The Effect of H_2O on the 410-Kilometer Seismic Discontinuity

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The 410-kilometer seismic discontinuity is generally considered to be caused by a phase transformation of the main constituent of the upper mantle, olivine, α-$(Mg,Fe)_2SiO_4$, to β-$(Mg,Fe)_2SiO_4$. Recent data show that H_2O dissolves in olivine and other nominally anhydrous mantle minerals and that the partitioning of H_2O between olivine and β-$(Mg,Fe)_2SiO_4$ is about 1:10. Such behavior strongly affects the region over which the α to β phase transformation occurs and hence the seismic discontinuity that results. The observed width of the discontinuity constrains the maximum H_2O content of upper mantle olivine to about 200 parts per million by weight.

The seismic discontinuities at depths of 410 and 660 km correspond to important jumps in mantle density [5 and 10%, respectively (*1*)] and in *P*-wave and *S*-wave velocities. The discontinuities are correlated with phase transformations in the major olivine, α-$(Mg,Fe)_2SiO_4$, component of peridotitic mantle, which converts to β-$(Mg,Fe)_2SiO_4$ at 14 GPa (a depth of 410 km) (*2, 3*), then through γ-$(Mg,Fe)_2SiO_4$ to $(Mg,Fe)SiO_3$ perovskite plus (Mg,Fe)O magnesiowüstite at 23 GPa (a depth of 660 km) (*3, 4*). An important, long-standing question is whether these discontinuities are isochemical transformations or whether they are accompanied by changes in the bulk chemical composition of the mantle (*5, 6*).

The main constraints on hypotheses about phase or compositional changes are the observed intensities and widths of the seismic discontinuities. Recent seismological studies using high-frequency reflected and converted waves indicate that both the 410- and the 660-km discontinuities are sharp and that the changes in physical properties associated with them occur over small depth intervals (*7, 8*). For the 660-km discontinuity, a width of 5 km is consistent with the seismic data (*7, 8*), and a width of <10 km has been suggested for the 410-km discontinuity (*9*).

The implication for the phase change hypothesis is considerable. The chemical system of the mantle is multicomponent, and simple phase relations show that the transformation from olivine to the β phase must occur in a divariant loop (Fig. 1), giving a broad pressure interval over which the transition occurs. The seismic observations at 410 km indicate that the transition is sharp, however, which is explicable by a maximum interval of 8 km (*10*). This is at the lower limit of values predicted from Fe-Mg partitioning between the two phases (*10, 11*). For such calculations, it is generally assumed that the chemical system of the Earth is MgO-FeO-SiO_2 and that other components such as H_2O have no effect on the phase transformations. It is now established, however, that some H_2O is structurally bound in the nominally anhydrous minerals of the upper mantle including olivine (*12*), and recent measurements (*13–15*) demonstrate that H_2O is much more soluble in the β phase than in olivine. I now show that the strong preference of H_2O for the β phase must, at very low concentrations of H_2O in the mantle, greatly affect the width of the transition interval, with implications for the correlation between seismic observations and phase relations.

Smyth (*16, 17*) proposed that the replacement of one of the O atoms (O1) in β-Mg_2SiO_4 by an OH group is energetically favored and that the β phase could be a host for large amounts of H_2O below depths of 410 km. Charge compensation would come through the creation of cation vacancies in the Mg sublattices. New experiments (*13–15*) indicate a solubility of up to 3% H_2O (by weight) in the β phase and a partitioning of H_2O between the β phase and olivine of greater than 10:1 in favor of the former (*15*). The hypothetical end-member has the formula $Mg_7Si_4O_{14}(OH)_2$, and in a mantle saturated with $(Mg,Fe)_2SiO_4$ and the $(Mg,Fe)SiO_3$ component of pyroxene, its formation may be represented by the equilibrium

$$\underset{\beta\ \text{phase}}{3Mg_2SiO_4} + \underset{\text{Pyroxene}}{MgSiO_3} + H_2O = \underset{\beta\ \text{phase}}{Mg_7Si_4O_{14}(OH)_2} \qquad (1)$$

This creates a β-phase solid solution in which one-eighth of the available O sites (O1) may form OH groups with charge-compensating vacancies on the Mg sites. At low concentrations of OH, the solution of this component must, through the configurational entropy of disorder, stabilize the β phase to lower pressure. If we assume Henry's law solution of H_2O, the chemical potentials of major Mg_2SiO_4 and Fe_2SiO_4 components are given by

$$\mu^{\beta}_{Mg_2SiO_4} = \mu^{0}_{Mg_2SiO_4} + RT\ln[X^2_{Mg}\gamma_{Mg}(1 - X_{OH})^{0.5}] \qquad (2)$$

$$\mu^{\beta}_{Fe_2SiO_4} = \mu^{0}_{Fe_2SiO_4} + RT\ln[X^2_{Fe}\gamma_{Fe}(1 - X_{OH})^{0.5}]$$

where *R* is the Boltzmann constant and *T* is temperature. In Eq. 2, X_{Mg} and X_{Fe} refer to atomic fractions of Mg and Fe, respectively, on the large cation positions, whereas X_{OH} is the fraction of O1 sites that are OH 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 nonideal Mg-Fe mixing (*18*), combined with (nominally) ideal mixing of vacancies, which from stoichiometry have a mole fraction one-eighth of that of OH on the O1 positions.

In olivine, the much lower solubility of structurally bound H_2O is dependent on the fugacities fH_2 and fO_2 and the activity of $MgSiO_3$ in the system (*19*). On the basis of low-pressure data, Bai and Kohlstedt (*19*) derived a solution model for H_2O in which H complexes with interstitial O atoms, O_i'', with the concentrations of interstitials dependent on the thermodynamic state of the system. A simple representation of their model is, in Kröger-Vink notation,

$$O_i'' + H_2O = 2OH_i' \qquad (3)$$

In this case, calculation of the chemical

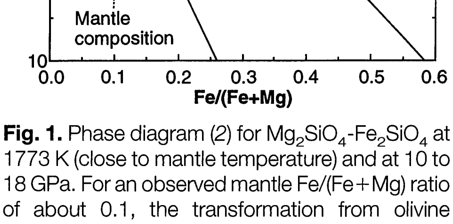

Fig. 1. Phase diagram (*2*) for Mg_2SiO_4-Fe_2SiO_4 at 1773 K (close to mantle temperature) and at 10 to 18 GPa. For an observed mantle Fe/(Fe+Mg) ratio of about 0.1, the transformation from olivine [α-$(Mg,Fe)_2SiO_4$] to β-$(Mg,Fe)_2SiO_4$ takes place through an interval of about 0.25 GPa where both phases coexist. This should result in an apparent seismic discontinuity spread over a 7-km depth interval.

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potential of the Mg_2SiO_4 component in the partially hydrated olivine, relative to H_2O-free olivine under the same conditions, is given by

$$\mu^{\alpha}_{Mg} = \mu^{0}_{Mg_2SiO_4} + RT\ln [X^2_{Mg}\,\gamma_{Mg}(1-X_{OH})^4/(1-0.5X_{OH})^4] \quad (4)$$

The chemical potential of the Fe_2SiO_4 component has a similar form. In Eq. 4, I have taken explicit account of the fact that creation of OH defects destroys half as many preexisting O interstitials (denominator on the right) and the standard state values μ^0 refer to hypothetical olivine free of O interstitials. Activity coefficients γ_{Mg} and γ_{Fe} were estimated from the symmetric solution model (*20*), and the phase relations for partially hydrated olivine and β-$(Mg,Fe)_2SiO_4$ were calculated (*21*).

As shown in Fig. 2, the effect of as little as 500 ppm H_2O on the transition from olivine to the β phase is dramatic; the β phase appears at a pressure approximately 0.6 GPa lower in the H_2O-bearing than in the anhydrous system. The first β phase to appear has, with 10:1 partitioning, 5000 ppm H_2O, whereas olivine disappears at high pressure as its H_2O content reaches 50 ppm and the H_2O content of the β phase reaches 500 ppm. The width of the two-phase region is enlarged from 0.25 GPa in the dry system to 0.8 GPa when the H_2O content is 500 ppm (Fig. 3), so that the transition interval would be approximately 22 km wide if upper mantle olivine contained 500 ppm H_2O. The calculation is, of course, performed relative to the anhydrous system, and so the result depends on the assumed width of the transformation interval when there is 0 ppm H_2O in the system. I assumed an anhydrous interval of 7 km (0.25 GPa), which is at the lower limit calculated from Fe-Mg partitioning (*10*). Therefore, the calculated widths shown in Figs. 2 and 3 for H_2O-bearing olivine and β phase are similarly lower bounds.

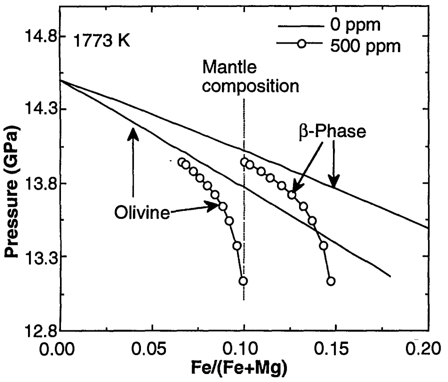

Fig. 2. The calculated effect of 500 ppm H_2O (by weight) on the α+β region of Fig. 1; β-$(Mg,Fe)_2SiO_4$ appears at a pressure 0.6 GPa lower (16 km higher in the mantle) than in the anhydrous case, and the α+β loop is expanded from 7 to 22 km.

The effects of H_2O contents from 0 to 1000 ppm on the olivine–β-phase transformation interval are shown in Fig. 3. Clearly, H_2O contents in upper-mantle olivine of 500 or 1000 ppm are inconsistent with seismological observations at high frequency, which imply that the 410-km discontinuity is less than 10 km wide (*7–9*). The maximum permissible H_2O content of olivine at the 410-km seismic discontinuity is, from Fig. 3, about 200 ppm. Thus, the seismic discontinuity is strongly affected by the H_2O content of the mantle and should not be regarded as a passive bystander as arbitrary amounts of H_2O are assigned to the β phase below 410 km. Although there is some uncertainty about the width of the olivine–β-phase transition for 0 ppm H_2O, some investigators favor values >7 km (*2*, *18*), which would constrain the H_2O content of mantle olivine to less than 200 ppm.

Uncertainties in the H_2O solution model for the β phase affect the calculation more than any other potential source of error. I adopted a model (*16*) in which H bonds with O atoms on O1 sites. I also assumed that OH species mix randomly with unprotonated O1 atoms and that cation vacancies, V_{Mg}, mix randomly with Mg and Fe atoms. Several different assumptions might be made. First, following Downs (*22*), it is possible that both O1 and O2 atoms in hydrous β-$(Mg,Fe)_2SiO_4$ may be protonated. This would explain the presence of two intense OH absorption bands in the infrared spectrum of β-Mg_2SiO_4 (*13*, *23*).

Adopting the Downs (*22*) model makes, however, a negligible difference in the results in the concentration range shown in Fig. 3, where β-$(Mg,Fe)_2SiO_4$ contains a maximum of 10,000 ppm H_2O. For example, when olivine contains 1000 ppm H_2O and the β phase contains 10,000 ppm H_2O, the latter should appear 40 km above the point of 100% transformation (Fig. 3). With the Downs model this value is 37 km. The point of the initial appearance of the β phase when olivine contains 500 ppm H_2O (Fig. 3) is shifted from 22 to 21.25 km above the β-phase zone, whereas at 200 ppm H_2O in olivine the curve is moved from 13.54 to 13.46 km.

Larger differences in my results are obtained if it is assumed that cation vacancies are long-range–ordered, as suggested recently by Smyth (*17*). In this case, the entropy of disorder is about 30% less than in my model, so that the effect of H_2O at any particular concentration would be about 0.7 times that depicted in Fig. 3. A recent single-crystal x-ray study of hydrated β phase of end-member $Mg_7Si_4O_{14}(OH)_2$ composition (*24*) shows, however, that there is no long-range ordering of cation vacancies. The space group (*Imma*) is the same as that of anhydrous β-Mg_2SiO_4, and valence sum calculations indicate that the O1 site is protonated (*24*). Both observations support my model of hydrated β phase. Some short-range ordering of vacancies onto M3 and M1 Mg sites was reported (*24*), but this has little effect on the entropy of disorder at the H_2O concentrations of interest.

The phase transformation from γ-$(Mg,Fe)_2SiO_4$ to $(Mg,Fe)SiO_3$ perovskite plus (Mg,Fe)O magnesiowüstite at 660 km may also be sensitive to H_2O content [H_2O has recently been shown to be soluble in both γ-$(Mg,Fe)_2SiO_4$ (*15*) and the perovskite phase (*25*)]. Provided H_2O partitioning between the two phases is, like that for the olivine–β-phase transition, on the order of 10:1 in favor of either, then the transformation interval must be broadened. If H_2O favors perovskite, then the transformation interval would be broadened to lower pressures compared to the anhydrous case (compare the olivine–β-phase transition), whereas a preference for γ-$(Mg,Fe)_2SiO_4$ would broaden the transformation to higher pressure. Calculations like those above indicate that the observed width of the discontinuity of <5 km (*7*, *8*) would, if the discontinuity is isochemical, be consistent only with <1000 ppm H_2O in γ-$(Mg,Fe)_2SiO_4$.

Results of seismic tomography in regions of subduction zones (*26*, *27*) suggest that H_2O may be released from the subducting lithosphere in two depth intervals, one

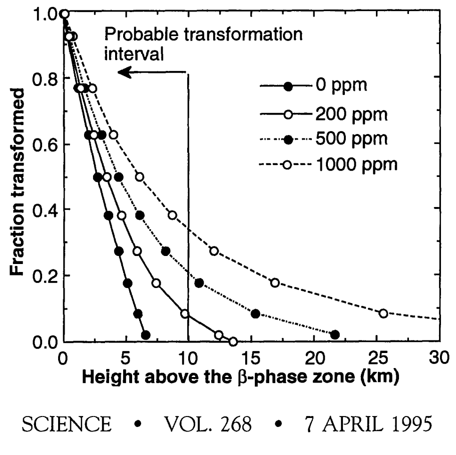

Fig. 3. The olivine–β-phase transition interval for initial H_2O contents of olivine of 0, 200, 500, and 1000 ppm. Addition of H_2O elevates the point at which β-$(Mg,Fe)_2SiO_4$ appears (shifts it to lower pressure) and broadens the transformation interval. Given a seismically determined transformation interval of <10 km, the maximum H_2O content of upper mantle olivine at a depth of 400 km is constrained to about 200 ppm.

shallower than 100 km and the other 300 to 500 km deep. Nolet and Zielhuis (*27*) have argued that in the latter case low S-wave velocities above an ancient subduction zone could only reasonably be accounted for by the weakening of the shear modulus because of the presence of H_2O or small amounts of hydrous partial melt. My calculations (Fig. 3) indicate that in H_2O-rich regions, the 410-km discontinuity should be elevated and broadened relative to more normal regions where H_2O contents are lower. This suggests the need for further seismic experimentation on the nature of the 410-km and perhaps 660-km discontinuities in the region of subduction zones. Broadening and elevation of the 410-km discontinuity and broadening of the 660-km discontinuity in "wet" areas of the mantle would indicate that the discontinuities are due to isochemical phase changes. The absence of such effects would support models that invoke combined phase and bulk compositional changes.

Given a maximum H_2O content of olivine of close to 200 ppm at the 410-km discontinuity, an important question concerns how this relates to the bulk H_2O content of the upper mantle and transition zone. Olivines in low-pressure mantle xenoliths generally have structurally bound H_2O contents an order of magnitude lower than coexisting, nominally anhydrous pyroxenes (*12, 28*) but somewhat higher than the dominant aluminous phase, garnet (*12*). Despite the implication that the major mineral, olivine, may not be the major H_2O reservoir, several lines of evidence suggest that it is a more important host for H_2O at the 410-km discontinuity than it is in the shallow mantle. First, the proportion of pyroxene declines with depth as it dissolves into garnet (*29*), so that a relatively H_2O-rich mineral is replaced by a H_2O-poor one. Second, data on natural samples (*30*) indicate a stronger pressure effect on H_2O solubility in olivine than in pyroxene, such that Bell *et al.* (*30*) argued that olivine is the major reservoir for H_2O below a depth of 200 km. Finally, experimental results on pyroxene synthesized at 13 GPa indicate a H_2O content similar to that of olivine under the same conditions (*31*). Therefore, although the exact relation between the H_2O content of olivine and that of the whole rock is unknown, they should not differ greatly.

The presence of structurally bound H_2O may help explain the apparent breadth of the phase transition measured experimentally, which is about 0.5 GPa at 1600°C (*2*). Calculations based solely on Fe-Mg partitioning and assuming completely anhydrous conditions suggest transition intervals of 0.2 to 0.3 GPa (*10, 11*). Because it is virtually impossible to exclude H_2O from these 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.

Finally, it is pertinent to ask whether there is some other minor element that affects the olivine–β-phase transition and that might, perhaps, make it narrower rather than broader. Such an element would have to partition strongly into olivine and would need to be present at about the 1 mol % level. Recent experimental data (*32*) show no evidence that any of the principal trace elements in olivine (Ni, Cr, Al, and Mn) behave in this way, which indicates that the effect of H_2O is the most important.

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21. The combined effect of H_2O and Fe on the olivine–β-phase transition may be calculated by fixing the bulk Fe/(Fe + Mg) ratio and H_2O content of mantle olivine at a point just above the depth at which the β phase appears and then calculating the shift in equilibrium pressure relative to the value for pure anhydrous Mg_2SiO_4. The Fe-Mg exchange equilibrium was fixed from the standard-state free energy change, ΔG^0, of the equilibrium:

$$\text{Mg(olivine)} + \text{Fe}(\beta\text{ phase}) = \text{Fe(olivine)} + \text{Mg}(\beta\text{ phase}) \tag{5}$$

The experimental results on this equilibrium (*2*) indicate minimum values of ΔG^0 of about 5.5 kJ, yielding a two-phase loop in the anhydrous system that is about 0.25 GPa (7 km) wide (Figs. 2 and 3). Proportions of phases through the two-phase region were calculated as follows. The Fe/(Fe+Mg) ratio of the olivine was set at a value less than or equal to the value just above the transition zone. The Fe/(Fe+Mg) ratio of the coexisting β phase was then obtained from ΔG^0 of Eq. 5, taking into account Fe-Mg nonideality. Then, from the Fe/(Fe+Mg) ratio of the initial mantle olivine, phase proportions were simply solved from the lever rule. Given proportions of olivine and the β phase, the concentrations of H_2O in the two phases were calculated from the partition coefficient of 10:1 and the fixed H_2O content of the system. The equilibrium pressure was then calculated from (*33*) such that

$$(P - P^0)\Delta V^0 = -RT\ln[X^2_{Mg}\gamma_{Mg}(1 - X_{OH})^{0.5}]_\beta + RT\ln[X^2_{Mg}\gamma_{Mg}(1 - X_{OH})^4/(1 - 0.5X_{OH})^4]_{ol} \tag{6}$$

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

$$\underset{\text{Olivine}}{Mg_2SiO_4} = \underset{\beta\text{ phase}}{Mg_2SiO_4} \tag{7}$$

and ΔV^0 refers to the volume change of this reaction at the pressure and temperature conditions of interest. I performed the calculations at 1773 K and took P^0 to be 145 kbar (Fig. 2). I calculated the volumes of the two phases at P and T from the Murnaghan equation of state, using the following thermodynamic properties for olivine and β phase, respectively. Volume: 43.670 and 40.520 $cm^3\ mol^{-1}$; K_s (adiabatic bulk modulus at 298 K), 128.0 and 173.0 GPa; K' (pressure derivative of K_s), 5.2 and 4.8; α (coefficient of thermal expansion), 4.00×10^5 and 3.57×10^5 K^{-1}; δ_s (Anderson-Grüneisen parameter), 4.0 and 4.3; and γ_{th} (Grüneisen parameter), 1.20 and 1.30.
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31. D. L. Kohlstedt (personal communication) reports an H_2O content of Mg,Fe clinopyroxene synthesized from olivine and talc at 13 GPa and 1100°C that, in weight terms, is very similar to that obtained in olivine under similar conditions (*15*). This implies that olivine, by virtue of its higher modal proportion, should be the major carrier of H_2O in peridotitic mantle at a depth of around 400 km, a conclusion independently reached by Bell *et al.* (*30*).
32. A trace element partitioning experiment performed at 16 GPa and 1600°C at the Bayerisches Geoinstitut (B. J. Wood, unpublished results) yielded coexisting olivine and β-$(Mg,Fe)_2SiO_4$. The Fe-Mg partitioning between the two phases is consistent with that found in earlier work (*2*). The elements Ni, Al, and Cr were all found to prefer the β phase, whereas Mn preferentially entered olivine. The partition coefficients are not, however, sufficiently different from 1.0 to have a marked effect on the olivine–β-phase relations. The greatest calculated effect, using an analysis similar to that described above, is due to Ni. At mantle concentrations of 3000 to 4000 ppm, Ni should broaden the transition interval by about 1 km, an effect that is extremely small compared to that of H_2O.
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34. I thank D. Kohlstedt for permission to cite unpublished data and D. Rubie for help in setting up the trace element partitioning experiments. Comments on the manuscript by G. Helffrich and two anonymous reviewers improved it greatly. Work in Bristol is supported by Natural Environment Research Council (UK) grant GR3/8362 and in Bayreuth by European Community Large Facility contract ERBCHGECT940053.

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