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2.7. High-pressure devices

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2.7.1. Introduction

Although life in the biosphere of Earth exists within narrow limits of temperature and pressure, these thermodynamic conditions are unusual *on* Earth and in the Universe. Most of the matter in the Universe is contained in black holes, stars and planets, where it is exposed to extreme temperature and pressure. On the other hand, interstellar space constitutes most of the Universe's volume, where both pressure and temperature are close to their absolute-zero values. On Earth's surface at sea level, atmospheric pressure is about 1000 hPa [1 atm = kG cm^{-2} = 9.807×10^4 Pa $\simeq$ 0.1 MPa; currently, the pascal (abbreviated Pa) is the generally accepted pressure unit recommended by the International System of Units]. Under water on Earth, the pressure increases by 0.1 MPa for every 10 m depth, and rises to 120 MPa at the bottom of the Mariana Trench, 11 km below the sea's surface. A relatively low pressure change, to about 0.3 MPa at a depth of 20 m, affects the dissolution of nitrogen in human blood and can lead to decompression sickness (caisson disease); at 300 m in the oceans (3 MPa) and 288 K, methane forms stable hydrates, which constitute the most abundant deposits of carbon on Earth. All geological deposits are exposed to some pressure; at a depth of 1000 m this is about 300 MPa. Consequently, the structure and properties of very many minerals, formed and deposited in the crust, can transform considerably after their exposure to the surface. The syntheses of numerous minerals require high-pressure conditions. Thus, high-pressure experiments can provide indispensable information about the geological and stellar mechanisms, transformations and properties governing the matter forms, properties and distribution inside stars and planets.

Therefore, the pressure dependence of crystal structures is of primary interest to geologists, planetologists and astrophysicists (Hazen, 1999; Merlini *et al.*, 2012). The most cited examples of the effects of extreme conditions are thermonuclear synthesis, the formation of diamond (the dielectric carbon allotrope), the formation of stishovite (the dense form of SiO_2) and the propagation of seismic waves through the Earth's crust. The understanding of these and other phenomena requires that extreme conditions be reproduced and crystal structures investigated in laboratories. Most importantly, the conditions that are ubiquitous across the Universe are viewed as extreme only from our perspective of a narrow thermodynamic space, of a few tens of kelvin and a few megapascals around the triple point of water. From this narrow thermodynamic space, most of our knowledge of materials science has been developed. Extreme conditions allow theories to be verified and developed to a more general level. Moreover, extreme conditions can be utilized to produce new materials with desired properties (Hanfland *et al.*, 2011; Senyshyn *et al.*, 2009), including diamond or its other super-hard substitutes, or new forms of pharmaceutical drugs (Boldyreva, 2010; Boldyreva *et al.*, 2002, 2006; Fabbiani, 2010; Fabbiani & Pulham, 2006; Fabbiani *et al.*, 2004, 2005, 2009). The key element for such research is a sample-environment device for generating high pressure in the laboratory.

The pressure at the centre of Earth is about 364 GPa, one order of magnitude higher again inside the giant planets Jupiter and Saturn, and over 1 000 000 GPa (*i.e.* 1000 TPa) inside small stars like the Sun. Structural determinations under varied thermodynamic conditions are essential for the general understanding of physical and chemical phenomena, and to gain knowledge about the properties of materials and to describe the world around us. Indeed, the biosphere where we live is confined to a range from 0.33 atm (0.033 MPa) at the top of Chomolungma (Mt Everest), 8848 m above sea level, to about 1200 atm (120 MPa). The most commonly discussed and studied thermodynamic parameters are temperature (T), pressure (P) and composition (X). In principle, they affect the structure of matter differently. For example, the primary change induced by temperature is in the energy of atomic, molecular and lattice vibrations, whereas increasing pressure always reduces the volume. These changes are interdependent, and the compression of a structure can also reduce its thermal vibrations, change the types of cohesion forces and reverse the balance between competing compounds of different composition. This concerns all compounds, not only minerals deep under the Earth's surface. An exciting example of a molecular compound undergoing such transformations is water, transforming between at least ten polymorphic structures at high pressure, and also forming hydrates, depending on the thermodynamic conditions. Hence, pressure is now utilized to generate new polymorphs and solvates that cannot be obtained under normal conditions (Patyk *et al.*, 2012; Tomkowiak *et al.*, 2013; Fabbiani, 2010; Boldyreva, 2010).

For these reasons, high-pressure techniques have been developed dynamically, and the breakthrough invention of the diamond-anvil cell and its development in the second half of the 20th century greatly intensified high-pressure research. Today, the effects of high pressure on various materials and their reactions are studied both in small laboratories in universities and at large facilities, which provide powerful beams of X-rays from synchrotrons and beams of neutrons from reactors and spallation targets. The large facilities are either international initiatives, like the European Synchrotron Radiation Facility (ESRF) and Institute Laue–Langevin (ILL) in Grenoble, France, or national ones, like the Diamond Light Source and ISIS at the Rutherford Appleton Laboratory in Oxfordshire, UK, the Deutsches Elektronen Synchrotron (DESY) in Hamburg, Germany, the Photon Factory in Tsukuba, SPring-8 (Super Photon ring – 8 GeV) in Hyōgo Prefecture and the Japan Proton Accelerator Research Complex (J-PARC) in Tokal near Tokyo, Japan, the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory, USA, the Advanced Photon Source (APS) at Argonne National Laboratory and Los Alamos National Laboratory (LANL), New Mexico, USA, the Lawrence Livermore National Laboratory, California, USA, the Joint Institute for Nuclear Research (JINR) in Dubna, Russian Federation, the Spallation Neutron Source (SNS) at Oak Ridge National Laboratory, USA, and others. They provide access to the beams and high-pressure equipment to the general scientific community.

2.7.2. Historical perspective

The earliest concepts of pressure are often associated with Evangelista Torricelli's famous statement '*Noi viviamo sommersi nel fondo d'un pelago d'aria*' ('We live submerged at the bottom of an ocean of air') in 1643, Otto von Guericke's experiment pitting the force of six horses against atmospheric pressure acting to squeeze together two hemispheres evacuated using the vacuum pump he had constructed in Magdeburg in 1654, and Blaise Pascal's measurements of pressure differences at different altitudes and his demonstrations of barrels being blown up by the force of water poured in through a tall pipe. The subsequently developed high-pressure devices were mainly of the piston-and-cylinder type.

At the beginning of the 19th century, pressures of about 400 MPa could be obtained, and at the beginning of the 20th century, often referred to as the end of the pre-Bridgman era, pressures up to about 2 GPa could be achieved. Then Percy W. Bridgman's remarkable inventions extended the pressure range greatly, to over 10 GPa (Bridgman, 1964). He devised new techniques for sealing pressure chambers, developed the opposed-anvils apparatus and introduced methods for the controlled measurement of various phenomena. Moreover, he used his new methods to describe a vast number of observations and properties of matter at high-pressure ranges hitherto unexplored. Bridgman's ingenious designs of high-pressure devices, such as the opposed-anvils apparatus, paved the path for future researchers. His scientific achievements won him the Nobel Prize in Physics in 1946.

The Bridgman era in high-pressure research ended in the late 1950s, when the diamond-anvil cell, often abbreviated to DAC, was invented (Weir *et al.*, 1959; Jamieson *et al.*, 1959; Piermarini, 2001). Soon after, the DAC became the main tool of high-pressure researchers; it gradually increased the range of attainable pressure by more than an order of magnitude, and under laboratory conditions it surpassed the pressure level at the centre of the Earth. Most importantly, the DAC allowed many new measuring techniques, particularly X-ray diffraction and optical spectroscopy, to be utilized. Before that, spectroscopic studies were limited to about 0.5 GPa. High-pressure X-ray diffraction, pioneered by Cohen (1933) in Berkeley for powders and by Vereshchagin *et al.* (1958) in Moscow for a single crystal of halite at 0.4 GPa in a beryllium high-pressure vessel, had been expensive, inefficient and inaccurate.

The DAC has become commonly available because of its low cost and easy operation. Today, the DAC continues to be the main and most versatile piece of laboratory pressure equipment and a record-breaking high-pressure apparatus. However, other sample environments provide complementary means of structural studies. For example, the large-volume press can be advantageous for neutron diffraction studies and in experiments where very stable high-pressure/high-temperature conditions are required. Naturally, the success of many high-pressure methods would not be possible without the development of other sciences and technologies, including computers, powerful sources of X-rays and neutrons and their detectors, and lasers.

2.7.3. Main types of high-pressure environments

High-pressure methods can be classified as dynamic or static. In the traditional dynamic methods, the pressure is generated for microseconds, usually at an explosion epicentre or at targets where ultra-fast bullets or gas guns are fired at the sample. The explosions are carried out either in special chambers or in bores underground (Batsanov, 2004; Ahrens, 1980, 1987; Keller *et al.*, 2012).

Even shorter, of a few nanoseconds' duration, the shock compression generated in targets using laser drivers coupled to the powerful X-ray pulses of a free-electron laser, or an otherwise generated X-ray beam, can further extend the attainable pressure limits. While this laser shock generates both high pressure and high temperature in the sample (the so-called Hugoniot compression path), in the ramp compression, also termed the off-Hugoniot path, the signal of the designed profile from an optical laser affords terapascal compression and approximates isothermal conditions (Wicks *et al.*, 2018; Smith *et al.*, 2014; Wang *et al.*, 2016).

The advantage of the gas and laser shock-wave and ramp-compression methods is that the attainable pressure is not limited by the tensile strength of the pressure chamber. Disadvantages include the inhomogeneous pressure, difficulties in controlling the temperature, the requirement for very fast analytical methods and the very high cost. The kinetic products generated during the explosion and in the shock waves can be different from the products recovered after the explosion, and different again from those formed under stable conditions. In most cases the laser-generated shock annihilates the sample.

Static methods are at present more suitable for crystallographic studies. The first variable-temperature sample-environment devices for structural studies of liquids and solids were designed soon after the inception of X-ray diffraction analysis. Structural investigations at high and low temperature at ambient pressure were mainly performed either by blowing a stream of heated or cooled gas onto a small sample (Abrahams *et al.*, 1950) or by placing the sample inside an oven or a cryostat. At present, a variety of attachments for temperature control are commercially available as standard equipment for X-ray and neutron diffractometers. Open-flow coolers using gaseous nitrogen and helium are capable of maintaining temperatures of about 90 K and a few kelvin, respectively, for days and weeks. They are easy to operate and pose no difficulties for centring the sample crystal, because the crystal is mounted, as in routine experiments, on a goniometer head with adjustable x–y–z translations and is visible at all positions through a microscope attached to the diffractometer. Cryostats and furnaces obscure the visibility of the sample and are usually heavy, and hence require strong goniometers; however, they often have the advantage of higher stability, a larger homogeneous area in the sample and a larger range of temperature (see Chapter 2.6).

Devices for static high-pressure generation are more difficult to construct because of the obvious requirement for strong walls capable of withstanding the high pressure applied to the sample. There are several types of high-pressure device and they can be classified in several ways. The piston-and-cylinder (PaC) press is the oldest type of pressure generator. However, the pressure range is limited in most advanced constructions (of multilayer negatively strained cylinders, like one shown in Fig. 2.7.1) to 3.0 GPa (Baranowski & Bujnowski, 1970; Besson, 1997; Dziubek & Katrusiak, 2014). PaC presses are ideal for volumetric measurements on a sample enclosed in the cylinder and for generating pressure in a hydrostatic medium transmitted through a capillary to other external high-pressure chambers containing the sample and optimized for a chosen measurement method, usually optical spectroscopy and diffraction. The external devices include chambers for loading the PaC with gas, which is either the hydrostatic medium or the sample itself (Tkacz, 1995; Rivers *et al.*, 2008; Couzinet *et al.*, 2003; Mills *et al.*, 1980; Yagi *et al.*, 1996; Kenichi *et al.*, 2001). In some pressure generators, a cascade of two or three PaC presses is applied for highly compressible pressure-transmitting media (gases) before the final setup stage.