

Mineral physics of the mantle

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The last few years have seen intense interest in the global environment and climate change, and with it an increasing appreciation for the interactions between the atmosphere, biosphere, oceans and the solid earth. In solid earth geophysics, the traditional boundaries between the earth's fluid and solid spheres have been breached by the growing body of evidence that they may physically communicate on a massive scale, that atmospheric constituents, under certain conditions, may be transported to and stored within the deepest parts of the earth. Of course there has for some time been an appreciation for influence of mantle dynamics, the driving force of plate tectonics, volcanism, and seismicity, on surface processes. However, perhaps nothing illustrates the essential connections better than visualizing, now with some experimental and observational support, a tropospheric molecule, transported through sedimentary and tectonic agents 3000 km to the core-mantle boundary, only to rise again, perhaps many millions of years later in a volcanic eruption.

In this very brief review of a very large and rapidly growing field, I have made no attempt to be comprehensive. Because of space limitations, I have focused on only a few of the exciting developments since 1991 [see *Wolf et al.*, 1991 for a review of literature prior to 1991]. Included is recent work on the possible state of volatiles in the deep interior, especially on the structure and high pressure stability of volatile-bearing crystalline phases. These types of studies may eventually have their greatest impact on our understanding of the atmospheres and oceans, for the simple reason that 1 wt% H₂O, dynamically stored in the mantle, is equivalent to the weight of 30 hydrospheres. Volatiles, as well as phase-transition induced faulting and metastable wedges, have been enlisted to help explain the mechanisms by which sub-lithospheric earthquakes occur. Small amounts of volatiles can also have a large effect on transport properties, and phase stability, especially melting, and may eventually alter our understanding of bulk mantle composition and petrogenesis. The determination of hydrous melting and dehydration reactions at upper mantle pressures advanced considerably in the last few years, although our picture of lower mantle melting is in a state of flux. As the characterization of volatile-bearing phases continues, so does the pursuit of one of the central questions of mineral physics: determining the bulk composition of the mantle from seismological observations. Comparison of experimentally or theoretically determined equations of state is the only way we have of extracting compositional information from the high quality seismological data base. Complementing this extensive effort are a growing number of samples of the mantle below 200 km depth. Our understanding of the minor and trace element

chemistry of the mantle, and with it our understanding of the earth's origins, evolved substantially as traditional views of core-mantle equilibrium were challenged.

The last few years have seen major advances in the characterization of volatiles in nominally anhydrous phases, the stability of high pressure hydrous silicate phases, and understanding the behavior of more common volatile-bearing phases, such as calcite and micas. This work has given us a new picture of volatile distribution in the earth, one in which the volatile budget is not restricted to the oceans and atmospheres, but may be concentrated in the mantle.

There are certainly no shortage of mineral structures in which to store volatiles in the deep earth. Stabilization of OH in wadsleyite, a major transition zone phase, was anticipated on the basis of its unusual structure [*Smyth*, 1987]. Structurally a sorosilicate, but stoichiometrically an orthosilicate, this mineral contains oxygen atoms with undersaturated bonds which are ideal places to bind excess protons [0.4 wt% as H₂O; *Young et al.*, 1993]. Spectroscopic investigations of other nominally anhydrous phases, without such unusual structural features, show that nearly all common mantle minerals may host measurable quantities of water, ranging from 1-5 ppm H₂O by weight in olivine to 200-500 ppm in pyroxene [*Bell and Rossman*, 1992]. Stishovite [*Pawley et al.*, 1993], and a synthetic sample of MgSiO₃ perovskite [*Meade et al.*, 1994] were recently found to contain measurable amounts of hydrogen.

At least 8 high pressure phases have been proposed in the MgO-SiO₂-H₂O system [*Thompson*, 1992], with water contents ranging from 3-12 wt% and stability fields reaching 1700 K at 23 GPa [*Kanzaki*, 1991; *Gasperik*, 1993]. A crucial, but difficult aspect of the characterization of these phases is the determination of their crystal structures. Among the 8 proposed phases, the crystal structures of Phase B, superhydrous B and Phase E have been solved [*Finger et al.*, 1991; *Pacalo and Parise*, 1992; *Kanzaki et al.*, 1993]. Other important problems will be to investigate the effects of Fe and other elements on the stability of these phases and to determine their elastic properties [*O'Neill et al.*, 1993]. This will allow us to fit these potential new mantle phases into our seismologically based picture of deep earth composition. Characterization of rheological parameters and electrical conductivity [*Li and Jeanloz*, 1991] will also be important as diagnostics of mantle volatile content since transport properties are expected to depend strongly on H and C concentration. The high pressure behavior of other phases in this system, including the humite series [*Faust and Knittle*, 1994a], and other hydrous silicate phases, such as muscovite [*Faust and Knittle*, 1994b] are now being investigated.

The characterization of comparatively simple non-silicate volatile-bearing phases has progressed rapidly. The equations of state of portlandite [Ca(OH)₂; *Meade and Jeanloz*, 1989], diaspore [AlO(OH); *Xu et al.*, 1994; *Mao et al.*, 1994], magnesite [MgCO₃; *Redfern et al.*, 1993], calcite (CaCO₃), and dolomite (CaMgC₂O₆) [*Fiquet et al.*, 1994] have now been measured at room temperature to mantle pressures. In a pio-

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neering study, *Parise et al.* [1994] have determined deuterium positions in a deuterated brucite at high pressure, revealing an enhancement of hydrogen bonding relative to ambient conditions. Measurements at simultaneously high temperatures have been performed on brucite [Mg(OH)_2 ; *Duffy et al.*, 1991; *Fei and Mao*, 1993] and ice VII [*Fei et al.*, 1993] and have helped constrain the high pressure melting curve of ice and the stability of brucite. Raman studies of carbonate phases, including calcite, magnesite, aragonite and dolomite [*Kraft et al.*, 1991; *Williams et al.*, 1992; *Gillet et al.*, 1993] have demonstrated that these minerals have very wide stability fields, some extending into the shallow lower mantle.

Important issues which remain to be addressed are the temperature range of stability of many hydrous phases - are they stable only in relatively cold subduction environments, or are they also stable in the ambient mantle? The way in which these phases might be transported to the mantle also needs to be better understood [*Thompson*, 1992]. The problem is difficult because the presence of volatiles increases the complexity of the relevant phase diagrams considerably.

Mantle volatiles may help explain a long standing problem in geophysics, that of the cause of sublithospheric earthquakes. The strength of rocks is such that they deform by ductile flow below about 100 km depth, so that deep earthquake mechanisms must be very different from what we are familiar with at the surface. The idea that phase transitions might cause deep earthquakes is an old one but has suffered from being unable to explain 1) the source mechanism, which has no significant isotropic component, as one would expect in a simple picture of a sudden volume collapse, and 2) the broad depth distribution of earthquakes within slabs, e.g. deep earthquakes do not occur at discrete depths as equilibrium phase transitions do. Instead it has been proposed that some deep earthquakes (depths < 300 km), can be explained by gradual devolatilization of hydrous minerals such as serpentine [*Meade and Jeanloz*, 1991].

At greater depths, a different type of transition, one in which crystalline order is gradually lost as the pressure increases, may be responsible [*Meade and Jeanloz*, 1991]. The list of silicates which undergo these so-called pressure-induced amorphization transitions continues to grow [*Serghiou and Hammack*, 1993; *Zhang and Ong*, 1993; *Guyot and Reynard*, 1992; see also *Wolf et al.*, 1991]. The ubiquity of these transitions may indicate the presence of significant amounts of amorphous phases in the earth, at least in subduction environments. Other proposed sources of deep earthquakes include a mechanism involving the development of faults during the olivine-wadsleyite transition [*Green and Burnley*, 1989; *Kirby et al.*, 1991]. Acoustic emissions resulting from this mechanism were observed for the first time by *Green et al.* [1992]. In this mechanism, the wide depth distribution of seismicity is explained by kinetic hindrance of the transition in the cold subducted slab. Recent seismic studies seem to support the existence of a metastable wedge of olivine in at least some subducting slabs [*Vidale et al.*, 1991; *Iidaka and Suetsugu*, 1992].

Volatiles are known to have a large effect on silicate melting temperatures at lithospheric and upper mantle pressures [*Inoue*, 1994]. Whether this is also true at high (e.g. lower mantle) pressures is less well constrained [*Thompson*, 1992], in part because our understanding of the anhydrous end-member is in a state of flux. In the last year, two different groups have determined melting curves of $(\text{Mg},\text{Fe})\text{SiO}_3$ perovskite with results that differ by more than 1700 K at 60 GPa [*Zerr*

and *Boehler*, 1993; *Sweeney and Heinz*, 1993]. This lies far outside the quoted experimental uncertainties. It should be noted that these are extremely difficult, state of the art experiments and represent some of the highest pressure static melting determinations ever attempted, surpassed only by determinations of the iron melting curve. Nevertheless a resolution of this issue is geophysically crucial as the differences between the two experiments mean the difference between a very stringent upper bound on lower mantle temperatures (3000 K at mid lower mantle depths) on the one hand, or possibly much higher lower mantle viscosities than previously thought, which would be expected to affect lower mantle flow [*van Keken et al.*, 1994].

One of the central goals of mineral physics over the past decade has been to determine the bulk composition of the mantle by comparing experimental measurements of candidate compositions with seismological observables. Until recently, technical difficulties limited laboratory measurements of seismic velocities to lithospheric pressures and of density to either room temperature isotherms or ambient pressure isobars. This program has made deep mantle constituents some of the best characterized of all minerals in terms of bulk thermodynamic properties, but still leaves us short of a direct comparison with the earth. Now, the elastic constants of a mantle phase have been measured at mantle pressures for the first time in static experiments [*Zaug et al.*, 1993]. Important advances have also been made in the determination of elastic wave velocities in shock wave experiments [*Duffy and Ahrens*, 1992]. The first measurements of the equations of state of mantle minerals at simultaneously high pressures and temperatures [*Mao et al.*, 1991; *Fei et al.*, 1992a] were used to analyze the composition of the lower mantle in terms of its seismologically observed density and bulk sound velocity profiles [*Stixrude et al.*, 1992]. These types of measurements [see also *Fei et al.*, 1992b; *Meng et al.*, 1993] will soon allow mineral physics to make connections to what has been one of the most exciting developments in seismology in the last decade, the determination of the three-dimensional structure of the mantle. The density of a mantle mineral (MgSiO_3 perovskite) was measured at mantle pressure-temperature conditions for the first time [*Funamori and Yagi*, 1993]. These measurements, and an independent and simultaneous prediction based on first principles theory [*Stixrude and Cohen*, 1993] gave the first positive indication that MgSiO_3 perovskite, believed to be the most abundant mineral in the earth, is stable in its observed orthorhombic form at mantle temperatures.

The stability of orthorhombic perovskite leaves open the question of how to account for the growing body of evidence for seismic reflectors within the lower mantle [*Revenaugh and Jordan*, 1991; *Wicks and Richards*, 1993; *Kawakatsu and Niu*, 1994]. One possible explanation of these features is a transition in SiO_2 from stishovite to a CaCl_2 type structure, predicted to occur at 45 GPa at low temperature from first principles theory and recently confirmed experimentally [*Cohen*, 1991; *Kingma et al.*, 1995]. Though changes in crystal structure and density are subtle, the effect of this transition on the shear elastic modulus is large. If this transition were identified as the cause of the 720, 900 or 1200 km reflectors, it would force an important change in our understanding of lower mantle composition, which has generally been taken to be silica-undersaturated. On the other hand, the reflectors may be localized features, perhaps caused by compositional heterogeneity, associated, for instance with subducting slabs which have penetrated into the lower mantle. In this context, important

new work has lead to the surprising conclusion that the enrichment of Fe and Al expected in garnets in the oceanic crust stabilizes garnet-majorite to pressures greater than 50 GPa, well into the lower mantle [O'Neill and Jeanloz, 1994].

The problem of determining the major element composition of the mantle would not be so difficult were it not for the fact that the deep mantle is so inaccessible - we have tangible samples (xenoliths) only from the upper 200 km [Nixon, 1987]. These have always played an important role in the mantle composition problem, but they have left open the question of whether the mantle below 200 km has a substantially different bulk composition. Mantle models containing two or even three distinct compositional layers have been proposed as the best explanation of the seismic data; the boundaries occurring near the major seismic discontinuities at 410 and 660 km depth. Now we may be able to test these hypotheses against a growing number of actual samples of the mantle transition zone and the lower mantle [Haggerty and Sautter, 1990; Sautter et al., 1991; Kesson and Fitz Gerald, 1992]. A major problem in the coming years will be to recognize and collect more of these ultradeep xenoliths and diamond inclusions, characterize them and try to unravel their complex petrologic history [Doukhan et al., 1994].

A long standing problem in the minor element chemistry of the mantle has been the pattern of siderophile element abundances. These elements are depleted relative to a postulated chondritic bulk earth composition because they were segregated into the iron rich fluid as it traversed the mantle on its way toward forming the core. The problem is that the depletions are much less than expected based on laboratory measurements of silicate-iron partition coefficients. Many explanations have been advanced, including a so-called "late veneer": the addition, late in earth's accretion history, of a thin layer of siderophile rich material. However, the answer may be much simpler than has been imagined, and may be that the early earth was much hotter than typical partitioning experiments. One expects on general grounds for partition coefficients to tend toward unity with increasing temperature - entropy is maximized by an even distribution of elements between phases - offering a possible explanation of the smaller than expected compositional effect of the migrating metallic fluid. Essentially this explanation, advanced by Murthy [1991], has now received some experimental support from some of the highest pressure-temperature partitioning experiments ever attempted [Walker et al., 1993]. Experimental tests of Murthy's hypothesis are vital because many of the relevant partition coefficients are far from unity, indicating that simple geometrical arguments relevant to the high temperature limit may not be appropriate. Much more work still needs to be done on this contentious issue [Jones and Drake, 1992; O'Neill, 1992; Murthy, 1992; Capobianco et al., 1993; Hillgren et al., 1994].

As mineral physics enters its fifth decade following Birch's classic 1952 paper, it finds itself on the verge of being able to routinely conduct precise measurements at the pressure and temperature conditions of the deep earth in the laboratory. As it strengthens its base in the materials science of earth constituents, it is becoming increasingly capable of advancing and testing geophysical hypotheses concerning the working of the earth's interior.

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