Ultrahigh Pressure: New Highs Spur Pursuit of Exotic Goals

High-pressure researchers have been trying for years to produce, in the laboratory, sustained pressures in excess of 1 million atmospheres and to devise calibration schemes capable of verifying the attainment of such pressures. Recently they have succeeded on both counts.

The achievement of sustained pressures of about 1.5 million atmospheres is having a strong impact on two diverse fields of research. It has shown that the study of rocks under the conditions prevailing at the boundary between the earth's mantle and liquid core is practical. Routine experiments at lower pressure by means of the same techniques are now helping to explain the structure of the earth's mantle directly, rather than by deduction from seismic wave studies. In addition to being a spur to geophysical studies, the refinement of high-pressure techniques has stirred considerable interest in the conversion of molecular hydrogen into its exotic but still hypothetical metallic form, which might be used in many ways, from superconducting electrical generators to controlled nuclear fusion. How close this goal may be has been a matter of some debate, and unrealistic expectations have abounded in the past. But the recent advances together with related high-pressure research have promoted a certain amount of restrained optimism.

The generation of very high pressures, and temperatures, has been made possible by the refinement of the diamond anvil or diamond-window pressure cell (*Science*, 5 December 1975, p. 967), an instrument in which two tiny diamond faces are squeezed together with a solid sample in between. Previously, high pressures had been approached by applying very large forces to relatively large surface areas. But the massive machines required for this have fallen out of favor for ultrahigh-pressure studies as the diamond cell has demonstrated its superiority.

The diamond cell strikes a different balance between force and area (pressure is force per unit area). High pressures are generated by applying modest forces to very small areas (a few hundred micrometers in diameter). The problem with this approach is the possible failure of the diamonds themselves. Even carefully selected and shaped diamonds (at a cost of as much as $500 each) will crack and shatter into so much diamond dust if not properly aligned and supported.

The most successful effort to keep the opposing diamonds intact under ultrahigh pressures has apparently been that of Ho-Kwang Mao and Peter Bell of the Carnegie Institution of Washington's Geophysical Laboratory. These investigators believe that they have reached 1.7 megabars, which would be the highest sustained pressure ever recorded by direct measurement. Although one or the other of the pair of diamonds in other experiments at Carnegie eventually failed at slightly lower pressures, the pair subjected to 1.7 megabars pressure did not fracture. However, one of the diamonds was deformed by the pressure. It would appear that the effective strength of diamond, the hardest substance known, may be the limiting factor in ultrahigh-pressure research, but no one is certain what diamond's ultimate useful strength may be.

Diamond Strength Debated

Arthur Ruoff of Cornell University believes that, under the conditions of Mao and Bell's experiments, diamond cannot support the pressures that have been claimed. Ruoff and J. Wanagel of Cornell have also used a diamond cell, but it consists of a flat plate and a spherically tipped needle, or indentor, whose area of contact is only 1.6 micrometers in diameter. This configuration allows contact to be made on perfect diamond crystal in between imperfections that would cause failure under pressure, they believe. The indentor technique is limited at present by the small area under compression, which does not allow the use of most of the analytical techniques that have made the diamond anvil so popular. The indentor does allow a unique direct determination of the pressure up to 0.5 megabar, but the method is limited to this apparatus. It compared well with a theoretical calculation involving the size of the indentor, the applied force, and the elastic properties of diamond. Using this method, they concluded that a pressure of 1.4 megabars had been created in their indentor experiments.

Conflicting claims have been frequent in high-pressure research, partly because methods for generating very high pressures usually outrun the accepted methods for calibrating the pressures that they create. Such is still the case, but recent work by Mao and Bell, together with John Shaner and Daniel Steinberg of Lawrence Livermore Laboratory, has lead to considerable agreement within the high-pressure community on the calibration methods used up to 1 megabar, the point from which higher measurements have been extrapolated. They compared the ruby fluorescence calibration method, which is routinely used with the diamond anvil, with the widely accepted marker substance method developed in shock wave studies over the last several decades.

Neither of these methods directly measures pressure. Rather, some physical property that varies in a known way with pressure is measured. Determining the relation between the physical property and the pressure usually presents the greatest problems. The wavelength of ruby fluorescence increases linearly with increasing pressure up to 0.5 megabar, but the physical basis for this behavior is not completely understood, and no reliable standard exists for comparison at higher pressures. The increase in the density of metals, or marker substances, with increasing pressure has been firmly linked to fundamental physical principles in this range, but the pressures had been generated for only a microsecond at high temperatures by explosive shock waves. Mao's group linked the two methods by compressing both the metallic marker substances and ruby crystals in the same sample. They believe that the error in the ruby fluorescence calibration, up to 1 megabar, is now 6 percent. Mao and Bell estimate that the error at 1.7 megabars is no more than 20 percent.

This general approach to the measurement of sustained high pressures has received broad support, at least in the range below 1 megabar. Nonetheless, objections have been raised. One is the suggestion that some assumptions made when relating the conditions of the shock wave experiments to those of the diamond anvil were faulty. Steinberg responds that any of a wide range of assumptions would still give pressures within 10 percent of their results. Concerning the question of the strength of diamond, as raised by Ruoff, Mao points out that the available data are not as good as might be hoped. In addition, he says, a substance can be subjected to pressures exceeding its experimentally determined strength if it is properly supported, as has been demonstrated in the

0036-8075/78/0804-0429$00.50/0

case of tungsten carbide. Mao believes that the present design of the diamond cell may allow pressures above 2 megabars to be achieved, but higher pressures would require complete redesign of the support for the diamonds. Echoing the opinion of many specialists, Stanley Block of the National Bureau of Standards, Gaithersburg, Maryland, thinks that the linking of the tried-and-true calibration by means of marker substances with the rapid ruby fluorescence method is reasonable and is the best approach available at present.

Crystal Structures in the Mantle

The ability to subject samples to pressures of up to about 1.5 megabars and to make simultaneous observations should allow high-pressure geophysicists to extend their studies to the conditions prevailing at the bottom of the earth's mantle, 2800 kilometers below the surface. Among other questions, they want to know what changes in mineral structure and composition could be responsible for the sharp density changes with depth observed by seismic methods. These density changes at great depth may affect the slow convection postulated to occur in the mantle. Mantle convection may be a driving force for the motion of continents and the expansion of ocean basins as described by the plate tectonics theory.

Recent diamond anvil experiments by Lin-gun Liu of the Australian National University, Canberra, and by Mao and Bell have helped establish the perovskite-type crystal structure as a major form for mantle rock above 0.3 megabar, which is equivalent to a depth of about 650 kilometers. Geochemical and geophysical evidence indicates that the mantle is composed largely of oxygen, silicon, magnesium, and iron, but there is less agreement about how these elements are grouped to form minerals and how the mineral structures adjust to different pressures and temperatures at different depths. A likely combination of mantle minerals is the three silicates—olivine, pyroxene, and garnet. Liu has suggested that a sudden large change in density at 650 kilometers in part results from the atoms in the olivine crystal adjusting to the pressure by changing into the denser perovskite form in which the oxygen atoms are closer to each other. Minerals having the perovskite crystal structure are at least 20 percent denser than minerals having a low pressure structure. A number of other minerals likely to occur in the mantle have been observed to make the same transition when heated by an infrared laser under high pressures in a diamond anvil press.

The shift to the perovskite crystal structure may not be the last accommodation to increasing pressure within the mantle. Shock wave experiments have already provided some evidence that transition to even denser forms may occur. Since rocks at the bottom of the mantle are under about 1.5 megabars of pressure, such transitions are now within the range of controlled laboratory experiment.

The same high-pressure technique that allows the probing of conditions deep within the earth has also sparked considerable interest in creating metallic hydrogen, the exotic substance that probably makes up the interior of the planet Jupiter (*Science*, 27 April 1973, p. 398). The achievement of this goal would have an impact far beyond the field of planetary science. According to many experts and a Rand report,* the potential usefulness of metallic hydrogen is extraordinary. It may be a superconductor at room temperature, would have an energy content 300 times greater than the best aircraft fuel, and may be an explosive 35 times more powerful than TNT. It could even be useful in laser-induced nuclear fusion and nuclear weapons, a fact that has apparently both encouraged as well as discouraged efforts to create it.

While there is general agreement that molecular hydrogen (two protons bonded by two electrons into a single molecule) can be squeezed under high pressure into metallic hydrogen (protons embedded in a sea of electrons), there remain the questions of how much pressure is required and how long metallic hydrogen will exist once the pressure is released. Like diamond, the high-pressure form of carbon, metallic hydrogen may persist under low pressure even though the molecular form is more stable. Theoreticians are not optimistic that it will, but neither are they committing themselves. Neil Ashcroft of Cornell University points out that the field of high-pressure theory has had a few surprises before, so that no one is anxious to make a firm prediction on the basis of the current limited theoretical understanding.

The theoretical prediction of the transition pressure is not on much surer footing, the predictions ranging from 1 megabar to more than 10 megabars. The increasing capabilities of the diamond anvil press, as well as some recent laboratory results, however, have encouraged at least a half-dozen groups to start metallic hydrogen projects. These efforts, largely involving diamond anvil presses, follow announcements of the last few years from laboratories in Japan and the Soviet Union that metallic hydrogen had been created with the use of massive presses. These reports are now regarded in the United States as having been erroneous. (Some reports from researchers traveling abroad suggest that even the investigators involved in these experiments are no longer claiming unequivocal success.) The great difficulty of analyzing the sample within the bowels of these machines, it is thought, produced misleading observations. Thus, the extension of the ruby fluorescence calibration technique and the ready accessibility of the sample through the diamonds to other types of analysis, including microscopic observations, have prompted renewed interest in metallic hydrogen.

Metallic Hydrogen at 2 Megabars?

Also adding to the recent upsurge in interest is the posssible creation, however briefly, of metallic hydrogen by means of explosive compression. Ronald Hawke of Lawrence Livermore Laboratory placed liquid hydrogen inside the innermost of two concentric metal tubes. High explosives surrounding the entire apparatus then compressed a magnetic field that was generated between the tubes, which in turn compressed the sample tube. During the instant before the sample was destroyed, Hawke detected a sharp increase in electrical conductivity that, he feels, can be best interpreted as a transition to metallic hydrogen. The apparent transition pressure was about 2 megabars, but it could have been as low as 1.5 megabars. A relatively moderate transition pressure of 1.5 to 3.0 megabars is also anticipated by Ruoff, on the basis of his recent study of another nonmetal-metal transition.

Pressure considerations are not the only obstacle. Some researchers believe that the combination of high compressibility and small molecular size may present considerable difficulties in handling hydrogen under high pressure. In fact, recent expectations of early success appear to be giving way to less ambitious, more methodical approaches. For example, some researchers are now using xenon to work out techniques before tackling hydrogen. Donald Liebenberg of Los Alamos Scientific Laboratory notes only half jokingly that, in light of these difficulties, it may in the end be easier to mine metallic hydrogen from Jupiter than to create it in the laboratory.—RICHARD A. KERR

*M. Ross and C. Shishkevish, *Molecular and Metallic Hydrogen*, R-2056-ARPA (The Rand Corporation, Santa Monica, Calif., 1977).