibrium pressure was then calculated from (cf. Wood 1990)

$$\begin{aligned}(P - P^0)\Delta V^0 = {} & -RT\ln\{X_{\mathrm{Mg}}^{2}\gamma_{\mathrm{Mg}} \cdot (1 - X_{\mathrm{OH}})^{0.5}\}_{\beta} \\ & + RT\ln\{X_{\mathrm{Mg}}^{2}\gamma_{\mathrm{Mg}} \cdot (1 - X_{\mathrm{OH}})^4/(1 - 0.5X_{\mathrm{OH}})^4\}_{\mathrm{ol}},\end{aligned} \tag{3.6}$$

where P^0 refers to the equilibrium pressure for the end-member reaction

$$\underset{\text{olivine }(\alpha)}{\mathrm{Mg_2SiO_4}} = \underset{\beta}{\mathrm{Mg_2SiO_4}} \tag{3.7}$$

and ΔV^0 refers to the volume change of this reaction at the P, T conditions of interest. We performed the calculations at 1773 K and took P^0 to be 14.5 GPa (figure 3). The volumes of the two phases at P and T were calculated from the Murnaghan equation of state using the thermodynamic properties of table 1, as discussed by Wood (1995).

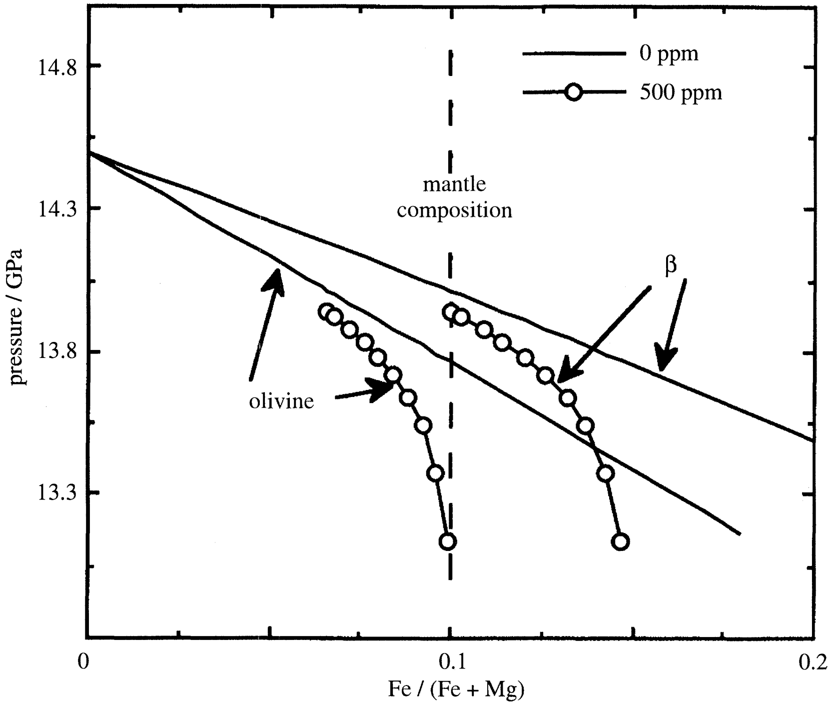

Figure 3. The effect of 500 ppm water on the olivine-β transition loop (note that this is strictly a projection from Mg_2SiO_4–Fe_2SiO_4–H_2O space back onto the front face). The first β-$(Mg,Fe)_2SiO_4$ to appear at 13 GPa has 5000 ppm water and coexists with olivine with 500 ppm. Olivine disappears when it has 50 ppm water and β-phase has 500 ppm, together with Fe/Fe + Mg of 0.1.

Table 1. *Thermophysical properties of olivine and β-phase*

	olivine	β-phase
volume/(cc mol^{-1})	43.670	40.520
K_S (298 K) GPa	128.0	173.0
K'	5.2	4.8
α ($\times 10^5$) K^{-1}	4.00	3.57
δ_S	4.0	4.3
γ_{th}	1.20	1.30

Figure 3 shows a comparison of the phase transition with 0 ppm and with 500 ppm by weight of H_2O in mantle olivine above the transition zone. The effect of as little as 500 ppm water is dramatic, β-$(Mg,Fe)_2SiO_4$ appearing approximately 0.6 GPa lower in the water-bearing than in the anhydrous system. In this case, the first β-$(Mg,Fe)_2SiO_4$ to appear contains 5000 ppm water, while olivine disappears at high pressure as its water content reaches 50 ppm and that of β 500 ppm. The width of the two-phase region is enlarged from 0.25 GPa in the dry system to 0.8 GPa when there is 500 ppm water (figure 3), so that the transition interval would be approximately 22 km wide if upper-mantle olivine contained 500 ppm water. Figure 4 shows

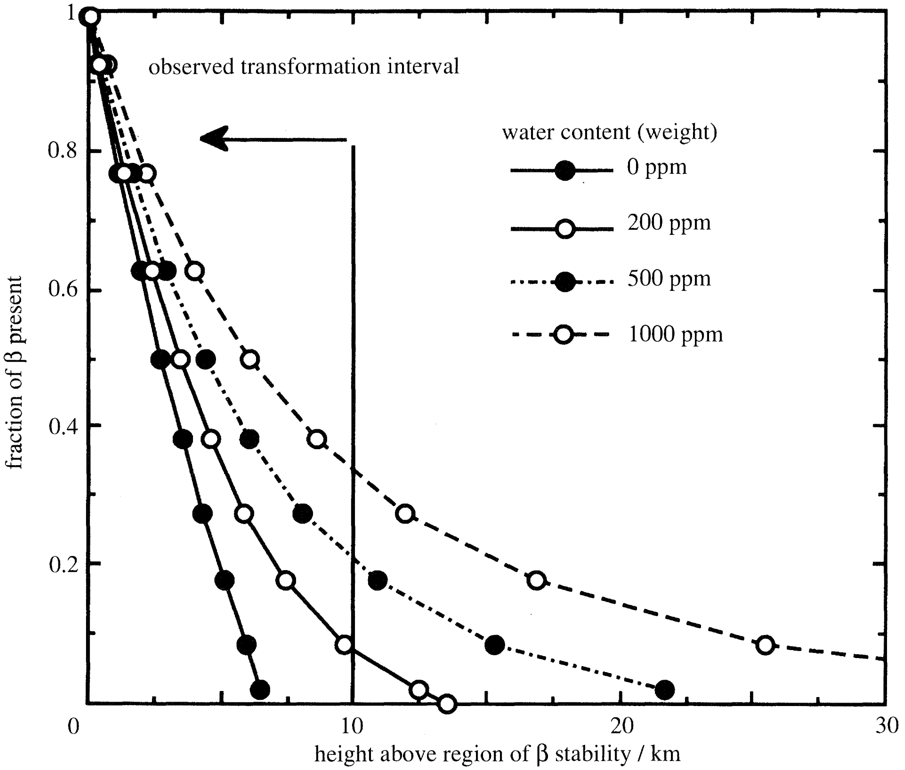

Figure 4. The olivine to β-(Mg,Fe)$_2$SiO$_4$ phase transition interval from figure 3 showing the effects of varying water content. Note that 500 ppm water produces a transition interval substantially greater than 10 km, the maximum likely from seismic observations.

the effects of variable water content on the transformation interval from olivine to β. In this case, the anhydrous interval is taken to be 7 km (0.25 GPa) as discussed previously. It can clearly be seen that, given this 'intrinsic' width to the phase transformation, water content in upper-mantle olivine of 500 or 1000 ppm is inconsistent with seismological observations, implying that the 410 km discontinuity is less than 10 km wide (Paulssen 1988; Benz & Vidale 1993; Yamazaki & Hirahara 1994). The maximum permissible water content would be even lower if the 'intrinsic' width of the transformation were greater. Thus, the seismic discontinuity is strongly affected by the water content of the mantle and should not be regarded as a passive bystander as arbitrary amounts of water are assigned to the transition zone.

A sensitivity analysis shows that the results are insensitive to the assumed partitioning behaviour of H_2O between the two phases and most dependent on the defect model for H_2O solution in β-(Mg,Fe)$_2$SiO$_4$. The X-ray data of Kudoh *et al.* (1994) indicate that OH occupies the O(1) position and that there is no long-range ordering of cation vacancies. Thus, our solution model is essentially correct. Explicit provision for the entropic effect of short-range ordering of cation vacancies onto M3 sites found by Inoue *et al.* (1995) has almost no effect on the results.

Results of seismic tomography in regions of subduction zones indicate a low S-wave velocity zone at 300–500 km depth which Nolet & Zielhuis (1994) interpret as due to release of water from the subducting slab. If the latter low-velocity zone is indeed a zone where fluids or hydrous melts are present, then, from figure 4, one would expect the high water content to affect the olivine to β-(Mg,Fe)$_2$SiO$_4$ transition. In particular, one would expect the 410 km discontinuity to be elevated and smeared-out relative to more normal regions of the mantle where the water contents are lower. Although this hypothesis is difficult to test seismically because of other mechanisms of apparent discontinuity broadening (e.g. defocusing due to topography), we note that, as discussed above, observed high-frequency reflections locally constrain water contents to be low. It is possible that seismic experimentation can test for correlation between discontinuity broadening and regions where petrological models indicate high water content.

The calculated effect of water may also explain the apparent breadth of the phase transition measured experimentally, which is about 0.5 GPa at 1600 °C (Katsura & Ito 1989). Calculations based solely on Fe–Mg partitioning and assuming completely anhydrous conditions (Bina & Wood 1987; Helffrich & Wood 1994) suggest transition intervals in the range 0.2–0.3 GPa. Since it is virtually impossible to completely exclude water from high-pressure experiments, it is quite likely that some of the experimentally observed width of the two-phase loop is due to the presence of small amounts of H_2O in the sample cell, so that the discrepancy between calculation and experiment may be an experimental artifact rather than a problem with the theory.

4. Effects of other minor components on the 410 km discontinuity

Mantle olivines contain small amounts of trace components (particularly Ni, Mn and Cr) in addition to H_2O and it is pertinent to consider whether these would also affect the width of the α–β transition interval. In order to reduce the interval, a particular element would have to partition preferentially into olivine. We have performed an experiment at 16 GPa and 1600 °C and produced coexisting α- and β-(Mg,Fe)$_2$SiO$_4$. The Fe/Mg ratios of the two phases are consistent with the values given by Katsura & Ito (1989). Figure 5 shows that all of these trace elements, with the exception of Mn, partition preferentially into β-(Mg,Fe)$_2$SiO$_4$ relative to olivine and that they would therefore tend to broaden the interval. The effects are much less dramatic than H_2O, however, and can be calculated from the approximate relationship

$$\mathrm{d}P/\mathrm{d}X_{\mathrm{tr}} \simeq 2RTD/(X_{\mathrm{Mg}}\Delta V^0),$$

where X_{tr} and X_{Mg} are the mole fractions of the trace component and Mg on the Fe–Mg sublattices in the structure, D is the partition coefficient (β/α) and ΔV^0 is the standard state volume change of reaction (3.7), about $-0.224\ \mathrm{J\ bar^{-1}}$ under the conditions of the 410 km discontinuity. This means that for Ni, which is the most abundant of these elements in mantle olivine having X_{tr} of about 0.003, the transformation interval is broadened by about 450 bar or about 1.3 km. Clearly this effect is minor relative to that of water.

5. Water and the 660 km discontinuity

Since water has such a large effect on the width of the olivine to β-(Mg,Fe)$_2$SiO$_4$ transformation, it is reasonable to consider whether its influence on the reaction

$$\underset{\gamma-\text{spinel}}{(\mathrm{Mg,Fe})_2\mathrm{SiO}_4} = \underset{\text{perovskite}}{(\mathrm{Mg,Fe})\mathrm{SiO}_3} + \underset{\text{magnesiowüstite}}{(\mathrm{Mg,Fe})\mathrm{O}} \qquad (5.1)$$

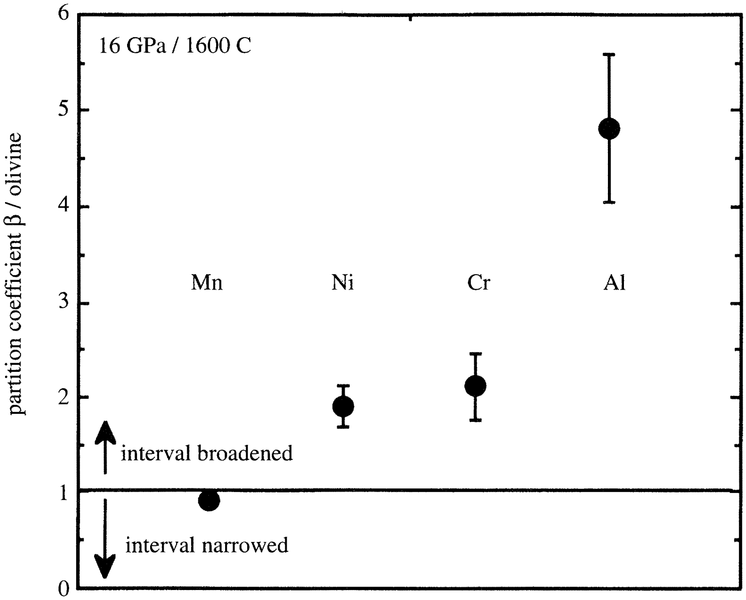

Figure 5. Measured partitioning of Mn, Ni, Cr and Al between β-(Mg,Fe)$_2$SiO$_4$ and olivine at 16 Gpa, 1600 °C. Note that data imply that these elements will tend to broaden the olivine-β two-phase loop but only by very small amounts (see text).

is comparable. In this case, the phase transformation is correlated with the 660 km discontinuity (see, for example, Ito & Takahashi 1989), but it is possible that there is also a change in bulk composition (see, for example, Zhao & Anderson 1994), in which case nothing could be deduced about the water content of the mantle from the width of the discontinuity. Meade *et al.* (1994) have observed small amounts of OH in synthetic MgSiO$_3$ perovskite and, by analogy with olivine, it is likely that addition of Fe^{3+} and Al will greatly enhance water solubility in this lower mantle phase.

Assuming that H$_2$O partitions preferentially into the perovskite plus magnesiowüstite assemblage, then a similar analysis to that performed earlier shows that 1000–2000 ppm of water would broaden the transformation beyond the width required by observed high-frequency reflections from the 660 km discontinuity (Benz & Vidale 1993; Yamazaki & Hirahara 1994). This calculation is for an intrinsic 0 ppm width of 1 km, which is within the range required by the Fe–Mg partitioning data (Ito & Takahashi 1989; Wood 1990) and greater transformation widths would place tighter constraints on the water content of the lower mantle.

In conclusion, although water is very soluble in β-(Mg,Fe)$_2$SiO$_4$ and conceivably quite soluble in perovskite, suggestions that there are high concentrations of H$_2$O in the nominally anhydrous phases of the lower mantle and transition zone must take into account the effects of these components on the well-established phase transformations. If the 410 and 660 km seismic discontinuities are due solely to phase transformations, then the water contents of β-(Mg,Fe)$_2$SiO$_4$ in the transition zone and perovskite in the lower mantle are limited to less than 500 and about 1000 ppm, respectively. The calculated large effect of water on the phase transitions is testable experimentally and seismic data may, under favourable circumstances, constrain geographic variations in mantle water content.

6. Carbon and carbonate

Analysis of the CO_2 contents of MORB glasses lead to an estimated carbon content of the degassed upper mantle of about 80 ppm. Estimates of carbon content of the bulk silicate Earth vary from 900 to 3700 ppm based on the correlation between C and ^{36}Ar in chondritic meteorites (Jambon 1994), assuming that the C content of the core is negligible. A recent analysis of $C/^4He$ and $C/^3He$ in peridotite xenoliths and in basalts by Trull *et al.* (1994) led to the conclusion that, using a two-reservoir model, the upper mantle contains 35–400 ppm C and the lower undegassed mantle about 2500 ppm C. Assuming an initial CO_2 content of MORB and hotspot basalts of about 0.3 wt%, then the Earth is degassing about 2×10^{14} g of CO_2 per year (Staudigel *et al.* 1989). Measurements of carbonate in altered oceanic crust by Staudigel *et al.* (1989) indicate that the amount of CO_2 being recycled in subduction zones is similar to that being evolved at ridges and hotspots. The important questions are whether recycled carbonate is stable in the deep mantle and how primordial and recycled carbon is stored in the Earth.

The presence of CO_2-rich fluids and carbonate magmas demonstrate that oxidized carbon occurs at depth. Similarly, native carbon as both graphite and diamond occurs in kimberlites and in deep-seated xenoliths associated with kimberlites. This suggests that the form in which carbon is stored is related to tectonic environment or depth and it is appropriate to consider the interactions between P, T and oxidation state.

In terms of high temperature stability, carbonates are much more refractory than hydrates, as may be seen from figure 6 (White & Wyllie 1992; Brey *et al.* 1983). At moderate mantle depths (less than 100 km), dolomite, $Ca(Mg,Fe)(CO_3)_2$, is stable, coexisting with anhydrous peridotite. At greater depths, dolomite transforms to magnesite, $(Mg,Fe)CO_3$, through a reaction which may be approximated as

$$\underset{\text{dolomite}}{Ca(Mg,Fe)(CO_3)_2} + \underset{\text{orthopyroxene}}{2(Mg,Fe)SiO_3} = \underset{\text{clinopyroxene}}{Ca(Mg,Fe)Si_2O_6} + \underset{\text{magnesite}}{(Mg,Fe)CO_3}\,.$$

In the peridotitic assemblage, magnesite is thermally stable to lower-mantle pressures (Redfern *et al.* 1993; Biellmann *et al.* 1993).

When compared to realistic mantle temperatures, carbonate should be stable anywhere in the continental lithosphere and could occur on the mantle adiabat at any depth below 200 km (figure 6, Redfern *et al.* 1993). When subduction zone P–T paths are plotted on figure 6, it appears that magnesite would be stable in any peridotitic assemblage virtually anywhere within the subducting lithosphere. The normal form of subducted carbonate in the basaltic part of the oceanic plate is calcite rather than magnesite (Staudigel *et al.* 1989), but high-pressure experiments indicate that this is converted to stable magnesite or dolomite in basaltic compositions, not disappearing before the beginning of melting at 1.5–3.5 GPa (Yaxley *et al.* 1994). Therefore, we can assume that virtually all subducted carbonate is returned to the mantle, indicating, as discussed earlier, that the rate of degassing of CO_2 at mid-ocean ridges is approximately balanced by recarbonation in subduction zones.

Given that reasonable quantities of carbonate are returned to the mantle, it is of interest to consider whether it remains stored as carbonate or is converted into diamond or graphite. Diamonds commonly contain inclusions of high-pressure silicate minerals such as garnet, sodic pyroxene (eclogitic suite), olivine and orthopyroxene (peridotitic suite). Of the two inclusion suites (Meyer 1987), the peridotitic suite is correlated with common mantle minerals while the eclogitic suite may have its origin as subducted basaltic crust (see, for example, Kesson & Ringwood 1989). Carbon

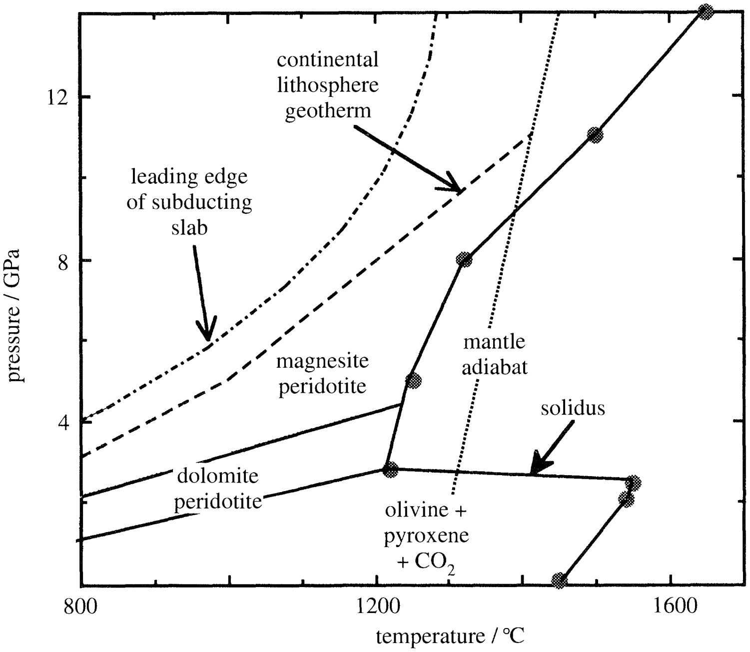

Figure 6. The stability of carbonate (magnesite and dolomite) in the mantle. Note that carbonates are much more refractory than hydrates and are thermally stable in subduction zones and throughout most of the mantle. Line labelled 'leading edge of subducting slab' from figure 1.

isotope analysis is generally equivocal, but some diamonds of the eclogitic suite have very light $^{12}C/^{13}C$ ratios, indicating a crustal component of carbon. It is plausible that diamonds of this suite formed by reduction of a mixture of subducted carbonate and organic carbon (Kesson & Ringwood 1989).

The two most important elements involved in redox reactions in the Earth are C and Fe. In the upper mantle Fe is dominantly present as reduced 'FeO' (about 8 wt%), but the concentration of Fe^{3+} is also considerable (about 0.2% as Fe_2O_3, O'Neill *et al.* 1993). Given these concentrations, which are robust and based on analyses of peridotites by Mössbauer spectroscopy, then the oxidation state of Fe should dominate that of carbon, given that the latter is present at a level of 80 ppm. The oxidation state of Fe is reflected by the oxygen fugacity, which has been measured for peridotites from a wide range of localities by oxygen thermobarometry (Wood *et al.* 1990; Bryndzia & Wood 1990). The results demonstrate that oxygen fugacity depends on tectonic environment (Wood *et al.* 1990). At oceanic ridges and in continental rift zones the mantle is relatively reduced, with f_{O_2} values extending from two log units below the fayalite–magnetite–quartz (FMQ) reference buffer up to about FMQ. Mantle peridotite from above subduction zones and in non-rift continental environments is more oxidized, extending to about one log unit above FMQ. This leads to the spread of asthenosphere (rift) and lithosphere values shown in figure 7.

The results shown in figure 7 all apply to the (aluminous) spinel peridotite facies of the upper mantle, which extends from the surface to depths of about 90 km. Deeper samples of the lithosphere are provided by garnet peridotite xenoliths in kimberlites, and oxygen barometry for limited suites of such samples suggest that the deeper parts of the lithosphere may have slightly more reduced f_{O_2} conditions than the spinel lherzolite facies of the asthenosphere and continental lithosphere

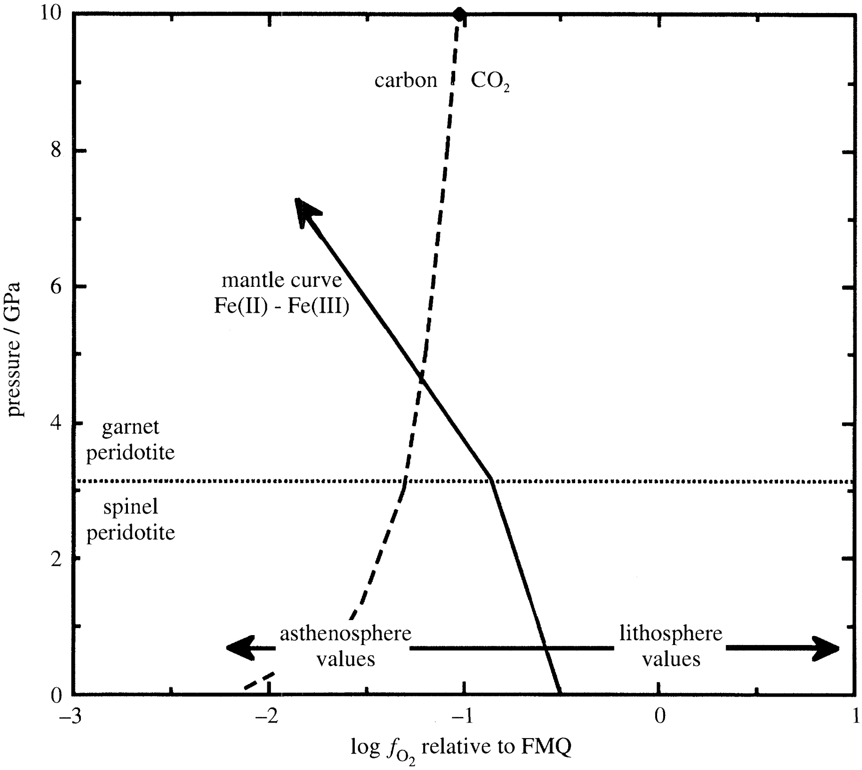

Figure 7. Line with arrows represents oxygen fugacity in the mantle relative to the FMQ buffer as a function of depth. The deeper parts of the upper mantle (garnet peridotite) and the transition zone are relatively reduced. Curved line separates reduced from oxidized carbon (experimentally measured to 300 km, extrapolated above). Carbon is oxidized in the lithosphere (CO_2 or carbonate) and stored as reduced diamond in the deeper parts of the upper mantle and transition zone.

(Gudmundsson & Wood 1996). Taking the bulk composition of the upper mantle to be approximately constant with 0.2% Fe_2O_3 distributed at low pressure between aluminous spinel (main host for Fe^{3+}) and pyroxene, and at higher pressures between garnet (main host for Fe^{3+} and pyroxene), then there is a simple pressure effect on the relative f_{O_2} of the mantle.

At low pressure the dependence of f_{O_2} on pressure may be represented by the equilibrium

$$\underset{\text{olivine}}{6Fe_2SiO_4} + O_2 = \underset{\text{spinel}}{2Fe_3O_4} + \underset{\text{orthopyroxene}}{6FeSiO_3}\ . \tag{6.1}$$

The volume change of the solids in this reaction (+8.6 cm^3) is about half that for the FMQ buffer (+17.95 cm^3) with the result that, at fixed composition, f_{O_2} declines by about 0.25 log units relative to FMQ for every 1 GPa increase in pressure. In the garnet stability field, the pressure effect on f_{O_2} may be estimated from the equilibrium

$$\underset{\text{olivine}}{4Fe_2SiO_4} + \underset{\text{opx}}{2FeSiO_3} + O_2 = \underset{\text{garnet}}{2Fe_3^{2+}Fe_2^{3+}Si_3O_{12}}\ .$$

In this case, the volume change of the solids is $-8.6\ cm^3$ (Gudmundsson & Wood 1996), meaning that ferric iron has a relatively low partial molar volume in garnet and that f_{O_2} in the garnet field, at fixed composition, declines by about 0.9 log units relative to FMQ for every 1 GPa increase in pressure. This effect is purely crystallochemical in origin and must occur even at fixed composition. It is compounded by the breakdown of pyroxene to majorite garnet which dilutes the Fe^{3+} in garnet and hence lowers f_{O_2} still further. The overall effect, a gradual decline in f_{O_2} relative to FMQ with increasing depth, is shown schematically in figure 7.

To determine whether native C or CO_2 (or carbonate) are stable under mantle conditions, we may plot the position of the equilibrium

$$C + O_2 = CO_2 \ (CCO)$$

on figure 7 and compare it with the curve for mantle f_{O_2}. Our recent measurements of this equilibrium to 8 GPa may be represented along a typical mantle adiabat by

$$\log f_{O_2} = \text{FMQ} - 1.5562 + 0.5298 \log P,$$

where P is in GPa.

This means that if the C content of the upper mantle is of the order of 80 ppm and Fe dominates the redox properties then, in much of the asthenosphere and lithosphere, CO_2 and carbonates should be stable, while deeper in the mantle CO_2 (or carbonate) will be reduced by the FeO-rich mantle minerals to produce diamond/graphite and higher concentrations of 'Fe_2O_3' in major mantle minerals:

$$4'\text{FeO}' + CO_2 = 2'\text{Fe}_2\text{O}_3' + C.$$

The implication is that, although carbonate is thermally stable in subduction zones (figure 6), it will generally be reduced to diamond within the upper 200–300 km of the mantle and will be stored and recycled as diamond rather than carbonate, as suggested by Kesson & Ringwood (1989). Similarly reduced carbon tends to be oxidized by Fe^{3+} during asthenospheric upwelling (Ballhaus & Frost 1994).

Recent studies of Fe^{3+} in β- and γ-$(Mg,Fe)_2SiO_4$ by Hazen *et al.* (1990) and O'Neill *et al.* (1993) indicate that both these phases have $Fe^{3+}/(Fe^{2+} + Fe^{3+})$ ratios of close to 0.1. This contrasts with the very low values (less than 0.02) found in the low-pressure analogue, olivine (Dyar *et al.* 1989). In the transition zone, therefore, ferric iron should be present at moderate concentrations in the major β- and γ-$(Mg,Fe)_2SiO_4$ phases rather than being forced at high concentrations into minor phases such as aluminous spinel. The implication (O'Neill *et al.* 1993) is that f_{O_2} in the transition zone is much lower than in the upper mantle, since the ease with which ferric iron is accommodated in the major phases means, even at fixed composition, a very low chemical potential for Fe^{3+} components. In the lower mantle, Fe partitions strongly into magnesiowüstite relative to perovskite (Ito & Takahashi 1989). Since magnesiowüstite can accomodate $Fe^{3+}/(Fe^{3+} + Fe^{2+}) > 0.5$ (see, for example, Wood & Nell 1991), it is possible that the lower mantle mirrors the upper mantle in that a minor phase (magnesiowüstite rather than aluminous spinel) contains most of the Fe^{3+} with the result that oxygen fugacity is relatively high. From the point of view of carbon, storage in the transition zone should be as diamond. In the lower mantle, carbon should be oxidized and stored as thermally stable magnesite $(Mg,Fe)CO_3$.

7. Summary

Although H_2O and C are present in only trace amounts in the upper mantle and likely only at concentrations of 1000 ppm in the deep mantle, the properties of the mantle should not be regarded as independent of the concentrations and chemical form of these two components. The width of the α–β transition in $(Mg,Fe)_2SiO_4$ is extremely sensitive to the water contents of the anhydrous minerals in the mantle and the position and width of the 410 km seismic discontinuity constrains the water content of olivine to be 0–500 ppm. A similar constraint probably applies at 660 km, but quantification awaits data on partitioning of H_2O between the different phases.

Carbon is much more refractory than H_2O and an analysis of the stabilities of carbonates indicates that most carbon in the subducting oceanic lithosphere is returned to the deep mantle. Because, however, of the redox relationship between carbon and iron, carbonate is reduced to diamond or graphite within the upper mantle and storage in the transition zone is as diamond rather than carbonate. Partitioning of Fe amongst lower-mantle minerals shows that Fe^{2+} and possibly Fe^{3+} are concentrated in the magnesiowüstite phase. The implication is that relative f_{O_2} is higher in the lower mantle than in the transition zone and that carbonate, rather than diamond, is stable. A potential test of this hypothesis is provided by electrical conductivity data. Wood & Nell (1991) showed that, if Fe-rich magnesiowüstite is the phase responsible for the observed conductivity of the lower mantle then the latter is consistent with an Fe^{3+}/Fe^{2+} ratio indicative of relatively oxidizing conditions close to the FMQ buffer.

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