High-Pressure Geophysics: A Window on the Lower Mantle

Information about the earth's deep interior is scanty, and even inferences drawn from seismic and electrical conductivity measurements include assumptions about the relevant mineral species and their properties. Creating in the laboratory pressures and temperatures characteristic of the lower mantle (300 to 1500 kilobars) has proved difficult, except under transient conditions in shock wave apparatus. But these barriers appear to be falling as geophysicists apply an improved technique for studying materials under extremely high pressures and temperatures. Already investigators have found evidence that suggests major revisions in the accepted picture of the lower mantle. The most recent discovery bears on the chemical evolution of the earth, specifically the separation of a metallic iron core from the iron oxide of the mantle; the new evidence, which has attracted considerable attention among geophysicists, would appear to strengthen the hand of those who believe the earth evolved from an initially homogeneous mass.

The key to these new results is a device known as a diamond-anvil or diamond-window pressure cell. It is not new, having been developed in the late 1950's by a group at the National Bureau of Standards, but it is only recent improvements—in the cell itself and in means of measuring high pressures and of heating samples within the cell—that have made possible significant applications to geophysical and other research problems. If its development has been evolutionary rather than revolutionary, however, the capability of the technique is nonetheless remarkable. Two laboratories have now reported measurements at pressures of 500 kilobars—equivalent to the pressures found at a depth of about 1000 kilometers within the earth.

Perhaps the most striking feature of a diamond-anvil cell to one who is unfamiliar with it is the extremely small size of an apparatus capable of such high pressures (Fig. 1). The small size contrasts with more established high-pressure techniques based on tungsten carbide anvils, which are massive and expensive, although they permit the use of larger samples. In the diamond cell, a spring-lever arm or similar mechanism presses a hardened steel piston containing an anvil-shaped diamond against an opposing diamond anvil. The experimental sample is contained in a metal gasket between the two diamonds, which are cut from gem quality stones of about 0.3 carat. High pressures are achieved because the area of the piston is much larger than that of the diamonds, which are in turn larger than the sample—about 0.25 to 0.3 millimeter across, depending on the apparatus. The whole assembly is small enough to fit in the palm of the hand or, more to the point, under the objective lens of a conventional microscope. The special virtue of the diamonds is their transparency to visible and infrared light, to x-rays, and to gamma rays, which allows investigators to heat the experimental samples with laser beams, directly observe the transformations that occur, and collect information on the temperature and pressure within the cell.

Several groups have led in the refinement of the cell and its applications, including Gasper Piermarini and Stanley Block of the National Bureau of Standards, Ho-kwang Mao and Peter Bell at the Geophysical Laboratory of the Carnegie Institution of Washington, and William Bassett and Li-Chung Ming of the University of Rochester. Piermarini and Block developed a means of calibrating the pressures obtained with the cell, without which its capabilities are of little use, and the Carnegie and Rochester groups have pioneered its application to geophysical investigations in which high temperatures, as well as high pressures, are needed.

The Bureau of Standards technique for pressure measurements, an optical method, involves placing small fragments of ruby in the diamond cell along with an experimental sample. When high-intensity light from a mercury-arc lamp or a laser is directed onto the ruby, it fluoresces, emitting light at a characteristic wavelength that is sensitive to pressure. As pressure increases, the fluorescence line shifts into the red region of the spectrum. By comparing the fluorescence wavelength to electrical conductivity transitions in a variety of materials, which occur at pressures that are reasonably well known below 150 kilobars (the so-called fixed-point scale), Piermarini and Block have established that the ruby shift is linear over a wide range of pressures.

The highest calibrated point on the ruby pressure scale is about 290 kilobars, the pressure at which sodium chloride crystals undergo a transition to a high-pressure phase; the interatomic distances in the NaCl were measured by x-ray diffraction techniques and the pressure was then calculated from an equation of state, so that even this point on the pressure scale is no more accurate than the equation of state. But the fixed-point scale itself is open to question; above 150 kilobars it gives higher pressures than does the ruby technique. Equally important, perhaps, the ruby technique is easy to use; it has been widely adopted. Block and Piermarini report reaching pressures above 500 kilobars, as measured on the ruby scale.

Many basic crystal studies can be done at high pressure without heating the experimental samples. But to reach temperatures of geophysical interest, the Rochester and Carnegie groups have developed means of heating samples to 2000°C or more with a neodymium-doped yttrium aluminum garnet (Nd:YAG) laser. The Nd:YAG laser emits in a spectral region (1.064 micrometers) that is particularly suitable for geochemical and geophysical investigations; many iron-bearing minerals absorb heat readily at this wavelength, but diamonds do not. The laser beam is focused onto the sample with the lens of the microscope that is used to observe the experiment. Temperature is measured optically to within about 25°C with a pyrometer, again using the microscope optics and

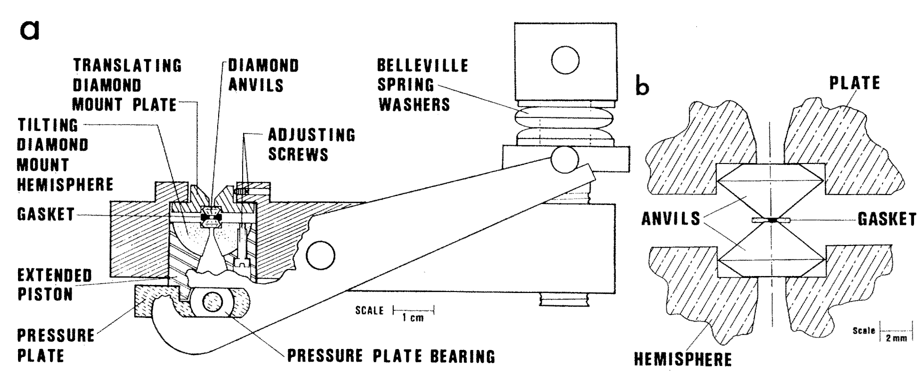

Fig. 1. (a) Schematic of one version of a high-pressure diamond cell. (b) Enlarged schematic showing diamonds, gasket, and experimental sample. [Source: G. J. Piermarini and S. Block, National Bureau of Standards]

a system of filters to channel the infrared radiation given off by the heated sample to the device.

Bassett and Ming have used their equipment to investigate the mineral constituents of the lower mantle. The chemical composition of the mantle is thought to be essentially that of ferromagnesium silicate, which commonly occurs in the upper mantle as the mineral olivine or, at higher pressures and temperatures, as spinel. Shock wave experiments had indicated the existence of still other, and denser, forms of unknown nature. What Bassett and Ming find, however, is that at pressures above 250 kilobars and temperatures above 1000°C, the ferromagnesium silicate breaks down into simple oxides of iron, magnesium, and silicon. Below 650 kilometers, they believe, these oxides constitute the main mineral species in the mantle. They have confirmed the presence of the oxides in their experiments with lengthy x-ray diffraction measurements, and they note that, in agreement with the shock wave data, the oxides are denser than spinel.

Iron oxides are of particular interest since they control the optical, electrical, and thermal properties of the mantle and are thought to have played a principal role in the evolution of the earth. In what could prove a major discovery, Mao and Bell find that iron oxide is not stable at very high pressures and temperatures, and can break down from the ferrous oxidation state (FeO) into metallic iron and higher oxidation states. They heat samples of an iron-rich basaltic glass in a diamond cell at pressures above 300 kilobars and recover metallic iron and ferric oxides (Fig. 2), which suggests that both species can coexist deep within the mantle. If so, what some investigators have held to be a major constraint on the earth's evolution, the impossibility of simultaneously forming both a highly oxidized crust and a metallic core from an originally homogeneous ferrosilicate mixture, would appear to be obviated. Thus, Mao and Bell argue, it is no longer essential to consider more complicated evolutionary histories, such as an initially inhomogeneous earth, because the breakdown of FeO provides a mechanism for forming a metallic core.

Not only the mineral constituents of the lower mantle but also their chemical and physical properties are beginning to be looked at, and there appear to be some unexpected phenomena. Mao and Bell, for example, found that above 100 kilobars olivine, spinel, and many other iron-bearing minerals undergo a marked increase in electrical conductivity, accompanied by a change in the way they absorb light. The investigators propose that the more efficient conduction at high pressure is due to changes in the electronic orbitals of a group of atoms when radiation is absorbed, a process known as charge transfer. Since estimates of the earth's internal temperatures are determined from models that depend on electrical conductivity, the pressure effect will alter those estimates.

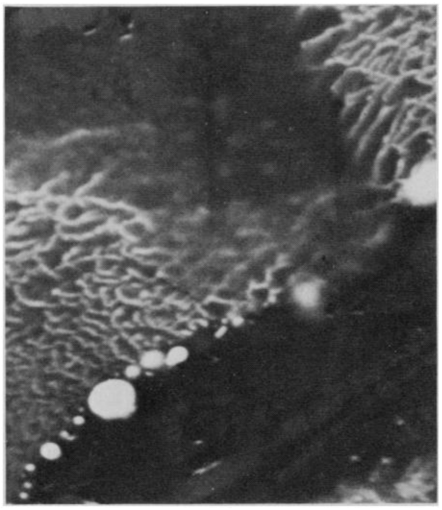

Fig. 2. Sample of basaltic glass under high pressure in a diamond cell; the bright circular spots are beads of metallic iron formed when the sample was heated with a laser beam. [Source: H. K. Mao, Carnegie Geophysical Laboratory]

Thermal conductivity, which also bears on internal temperatures, is also being reassessed. Heat transfer within the lower mantle is thought to occur primarily by radiation. But according to Mao and Bell, the transformation of FeO, which is largely transparent to thermal radiation, to Fe and higher oxides, which are opaque, would effectively block radiative heat transfer. On the other hand, metallic iron and high-pressure forms of iron oxides tend to have high thermal conductivities. It is too early to say what the net effect of higher electrical and thermal conductivity and diminished radiative heat transfer will be on temperature estimates within the earth, but Bell thinks it may well turn out to mean significantly higher temperatures than those now generally accepted.

Still other properties are being explored. Bassett and Edward Brody, also of Rochester, for example, have developed a technique for determining the speed of sound within the tiny sample contained in a diamond cell, from which elastic constants, compressibility, and other properties of interest to seismologists can be calculated.

The diamond-cell technique is not without its flaws. Some earth scientists have been skeptical of the recent results because pressure and temperature are not uniform within the diamond cell. Most investigators now fill the cell with a fluid to achieve an even, hydrostatic pressure on the experimental sample at pressures below 100 kilobars. Above this point, however, even such preferred liquids as methanol-ethanol mixtures freeze and become glassy, so that the pressure distribution is not entirely uniform. Temperature uniformity is also a problem, since diamond is an extremely efficient thermal conductor.

But those active in the field believe that they overcome these limitations by experimental technique and by a range of sophisticated analytical tools—x-ray diffraction, nuclear magnetic resonance measurements, and a host of optical methods—with the result that accurate characterization of high-pressure phenomena is possible. Bassett, for example, has turned the lack of pressure uniformity into a virtue and is using it to study stresses and yield strengths in samples—information of interest to those who model mantle connection. And the investigators believe that further improvements are possible; most are optimistic that pressures higher than 500 kilobars can be achieved.

While very high pressures and temperatures are particularly significant for geophysical investigations, high-pressure techniques have made substantial contributions to basic physics and chemistry. Harry G. Drickamer of the University of Illinois, for example, has made extensive measurements of the electronic states and chemical reactivity of many materials; many of his results stem from optical, electrical resistance, and Mössbauer resonance techniques in a tungsten carbide cell of special design at pressures up to 275 kilobars. Drickamer and others have found that high pressure allows them not only to characterize the electronic behavior of their samples but also to test theories of matter in the solid state. Physicists have also begun to use the diamond cell, with excellent results. At the Bell Laboratories, for example, A. Jayaraman has discovered the existence of valence states intermediate between two integer values. He finds that these curious states come about as the result of an electronic phase transition at high pressure in many rare earths.

There is every indication that interest in the diamond cell and other high-pressure techniques will continue to grow among crystallographers, solid state physicists, and geophysicists. Some of the latter, for example, are said to have recently rushed out to purchase duplicate systems after seeing those at some of the research centers mentioned above. Thus earth scientists may have at last found what they have long needed, a (diamond) window on the lower mantle.

—ALLEN L. HAMMOND