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# Mantle Discontinuities

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## INTRODUCTION

The nature of the discontinuities evident in seismic velocity profiles of the Earth's mantle has been a topic of active research since the work of Birch in the 1950s. The chemical, mineralogical, and thermal properties of these features have important implications outside the fields of seismology and mineral physics, constraining as they do the overall dynamics of the Earth's interior, the deep return flow for plate tectonics, and the geochemical signatures of source regions of igneous rocks.

In the period 1987–1990, great strides have been made in identifying and characterizing mantle discontinuities from a seismological standpoint. Advances in detailed observation of reflected and converted phases, analysis of multiple ScS reverberations, stacking of global digital data, application of seismometer arrays, and broadband data collection have permitted improved determination of the location, magnitude, and sharpness (depth-extent) of rapid seismic velocity changes in the mantle. Notable among such advances are the global stacking study of *Shearer* [1990] and the SH-polarized mantle reverberation studies of *Revenaugh and Jordan* [1987, 1989, 1990a, 1990b] which systematically investigate the fine structure of seismic velocity variations in the mantle.

Important progress has also been made in understanding the physical and chemical properties of mantle discontinuities by better constraining the effects of pressure, temperature, and compositional variations upon the crystal structures and elastic moduli of the mantle's constituent minerals. Advances in multi-anvil press and diamond-anvil cell high-pressure technology, calorimetric study of mineral thermochemical properties, synchrotron radiation analysis of crystal structures, and first-principles computation of crystal properties have allowed better constraints upon both the stability fields and thermoelastic properties of mantle mineral assemblages. Notable among these advances are the detailed experimental study of post-spinel phase transformations by *Ito and Takahashi* [1989] and the subsequent thermodynamic analysis by *Wood* [1989, 1990].

Taken together, these advances allow more meaningful correlation of seismological features with mineralogical changes. While this permits the placing of stronger constraints upon the composition, structure, and dynamics of the interior, there remain significant uncertainties and ambiguities. Here I review fundamental advances in both the seismological and mineralogical understanding of mantle discontinuities which have taken place during the period 1987–1990, as well as briefly discussing some implications for mantle thermal structure and dynamics. While I have endeavored to compile as complete a reference list as possible, the lesser number of references directly discussed in the text necessarily reflects my own interests and familiarity with the literature. I conclude by outlining the picture of mantle structure and composition which is emerging from these efforts while indicating the remaining major uncertainties.



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## SEISMOLOGY

The seismological characterization of mantle discontinuities in both the upper and lower mantle has followed several avenues of inquiry. Investigation has focused upon establishing the presence or absence of seismic discontinuities, determining whether they are global or local in extent, measuring the topographic variability of their depth of occurrence, and quantifying the magnitude and sharpness of their velocity changes. In addition to numerous local and regional studies, notable advances of the last four years include the use of SH-polarized mantle reverberations [*Revenaugh and Jordan*, 1987, 1989, 1990a, 1990b] and the stacking of five years of global long-period data [*Shearer*, 1990] to better constrain the fine structure of mantle seismic discontinuities. Work continues [B. Kennett, pers. comm., 1989] on a new radial Earth model (IASPR) to fit global body-wave travel times more closely than the currently-used radial model PREM [*Dziewonski and Anderson*, 1981] while retaining those features of PREM structure which provide a good fit to free oscillation data. Recently reported depths and magnitudes of mantle seismic discontinuities are summarized in Table 1.

Below the crust-mantle boundary, upper mantle seismic velocity structure is dominated by a velocity increase at about 410 km depth, followed by an anomalously high velocity gradient throughout the region between this 410 km discontinuity and the base of the upper mantle near 660 km depth. Recent work also indicates the presence of a smaller velocity increase near 520 km depth, as well as suggesting that reported velocity discontinuities near 220 km depth cannot be globally coherent features. Lower mantle velocity structure is dominated by a sharp velocity increase at about 660 km depth, marking the boundary between the upper and lower mantle, and by the core-mantle boundary (CMB) at 2890 km depth. The lowermost 200–300 km of the mantle (the D″ layer), just above the CMB, is characterized by anomalous velocity structures, consistent with the presence of a velocity discontinuity with strongly laterally varying properties.

TABLE 1. Summary of Reported Mantle Seismic Discontinuities

| Depth (km) | Study | Reference | Characteristics |
|---|---|---|---|
| 67 | S | Revenaugh [1989] | 5-8% impedance contrast |
| 86 | S | Revenaugh and Jordan [1989] | observed, W Pacific |
| 75-225 | S | Graves and Helmberger [1988] | LVZ, old Pacific |
| upper 100 | S | Revenaugh [1989] | LVZ onset, oceanic and tectonic, base not detected |
| 165-215 | P | LeFevre and Helmberger [1989] | LVZ, Canadian shield |
| 200 | P | Bowman and Kennett [1990] | 3.3% $V_P$ increase, NW Australia |
| ~220 | P,S | Shearer [1990] | not detected |
| ~220 | S | Revenaugh and Jordan [1989] | not detected, W Pacific |
| 232 | S | Revenaugh [1989] | 4% impedance contrast, NWC Australia |
| 300 | P'P' | Wajeman [1988] | Eurasia |
| 400 | P | Bowman and Kennett [1990] | 5.6% $V_P$ increase, NW Australia |
| 405 | P | LeFevre and Helmberger [1989] | 5% $V_P$ increase, Canadian shield |
| 405 | S | Graves and Helmberger [1889] | 3.6% $V_S$ increase, old Pacific |
| 410 | P,S | Shearer [1990] | topography <20 km |
| 414 | S | Revenaugh and Jordan [1987, 1989, 1990a,b] | refl. coef. 0.046±0.010, topog. ~12 km |
| 415 | P'P' | Nakanishi [1988,1989] | intermittent |
| 520 | P,S | Shearer [1990] | 3% impedance contrast |
| 520 | S | Revenaugh and Jordan [1990b] | reflection coef. 0.014 |
| 630 | P | Bowman and Kennett [1990] | 3.9% $V_P$ increase, NW Australia |
| 655 | P'P' | Nakanishi [1988,1989] | sharp |
| 659 | S | Graves and Helmberger [1889] | 6.8% $V_S$ increase, old Pacific |
| 660 | P | LeFevre and Helmberger [1989] | 4% $V_P$ increase, Canadian shield |
| 660 | P,S | Shearer [1990] | topography <20 km |
| 660 | S | Revenaugh and Jordan [1987, 1989, 1990a,b] | refl. coef. 0.072±0.010, topog. ~12 km, slab def. <40 km |
| 670 | P'P' | Davis et al. [1989] | not detected → 10 km topog. |
| 670 | P'P' | Wajeman [1988] | 7.5% $V_P$ contrast, Eurasia |
| 670 | P→S | Paulssen [1988] | sharp |
| 660-680 | S→P | Richards and Wicks [1990] | slab def. <50 km, Tonga |
| 710 | S | Revenaugh and Jordan [1989, 1990b] | refl. coef. ~0.020, tentative |
| 840 | P,S | Shearer [1990] | tentative |
| 900 | S | Revenaugh and Jordan [1989, 1990b] | tentative |
| 2546 | P | Baumgardt [1989] | 2.75% $V_P$ increase |
| 2600 | P | Davis and Weber [1990] | 3% $V_P$ increase, N Siberia |
| 2610 | S | Young and Lay [1987a] | 2.75% $V_S$ increase, Indian Ocean |
| ~2610 | S | Revenaugh and Jordan [1989] | not detected, W Pacific |

Studies are of P-waves (P), S-waves (S), both (P,S), underside reflections (P'P'), and converted phases (P→S, S→P). LVZ denotes low velocity zone. Magnitudes are given as velocity increases, impedance contrasts, or normal-incidence reflection coefficients. Also noted are long-wavelength topography and apparent deformation by subducting slabs.

While there is a general lack of evidence for additional significant global discontinuities, minor velocity discontinuities tentatively have been suggested at intermediate depths in the lower mantle, and seismic reflectors also have been observed in subducting slabs. An additional conclusion of recent studies is that the 410 and 660 km discontinuities exhibit only small variations in depth, comprising perhaps 20–40 km of relief.

### *Shallow Mantle Discontinuities*

Using SH-polarized mantle reverberations, *Revenaugh* [1989] reports a reflector with a 5–8% impedance contrast at 67 km depth in the mantle, which he attributes to the phase transition from spinel lherzolite to garnet lherzolite. In addition, *Revenaugh and Jordan* [1989] find strong evidence for a discontinuity beneath the western Pacific, located at 86 km depth (or, ambiguously, in the lower 170 km of the mantle), which they suggest may represent the onset of partial melting.

In the ongoing debate over the question of a possible 220 km discontinuity, the stacking of five years of long-period P- and S-wave data by *Shearer* [1990] reveals no evidence for such a feature. This suggests that the discontinuity, which appears to be required in certain regional studies, cannot be a globally coherent feature. *Revenaugh and Jordan* [1989], using SH-polarized mantle reverberations, find no evidence for this discontinuity beneath the western Pacific. In modeling short-period waveforms from a hybrid array, however, *Bowman and Kennett* [1990] require the presence of a 3.3% velocity increase near 200 km depth in their upper mantle P-wave velocity profile (NWB-1) for northwest Australia. Furthermore, *Revenaugh* [1989] finds evidence for a 4% impedance contrast at 232 km depth beneath west-central and northern Australia using SH-polarized mantle reverberations. *LeFevre and Helmberger's* [1989] upper mantle P-wave velocity profile (S25) for the Canadian shield, determined from waveform modeling of long-period data, contains a low velocity zone in the 165–215 km depth range. *Graves and Helmberger's* [1988] upper mantle model for the old Pacific (PAC), derived from waveform modeling of long-period multibounce SH-waves, exhibits a low velocity zone in the 75–225 km depth range. *Revenaugh* [1989] reports evidence from mantle reverberations for the onset of a low velocity zone in the upper 100 km of oceanic and tectonically active regions, but he finds no evidence for a sharp (less than 50 km depth-extent) base to the low velocity zone.

### *The 410 km Discontinuity*

*Shearer's* [1990] global stacking study yields a best-fitting depth of 410 km for the "400 km discontinuity", with topography of less than 20 km. Using SH-polarized $ScS_n$ and $sScS_n$ mantle reverberations, *Revenaugh and Jordan* [1987, 1989, 1990a, 1990b] obtain a normal-incidence reflection coefficient of 0.046±0.010 at a depth of 414 km, for which they suggest a $V_S$ contrast of about 5.4% and a density contrast of 3.9%. Their travel time correlations are consistent with an exothermic (*i.e.*, positive P–T slope) phase transition near 400 km, with about 12 km of long-wavelength topography on the boundary. *Bock* [1988] reports observation of S–P conversions from 400 km depth beneath Australia, indicating that this discontinuity, at least locally, is quite sharp.

Furthermore, *Bowman and Kennett's* [1990] upper mantle P-wave velocity profile (NWB-1) for northwest Australia, from waveform modeling of short-period array data, prescribes an unusually large (5.6%) 400 km discontinuity in this area. Their study is also notable in that it prescribes only three mantle velocity discontinuities (at 200, 400, and 630 km depth) for this Australian region, rather than the numerous discontinuities evident in earlier studies [*e.g.*, *Leven*, 1985].

Using waveform modeling of long-period data, *LeFevre and Helmberger* [1989] determined an upper mantle P-wave velocity profile (S25) for the Canadian shield, complementing the S-wave velocity profile (SNA) previously determined by *Grand and Helmberger* [1984] for the same region and prescribing a 5% $V_P$ increase at 405 km depth. Their study reinforces earlier conclusions that contrasts in velocity profiles between shields and tectonically active regions drop to less than 1% below 400 km depth, a conclusion also supported by *Grand's* [1987] S-wave tomographic inversion below North America.

*Graves and Helmberger's* [1988] upper mantle model for the old Pacific (PAC), derived from waveform modeling of long-period multibounce SH-waves, exhibits a 3.6% S-wave velocity increase at 405 km depth.

### *The 520 km Discontinuity*

The question of whether an additional discontinuity between those at 410 and 660 km depth is required by seismological observations has long been a topic of debate, as such a feature was occasionally suggested by older refraction and slowness data [*e.g.*, *Fukao et al.*, 1982]. Upon stacking five years of long-period data, *Shearer* [1990] has observed two seismic phases which indeed appear to arise from a discontinuity near 520 km depth with an impedance contrast of roughly 3%. Using SH-polarized mantle reverberations, *Revenaugh and Jordan* [1990b] find evidence for a minor reflector near 520 km depth with a normal-incidence reflection coefficient of approximately 0.014.

### *The 660 km Discontinuity*

The best-fitting depth to the "670 km" upper/lower mantle boundary obtained by *Shearer's* [1990] global stacking study is 660 km, with topography of less than 20 km. By observing SH-polarized $ScS_n$ and $sScS_n$ mantle reverberations, *Revenaugh and Jordan* [1987, 1989, 1990a, 1990b] obtain a normal-incidence reflection coefficient of 0.072±0.010 at 660 km, for which they suggest a $V_S$ contrast of about 8.5% and a density contrast of 6.1%. Their travel time correlations are consistent with endothermic (*i.e.*, negative P–T slope) phase transitions near 650 km, with about 12 km of long-wavelength topography on the boundary. They find evidence for no more than 30–40 km of topography on the 660 km discontinuity beneath areas of deep subduction, considerably less than that predicted by rigorously stratified mantle models.

*Davis et al.* [1989] extend the search for elusive precursors to P′P′ by examining broadband data; they conclude that the almost total absence of such underside reflections from mantle discontinuities can be explained by either degrading the large, sharp impedance contrast across the 670 km discontinuity given by PREM [*Dziewonski and Anderson*, 1981] or by imposing 10 km topography on the discontinuity over 300 km length scales. *Wajeman* [1988], on the other hand, observes underside P-reflections from 670 km and 300 km depths beneath Eurasia upon stacking broadband data, with amplitude ratios consistent with an anomalously large (7.5%) $V_P$ contrast at 670 km. *Nakanishi* [1988, 1989] discusses constraints upon mantle discontinuities and their topography from P′P′ precursors, reporting such underside reflections from 655 km depth and somewhat weaker and more intermittent precursors from 415 km depth. *Paulssen* [1988] observes P-to-S converted phases from the 670 km discontinuity on short-period and broadband records, indicating that this discontinuity is, at least locally, very sharp. Details of waveform modeling of S-to-P conversions from mantle discontinuities are discussed by *Douglas et al.* [1990].

Other constraints on the depth and magnitude of this discontinuity have come from regional waveform modeling studies. Using long-period data, *LeFevre and Helmberger* [1989] determined an upper mantle P-wave velocity profile (S25) for the Canadian shield which features a 4% increase at 660 km depth. Using short-period data from a hybrid array, *Bowman and Kennett* [1990] constructed an upper mantle P-wave velocity profile (NWB-1) for northwest Australia, finding a 3.9% velocity increase at 630 km depth. From waveform modeling of long-period multibounce SH-waves, *Graves and Helmberger* [1988] derived an upper mantle model for the old Pacific (PAC) which exhibits a 6.8% S-wave velocity increase at 659 km depth.

### *Other Deep Mantle Discontinuities*

*Revenaugh and Jordan* [1989, 1990b], using SH-polarized mantle reverberations, find tentative evidence for a small impedance increase (reflection coefficient about 0.020) at 710 km and another at 900 km depth. On the basis of observed P- and S-wave multiples, *Shearer* [1990] suggests a possible discontinuity near 840 km depth. The compositional implications of variations in the seismic Poisson's ratio for the lower mantle are discussed by *Poirier* [1987].

### *The Core–Mantle Boundary Region*

*Young and Lay* [1987a] investigated the structure of the D″ layer beneath India and the Indian Ocean using SH and sSH seismograms, finding an abrupt 2.75% increase in $V_S$ about 280 km above the CMB. This is consistent with previous work by Lay and Helmberger in other regions, with the added complication that a negative $V_S$ gradient is required between this feature and the CMB. The case for such a discontinuity, as opposed to scattering or diffraction hypotheses, is analyzed by *Young and Lay* [1990]. *Davis and Weber* [1990] find evidence for a 3% increase in $V_P$ about 290 km above the CMB beneath northern Siberia using broadband data from the Gräfenberg (GRF) array, and *Baumgardt* [1989] finds evidence from short-period data for a 2.75% $V_P$ increase about 344 km above the CMB. Furthermore, these authors suggest that this may not be a coherent global feature but may be restricted to distinct localities and may exhibit depth variations of up to 50 km. *Revenaugh and Jordan* [1989], using SH-polarized mantle reverberations, find no evidence for this D″ discontinuity beneath the western Pacific.

Using slownesses of diffracted arrivals, *Wysession and Okal* [1988, 1989] find evidence for fast velocities in D″ beneath Asia and the eastern Pacific and slow velocities beneath New Guinea and the Solomon Islands, with variations of 3.1% and 3.5% in $V_P$ and $V_S$, respectively, in D″. Lateral velocity variations are further discussed by *Garnero et al.* [1988] and *Young and Lay* [1989], and scattering by inhomogeneities near the CMB is discussed by Haddon and *Buchbinder* [1987], *Bataille and Flatté* [1988], and *Doornbos* [1988]. From travel time residuals, *Morelli and Dziewonski* [1987] infer 6 km relief on the CMB. The dynamics and the seismological and thermal structure of D″ and the CMB are thoroughly reviewed by *Young and Lay* [1987b] and *Lay* [1989].

### *Subducting Slab Discontinuities*

Within the double-planed seismic zone beneath the Kanto district of Japan, *Obara and Sato* [1988] and *Obara* [1989] report S-wave reflections from 80–100 km depth, for which they suggest that the large impedance contrast may be due to the presence of liquid bodies or a low velocity layer near the upper surface of the subducting Pacific plate. *Helffrich et al.* [1989] undertook a thorough investigation of subduction zone seismic reflectors, ascribing some features to the possible elevation of exothermic phase transitions in the downgoing slab and others to preferred orientation of mineral textures.

From examination of P- and S-wave travel time anomalies, *Krishna and Kaila* [1987] conclude that the 400 km and 670 km seismic discontinuities are elevated in the subducting slab in the Tonga–Kermadec region relative to the surrounding mantle. From analysis of travel time residuals, however, *Iidaka and Suetsugu* [1990] find that the 400 km discontinuity is deflected downward, rather than upward, in the subducting slab beneath Japan. This suggests [*Geller*, 1990] that $\alpha$ olivine persists metastably into the modified spinel or spinel stability field in the downgoing slab, in accord with the transformation faulting hypothesis of *Kirby et al.* [1990] for the origin of deep earthquakes.

*Wajeman and Souriau* [1987] report P–S conversions from a dipping (20°) reflector beneath Kerguelen, located ambiguously at either 880 km or 600 km depth. *Richards and Wicks* [1990] report short-period S-to-P conversions beneath Tonga from 660–680 km depth in the northern part of the subduction zone and from 660–700 km depth in the southern portion. Since their observed rays travel within the subducted slab, they conclude that the slab deforms the 670 km discontinuity by less than 50 km. This is consistent with a phase transition origin for the discontinuity, since deformation greater than 100 km would be expected for a chemical discontinuity [*e.g.*, *Kincaid and Olson*, 1987].

## MINERAL PHYSICS

Investigation of the physics of mineralogical changes in phase or chemistry which may be associated with mantle seismic discontinuities has pursued two main courses. Firstly, the refinement of equilibrium phase relations between mantle mineral assemblages permits the determination of the depth of occurrence and sharpness of phase transitions in various mantle compositional models. Furthermore, the measurement of mineral thermochemical properties allows the thermodynamic calculation of such phase boundaries under conditions of pressure, temperature, and composition outside of the regime in which phase equilibrium experiments were performed. Notable advances in this area include the detailed experimental study of post-spinel phase transformations by *Ito and Takahashi* [1989] and the subsequent thermodynamic analysis of *Wood* [1989, 1990]. Secondly, determination of the thermoelastic properties of mineral phases allows better calculation of the densities and seismic velocities of candidate mineral assemblages as functions of pressure, temperature, and composition, thus permitting direct comparison of compositional models with seismic velocity profiles. In this area, notable advances include the calculation of densities for various lower mantle compositional models by *Jeanloz and Knittle* [1989], using their measured perovskite thermoelastic properties, and the comparison of these model calculations to seismological density estimates.

Below the low velocity zone, upper mantle mineralogy is dominated by two sets of phase transformations: the olivine-spinel transitions and the eclogite-garnetite transitions. In the former, the $\alpha$ phase of olivine transforms to the $\gamma$ spinel structure with increasing depth, passing through the intermediate $\beta$ modified-spinel structure in compositions with high Mg/Fe ratios. In the latter, Alpoor pyroxene gradually dissolves into Al-rich garnet with increasing depth to form a garnet-majorite solid solution. Additional phase changes and some degree of partial melting may also occur at shallower depths. Lower mantle mineralogy is dominated by the perovskite transformations: that of $\gamma$ spinel to perovskite plus magnesiowüstite and that of garnet-majorite to perovskite. The possible stability of silicate ilmenite phases and further high pressure structural changes in perovskite or in stishovite ($SiO_2$) have also been suggested.

The construction of mantle mineralogical profiles for model bulk compositions and the calculation of their associated seismic velocity profiles continues. *Weidner and Ito* [1987] computed mineralogies and seismic velocity profiles for different mantle compositions, concluding that while a uniform pyrolite composition is compatible with available data, uncertainties are sufficiently large as to permit a wide variety of compositions. *Duffy and Anderson* [1989], too, obtain a wide range of acceptable compositions but suggest that the more eclogitic compositions are more suitable. Similar calculations by *Akaogi et al.* [1987] and *Bina* [1987] suggest that peridotitic compositions, such as pyrolite, provide a better fit to seismological data than more eclogitic compositions. *Irifune* [1987], *Irifune and Ringwood* [1987a], and *Bina and Wood* [1987] also find a good fit with pyrolite, and *Bina* [1989] notes that such compositional estimates depend not only upon the assumed elastic moduli pressure and temperature derivatives but also upon choice of seismic velocity parameterization. The major phase changes expected to occur in the mantle and in subducting slabs are reviewed by *Anderson* [1987].

### *Low Velocity Zones*

The presence in many velocity profiles of a low velocity zone in the uppermost mantle, falling somewhere between 50 km and 220 km depth, is often taken to indicate the presence of partial melt at these depths. However, *Sato et al.* [1988, 1989] and *Sato and Sacks* [1989] measured seismic velocities in peridotites as functions of partial melt fraction and homologous temperature (*i.e.*, the ratio of temperature T to the solidus temperature $T_m$). They find that seismic velocities, like the attenuation $Q^{-1}$, exhibit a strong homologous temperature dependence, and they conclude that a velocity drop of up to 6% in the low velocity zone can be accommodated merely by the effects upon velocities of subsolidus temperature increases. Thus, partial melts need not be ubiquitous throughout low velocity zones.

### *Olivine–Spinel Transitions*

An experimental phase equilibrium study of the olivine-spinel transitions by *Katsura and Ito* [1989] confirms that the $\alpha$ olivine to $\beta$ modified-spinel (ringwoodite) transition occurs exothermically (*i.e.*, with positive P–T slope) at pressures and temperatures appropriate to approximately 400 km depth. They also determined that this transition occurs over a narrow pressure interval, narrowing further with increasing temperature, in agreement with the predictions of *Bina and Wood's* [1987] thermodynamic analysis. *Katsura and Ito* [1989] also determined the conditions under which the more gradual $\beta$ modified-spinel to $\gamma$ spinel transformation occurs. *Yagi et al.* [1987a] report *in situ* observation of the $\alpha$–$\gamma$ transition in $Fe_2SiO_4$ using synchrotron radiation.

Analyses of the thermochemical properties of the olivine polymorphs were performed using calorimetry [*Ashida et al.*, 1987; *Watanabe*, 1987; *Akaogi et al.*, 1989], shock wave analysis [*Brown et al.*, 1987], and spectroscopy [*Hofmeister et al.*, 1989]. The crystal chemistry of the $\beta$ phase is discussed by *Sawamoto and Horiuchi* [1990]. Using the most recent available thermodynamic and phase equilibrium data, thorough thermodynamic modeling of the olivine phase transformation series was performed by *Akaogi et al.* [1989] and by *Fei et al.* [1990a, 1990b]. The stress-dependence of the transformation mechanism of the $\alpha$–$\gamma$ transition in the $Mg_2GeO_4$ olivine analogue was studied by *Burnley and Green* [1989], while the kinetics of these phase transitions in germanates were investigated by *Will and Lauterjung* [1987]. *Rubie et al.* [1990] found the kinetics of the $\alpha$–$\gamma$ transition in a nickel silicate olivine analogue to be sufficiently sluggish as to predict the metastable persistence of olivine to significant depth in slabs, thus supporting the seismological results of *Iidaka and Suetsugu* [1990].

Given the coincidence of the $\alpha$–$\beta$ transition and the 410 km seismic discontinuity, upper mantle composition may be estimated by comparing the magnitude of the velocity increase in the Earth to the magnitude of that expected for the phase transition in olivine under upper mantle pressure and temperature conditions. Thus, it is important to constrain the thermoelastic properties of the olivine polymorphs. *D. L. Anderson* [1988] and *Duffy and Anderson* [1989] predicted pressure and temperature derivatives of the elastic constants of the olivine polymorphs through analyses of the systematics of other compounds. *Isaak et al.* [1989a] measured the elastic constants of $Mg_2SiO_4$ $\alpha$ olivine (forsterite) as functions of temperature using the rectangular parallelopiped resonance (RPR) method, and *Brown et al.* [1989] measured single-crystal $\alpha$ olivine elastic constants via a new impulsive scattering technique. *Gwanmesia et al.* [1990] report measurements of the pressure dependence of $\beta$–$Mg_2SiO_4$ elastic moduli, noting the strong dependence of upper mantle compositional estimates upon assumed values of elastic moduli temperature dependence.

The hypothesis that the $\beta$ phase of olivine might serve as a host for water in the upper mantle was put forward by *Smyth* [1987], and the occurrence of OH or $H_2O$ in this phase was confirmed spectroscopically by *McMillan et al.* [1987]. The possibility of water storage in mantle minerals has been pursued further [*Ahrens*, 1989; *Pool*, 1989; *Finger and Prewitt*, 1989; *Rossman and Smyth*, 1990], both with spectroscopic and structure-refinement techniques. *Finger et al.* [1989] determined the structure of the hydrous magnesium silicate "phase B" and concluded that it should be a stable host for water, at least in the upper mantle. If significant amounts of water can be accommodated in certain mantle phases, then phase transitions involving such minerals may mark changes in the degree of hydration of the mantle as well as the usual changes in its elastic properties.

*Eclogite–Garnetite Transitions*

The equilibrium phase diagram of the eclogite-garnetite transition in $MgSiO_3$ at high pressures and temperatures was determined experimentally by *Sawamoto* [1987]. Further experimental studies of the eclogite-garnetite transitions performed by *Irifune* [1987] and *Irifune and Ringwood* [1987a, 1987b] confirm that these transitions occur in a gradual multivariant (*i.e.*, continuous) fashion, as predicted by the thermodynamic analysis of *Bina and Wood* [1984], rather than in the nearly univariant (*i.e.*, sharp) fashion necessary to produce a seismic discontinuity. *Gasparik* [1989] reports experimental results on the dissolution of sodium-bearing pyroxene phases into garnet-majorite solid solutions. Calorimetric analyses of garnet, ilmenite, and perovskite thermochemical properties were performed by *Navrotsky* [1987].

With regard to the thermoelastic properties of garnetite phases, *Akaogi et al.* [1987] measured garnet elasticity along the enstatite-pyrope join in addition to performing a thermodynamic analysis of the eclogite-garnetite transitions. They concluded that these phase transitions do not produce any abrupt elasticity changes, in agreement with *Bina and Wood's* [1984] earlier thermodynamic model, and that bulk sound velocities calculated for pyrolite are in general agreement with mantle seismic velocity profiles. The elastic properties of garnet-majorite solid solutions were determined by *Yagi et al.* [1987b] using synchrotron radiation at high pressures and temperatures. *Bass* [1989] measured the elastic properties of grossular and spessartite garnet by Brillouin spectroscopy.

*Perovskite and Magnesiowüstite Transitions*

The ferromagnesian silicate perovskite phase equilibrium experiments of *Ito and Takahashi* [1989] reaffirm that the endothermic transformation of $\gamma$ spinel to perovskite plus magnesiowüstite occurs under pressure and temperature conditions appropriate to approximately 670 km depth. Moreover, they also demonstrate that the transition takes place over a depth interval of less than 6 km, thus occurring in the very sharp (nearly univariant) fashion necessary to produce a sharp seismic discontinuity. Based upon thermodynamic analysis of their data, *Wood* [1989, 1990] demonstrates that this maximum width is independent of the uncertainties in iron-magnesium partitioning. The partitioning of iron in perovskite is also discussed by *Jackson et al.* [1987] and *Wright and Price* [1989], while *Guyot et al.* [1988] present the results of diamond-anvil cell experiments on Fe–Mg partitioning between perovskite and magnesiowüstite.

*Irifune and Ringwood* [1987a] report exsolution of calcium silicate perovskite from Ca-bearing garnet-majorite solid solutions under certain upper mantle conditions. High pressure studies of $CaMgSi_2O_6$ diopside by *Irifune et al.* [1989] indicate that $CaSiO_3$ forms a cubic perovskite phase distinct from the $MgSiO_3$ orthorhombic perovskite, with a restricted mutual solubility of about 2%, in agreement with the results of *Tamai and Yagi* [1989] and *Irifune and Ringwood* [1987a]. The contrary finding of extensive mutual solubility by *Liu* [1987] and by *Takahashi and Ito* [1987] and *Ito and Takahashi* [1987b] may be due to analytical difficulties attendant upon the small sample size. *Mao et al.* [1989] found cubic perovskite to be the stable phase of $CaSiO_3$ under all lower mantle conditions, in agreement with the results of *Yagi et al.* [1989] and *Tarrida and Richet* [1989] and the predictions of *Hemley et al.* [1987] and *Wolf and Bukowinski* [1987]. *Kato et al.* [1987a, 1988b] find that calcium silicate perovskite is a ready host for many normally incompatible elements. A possible additional aluminocalcic lower mantle phase is proposed by *Madon et al.* [1989].

With regard to perovskite thermochemical properties, calorimetric analyses of garnets, ilmenites, and perovskites were performed by *Navrotsky* [1987] and spectroscopic analyses were reported by *Madon and Price* [1989]. *Williams et al.* [1987b, 1989] analyzed the vibrational spectrum of $MgSiO_3$ perovskite, and a computational model for ilmenite and perovskite phases was constructed by *Matsui et al.* [1987]. *Liu et al.* [1988] investigated the orthorhombic-tetragonal phase change in the germanate analogue of Ca-perovskite. Enstatite-perovskite transition kinetics are discussed by *Knittle and Jeanloz* [1987a].

Measurements of the elasticity of magnesiowüstite were extended by *Richet et al.* [1989] to 50 GPa and by *Isaak et al.* [1989b] to 1800 K. *Mehl et al.* [1988] and *Isaak et al.* [1990] also performed theoretical analyses of MgO properties at high pressures and temperatures. *Kubicki* [1988] pursued molecular dynamics modeling of both perovskite and MgO equations of state.

The determination of the thermoelastic properties of perovskites remains an active field of research. Experimental studies of the elastic properties of Mg-perovskite have been performed by *Horiuchi et al.* [1987], *Knittle and Jeanloz* [1987b], *Kudoh et al.* [1987, 1989], *Ross and Hazen* [1989, 1990], and *Yeganeh-Haeri et al.* [1989], while *Cohen* [1987b], *Bukowinski and Wolf* [1988], and *Hemley et al.* [1989] undertook theoretical studies of perovskite elasticity. A theoretical analysis of the stability and elasticity of Mg and Ca perovskites was performed by *Wolf and Bukowinski* [1987] who concluded that both pyrolite and pyroxenite lower mantle compositions are compatible with seismic data, and *Bukowinski and Wolf* [1990] noted the inherent biases in extracting lower mantle compositional estimates from adiabatic decompression analyses. *Mao et al.* [1989] conclude that the density and bulk modulus of cubic $CaSiO_3$ perovskite are so similar to those of ferromagnesian silicate perovskite as to render the calcic phase nearly indistinguishable seismologically. *Fischer et al.* [1989] studied a strontium titanate perovskite analogue.

Upon comparing the densities calculated for various lower mantle mineralogies to lower mantle seismological profiles, *Jeanloz and Knittle* [1989] concluded that the lower mantle must be enriched in iron relative to a pyrolitic upper mantle. *Bina and Silver* [1990] show that bulk sound velocity data require such iron enrichment to be accompanied by silica enrichment, but they also demonstrate the sensitivity of such conclusions to uncertainties in the mineralogical and seismological data. In particular, hypotheses as to compositional differences between the upper and lower mantle hinge primarily upon the behavior of the volume coefficient of thermal expansion ($\alpha$) of perovskite with increasing pressure and temperature. Debate continues over the behavior of the perovskite thermal expansion coefficient ($\alpha$) at high temperatures [*Jeanloz and Knittle*, 1989; *Ross and Hazen*, 1989; *Navrotsky*, 1989; *Hill and Jackson*, 1990] and its dependence ($\delta_T$) upon pressure [*Wolf and Bukowinski*, 1987; *Cohen*, 1987b; *D. L. Anderson*, 1988; *Hemley et al.*, 1989]. Results with respect to the latter are particularly polarized, with some [*Chopelas*, 1990a, 1990b; *Chopelas and Boehler*, 1989; *Anderson et al.*, 1990; *Reynard and Price*, 1990] advocating a pressure-independent $\delta_T$ while others [*Isaak et al.*, 1990; *Agnon and Bukowinski*, 1990] conclude that $\delta_T$ is pressure-dependent.

*Kato et al.* [1987b] performed high pressure melting experiments demonstrating that majorite garnet fractionation from a chondritic parental mantle — a hypothesis suggesting a silica-enriched lower mantle composition — cannot explain the subchondritic silica content of the upper mantle. Chemical stratification by early-stage melting is discussed by *Ohtani* [1988]. Additional melting experiments are discussed by *Heinz and Jeanloz* [1987], *Ito and Takahashi* [1987a], *Kato et al.* [1988a], *Agee et al.* [1989], *Bassett and Weathers* [1989], and *Knittle and Jeanloz* [1989a].

### *Silica Transitions and Reactions*

While most models of mantle composition are undersaturated in silica ($SiO_2$), the possibility remains that free silica might be present in the mantle. In this case, transitions between the silica polymorphs — quartz, coesite, stishovite, and possibly others — could be important in determining mantle structure. The elastic properties of stishovite were measured experimentally to 16 GPa pressure by *Ross et al.* [1990]. *Hemley* [1987] examined the thermodynamics and stability of silica polymorphs using pressure-dependent Raman spectroscopy, and *Cohen* [1987a] studied stishovite instabilities numerically using a potential-induced breathing model. *Park et al.* [1988], on the basis of first-principles electronic structure calculations, predict a modified flourite ($Pa\bar{3}$) structure for $SiO_2$ at pressures greater than about 60 GPa. *Tsuchida and Yagi* [1989] find experimentally that stishovite transforms to the $CaCl_2$ structure at pressures appropriate to the base of the mantle, with a volume change of less than 1%.

From experimental studies, *Knittle and Jeanloz* [1989b] suggest that free silica, as well as Fe–Mg–O and Fe–Si alloys, may form from complex chemical reactions between mantle and core in the D″ region. Simple chemical relationships near the CMB are discussed by *Sherman* [1989] and *Svendsen et al.* [1989]. Based upon thermodynamic analysis of silicate melting relations, *Stixrude and Bukowinski* [1990] conclude that silicate perovskite cannot be a stable constituent of the D″ region, proposing instead a mixture of magnesiowüstite and $SiO_2$. *Jeanloz* [1989] points out that extrapolation of *Tsuchida and Yagi's* [1989] phase boundary for the stability of the $CaCl_2$ form of $SiO_2$ to lower mantle pressures and temperatures places the transition at 270±160 km above the CMB, thus making it a plausible contributor to D″ seismic structure.

## THERMAL STRUCTURE AND DYNAMICS

The coincidence of mantle seismic discontinuities and phase transitions can be used to place constraints upon mantle geotherms. Using the most recent experimentally determined phase diagrams, *Ito and Katsura* [1989] calculated a model temperature profile for a mantle transition zone of $(Mg_{0.89}Fe_{0.11})_2SiO_4$ composition. By requiring the $\alpha \rightarrow \beta$ and $\gamma \rightarrow$pv+mw transitions to coincide with the 400 km and 670 km discontinuities, respectively, they find that mantle temperatures should increase from about 1400°C near 350 km depth to 1600±100°C at 655±5 km depth, a temperature gradient which is nearly adiabatic. In contrast, *Jeanloz and Morris* [1987] argue that the lower mantle geotherm should be significantly subadiabatic.

The question of whether mantle seismic discontinuities represent isochemical phase transformations or whether they constitute changes in bulk chemical composition is of profound importance for mantle dynamics. While subducting slab material may penetrate a phase transition boundary with little resistance, the intrinsic density contrast associated with a chemical discontinuity may constitute a serious impediment to throughgoing convection [*e.g.*, *Christensen and Yuen*, 1984]. Having significant bearing upon this question is the observation [*Revenaugh and Jordan*, 1987, 1989, 1990a, 1990b; *Davis et al.*, 1989; *Shearer*, 1990] that the 410 and 660 km discontinuities exhibit less than 20 km of topographic variation in their depth of occurrence. Furthermore, the 660 km discontinuity is found [*Revenaugh and Jordan*, 1987, 1989, 1990a, 1990b; *Richards and Wicks*, 1990] to be deflected by less than 50 km beneath subduction zones. Since a subducting slab would be expected to deflect a chemical boundary by more than 100 km [*e.g.*, *Kincaid and Olson*, 1987], these observations argue against a mantle which is chemically stratified at transition zone seismic discontinuities and support the hypothesis of convective mass transfer from the upper to the lower mantle.

The kinetics of phase transformations in cold slab material also have implications for mantle dynamics. Under the common assumption of chemical equilibrium within the slab [*e.g.*, *Helffrich et al.*, 1989], the exothermic $\alpha \rightarrow \beta$ transition in olivine would be deflected upwards from its usual occurrence at 400 km to shallower depths within the subduction zone. Such an upward deflection of the phase boundary would impart a negative buoyancy to slab material immediately below the boundary relative to the surrounding mantle. However, the possible metastable persistence of olivine in the slab [*Iidaka and Suetsugu*, 1990; *Geller*, 1990; *Rubie et al.*, 1990] reverses this scenario. The corresponding downward deflection of the olivine phase change would impart a positive buoyancy, relative to the surrounding mantle, to material immediately above the boundary.

The possible trapping between the upper and lower mantle of intrinsically buoyant components of subducted lithosphere is discussed by *Ringwood and Irifune* [1988] and *Christensen* [1988]. However, *Richards and Davies* [1989] present dynamical arguments against such separation of slab components during passage through the transition zone. The dynamical, geochemical, and seismological arguments for and against chemically distinct upper and lower mantles are thoroughly reviewed by *Silver et al.* [1988] and *Olson et al.* [1990].

## CONCLUDING REMARKS

The picture of mantle structure and composition which is emerging from these discontinuity-related studies is outlined below and in Figure 1. Our understanding of the crust-mantle boundary and the uppermost mantle, with its various and occasional reflectors and low velocity zones, is still somewhat uncertain. It does not appear necessary to invoke widespread partial melting to explain low velocity zones, however, since the hypothesis that high homologous temperatures can yield subsolidus velocity decreases has been demonstrated experimentally.

The 410 km discontinuity corresponds to the relatively sharp exothermic α–β transition in olivine. While upward deflection of this equilibrium phase change by cold slabs has been invoked to account for some seismic reflectors in subduction zones, recent evidence points to downward deflection of this phase transition due to sluggish kinetics in the cold slab interior. The smaller 520 km discontinuity corresponds to the broader exothermic β–γ transition in olivine. The high velocity gradient which extends from approximately 410 to 660 km depth corresponds to the significantly broader exothermic eclogite-garnetite transformation and possibly to the exsolution of calcium perovskite [*Gasparik*, 1990]; the onset or completion of either of these phase changes may also play a rôle in the 520 km feature. The possible role of silicate ilmenite in all of this is unclear, as it may only be stable in anomalously cold or silica-rich environments.

The 660 km discontinuity corresponds to the extremely sharp transformation of γ spinel to silicate perovskite and magnesiowüstite, with a somewhat broader transformation of garnet-majorite to perovskite occurring at a similar depth. The velocity increase 200–300 km above the core-mantle boundary, as well as other more tentative lower mantle features, may be related to subsequent distortions or breakdown of the perovskite structure, to the appearance of other aluminocalcic phases, to subsequent transformations in free silica, or to metal-silicate chemical reactions between mantle and core, to list a few possibilities.

Thus, the gross structure of the mantle is consistent with the occurrence of isochemical phase transformations in a mantle of uniform peridotitic bulk composition [*e.g.*, *Wood and Helffrich*, 1990]. While such isochemical phase transitions provide a good match to the characteristics of seismic discontinuities with regard to their sharpness and depth of occurrence, confident matching of the magnitudes of their associated velocity changes awaits

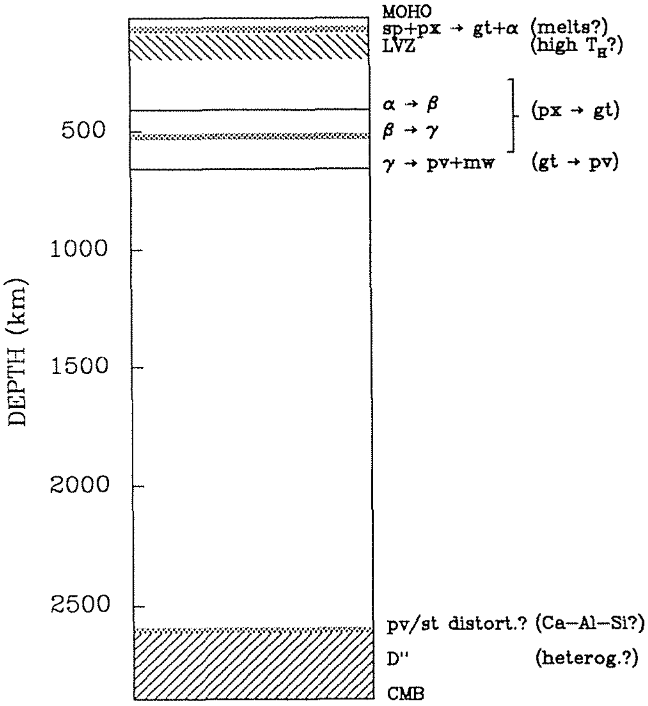


Fig. 1. Summary of mantle discontinuities and corresponding mineralogical changes. Sharp discontinuities are designated by solid lines. Phases are spinel (sp), pyroxene (px), garnet (gt), olivine (α), modified silicate spinel (β), silicate spinel (γ), silicate perovskite (pv), magnesiowüstite (mw), and stishovite (st). Also shown are crust-mantle boundary (MOHO), low velocity zone (LVZ), and core-mantle boundary zone (D″ and CMB).

better constraints upon mineral thermoelastic properties. A peridotitic upper mantle, perhaps approximating a pyrolite composition, is consistent with studies of mantle xenoliths [*e.g.*, *Schulze*, 1989], but precise constraints upon the silica content of the upper mantle must rely upon future determination of the temperature dependence of the elastic moduli of β and γ spinel [*cf. Gwanmesia et al.*, 1990]. The precise determination of upper mantle composition remains a matter for further study, and some degree of chemical heterogeneity may certainly be present, but currently available data and their uncertainties do not require chemical stratification within the upper mantle.

The resolution of possible differences in major element chemistry between the upper and lower mantle requires the determination of such subtle parameters as the temperature and pressure dependence of the volume coefficient of thermal expansion (α) for perovskite (*i.e.*, second- and third-order partial derivatives of density), as well as upon more detailed determination of mantle seismic velocities and densities [*cf. Bina and Silver*, 1990]. The dynamical implications of discontinuity topography [*e.g.*, *Richards and Wicks*, 1990], however, argue against such chemical stratification of the mantle. The anomalous velocity features in the lowermost 200 or 300 km of the lower mantle may be due to a variety of phenomena, from simple phase transformations in silica or aluminocalcic phases to radial and lateral variations in bulk chemical composition. Understanding of this D″

region must await more detailed seismological mapping of the core-mantle boundary as well as further experimental investigation of mineral behavior under lower mantle pressure and temperature conditions.

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