



Materials under pressure

Anita Zeidler and Wilson A. Crichton, Guest Editors

Pressure is a key parameter in manufacturing, physical sciences, and life sciences in defining the state of matter. In this issue of *MRS Bulletin*, we focus on several of the many and diverse domains of advanced materials research where applied pressure (or stress) is used to alter, or otherwise garner information on, material properties. We give an overview of research in which the application of high pressure—often combined with high temperatures and advanced analysis—has led to technological progress, such as in the preparation of superhard materials, in discovering new chemistry for dense forms of low-Z elements, and in the interplay and mimicking of chemical-induced versus pressure-induced structural and electronic changes to prepare new magnetic and energy materials. In addition, the response of materials such as glasses and perovskites to high-stress conditions is discussed, where pressures in the gigapascal regime can easily be achieved in everyday usage. Finally, the structural, dynamical, and phase behavior of biological systems under pressure is explored.

Introduction

On Earth, pressures can range from one bar (10^{-4} GPa) at the surface, to a few hundreds of bars (on the order of 10^{-2} GPa) at the bottom of the oceans, to around 3.6×10^6 bar (360 GPa) at the Earth's center¹ (**Figure 1**). In comparison, the pressure at the center of the sun is estimated to be around 26.5×10^6 GPa. For many years, scientists have been motivated to attain ever higher pressures in the laboratory, to reproduce and study some of the phenomena seen in real life, and to create novel materials with new and unique properties.^{2–6} The applied pressure can be varied almost continuously by more than seven orders of magnitude above ambient pressure, and its influence can have a profound effect on the electronic structure, bonding, and coordination environments of atoms, the rates and types of possible reactions, and the microscopic to macroscopic volumetric response and deformation to such loads. The state of matter can be changed in a controlled way. In addition, advances in instrumentation are enabling completely new regions of phase space to be explored by experiment, while at the same time giving enhanced access to the information required to solve materials-related issues.

The definition of “high pressure” depends on the field of interest. Pressures can be small, at just a few tens of MPa, as in the investigation of biological systems such as the extremophile organisms that live at the bottom of the oceans or the study of protein folding, or they can be in excess of 1 TPa, which are not

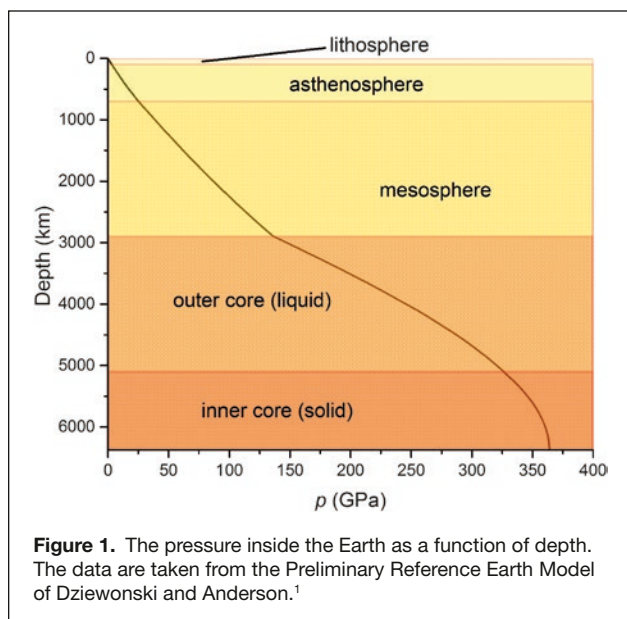
found naturally on Earth, but are achievable in shock compression experiments that are leading to the discovery of novel states of matter and novel physicochemical phenomena.⁷ The theme of this issue is “Materials under pressure.” It presents an overview of recent advances in high-pressure experimental methods and instrumentation (such as diamond anvil cells [DACs],⁸ multianvil presses,⁹ or the Paris-Edinburgh press¹⁰ [**Figure 2**]) to study matter in materials science, physics, chemistry, engineering, and biology.

Superhard materials

In their article in this issue, Sumiya reports on current progress in the development of ultrahard materials for abrasives, cutting tools, and wire dies.¹¹ This work extends the discussion of the March 2003 issue of *MRS Bulletin* on “Superhard coating materials”¹² toward the nanoscale, illustrating binderless nanopolycrystalline diamond and cBN phases. The physical properties of these synthetic ultrahard materials surpass those of microscopic and single-crystal materials through loss of binder and the absence of cleavage and anisotropy.¹³ Sumiya discusses the industrial significance of the high-pressure and -temperature sintering processing of these materials, their influence on the microstructure, as well as their mechanical properties. They also discuss how these tie to the eventual improved application of both nanophase diamond and cBN in high-precision machining of

Anita Zeidler, University of Bath, UK; az207@bath.ac.uk

Wilson A. Crichton, European Synchrotron Radiation Facility, France; wilson.crichton@esrf.fr
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nonferrous advanced alloys and ceramics, and for ferrous materials, respectively.^{14,15}

Superhigh pressures

At the extreme pressures occurring deep in planets and stars, which until now had not been studied, different chemistries form extended and dense forms of low-*Z* compounds. The article by Yoo¹⁶ in this issue draws from the behavior of ices,¹⁷ CO₂,^{18,19} and nitrogen^{20–22} to illustrate some of the structures that have been discovered and their associated properties. This work opens up the opportunity to make novel compounds with, for example, new piezoelectric, ferromagnetic, or superconducting functionality,^{23,24} or extremely high energy densities. It may prove possible to recover to ambient conditions long-lifetime metastable materials with transformative properties, as illustrated by the existence of diamond with superhard properties.

Chemistry at high pressure

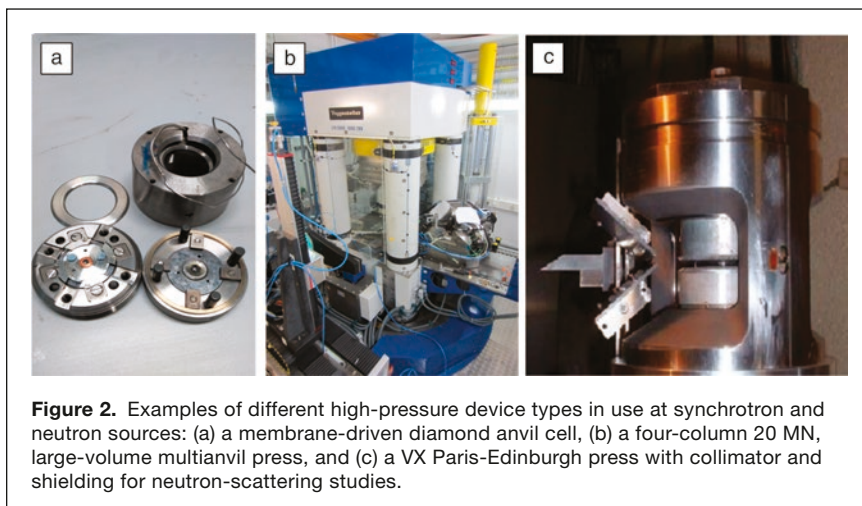
Pressure can be used as a method to access and tune structural and electronic configurations not available at atmospheric conditions. Once the desired property is identified and the structure is determined, an attempt can be made to reproduce this structure using alternative synthesis methods. In their article in this issue, Postorino and Malavasi illustrate these effects with two classes of modern technological materials.²⁵

First, the pressure-induced variation of the properties of hybrid perovskites for solar-energy cells (see also *MRS Bulletin*, May 2014²⁶ and August 2015²⁷) are illustrated and discussed in parallel with the chemically induced changes that occur by substituting different halides or organic ligands.^{28–30} The authors illustrate how the bandgap and carrier lifetime—both critical for solar application—could be influenced by substitution or by substrate selection, thus suggesting new (potentially pressure-influenced) directions of approach to longstanding issues. The second class of materials are manganites, which show exceptional magnetic and electronic functional diversity.³¹ They exhibit phenomena that range from high-temperature superconductivity to colossal magnetoresistance.

Postorino and Malavasi demonstrate the wide applicability of the diamond anvil cell (DAC) to combined measurements of the structural, optical, electronic, and magnetic properties of these materials, often carried out in parallel. With the DAC, they describe influencing the many degrees of freedom that affect the previously mentioned phenomena, intrinsic (e.g., chemistry, ionic radii) as well as extrinsic (e.g., temperature, pressure, applied field). These investigations illustrate the rich phase diagrams of manganites,^{32,33} with possible metallic, insulating, charge-ordered, or various magnetic phases.

Plastic deformations

How elastic moduli, which control fundamental mechanical properties of deformation and rheology, are affected by pressure is discussed in the article by Carrez and Cordier in this issue.³⁴ The fact that the elastic moduli and pressure scales are of a similar order implies that they will have a significant effect on the bonding, strength, and dynamics of materials studied under load. This is further complicated by the presence of defects—point defects, dislocations, and grain boundaries—in materials, and to the dependence of these defects on the class of material. The authors draw on examples from calculations on the pressure response to defect behavior in body-centered-cubic (bcc) metals,^{35,36} and in ionic³⁷ and covalent systems to illustrate the wide variation possible. They extend this discussion to illustrate the contrasting behavior of two forms of MgSiO₃, the perovskite³⁸ and the post-perovskite.³⁹ The transformation between the two is one of the more fundamental transformations in the Earth's deep mantle.



Glasses under pressure

Increasing defect density further, the article by Salmon and Huang⁴⁰ discusses the inherently disordered nature of glasses that makes investigations into its structural response a complex task. Much ground has, however, been covered in recent years in the characterization of glasses at all length scales.^{41,42} The local atomic environments such as bonding, coordination, and angular distribution of adjacent units, and their organization on an intermediate scale, have been investigated. These have been linked to the macroscopic mechanical bulk responses to increased load or strain.⁴³

Salmon and Huang discuss the importance of pressure on the ability to control and understand the mechanical properties of a glass. They illustrate that harder, more robust, denser glasses are desirable for scratch resistance, or for changing optical properties, where the power of lenses, or the resolution of a microscope, are given by functions of the refractive index, which generally varies with density. As in other materials, glasses can be affected by both mechanical and chemical pressure, thereby changing the structure and properties of these materials.^{44,45} High pressures in the GPa regime are produced under the tip of an indenter, which is used to simulate the scratching or deformation of the surface of the glass.^{46,47} Glasses can have inherently long relaxation times. This means that it is possible to recover new materials from high-pressure conditions in a densified form, which may lead to more fracture-resistant materials. Experimental and computational approaches can now be used to investigate the response of glasses to tests of these functionalities through detailed understanding of their structure–property relations.^{48,49}

Biological systems under pressure

High pressure is also an important parameter in natural systems, with augmented interest in biotechnological applications. As in inorganic systems, the application of pressure affects reactions, activation barriers, and reaction rates. In their article, Czeslik et al. discuss the complex processes involved and the methods employed for investigating how reactions in biological systems can be altered by the application of hydrostatic pressure, using enzymes as an example.⁵⁰ As enzymes are natural catalysts, they are key to developing more advantageous biotechnologies,^{51,52} particularly when pressure can be used to enhance reaction rates when other extrinsic parameters cannot (e.g., when higher temperatures might cause denaturation).^{53,54} Other features such as strengthened hydrogen bonds, interrupted hydrophobic and hydrophilic interactions, formation of new conformations, tuned flexibility in structural conformation, and overall energetic description of the process all play a role.⁵⁵ The authors illustrate such enzyme activity using stopped-flow technology in a well-chosen model system that reveals how pressure could be useful to biotechnological applications.^{56,57} The pressures involved in this case are orders of magnitude smaller (in the MPa regime) than in the inorganic systems discussed earlier.

Summary

Pressure can have a dramatic effect on the structure and properties of materials and hence it can be used as a means for manipulating and probing materials of technological and biological interest.

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Wilson A. Crichton is a scientist at the European Synchrotron Radiation Facility, France. He leads the large-volume press at the beamline ID06, following positions on beamlines ID09A, ID27, and ID30. He obtained his PhD degree at University College London, UK, in 2000. He earned his BSc degree in geology and applied geology from the University of Glasgow, UK, and his MSc degree in crystallography from Birkbeck, University of London. He is a former editorial board member of *Mineralogical Magazine*, and a Fellow of the Mineralogical Society of America. Crichton can be reached by phone at +33(0)4 76 88 22 69 or by email at wilson.crichton@esrf.fr.



Anita Zeidler is a Royal Society–Engineering and Physical Sciences Research Council Dorothy Hodgkin Research Fellow at the University of Bath, UK. She completed her undergraduate studies in chemistry at Phillips University of Marburg, Germany, in 2005, and her PhD degree in physics at the University of Bath in 2009. She is the recipient of the 2015 Sir Alastair Pilkington Award from the Society of Glass Technology, the 2014 B.T.M. Willis Prize from the Royal Society of Chemistry and the Institute of Physics (IOP), and the 2013 Liquids and Complex Fluids Early Career Award from the IOP. In 2016, she was the Gordon S. Fulcher Distinguished Scholar

at Corning Inc. Zeidler can be reached by phone at +44 (0)1225 384565 or by email at az207@bath.ac.uk.

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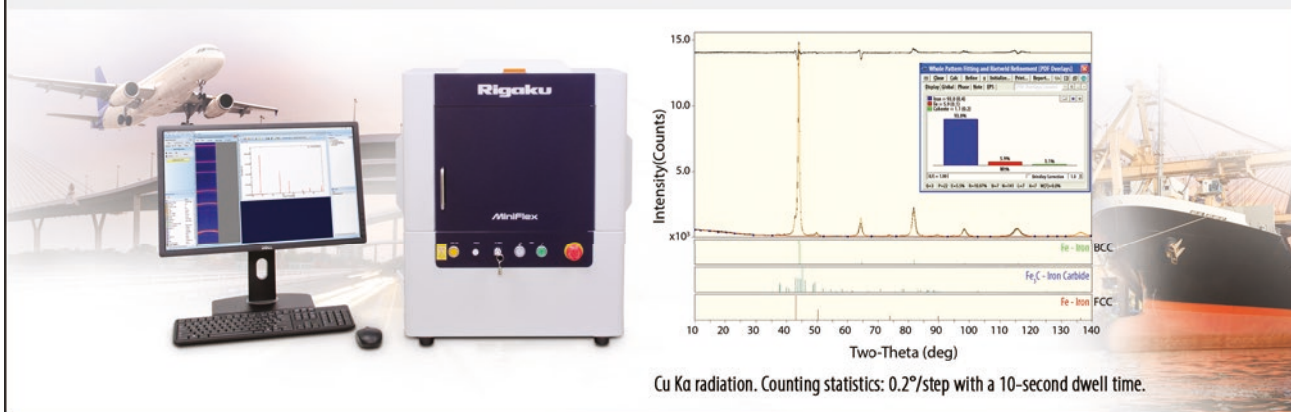
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RETAINED AUSTENITE ANALYSIS



Steels and steel alloys are an essential component in many everyday applications. Quality control is crucial to maintaining the structural stability of these materials. During the processing of these heat-treated steel alloys, austenite may be retained, which could weaken the overall structural integrity of the material used to manufacture our buildings, cars, bridges and much more. In this experiment, retained austenite analysis was performed on a typical metal sample. The retained austenite phase was identified in the pattern below, taken with Rigaku's MiniFlex benchtop diffractometer, in a 5.9(0.1)% concentration.



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