2.01 Overview – Mineral Physics: Past, Present, and Future

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Mineral physics involves the application of physics and chemistry techniques in order to understand and predict the fundamental behavior of Earth materials (e.g., Kieffer and Navrotsky, 1985), and hence provide solutions to large-scale problems in Earth and planetary sciences. Mineral physics, therefore, is relevant to all aspects of solid Earth sciences, from surface processes and environmental geochemistry to the deep Earth and the nature of the core. In this volume, however, we focus only on the geophysical applications of mineral physics (see also Ahrens (1995), Hemley (1998), and Poirier (2000)). These applications, however, are not just be constrained to understanding structure the Earth (see Volume 1) and its evolution (see Volume 9), but also will play a vital role in our understanding of the dynamics and evolution of other planets in our solar system (see Volume 10 and Oganov *et al.* (2005)).

As a discipline, mineral physics as such has only been recognized for some 30 years or so, but in fact it can trace its origins back to the very foundations of solid Earth geophysics itself. Thus, for example, the work of Oldham (1906) and Gutenberg (1913), that defined the seismological characteristics of the core, led to the inference on the basis of materials physics that the outer core is liquid because of its inability to support the promulgation of shear waves.

A landmark paper in the history of the application of mineral physics to the understanding of the solid Earth is the *Density of the Earth* by Williamson and Adams (1923). Here the elastic constants of various rock types were used to interpret the density profile as a function of depth within the Earth that had been inferred from seismic and gravitational data. Their work was marked by taking into account the gravitationally induced compression of material at depth within the Earth, which is described by the Williamson–Adams relation that explicitly links geophysical observables ($g(r)$, the acceleration due to gravity as a function of radius, r, and the longitudinal and shear seismic wave velocities V_p and V_s) with

mineral properties (K_s, the adiabatic bulk modulus and density, ρ), via

$$d\rho(r)/\rho(r) = -g(r)dr/\varphi(r) \qquad [1]$$

where $\varphi(r)$ is the seismic parameter as a function of radius, and is given by

$$\varphi(r) = V^2_p(r) - (4/3)V^2_s(r) = K_s(r)/\rho(r) \qquad [2]$$

Further progress in inferring the nature of Earth's deep interior rested upon the experimental determination of the elastic properties of rocks and minerals as a function of pressure and temperature. Notably, this work was pioneered over several decades by Bridgman (1958). In parallel with experimental studies, however, a greater understanding of the theory behind the effect of pressure on compressibility was being made by Murnaghan (1937) and Birch (1938). These insights into the equations of state of materials enabled Birch (1952) (see **Figure 1**) to write his classic paper entitled *Elasticity and the Constitution of the Earth's Interior*, which laid the foundations of our current understanding of the composition and structure of our planet.

One notable outcome from the investigation of the effect of pressure and temperature on material properties was the discovery of new high-density polymorphs of crustal minerals. Thus, Coes (1953) synthesized a new high-density polymorph of SiO_2 (subsequently named coesite), and Ringwood (1959) reported the synthesis of the spinel structured Fe_2SiO_4 (that had previously been predicted by Bernal (1936)). Ringwood and colleagues went on to make a variety of other high-density silicate polymorphs, including the phases, which are now thought to make up the transition zone of the mantle, namely the spinelloids wadsleyite (β-Mg_2SiO_4) and ringwoodite (γ-Mg_2SiO_4), and the garnet-structured polymorph of $MgSiO_3$ (majorite). Further insights into the probable nature of deep Earth minerals came from Stishov and Popova (1961) who synthesized the rutile-structured polymorph of SiO_2 (stishovite) that is characterized by having Si in

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Figure 1 Francis Birch (1903–92), Royal Astronomical Society Medalist 1960; Bowie Medalist 1960.

octahedral coordination and from Takahashi and Bassett (1964) who first made the hexagonal close-packed polymorph of Fe, which is today thought to be the form of Fe to be found in the Earth's core (but *see* Chapter 2.05). As high-pressure and -temperature experimental techniques evolved, still further phases

were discovered, the most important of which was the 'postspinel, perovskite-structured polymorph of $MgSiO_3$ (Liu, 1975). It was thought for sometime that this discovery and the subsequent work on the details of the high-pressure phase diagrams of silicate minerals had enabled a robust mineralogical model for the mantle to be established. This view, however, has had to be revised in the past few years, after the recent discovery of a 'postperovskite' phase (Murakami *et al.*, 2004; Oganov and Ono, 2000), which may be stable in the deepest part of the lower mantle.

Notwithstanding, however, the possibility of further new discoveries, the mineralogy, and composition of the mantle and the core are now relatively well defined. The current view of the mineralogy of the mantle is summarized in **Figure 2**, while as suggested by Birch (1952), the core is considered to be composed of iron (with minor amounts of nickel) alloyed with light elements (probably O, S, and or Si). The solid inner core is crystallizing from the outer core, and so contains less light elements. The current status of our understanding of the nature of the deep Earth is reviewed in detail in Chapters 2.02, 2.03, 2.04, and 2.05. Chap Stixrude provides a general overview of the structure of the mantle. The nature of the lower mantle is still relatively controversial, since generating lower mantle pressures ($\sim$25–130 GPa) and temperatures ($\sim$2000–3000 K) is still experimentally challenging, and mineral physics data and phase
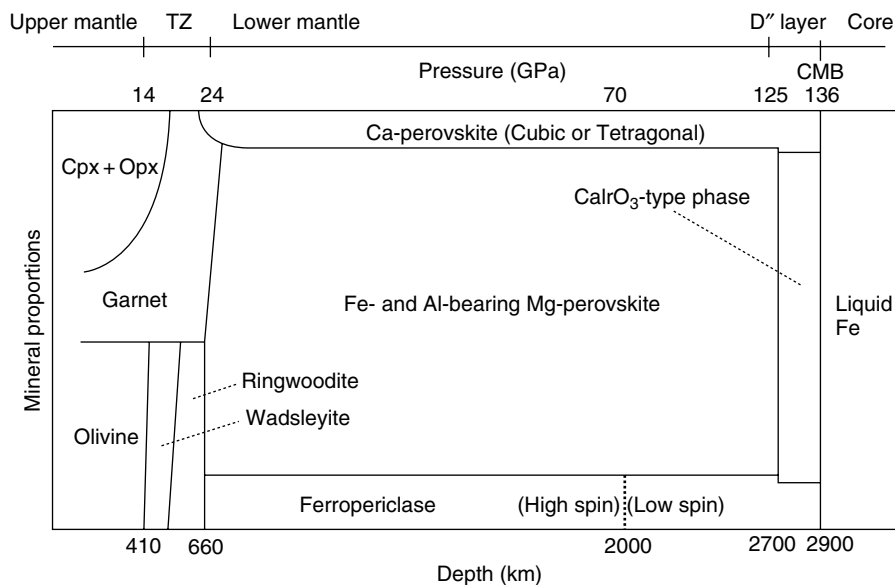

Figure 2 Phase relations of pyrolitic mantle composition as a function of depth. From Ono S and Oganov AR (2005) *In situ* observations of phase transition between perovskite and $CaIrO_3$-type phase in $MgSiO_3$ and pyrolitic mantle composition. *Earth and Planetary Science Letters* 236: 914–932.

relations for the minerals thought to be found here are less robust. Furthermore, the recent discovery of the postperovskite phase has added even greater uncertainty to the nature of the D″ zone and the core–mantle boundary. The problems of the lower mantle and the core–mantle boundary are therefore reviewed in Chapter 2.03. Although the major element chemistry of the mantle is quite well studied, it is probably fair to say that the understanding of the trace elements chemistry and the role of volatiles in the deep mantle is still in its infancy. This aspect of mantle chemistry, however, is vital if we are to fully understand the processes involved in planetary formation, core segregation, and subsequent evolution of the Earth (see Volumes 9 and 10). The Chapter 2.04 provides a review of our understanding of this aspect of the mantle, while the considerable progress in our understanding of the nature and evolution of the core is provided in Chapter 2.05.

As indicated above, our understanding of the lower mantle and core are limited to some extent by our inability easily to reproduce the high-pressure and -temperature conditions to be found in planetary interiors. To obtain greater insight, theory and experiment must be used together, and Chapters 2.06 and 2.13 present reviews of the theory underlying high-pressure, high-temperature physics, and the major experimental methods that are being developed to probe this parameter space. The Chapter 2.06 outlines the thermodynamic basis behind high-pressure–high-temperature behavior, and expands in greater detail on equations of state and the way in which the density and elastic properties of materials respond to changes in pressure and temperature. The macroscopic behavior of minerals depends upon the microscopic or atomistic interactions within the mineral structure. Thus, for example, free energy (and eventually phase stability) depends in part upon entropy, which in turn is dominated (for silicates at least) by lattice vibrations. Hence, in Chapter 2.07, a detailed analysis of lattice vibrations and spectroscopy of mantle minerals is presented. For the past 20 years, advances in computing power have enabled computational mineral physics to make a contribution to our understanding of the thermodynamic, thermo-elastic, and dynamical properties of high-pressure minerals. Initially, the results of simulations based on inter-atomic potentials provided semiquantitative insights into, for example, the lattice vibrations and the thermodynamics of mantle phases (e.g., Price *et al.*, 1987; Wall and Price, 1988). But more recently, quantum mechanical simulations of mantle and core phases have been able to achieve a precision

and accuracy that is comparable with that achievable experimentally, and as such *ab initio* modeling must now be seen as a legitimate complement to experimental study. Therefore in this volume, the theory and results from *ab initio* studies of some deep Earth phases are reviewed in Chapter 2.13.

Despite the power and insight provided by theory, mineral physics is dependent upon quantitative high-pressure and -temperature experimental results. Such work was pioneered by Williamson, Adams (**Figure 3**), and Bridgman, and then taken up by others such as Ringwood, Bassett, Liu, and many groups in Japan (see, e.g., Akimoto (1987) and **Figure 4**), but in the past 30 years huge advances have been made and today, for example, laser-heated diamond anvil cells can be used to access temperatures and pressures up to ∼6000 K and 250 GPa. Such experiments, however, can only be carried out on very small sample volumes and for very short periods of time. Multianvil experiments can be used to study much larger volumes of material and are stable over a longer time interval. These techniques are, therefore, complementary and are both developing rapidly. Chap Ito provides a review of multianvil cell

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Figure 3 Leason Heberling Adams (1887–1969), American Geophysical Union (AGU) President 1944–47, Bowie Medalist 1950.
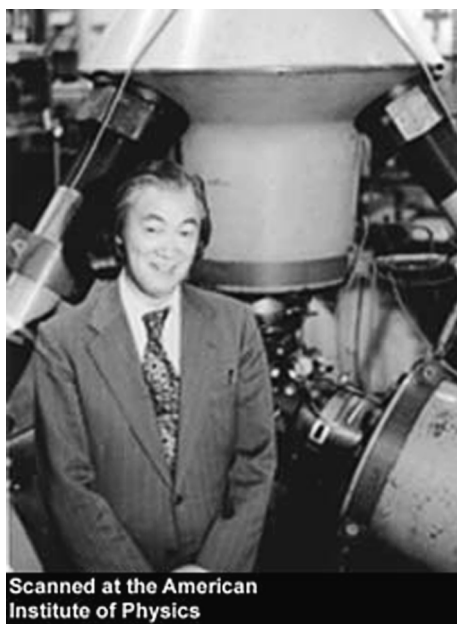
Figure 4   Syun-iti Akimoto (1925–2004), Royal Astronomical Society Medalist 1983, Bowie Medalist 1983.

methods, while Chap Mao gives an analysis of diamond-anvil cell techniques. A third technique for producing high pressures and temperatures is via shock compression. In this approach a high-velocity impact is produced by firing a projectile at a mineral target. Very high pressure and shock-produced heating can be obtained, but only for a few 100 ns. Analysis of the experimental results is not always straightforward, as a knowledge of some high P–T physical properties is usually needed to infer peak shock temperatures, and shock results are not always in agreement with static experiments (see, e.g., the debate on the high-pressure melting of Fe in Chapters 2.18 and 2.13). For more details on this techniques see Ahrens (1995), Poirier (2000), and Nellis (2002).

Achieving the high pressures and temperatures that occur in the deep Earth is, however, just the beginning of the challenge that faces experimental mineral physicists, since it is also necessary to measure a variety of physical properties under these conditions. Therefore in Chapters 2.10, 2.11, and 2.12 the specific techniques for measuring elastic and acoustic properties, electronic and magnetic properties, and rheological properties are described in greater detail.

The long-term goal of mineral physics research is to enable a full interpretation of seismic tomographic data (see Volume 1), and to provide a three-dimensional description of the mineralogy, composition, and thermal structure of the Earth's deep interior. To this end, we need not only full descriptions of the seismic properties of rocks and minerals, as a function of composition, pressure, and temperature (*see* Chapter 2.02), but also an understanding of the nature and origin of anisotropy in the Earth (*see* Chapter 2.16) and the significance and reasons for seismic wave attenuation (*see* Chapter 5.05).

In addition to being able to invert seismic data to provide an instantaneous picture of the Earth's interior, we desire to be able to describe the dynamic evolution of our planet (see Volumes 7 and 8). As such we need to be able to constrain, for example, geodynamical models of mantle convection, with the appropriate rheological descriptions of mantle phases (*see* Chapter 2.14), and self-consistent descriptions of heat flux and planetary thermal structure. Key to the latter is our understanding of thermal conductivity at high pressures and temperatures, which is an area where theory and experiment are still evolving and much progress is still required (*see* Chapter 2.19). Similarly, our ability to describe the dynamics of core convection, and hence the geodynamo, is critically dependent on our understanding of the physical properties of liquid and solid iron under core conditions (*see* Chapters 2.05, 2.13, 2.18, and Price *et al.*, 2004).

One particular problem in our understanding of the Earth is the nature of the core–mantle boundary. It has been variously suggested, for example, that it is a 'grave yard' for subducted slabs; a reaction zone with the core; associated with a postperovskite phase change; has pods of partially molten material; is enriched in iron; and is the source of deep mantle plumes (see Volume 7). To establish the importance of some of these hypotheses requires high-quality seismic data, but also tight constraints on the thermal structure of the core and the high-pressure melting behavior of mantle and core material (*see* Chapter 2.18). The melting of mantle material also obviously plays a vital role in volcanism and planetary evolution, and the migration of melts and their eruption or injection into the crust is central to our understanding of the dynamics of the upper mantle. The properties of melts are discussed in Chapter 2.15.

Another long-standing problem in geophysics is the energetics of the core and the driving force behind the geodynamo (see Volume 8). To be able to model this process, accurate descriptions of the melting of iron and the chemical compositions of the inner and outer core are essential (e.g., Nimmo *et al.*, 2004). The possible presence of radioactive elements

in the core (such as K^{40}) would be highly significant as such internal sources of heat would greatly influence the cooling rate of the core and hence the age and rate of growth of the inner core; but it is still an open question. The stability of the geodynamo may also be affected by thermal and electrical coupling with the mantle; hence, we need to fully understand the electrical properties of mantle phases (*see* Chapter 2.21). Finally, for example, insights into the past nature of the geodynamo, as its palaeo-intensity, can only be obtained from paleomagnetic data (see Volume 5), which requires a detailed understanding of rock minerals and magnetism (*see* Chapter 2.20).

In the following chapters in this volume, the great progress that has been made in our understanding of the physics and chemistry of minerals is clearly laid out. However, each author also highlights a number of issues which are still outstanding or that need further work to resolve current contradictions. The resolution of some of the problems outlined above, and in the subsequent chapters, will depend on more precise or higher-resolution geophysical measurements (e.g., the exact density contrast between the inner and outer core), while others will be solved as a result of new experimental or computational techniques. The combination, for example, of intense synchrotron radiation and neutron sources with both diamond anvil and multianvil cell devices promises to yield much more information on high pressure seismic (or equivalently elastic) properties of deep Earth phases. In the foreseeable future, developments in anvil design will see large-volume devices that can be used to determine phase equilibria to 60 GPa, or to study high-pressure rheology to 30 GPa and beyond. But more predictably, the continued development of increasingly powerful computers will see the role of computational mineral physics grow still further, as the study of more complex problems (like rheology and thermal transport) becomes routine. In addition, the use of more sophisticated *ab initio* methods (like quantum Monte Carlo techniques) will become possible, and accurate studies of the band structure and electrical properties of iron bearing silicates will be performed. Finally, the pressures of the Earth's interior (up to 360 GPa) will not represent the limit of interest for mineral physicists. Already extra-solar system, giant, Earth-like planets are being considered, and understanding their internal structure will open up even greater challenges (e.g., Umemoto and Wentzcovitch, 2006 Umemoto *et al.*, 2006).

In conclusion, therefore, this volume contains a comprehensive review of our current state of understanding of mineral physics, but without doubt there is still much that is unknown, but the prospect for further progress is excellent, and it is certain that in the next decades many issues, which are still controversial today, will have been resolved.

References

Ahrens TJ (1995) *AGU Reference Shelf 2: Mineral Physics and Crystallography: A Handbook of Physical Constants*. Washington, DC: American Geophysical Union.

Akimoto S (1987) High-pressure research in geophysics: Past, present, and future. In: Manghnani MH and Syono Y (eds.) *High-Pressure Research in Mineral Physics*, pp. 1–13. Washington, DC: American Geophysical Union.

Bernal JD (1936) Discussion. *Observatory* 59: 268.

Birch F (1938) The effect of pressure upon the elastic properties of isotropic solids according to Murnaghan's theory of finite strain. *Journal of Applied Physics* 9: 279–288.

Birch F (1952) Elasticity and constitution of the Earth's interior. *Journal of Geophysical Research* 57: 227–286.

Bridgman PW (1958) *Physics of High Pressure*. London: G Bell and Sons.

Coes L (1953) A new dense crystalline silica. *Science* 118: 131–132.

Gutenberg B (1913) Uber die Konstitution der Erdinnern, erschlossen aus Erdbebenbeobachtungen. *Physika Zeitschrift* 14: 1217–1218.

Hemley RJ (1998) *Reviews in Mineralogy*, Vol. 37, *Ultrahigh-Pressure Mineralogy: Physics and Chemistry of the Earth's Deep Interior,* Washington, DC: Mineralogical Society of America.

Liu LG (1975) Post-oxide phases of olivine and pyroxene and the mineralogy of the mantle. *Nature* 258: 510–512.

Murakami M, Hirose K, Kawamura K, Sata N, and Ohishi Y (2004) Post-perovskite phase transition in $MgSiO_3$. *Science* 304: 855–858.

Murnaghan FD (1937) Finite deformations of an elastic solid. *American Journal of Mathematics* 59: 235–260.

Nellis WJ (2002) Dynamic experiments: An overview. In: Hemely RJ and Chiarotti GL (eds.) *High Pressure Phenomena*, pp. 215–238. Amsterdam: IOS Press.

Nimmo F, Price GD, Brodholt J, and Gubbins D (2004) The influence of potassium on core and geodynamo evolution. *Geophysical Journal International* 156: 363–376.

Oldham RD (1906) The constitution of the Earth as revealed by earthquakes. *Quarterny Journal of Geological Society* 62: 456–475.

Oganov AR and Ono S (2000) Theoretical and experimental evidence for a post-perovskite phase of $MgSiO_3$ in Earth's D″ layer. *Nature* 430: 445–448.

Oganov AR, Price GD, and Scandolo S (2005) *Ab initio* theory of planetary materials. *Zietschrift fur Kristallographie* 220: 531–548.

Ono S and Oganov AR (2005) *In situ* observations of phase transition between perovskite and $CaIrO_3$-type phase in $MgSiO_3$ and pyrolitic mantle composition. *Earth and Planetary Science Letters* 236: 914–932.

Poirier JP (2000) *Introduction to the Physics of the Earth's Interior*. Cambridge: Cambridge University Press.

Price GD, Alfè D, Vočadlo D, and Gillan MJ (2004) The Earth's core: An approach from first principles. In: Sparks RSJ and

Hawksworth CJ (eds.) *AGU Geophysical Monograph Series,* Vol. 150. *The State of the Planet: Frontiers and Challenges in Geophysics*, pp. 1–12. Washington, DC: American Geophysical Union.

Price GD, Parker SC, and Leslie M (1987) The lattice dynamics and thermodynamics of the Mg_2SiO_4 polymorphs. *Physics and Chemistry of Minerals* 15: 181–190.

Ringwood AE (1959) The olivine-spinel inversion in fayalite. *American Mineralogist* 44: 659–661.

Stishov SM and Popova SV (1961) A new dense modification of silica. *Geochemistry* 10: 923–926.

Takahashi T and Bassett WA (1964) A high pressure polymorph of iron. *Science* 145: 483–486.

Umemoto K and Wentzcovitch RM (2006) Potential ultrahigh pressure polymorphs of ABX(3)-type compounds. *Physical Review B* 74: 224105.

Umemoto K, Wentzcovitch RM, and Allen PB (2006) Dissociation of $MgSiO_3$ in the cores of gas giants and terrestrial exoplanets. *Science* 311: 983–986.

Wall A and Price GD (1988) A computer simulation of the structural, lattice dynamical and thermodynamic properties of $MgSiO_3$ ilmenite. *American Mineralogist* 73: 224–231.

Williamson ED and Adams LH (1923) Density distribution in the Earth. *Journal of Washington Academy of Sciences* 13: 413–432.