

whether the heating is external or internal. The range of pressure and temperature which each of these types can cover is shown in Fig. 1. Also shown are the estimated pressure and temperature within a portion of the earth. The complexity and ease of operation are not inversely related to the pressures attainable, both the externally heated devices being quite simple.

In Fig. 2 more detail is given on the first type, the cold seal test-tube pressure vessel which is the workhorse of much high-pressure research today in the range up to 5000 atm and 1000°C. This extremely simple device can be used to react a very wide range of materials, whether solid or liquid. The materials, whether simple silicates or concentrated HF or NaOH solutions, are sealed into platinum or gold capsules which transmit the hydrostatic pressure actually supplied by an inert

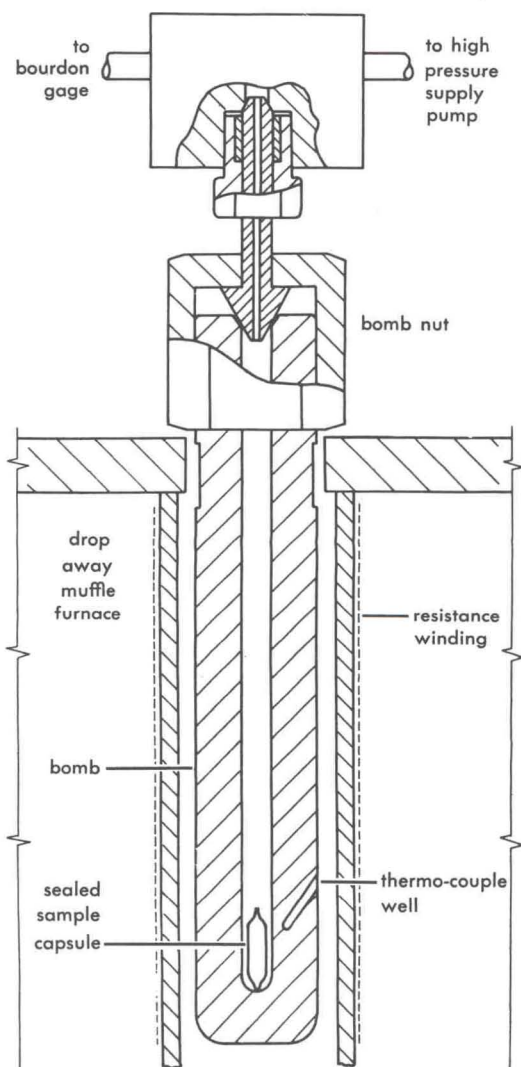


Fig. 2. Cold seal test-tube pressure vessel. Basic overall size of the test tube is 8 in. in length by 1 in. diameter.

fluid outside the capsule. These vessels are heated by an external furnace as illustrated. A related device, which also uses fluid pressure, has the furnace inside the vessel, which is cooled by flowing water. Such devices are ultimately limited by the fact that virtually all gases are frozen at room temperature when the pressure reaches 25,000–30,000 atm. The pressure-temperature ($p-t$) working range of these types of vessels can be compared by making reference to curves *a* and *b* respectively in Fig. 1.

The second and simpler type has been evolved from designs by P. W. Bridgman, a pioneer in high-pressure research. As shown in Fig. 3, it uses a hydraulic ram to apply a directed or uniaxial pressure on a small wafer of sample surrounded by a nickel ring and platinum foil pressed between appropriate small-area piston faces. Pressures up to 60,000 bars are possible with this setup, heated externally to temperatures approaching 650°C or slightly higher (conditions schematically shown in *c* of Fig. 1), depending on the material and design of the pistons. Complex mechanical buttressing of the pistons has been used in some modifications to raise the operating pressures to almost 200,000 atm.

The third type, the prototype of which was first described fully by L. Coes, is shown in Fig. 4. It is essentially an internally heated chamber with a piston and cylinder arrangement with the cylinder walls buttressed and cooled to support internal pressures of 60,000 atm at sample temperatures up to 2000°C. A number of variants of this type of apparatus as well as of the second type are being tried in the effort to reach higher pressures. Some use support from four pistons at tetrahedral angles; others use different ways of supplying the supporting pressure. At this time little systematic work has been reported on experiments with such apparatus, but it is apparent that temperatures of about 2000°C can be sustained for at least a few minutes at a pressure of 100,000 atm.

Another type of apparatus uses the energy of a shock wave to produce the high experimental pressures. Explosive charges or the impact of a rapidly moving column of gas is utilized to produce pressures of the order of 400,000 atm. The coincident temperatures and pressures are difficult to measure or calculate. The duration of these conditions is in microseconds, much too short to allow rearrangements of atoms or ions in crystalline structures and therefore of less interest to the geochemist. For example, although coesite, the dense form of silica, is made quite readily in hours at 20,000 atm and at 400–500°C, shock pressures of 200,000–400,000 atm have failed to accomplish this.

Synthesis of minerals and new materials. A good measure of the success of the earth scientist in the high-pressure field is the fact that since the synthesis of diamonds, it can now be claimed that any material which has been observed in nature can be made in the laboratory. To be sure, there

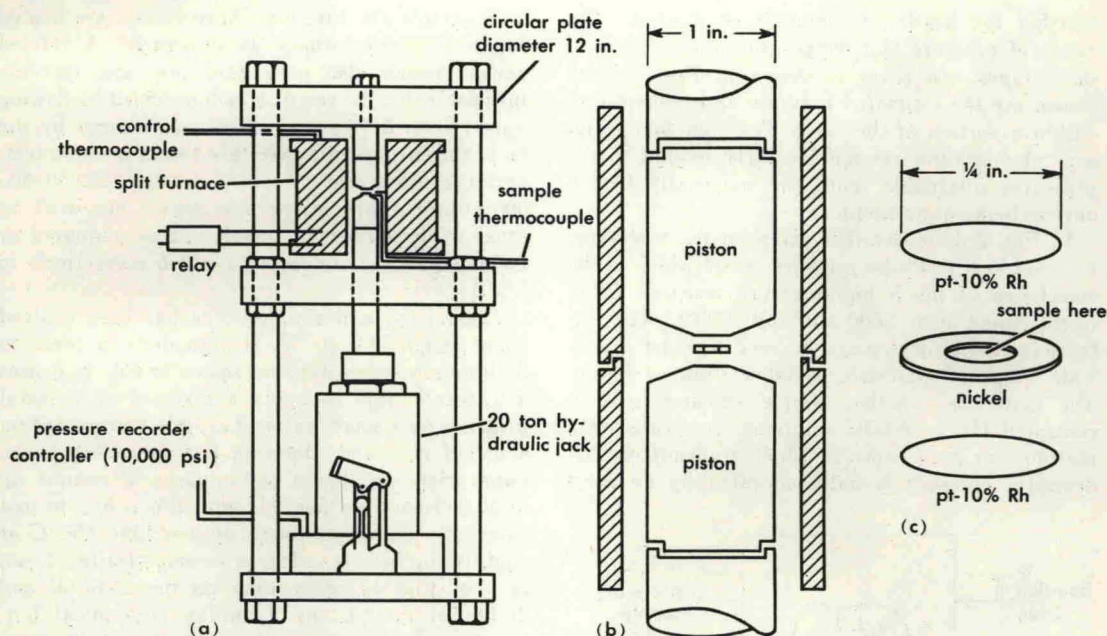


Fig. 3. (a) Schematic layout of uniaxial high-pressure apparatus with accessories. (b) Details of high-pressure pistons. (c) Sample assembly.

are many which have not been tried, but there is no reason to doubt that in every case the laboratory can duplicate the efforts of nature. See *DIAMOND; GEM, MANUFACTURED*.

First, one may mention the synthesis of the hard, dense phases which have presumably been thrust up rapidly from great depth. The most spectacular of the recent successes is the synthesis of diamonds in a few laboratories. Perhaps more important to the mineralogist has been the synthesis of the minerals jadeite, lawsonite, sillimanite, kyanite, and garnets such as pyrope, almandine, and andradite. All these phases were first synthesized in a dramatic breakthrough by Coes, using the apparatus shown in Fig. 4. Next is the extensive and

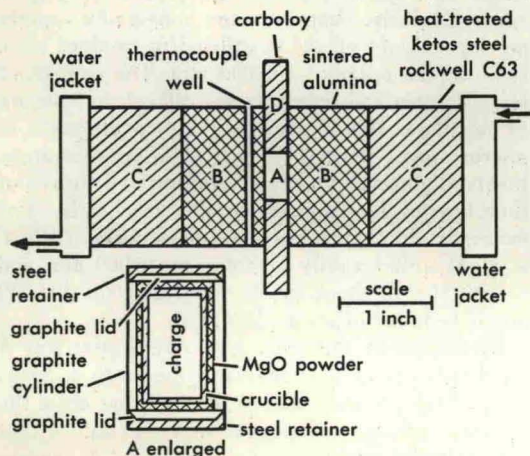


Fig. 4. Coes-type high-temperature-high-pressure apparatus.

systematic work on volatile-containing phases such as micas, clays, and complex carbonates. Under high water pressures all pure or end-member phases have been prepared and their properties studied and defined. Moreover, the extent of the systematic replacement of one ion by another has been studied. Isotopic fractionation effects in minerals have likewise been examined in the laboratory, using deuterium for hydrogen and O^{18} for O^{16} .

Many of the most interesting syntheses achieved have yielded phases which do not occur in nature and have never before been prepared. In some cases a long-expected phase was finally prepared, such as the hard cubic form of BN, analogous to diamond. In others, unexpected phases were found; thus, silica, SiO_2 , itself the most abundant substance on earth, gives a new form called coesite, some 10% denser than the usual form, quartz. New high-pressure forms of a large number of substances have been found. They cover the periodic table from B_2O_3 and BeF_2 through $MnPO_4$, MnF_2 , and $FePO_4$ to PbO_2 and U_3O_8 . It must be remembered that these changes include only those transformations which involve such a major rearrangement of strong bonds that, when the high pressure is removed rapidly, the reverse reaction is prevented and the high-pressure form is preserved metastable to ambient conditions. So far only simple compounds of monovalent cations have failed to yield new phases of this type.

Melting under volatile pressure. It is well known that the addition of one substance to another lowers the freezing point of the latter. This is true of the vast majority of substances; the addition of salt to