



**Figure 1.0** Dave Mao at the Geophysical Laboratory, Washington DC, 2018. For the color version, refer to the plate section.  
(photos courtesy of the Carnegie Institution for Science).

# 1

## Introduction to Static and Dynamic High-Pressure Mineral Physics

MICHAEL J. WALTER AND YINGWEI FEI

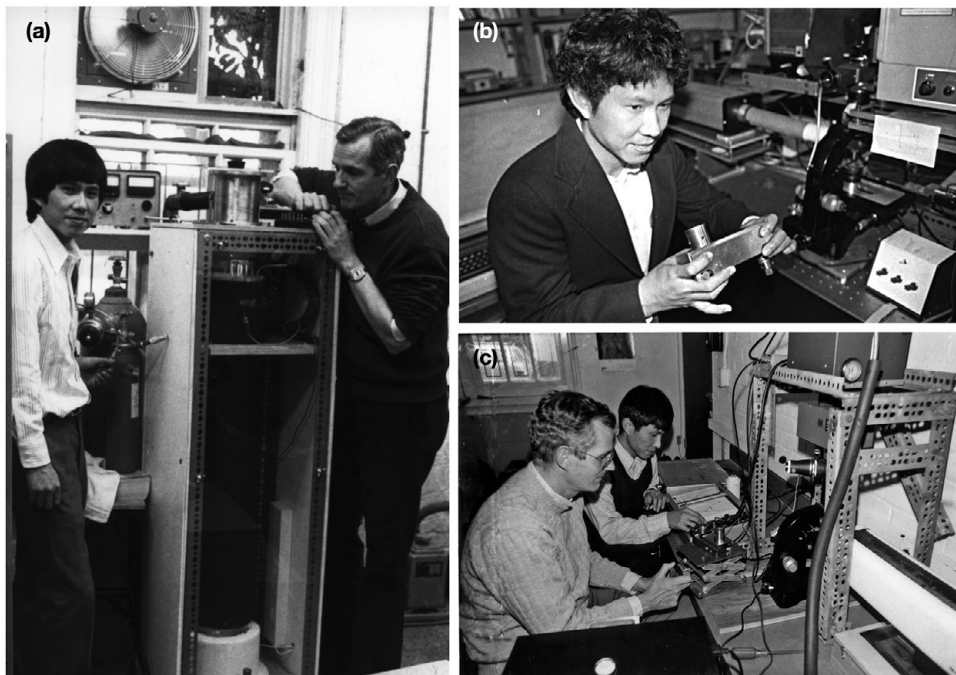
**In October of 2018, a group of scientists gathered at the Broad Branch Road campus of the Carnegie Institution for Science to celebrate 50 years of high-pressure research by Ho-Kwang “Dave” Mao at the Geophysical Laboratory. The celebration highlighted the growth of high-pressure mineral physics over the last half century, which has matured into a vibrant discipline in the physical sciences because of its intimate connections to Earth and planetary sciences, solid-state physics, and materials science. Dave’s impact in high-pressure research for over a half a century has been immense, with a history of innovation and discovery spanning from the Earth and planetary sciences to fundamental materials physics. Dave has always been an intrepid pioneer in high-pressure science, and together with his numerous colleagues and collaborators across the world he has driven the field to ever higher pressures and temperatures, guided the community in adopting and adapting a spectrum of new technologies for in situ interrogation of samples at extreme conditions, and relentlessly explored the materials that make up the deep interiors of planets. In this volume, we assemble 15 chapters from authors who have worked with, been inspired by, or mentored by Dave over his amazing career, spanning a range of subjects that covers the entire field of high-pressure mineral physics.**

### 1.1 Introduction

High-pressure mineral physics focuses on the physical properties of materials at high pressure, a field that has shaped our understanding of deep planetary interiors and revealed new material phenomena appearing at extreme conditions. Beginning in the early 1970s, the field has made major contributions to Earth and planetary sciences, condensed matter physics, and high-pressure materials synthesis, through ever-expanding capabilities for reaching higher pressures and probing smaller samples. Ho-Kwang “Dave” Mao has been at the forefront and led the growth of the field since its beginning. Dave started his epic adventure in high-pressure research as a doctoral student at the University of Rochester working in the lab of William A. “Bill” Bassett. After graduating in 1968, Dave began as a postdoctoral fellow at the Geophysical Laboratory (GL) of the Carnegie Institution of Washington, working closely with GL staff scientist Peter Bell. Shortly thereafter, in 1972,

Dave was appointed as a staff scientist by GL Director Hatten Yoder, and he retired in 2019 after more than 50 years of discovery, innovation, impact, and influence applying mineral physics in the realms of Earth and planetary science and fundamental materials science.

While a graduate student in Rochester, Dave was first introduced to an entirely new high-pressure technology, the diamond anvil cell, which had recently been developed at the National Institute of Standards and Technology (NIST)/National Bureau of Standards (NBS) (Piermarini, 2001). Dave's graduate work, measuring lattice parameters of iron and iron oxides using in situ X-ray diffraction, working together with diamond anvil cell (DAC) pioneer Bill Bassett and fellow student Taro Takahashi, set him on his path of high-pressure discovery (Mao et al., 1967, 1974). Upon his arrival at the Geophysical Lab, Dave worked together with Peter Bell (Figure 1.1) on improvements to the original lever-arm DAC design (Piermarini, 2001), and they were the first to achieve pressures of a megabar and above (Mao and Bell, 1978), opening up the lower mantle and core to relatively routine exploration by other eager high-pressure Earth scientists. Dave recognized that measuring pressure quickly and reliably was a prerequisite for this device to take hold in the high-pressure community, and Dave again leaped on a new method, the ruby fluorescence pressure scale developed at NIST/NBS, calibrating the scale using specific volume measurements of four metals combined with their shock wave equations of state to provide a



**Figure 1.1** Ho-Kwang “Dave” Mao in the early years at the Geophysical Laboratory, shown here with staff scientist Peter Bell (a,c) and holding a lever arm DAC (b) in preparation for an experiment using a first-generation laser heating system (photos courtesy of the Carnegie Institution for Science).

reliable, quasihydrostatic in situ pressure scale that is still widely used today (Mao et al., 1978, 1986).

The use of the DAC as a high-pressure device to address problems in Earth and planetary sciences, condensed matter physics, and materials sciences has drastically expanded by combining the DAC with laser heating to achieve simultaneous high pressure and temperature and coupling the DAC with synchrotron X-radiation for in situ measurements. Dave led both expansions to address a wide range of scientific questions in high-pressure science. Together with GL postdoctoral fellow Takehiko Yagi at the Geophysical Lab in the late 1970s, Dave was among the first to combine laser heating with the DAC to synthesize and investigate the structure and crystal chemistry of minerals at lower mantle conditions (Bell et al., 1979; Yagi et al., 1978, 1979), following the successful synthesis of the  $\text{MgSiO}_3$ -perovskite phase (bridgmanite) (Liu, 1976). The development of the double-sided laser-heating technique (Shen et al., 1996) and the symmetric DAC (Shen and Mao, 2017) further advanced the application of DAC techniques.

Dave recognized early on that the ability to probe samples in the DAC with focused energy at infrared, optical, and X-ray wavelengths permits a vast landscape of possible measurements to be made in situ at high pressure and often at high temperature. From his first forays into coupling synchrotron radiation with high-pressure experiments at the Brookhaven National Lab in the 1980s to his vision and dedication to the construction of large facilities dedicated to high-pressure science at the Advanced Photon Source (High Pressure Collaborative Access Team [HPCAT], HPSynC) and most recently the Shanghai Synchrotron Radiation Facility (SSRF), Dave and like-minded colleagues have led the community to its current state, where making measurements at megabar pressures and extreme temperatures while probing with energetic beams at scales reaching to the nanometric in scale has become commonplace and, importantly, easily accessible (Mao and Hemley, 1996; Shen et al., 1996, 2010; Mao et al., 2001a; Zhao et al., 2004; Hemley et al., 2005; Mao et al., 2016; Shen and Mao, 2017; Goncharov et al., 2019).

In the realm of Earth sciences, Dave has spent a career investigating the fundamental phase equilibria, thermodynamic, and physical properties of solid and liquid phases at pressure–temperature conditions relevant to Earth’s lower mantle and core – his body of work is truly remarkable and has been tremendously impactful. From his studies on deep mantle silicates and oxides to his extensive investigations on iron and iron alloys, there can be little doubt that our current understanding of Earth’s deep interior has Dave’s footprints all over the territory, and it is hard to find a path Dave has not trodden (Yagi et al., 1978; Mao and Bell, 1979; Jephcoat et al., 1986; Mao et al., 1989, 1997, 1998, 1990, 2001b, 2006b; Stixrude et al., 1992; Fei and Mao, 1994; Duffy et al., 1995; Saxena et al., 1995; Shen et al., 1998; Shieh et al., 1998; Badro et al., 1999; Hirose et al., 1999; Zha et al., 2000; Merkel et al., 2002; Li et al., 2004; Lin et al., 2005). One might argue that Dave’s most recently discovered path leading to new high-pressure hydrous phases and superoxide iron-rich phases, potentially tying together the Earth’s surface, mantle, and core, represents a fitting destination that began with his studies on iron and iron oxide phases as a graduate student (Hu et al., 2016; Liu et al., 2017, 2019; Mao et al., 2017; Zhang et al., 2018; Lin et al., 2020).

Expanding his horizons beyond the terrestrial landscape, Dave ventured into the realm of gas giants early in his career, aiming to probe the high-pressure behavior of hydrogen and leading the elusive search for its metallicity, the “holy grail” in high-pressure physics (Sharma et al., 1980; Hemley and Mao, 1988; Mao et al., 1988a, 1988b; Badding et al., 1991; Mao and Hemley, 1994; Loubeyre et al., 1996; Gregoryanz et al., 2003). This ultimately led to numerous investigations of a vast array of molecular compounds, exploration of novel new materials, and the search for room temperature superconductivity in materials at high pressure (Mao et al., 1988a, 2006a; Vos et al., 1993; Goncharov et al., 1996; Eremets et al., 2001; Meng et al., 2004; Yoshimura et al., 2006; Gregoryanz et al., 2007; Chen et al., 2008; Somayazulu et al., 2010; Zhu et al., 2013; Zhou et al., 2016; Zeng et al., 2017; Wang et al., 2018; Ji et al., 2019).

Perhaps the greatest legacy of Dave’s epic journey is the vast number of scientists (Figure 1.2) who he has trained, collaborated with, mentored, interacted with, and paved



**Figure 1.2** Dave Mao and colleagues in the 1990s and 2000s at the Geophysical Laboratory.

the way for over the last 50-plus years, a tradition that he continues to this day. The operation of the dedicated high-pressure beamline (HPCAT) at the Advanced Photon Source has further expanded Dave's collaborations with researchers around the globe (Figure 1.3). This volume, *Static and Dynamic High-Pressure Mineral Physics*, represents



**Figure 1.3** Dave Mao at HPCAT, the Advanced Photon Source. For the color version, refer to the plate section.



**Figure 1.4** Attendees at the symposium to honor Ho Kwang “Dave” Mao and 50 years of high-pressure science at the Geophysical Laboratory, held in October 2018, at the Broad Branch Road Campus of the Carnegie Institution for Science. For the color version, refer to the plate section.

(photo courtesy of the Carnegie Institution for Science).

an outgrowth of the workshop held in Dave’s honor at the Geophysical Lab in 2018 (Figure 1.4) celebrating his half-century journey in high-pressure science. Many of those who attended the workshop have contributed chapters to this book, together with collaborators and colleagues both old and new who have the pleasure of tagging along on Dave’s journey of discovery in high-pressure science.

## 1.2 Chapter Summaries

Leading off is Professor Takehiko Yagi (University of Tokyo) who worked with Dave as a postdoc at the Geophysical Laboratory in the late 1970s and who has himself been on a lifelong journey in high-pressure research. In Chapter 2, Yagi provides a unique historical perspective on the “Developments of Static High-Pressure Techniques and the Study of the Earth’s Deep Interior in the Last 50 Years and Its Future.” In this chapter, Yagi describes the evolution of both large-volume multi-anvil and diamond anvil techniques and the numerous kinds of experimental and analytical techniques that have been combined with these high-pressure devices to obtain what is now a mountain of information about the properties of minerals and melts at high pressures and temperatures. Yagi discusses how advances in coupling synchrotron radiation to the DAC played a key role in our understanding of the deep Earth and ends by describing current state-of-the-art efforts to extend the pressure range of the diamond anvil cell far beyond what is routinely capable in existing high-pressure devices in order to reach the next frontier in high-pressure science.

In Chapter 3, Guoyin Shen (Argonne National Laboratory), together with Wendy Mao (Stanford University), continues the theme of the key role that high-brilliance synchrotron radiation plays in high-pressure science in their contribution “Applications of Synchrotron

and FEL X-Rays in High-Pressure Research.” These authors provide an extensive review of developments in synchrotron and free electron laser (FEL) technology, and provide numerous examples of the many spectroscopic techniques that have been utilized in high-pressure research. They describe double-sided laser heating and how its coupling to X-ray diffraction through the use of small X-ray beams available at synchrotron light sources revolutionized high-pressure science in the DAC, including through X-ray mapping and the ability to make single-crystal and multigrain measurements. They discuss how techniques such as absorption and emission spectroscopy, inelastic scattering, nuclear forward scattering, X-radiography, and transmission X-ray microscopes enable determination of equations of state, interrogation of the electronic state of materials, spin transitions, site occupancies, magnetic transitions, thermodynamic properties, sound velocities, microstructural evolution, and more. These authors then highlight some active areas of development in high-pressure X-ray research and provide a forward-looking perspective on future opportunities becoming available with upgrades in both synchrotron and FEL facilities worldwide.

Low-Z materials are not easily noticed by X-rays and require other methods of interrogation, and in Chapter 4, “Neutron Diamond Anvil Cell Project at ORNL,” Reinhard Boehler and his colleagues Bianca Haberl and Jamie J. Molaison from the Oak Ridge National Laboratory (ORNL), together with Malcom Guthrie (European Spallation Source), report on a project to expand the pressure range of neutron diffraction in the DAC, which grew from Dave Mao’s vision as director of the Department of Energy (DOE) Energy Frontier Research in Extreme Environments (EFree). The team describes efforts to develop techniques for reaching much higher pressures than previously achieved while maintaining the relatively large sample sizes required for diffraction measurements at low neutron flux. These authors first recap high-pressure advances using neutrons in high-pressure science at ORNL over the previous decade, including the Spallation Neutrons at Pressure (SNAP) diffractometer. They then describe how breakthroughs in synthesizing multicarat diamond anvils grown by chemical vapor deposition (CVD), together with the latest developments in large anvil support designs and compact multiton hydraulic diamond cells and new gasket designs, have allowed neutron diffraction experiments at pressures approaching a megabar. They finish off with an example of neutron diffraction measurements on solid D<sub>2</sub>O (Ice VII) at 60 GPa.

While static compression experiments provide a wealth of high-pressure information, Chapters 5 and 6 highlight the importance of laboratory shock compression data for understanding the high-pressure behavior of silicates and other geological materials during planetary formation and shock metamorphism, and in deep Earth and other planetary objects. Shock experiments provide distinct, yet complementary, information to static experiments, and recently developed capabilities that allow for in situ examination of the atomic-level structure and exploration of material properties in the terapascal pressure range by laser- or magnetically driven dynamic compression have reinvigorated the field.

In Chapter 5, “Light-Source Diffraction Studies of Planetary Materials under Dynamic Loading,” Sally J. Tracy (Carnegie Institution for Science) highlights the recent experimental developments that make measurements possible during the nanosecond to



microsecond duration of shock experiments, especially at facilities that couple dynamic compression with high-flux X-rays for in situ X-ray diffraction under dynamic loading. Tracy provides a brief introduction into the theory of shockwave experiments and the different shock platforms and describes the ambiguity in determining features and phases formed during the compression and unloading processes due to the fast time scales of shockwave experiments. Tracy then describes developments at the Dynamic Compression Sector (DCS) at the Advanced Photon Source (APS) for in situ X-ray diffraction under plate impact shock loading that provide important information during compression and unloading, and provides examples of results in the systems  $\text{SiO}_2$ ,  $\text{Mg}_2\text{SiO}_4$ , and carbon. This is followed by a discussion of the new and exciting possibilities of laser shock studies at X-Ray Free Electron Laser Sources (XFEL) that generate ultrafast bursts (fs) of X-rays with peak X-ray brightness 10 orders of magnitude higher than synchrotron sources, and reviews recent results on silicate liquids and glasses, hydrocarbons, and carbides.

Thomas Duffy (Princeton University) builds on the theme of shock compression, and in Chapter 6, “New Analysis of Shock-Compression Data for Selected Silicates,” discusses issues with identification of the high-pressure phases formed under shock loading using density comparisons with static data or postmortem analysis of samples. Duffy then summarizes pressure-density shock wave data for garnet, tourmaline, nepheline, topaz, and spodumene and compares their Hugoniot compression behavior with data from static compression and theoretical studies. Duffy shows that there is good agreement with recent 300 K single-crystal X-ray diffraction data, illustrating the range of silicate behavior under shock loading. Duffy ends with a perspective on newly developed in situ X-ray experimental capabilities and the reflects on the many open questions that can be addressed with this new ability.

In Chapter 7, “Scaling Relations for Combined Static and Dynamic High-Pressure Experiments,” Raymond Jeanloz (University of California at Berkeley) shows how combining static and dynamic experiments can maximize material compression by tuning the viscous dissipation that occurs especially under shock loading. In this contribution, Jeanloz summarizes scaling relations for evaluating the internal energy ( $E$ ) dissipated as “waste heat” upon dynamic loading and shows that the dissipated energy increases rapidly with final compression. However, Jeanloz’s analysis shows that the waste heat is significantly reduced by precompressing the target sample. For a given final density, increased pre-compression pushes the dynamically loaded state toward an isentrope, and in the limit of numerous steps approaches isentropic ramp compression. This means that by combining static precompression and dynamic methods, final pressure–density–temperature ( $P$ – $\rho$ – $T$ ) states achieved in samples can be “tuned” to minimize final temperatures and maximum compression.

Accurate equations of state (EoS) for the solid phases that constitute planetary interiors are fundamental for modeling their density with pressure and temperature, and with the advent of synchrotron radiation as a primary tool in high-pressure science, the equation of state of “pressure markers” can be utilized to monitor pressure in situ in experiments. In Chapter 8, “Equations of State of Selected Solids for High-Pressure Research and Planetary Interior Density Models,” Yingwei Fei (Carnegie Institution for Science) reviews the

current state of the art of using thermal EoS in the Earth and planetary sciences. Fei begins by describing the experimental methods for making EOS measurements, including both static and dynamic approaches, and the importance of in situ X-ray diffraction at synchrotrons. Fei then presents a compilation of EoS parameters for a range of different solid materials that are commonly used as pressure standards in experiments, including platinum, gold, neon, MgO, and NaCl. He then discusses the internal consistency among the standards and compares their performance in extrapolation to the multimegabar pressure range. Fei then summarizes EoS data for key phases in Earth's mantle required to accurately model Earth's interior composition based on seismological measurements of density, including bridgmanite, ferropericlase, and CaSiO<sub>3</sub>-perovskite, and then discusses the effect of light elements on the EoS of iron (Fe) alloys relevant to Earth's core. Fei emphasizes how future work combining both static and dynamic EoS measurements are required to improve pressure standards and our understanding of deep planetary interiors.

After nearly a century of investigations, the compositions of the liquid outer core and the solid inner core are not uniquely known. Seismically deduced density and elastic wave velocities can potentially reveal the core composition, but only if these properties are known in candidate iron alloy compositions at the extreme high pressures and temperatures of Earth's core. In Chapter 9, "Elasticity at High Pressure with Implication for the Earth's Inner Core," Seiji Kamada (Tohoku University), Tatsuya Sakamaki (Tohoku University), and Eiji Ohtani (Tohoku University) take us on a journey to the core through the lens of the elasticity of iron and iron alloys. They provide the rationale for elasticity data to probe the secrets of core composition and describe how this line of experimental inquiry has developed since the pioneering work at megabar pressures of Dave Mao and colleagues in the early 1990s. Sakamaki and coauthors provide a comprehensive and informative review of the experimental methods for measuring compressional and shear-wave velocities at high pressures and temperatures (including ultrasonic, Brillouin spectroscopy; inelastic X-ray scattering; nuclear inelastic scattering; shock waves; pulsed laser; and radial diffraction). The authors provide a careful assessment of the wave velocity data at high pressure and room temperature on a range of iron alloy systems (e.g., Fe-C; Fe-O; Fe-S; Fe-Si; Fe-H), which is followed by an evaluation of much scarcer data obtained at combined high pressure and high temperature on iron alloys using inelastic X-ray scattering. The journey ends with an evaluation of the constraints placed on inner core compositions using extrapolations of data to inner core conditions, and a call for future studies especially in obtaining shear velocity data at high temperature.

Determining the correct structure of phases synthesized in diamond anvil cell experiments is the crucial first step for investigating materials at high pressure. In Chapter 10, "Multigrain Crystallography at Megabar Pressures," Li Zhang, Junyue Wang, and Dave Mao (Center for High Pressure Science and Technology Advanced Research) provide an in-depth look at how new developments in multigrain X-ray diffraction methods can revolutionize structural characterization of samples made in the laser-heated DAC at multimegabar pressures. In situ powder X-ray diffraction is the industry standard, but it has limitations for obtaining detailed structural information. While single-crystal X-ray diffraction is challenging at megabar pressures, multigrain crystallography provides an

innovative and powerful structural solution by taking advantage of separated reflection spots on diffraction images. Zhang and coauthors describe how several hundred submicron grains can be simultaneously indexed from an individual high-pressure experiment, and a nearly full convergence of the structure can be achieved when applying the multigrain method. To demonstrate the potential of this method, the authors present a schematic setup for data collection in a DAC at a synchrotron beamline and provide an example structure determination for seifertite at 129 GPa. They conclude with a discussion of future software developments that can facilitate wide and routine application of multigrain techniques.

Knowledge of how minerals deform at high pressures is key to understanding how planetary interiors evolve. In Chapter 11, “Deformation and Plasticity of Materials under Extreme Conditions,” Sébastien Merkel (Université de Lille) provides a stimulating review of the tremendous experimental advances made in the last quarter century, especially the coupling of high-pressure instruments with synchrotron radiation, for addressing the deformation and plasticity of materials under extreme conditions. Merkel discusses deformation experiments in both large volume presses and diamond anvil cells, noting their differences, advantages, and limitations, as well as new advances using torsion devices combined with tomographic measurements. Following on from Zhang and colleagues’ chapter, Merkel describes how studies of microstructures and plastic deformation have advanced to new heights using multigrain X-ray diffraction to study lattice-preferred orientation and microstructural elements to constrain plastic deformation mechanisms, and shows how deformation experiments are best interpreted using self-consistent methods that treat each grain of the polycrystal as an inclusion in a homogeneous yet anisotropic medium. Merkel then reviews applications of deformation experiments to deep Earth materials such as core-forming iron metal, and the lower mantle phases ferropericlase and bridgmanite, discussing how plastic deformation depends on the complex interplay between microstructure and the properties of each phase. Merkel provides an optimistic perspective of the future of deformation studies at high pressure, noting how improvements in high-pressure techniques and coupled in situ measurements will allow interrogation of samples at increasingly high pressures and over a wide range of strain rates.

The multi-anvil press (MAP) has for decades been a high-pressure experimental workhorse, and in Chapter 12, “Synthesis of High-Pressure Silicate Polymorphs Using Multi-Anvil Press,” Jie Li (University of Michigan) extols the virtues of the MAP for material synthesis, structure and property investigations, and studies of phase equilibria and chemical reactions in the geological and materials sciences. Li begins by providing the basics of pressure generation and the factors that limit sample size in the MAP and delves into the realms of pressure calibration and uncertainties as well as temperature generation, measurement, and variability. The main thrust of the chapter is in describing synthesis strategies for growing large (e.g., mm-sized), pure, single crystals at high pressure that are required for investigating the key properties needed to understand deep planetary interiors. Li discusses the theory of nucleation and growth of phases from melts and fluids and in solid-state transformations, and provides examples and phase diagrams for the key transition zone and lower-mantle phases wadsleyite, ringwoodite, and bridgmanite, including a discussion of the characterization of synthesis products through combination of

microanalytical techniques. Li concludes by stressing the importance of new initiatives to support construction of mammoth multi-anvil presses (e.g., ~60,000 tons) for synthesizing large single crystals and polycrystalline samples related to deep planetary interiors as well as for synthesis of superhard materials including polycrystalline nanodiamonds, carbides, and nitrides.

Recent technological advances make the diamond anvil cell an increasingly valuable petrological tool, and in Chapter 13, Yingwei Fei and Michael Walter (Carnegie Institution for Science), James Badro (Institut de Physique du Globe de Paris), Kei Hirose (Earth-Life Science Institute), Oliver T. Lord (University of Bristol), Andrew J. Campbell (University of Chicago), and Eiji Ohtani (Tohoku University) team up to describe in recent efforts in “Investigation of Chemical Interactions and Melting Using Laser-Heated Diamond Anvil Cell.” In this chapter, the authors describe how technical developments, especially focused ion beam (FIB) technology, allow ever more reliable investigations of element partitioning and melting phase relations at pressures approaching the center of the Earth. The authors begin with a discussion of temperature and pressure determination in the laser-heated DAC (LHDAC) and the importance of matching the temperature distribution to textural and chemical observations in recovered samples. They describe methods for preparing homogeneous starting materials, including ultrafast quenching methods such as aerodynamic levitation and ball-mill preparation of homogeneous metal alloys, and discuss new loading techniques using FIB fabrication. FIB technology is also key for *ex situ* chemical and textural analyses, allowing precisely milled cross sections of the heated spot at the micron and submicron scale. Examples utilizing these cutting-edge techniques are provided, including studies of metal-silicate interaction, melting phase relations of mantle compositions, and melting of core alloys. The chapter ends by advocating for coordinated collaborative efforts to share well-characterized starting materials, and a challenge to achieve a direct determination of melting relations at the inner core boundary with sample recovery for quantitative chemical analysis to help solve the longstanding problem of the composition of Earth’s core.

Knowledge of the behavior of light element molecular compounds (e.g., H, He, N) at extreme pressures is key to unlocking the secrets of gas giant planetary interiors as well as for understanding their fundamental physics. In Chapter 14, “Molecular Compounds under Extreme Conditions,” Alexander Goncharov (Carnegie Institution for Science) reviews experimental studies of molecular solids at high pressures over the past several decades. Goncharov emphasizes the importance of the pressure variable and the balance between intermolecular and intramolecular bonds leading to the formation of structurally complex crystals. Goncharov relates Dave Mao’s pioneering work and legacy in high-pressure research of molecular solids, especially in relation to hydrogen (metallization, clathrates), and the technical advances in experimental (e.g., gas loading) and analytical techniques needed to study these challenging materials at extreme pressures. Also described are the analytical developments that were crucial for probing the structure and behavior of low-Z molecular compounds, especially the three complementary optical spectroscopy techniques (Raman, Brillouin, and infrared), as well as X-ray scattering techniques. Goncharov describes a number of fascinating examples, including dense H<sub>2</sub>O ices (e.g., VII and X),

clathrate structures, nitrogen compounds, inclusion compounds (cocrystals), and “high-T” superconductors (e.g.,  $\text{H}_3\text{S}$ ). Goncharov suggests a promising future in further investigating these fascinating compounds by combining experimental static and dynamic high-pressure techniques to reach ever more extreme conditions and through further integrating experiments and theoretical approaches.

Achieving superconductivity in a solid material at room temperature has been a “holy grail” in solid-state physics for decades. In Chapter 15, “Superconductivity at High Pressure,” Mikhail I. Eremets (Max Planck Institute for Chemistry) presents a fascinating narrative of the search for high-temperature superconductivity and the progress that has been made in using high pressure to investigate candidate materials. The epic begins with the search for metallic hydrogen at the Geophysical Lab driven by Dave Mao and colleagues as they entered into the megabar realm using the diamond anvil cell. Eremets describes the elusive metallization of hydrogen and the exploration of other materials such as xenon and lithium and the early successes when the highest superconducting temperatures were of the order 20 K. But metallization of hydrogen remained elusive, and still does, and Eremets relates how the search moved to hydrogen alloys. The material landscape frontier expanded with the advent of *ab initio* calculations that could find new structures and make predictions of superconductivity coupled with improvements in DAC techniques that allowed multimegabar experiments. Eremets regales us with the tale of  $\text{H}_2\text{S}$ , a compound that metallizes at about a megabar with a superconducting temperature of the order 80 K, and how work on this and related compounds led to superconductivity measurements at megabar pressures in the range of 200 K (e.g.,  $\text{H}_3\text{S}$ ). The drama continues with the recent work on lanthanum hydrides, where superconductivity at temperatures approaching room temperature ( $\sim 250$  K) have been achieved. Eremets ends the tale with a forward-looking and optimistic perspective on the search for room temperature superconductivity and the best candidates for future research.

In Chapter 16, “Thermochemistry of High-Pressure Phases,” Alexandra Navrotsky (University of California at Davis) honors Dave Mao with a thoughtfully crafted review on the application of calorimetry to high-pressure research. The review begins with a concise treatment of the fundamental thermodynamic relationships related to the Gibbs free energy of reaction and the wide utility of thermochemical data, so long as it is made internally consistent in both values and format. Describing calorimetry as “the science and art of measuring heat effects,” Navrotsky explains how knowledge of the enthalpy of reaction,  $\Delta H$ , especially in combination with the entropy of reaction obtained from heat capacity measurements, provides the basis for posing the fundamental question of solid-state chemistry: “What structures can form at a given composition and why?” Navrotsky guides us through advances in calorimetric methodology, describing cryogenic heat capacity measurements in adiabatic calorimeters ranging from the large vessels holding grams of material to miniaturized “calorimeters-on-a-chip” to measure of micrograms of samples, as well as high-temperature solution and reaction calorimetry. This is followed by a systematic look at a range of materials including silicate spinels, perovskites, chalcogenides, nitrides, and carbides, as well as an enlightening discussion of water and defects in high-pressure phases and nanoscale effects. Navrotsky ends with a thoughtful

perspective of the important role of calorimetry in combination with high-pressure synthesis and phase equilibria, especially when integrated with crystallographic, spectroscopic, and theoretical studies, and how together they lead to essential insights into the structure and dynamics of the interior of the Earth and other planetary bodies.

### References

- Badding, J. V., Hemley, R. J., Mao, H. K. (1991). High-pressure chemistry of hydrogen in metals – in situ study of iron hydride. *Science*, **253**, 421–424.
- Badro, J., Struzhkin, V. V., Shu, J., et al. (1999). Magnetism in FeO at megabar pressures from X-ray emission spectroscopy. *Physical Review Letters*, **83**, 4101.
- Bell, P., Yagi, T., Mao, H. (1979). Iron-magnesium distribution coefficients between spinel [(Mg, Fe) 2SiO<sub>4</sub>], magnesiowüstite [(Mg, Fe) O], and perovskite [(Mg, Fe) SiO<sub>3</sub>]. *Year Book Carnegie Institute Washington*, **78**, 618–621.
- Chen, X.-J., Wang, J.-L., Struzhkin, V. V., Mao, H.-k., Hemley, R. J., Lin, H.-Q. (2008). Superconducting behavior in compressed solid SiH<sub>4</sub> with a layered structure. *Physical Review Letters*, **101**, 077002.
- Duffy, T. S., Hemley, R. J., Mao, H. K. (1995). Equation of state and shear-strength at multimegabar pressures – magnesium-oxide to 227GPa. *Physical Review Letters*, **74**, 1371–1374.
- Eremets, M. I., Struzhkin, V. W., Mao, H. K., Hemley, R. J. (2001). Superconductivity in boron. *Science*, **293**, 272–274.
- Fei, Y. W., Mao, H. K. (1994). In-situ determination of the NiAs phase of FeO at high-pressure and temperature. *Science*, **266**, 1678–1680.
- Goncharov, A. F., Kong, L., Mao, H.-k. (2019). High-pressure integrated synchrotron infrared spectroscopy system at the Shanghai Synchrotron Radiation Facility. *Review of Scientific Instruments*, **90**, 093905.
- Goncharov, A. F., Struzhkin, V. V., Somayazulu, M. S., Hemley, R. J., Mao, H. K. (1996). Compression of ice to 210 gigapascals: infrared evidence for a symmetric hydrogen-bonded phase. *Science*, **273**, 218–220.
- Gregoryanz, E., Goncharov, A. F., Matsuishi, K., Mao, H., Hemley, R. J. (2003). Raman spectroscopy of hot dense hydrogen. *Physical Review Letters*, **90**(17).
- Gregoryanz, E., Goncharov, A. F., Sanloup, C., Somayazulu, M., Mao, H.-k., Hemley, R. J. (2007). High P-T transformations of nitrogen to 170 GPa. *Journal of Chemical Physics*, **126**, 184505.
- Hemley, R. J., Mao, H.-k. (1988). Phase-transition in solid molecular-hydrogen at ultrahigh pressures. *Physical Review Letters*, **61**, 857–860.
- Hemley, R. J., Mao, H.-k., Struzhkin, V. V. (2005). Synchrotron radiation and high pressure: new light on materials under extreme conditions. *Journal of Synchrotron Radiation*, **12**, 135–154.
- Hirose, K., Fei, Y. W., Ma, Y. Z., Mao, H. K. (1999). The fate of subducted basaltic crust in the Earth's lower mantle. *Nature*, **397**, 53–56.
- Hu, Q. Y., Kim, D. Y., Yang, W. G., et al. (2016). FeO<sub>2</sub> and FeOOH under deep lower-mantle conditions and Earth's oxygen-hydrogen cycles. *Nature*, **534**, 241–244.
- Jephcoat, A. P., Mao, H. K., Bell, P. M. (1986). Static compression of iron to 78-GPa with rare-gas solids as pressure-transmitting media. *Journal of Geophysical Research – Solid Earth and Planets*, **91**, 4677–4684.
- Ji, C., Li, B., Liu, W., et al. (2019). Ultrahigh-pressure isostructural electronic transitions in hydrogen. *Nature*, **573**, 558–562.

- Li, J., Struzhkin, V. V., Mao, H. K., et al. (2004). Electronic spin state of iron in lower mantle perovskite. *Proceedings of the National Academy of Sciences of the United States of America*, **101**, 14027–14030.
- Lin, J. F., Struzhkin, V. V., Jacobsen, S. D., et al. (2005). Spin transition of iron in magnesiowustite in the Earth's lower mantle. *Nature*, **436**, 377–380.
- Lin, Y. H., Hu, Q. Y., Meng, Y., Walter, M., Mao, H. K. (2020). Evidence for the stability of ultrahydrous stishovite in Earth's lower mantle. *Proceedings of the National Academy of Sciences of the United States of America*, **117**, 184–189.
- Liu, J., Hu, Q. Y., Bi, W. L., et al. (2019). Altered chemistry of oxygen and iron under deep Earth conditions. *Nature Communications*, **10**(1), 1–8.
- Liu, J., Hu, Q. Y., Kim, et al. (2017). Hydrogen-bearing iron peroxide and the origin of ultralow-velocity zones. *Nature*, **551**, 494–497.
- Liu, L. G. (1976). Orthorhombic perovskite phases observed in olivine, pyroxene and garnet at high-pressures and temperatures. *Physics of the Earth and Planetary Interiors*, **11**, 289–298.
- Loubeyre, P., LeToullec, R., Hausermann, D., et al. (1996). X-ray diffraction and equation of state of hydrogen at megabar pressures. *Nature*, **383**, 702–704.
- Mao, H. K., Bassett, W. A., Takahashi, T. (1967). Effect of pressure on crystal structure and lattice parameters of iron up to 300 kbar. *Journal of Applied Physics*, **38**, 274–276.
- Mao, H. K., Bell, P. M. (1978). High-pressure physics – sustained static generation of 1.36 to 1.72 megabars. *Science*, **200**, 1145–1147.
- Mao, H. K., Bell, P. M. (1979). Equations of state of MgO and epsilon-Fe under static pressure conditions. *Journal of Geophysical Research*, **84**, 4533–4536.
- Mao, H. K., Bell, P. M., Shaner, J. W., Steinberg, D. J. (1978). Specific volume measurements of Cu, Mo, Pd, and Ag and calibration of ruby R1 fluorescence pressure gauge from 0.06 to 1 Mbar. *Journal of Applied Physics*, **49**, 3276–3283.
- Mao, H.-k., Chen, B., Chen, J., et al. (2016). Recent advances in high-pressure science and technology. *Matter and Radiation at Extremes*, **1**, 59–75.
- Mao, H. K., Chen, L. C., Hemley, R. J., Jephcoat, A. P., Wu, Y., Bassett, W. A. (1989). Stability and equation of state of CaSiO<sub>3</sub>-perovskite to 134-GPa. *Journal of Geophysical Research – Solid Earth and Planets*, **94**, 17889–17894.
- Mao, H. K., Hemley, R. J. (1994). Ultrahigh-pressure transitions in solid hydrogen. *Reviews of Modern Physics*, **66**, 671–692.
- Mao, H.-k., Hemley, R. J. (1996). Energy dispersive X-ray diffraction of micro-crystals at ultrahigh pressures. *International Journal of High Pressure Research*, **14**, 257–267.
- Mao, H. K., Hemley, R. J., Wu, Y., et al. (1988a). High-pressure phase-diagram and equation of state of solid helium from single-crystal X-ray-diffraction to 23.3-GPa. *Physical Review Letters*, **60**, 2649–2652.
- Mao, H. K., Hu, Q. Y., Yang, L. X., et al. (2017). When water meets iron at Earth's core-mantle boundary. *National Science Review*, **4**, 870–878.
- Mao, H. K., Jephcoat, A. P., Hemley, R. J., et al. (1988b). Synchrotron X-ray-diffraction measurements of single-crystal hydrogen to 26.5 gigapascals. *Science*, **239**, 1131–1134.
- Mao, H.-k., Kao, C., Hemley, R. J. (2001a). Inelastic X-ray scattering at ultrahigh pressures. *Journal of Physics: Condensed Matter*, **13**, 7847.
- Mao, H. K., Shen, G. Y., Hemley, R. J. (1997). Multivariable dependence of Fe–Mg partitioning in the lower mantle. *Science*, **278**, 2098–2100.
- Mao, H. K., Shu, J. F., Shen, G. Y., Hemley, R. J., Li, B. S., Singh, A. K. (1998). Elasticity and rheology of iron above 220 GPa and the nature of the Earth's inner core. *Nature*, **396**, 741743.

- Mao, H. K., Takahashi, T., Bassett, W. A., Kinsland, G. L., Merrill, L. (1974). Isothermal compression of magnetite to 320 kbar and pressure-induced phase-transformation. *Journal of Geophysical Research*, **79**, 1165–1170.
- Mao, H. K., Wu, Y., Chen, L. C., Shu, J. F., Jephcoat, A. P. (1990). Static compression of iron to 300 GPa and Fe<sub>0.8</sub>Ni<sub>0.2</sub> alloy to 260 GPa – implications for composition of the core. *Journal of Geophysical Research-Solid Earth and Planets*, **95**, 21737–21742.
- Mao, H. K., Xu, J., Bell, P. M. (1986). Calibration of the ruby pressure gauge to 800-kbar under quasi-hydrostatic conditions. *Journal of Geophysical Research-Solid Earth and Planets*, **91**, 4673–4676.
- Mao, H. K., Xu, J., Struzhkin, V. V., et al. (2001b). Phonon density of states of iron up to 153 gigapascals. *Science*, **292**, 914–916.
- Mao, W. L., Mao, H.-k., Meng, Y., et al. (2006a). X-ray-induced dissociation of H<sub>2</sub>O and formation of an O<sub>2</sub>-H<sub>2</sub> alloy at high pressure. *Science*, **314**, 636–638.
- Mao, W. L., Mao, H.-k., Sturhahn, W., et al. (2006b). Iron-rich post-perovskite and the origin of ultralow-velocity zones. *Science*, **312**, 564–565.
- Meng, Y., Mao, H.-k., Eng, P. J., et al. (2004). The formation of sp(3) bonding in compressed BN. *Nature Materials*, **3**, 111–114.
- Merkel, S., Wenk, H. R., Shu, J. F., et al. (2002). Deformation of polycrystalline MgO at pressures of the lower mantle. *Journal of Geophysical Research – Solid Earth*, **107**, (B11), ECV 3.1–EVC3.17.
- Piermarini, G. J. (2001). High pressure X-ray crystallography with the diamond cell at NIST/NBS. *Journal of Research of the National Institute of Standards and Technology*, **106**, 889–920.
- Saxena, S., Dubrovinsky, L., Häggkvist, P., Cerenius, Y., Shen, G., Mao, H. (1995). Synchrotron X-ray study of iron at high pressure and temperature. *Science*, **269**, 1703–1704.
- Sharma, S. K., Mao, H. K., Bell, P. M. (1980). Raman measurements of hydrogen in the pressure range 0.2–630 kbar at room-temperature. *Physical Review Letters*, **44**, 886–888.
- Shen, G., Mao, H.-k., Hemley, R. J. (1996). Laser-heated diamond anvil cell technique: double-sided heating with multimode Nd: YAG laser. *Computer*, **1**, L2.
- Shen, G., Wang, L., Ferry, R., Mao, H.-k., Hemley, R. J. (2010). A portable laser heating microscope for high pressure research. *Journal of Physics: Conference Series*, **215**, 012191.
- Shen, G. Y., Mao, H. K. (2017). High-pressure studies with X-rays using diamond anvil cells. *Reports on Progress in Physics*, **80**, 1–53.
- Shen, G. Y., Mao, H. K., Hemley, R. J., Duffy, T. S., Rivers, M. L. (1998). Melting and crystal structure of iron at high pressures and temperatures. *Geophysical Research Letters*, **25**, 373–376.
- Shieh, S. R., Mao, H. K., Hemley, R. J., Ming, L. C. (1998). Decomposition of phase D in the lower mantle and the fate of dense hydrous silicates in subducting slabs. *Earth and Planetary Science Letters*, **159**, 13–23.
- Somayazulu, M., Dera, P., Goncharov, A. F., et al. (2010). Pressure-induced bonding and compound formation in xenon–hydrogen solids. *Nature Chemistry*, **2**, 50–53.
- Stixrude, L., Hemley, R. J., Fei, Y., Mao, H. K. (1992). Thermoelasticity of silicate perovskite and magnesio-wüstite and stratification of the Earth's mantle. *Science*, **257**, 1099–1101.
- Vos, W. L., Finger, L. W., Hemley, R. J., Mao, H. K. (1993). Novel H<sub>2</sub>-H<sub>2</sub>O clathrates at high-pressures. *Physical Review Letters*, **71**, 3150–3153.



- Wang, Y., Ying, J., Zhou, Z., et al. (2018). Emergent superconductivity in an iron-based honeycomb lattice initiated by pressure-driven spin-crossover. *Nature Communications*, **9**, 1–7.
- Yagi, T., Bell, P., Mao, H. (1979). Phase relations in the system MgO-FeO-SiO<sub>2</sub> between 150 and 700 kbar at 1000 C. *Year Book Carnegie Institute Washington*, **78**, 614–618.
- Yagi, T., Mao, H. K., Bell, P.M. (1978). Structure and crystal-chemistry of perovskite-type MgSiO<sub>3</sub>. *Physics and Chemistry of Minerals*, **3**, 97–110.
- Yoshimura, Y., Stewart, S. T., Somayazulu, M., Mao, H.-k., Hemley, R. J. (2006). High-pressure X-ray diffraction and Raman spectroscopy of ice VIII. *Journal of Chemical Physics*, **124**, 024502.
- Zeng, Z., Yang, L., Zeng, Q., et al. (2017). Synthesis of quenchable amorphous diamond. *Nature Communications*, **8**, 1–7.
- Zha, C. S., Mao, H. K., Hemley, R. J. (2000). Elasticity of MgO and a primary pressure scale to 55 GPa. *Proceedings of the National Academy of Sciences of the United States of America*, **97**, 13494–13499.
- Zhang, L., Yuan, H. S., Meng, Y., Mao, H. K. (2018). Discovery of a hexagonal ultradense hydrous phase in (Fe,Al)OOH. *Proceedings of the National Academy of Sciences of the United States of America*, **115**, 2908–2911.
- Zhao, J., Sturhahn, W., Lin, J.-f., Shen, G., Alp, E. E., Mao, H.-k. (2004). Nuclear resonant scattering at high pressure and high temperature. *High Pressure Research*, **24**, 447–457.
- Zhou, Y., Wu, J., Ning, W., et al. (2016). Pressure-induced superconductivity in a three-dimensional topological material ZrTe<sub>5</sub>. *Proceedings of the National Academy of Sciences*, **113**, 2904–2909.
- Zhu, J., Zhang, J., Kong, P., et al. (2013). Superconductivity in topological insulator Sb<sub>2</sub>Te<sub>3</sub> induced by pressure. *Scientific Reports*, **3**, 1–6.