card?

H. T. Hall

AN i&ec REPRINT

3/4" bore
approx 50% larger than Bridgman's

Apparatus for Pressures of 27,000 Bars and Temperatures of 1400° C.

FRANCIS BIRCH, EUGENE C. ROBERTSON, AND SYDNEY P. CLARK, JR.
Harvard University, Cambridge, Mass.

Bi I-II 25,800 kg/cm^2

20,000 psi oil wax.

3/1 ratio of internal to external pressure

20,000 psi nitrogen introduced into cylinder.

upermost support ring has slight initial clearance.

13 ohms heater.

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HIGH PRESSURE

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Temperature, pressure, and other variables may be controlled and measured in the reaction zone with unusually high precision

THE SOLUTIONS to a number of geophysical and geochemical problems are to be found in the study of high-pressure minerals. They are important in interpreting the results obtained by seismic and other geophysical methods. A number of minerals commonly observed in rocks at the surface of the earth have not been synthesized at atmospheric pressure. In several cases it has been demonstrated that these phases are stable only at elevated pressure.

Chemical equilibrium in silicate systems is virtually unobtainable at room temperature; hence it is necessary to combine high temperatures with high pressures, to study equilibrium relations. Accurate knowledge of the physical conditions is also desirable.

These considerations led to the development of a modification of the apparatus which Bridgman has used so successfully to 30,000 bars. The present equipment is larger than Bridgman's, and provision is made for a furnace inside the pressure vessel. Nitrogen, rather than an organic liquid, is the pressure medium.

Tapered Cylinder. The most serious difficulty encountered in the present apparatus has been failure of the tapered cylinder (*A*, Figure 2). The failure has usually taken the form of a break normal to the axis a few inches from the upper end. A longitudinal crack characteristically accompanies this break, and there may be one or more additional transverse fractures further down the cylinder.

This breakage has been unpredictable; several cylinders have survived a large number of exposures to high pressure, but others have broken on the first exposure. Some have broken at pressures below 15,000 bars after having contained pressures over 25,000 bars without failure.

Two factors seem to account for the observed nature of the breaks. First, the internal pressure has a sharp discontinuity at the upper packing; the shearing stress must locally reach high values, and several breaks seem to be associated with this discontinuity. Second, the longitudinal stress, although compressive, is much lower than the radial stress; it decreases along the cylinder and vanishes at its upper, free

Apparatus

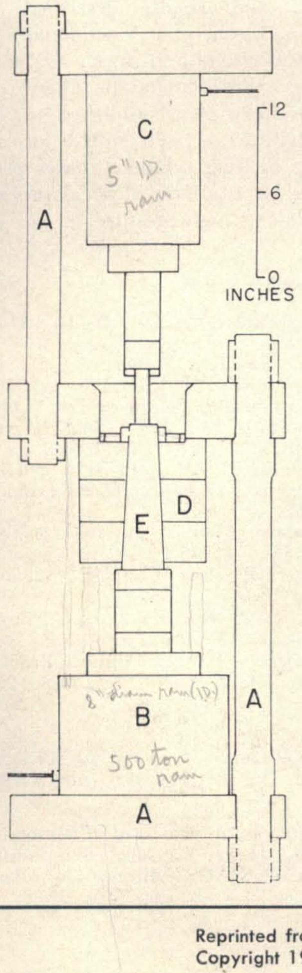

Figure 1. Section through apparatus used for measuring chemical equilibria. Tapered cylinder *E* is forced into supporting rings *D* by ram *B*, 8 inches in diameter with 500-ton thrust. Five-inch ram *C* generates pressure in *E*

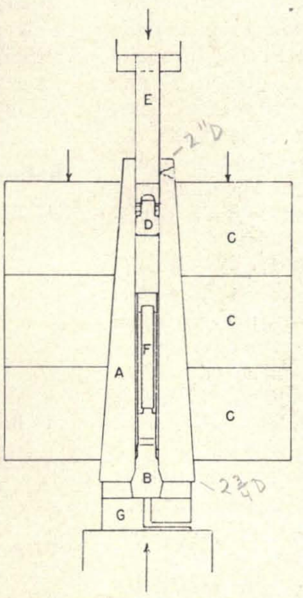

Figure 2. Tapered cylinder and supporting rings. Gas at 2000 bars is introduced at top. Pressure is measured with Manganin coil at *B*. Cylinder bore is $^3/_4$ inch

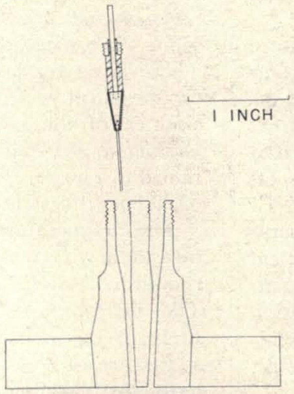

Figure 3. Bottom closure and insulated electrical lead. Horizontally ruled material is lava, diagonally ruled material is Teflon, and remaining parts are metal

Supporting Rings (C, Figure 2).
AISI 4340 steel forgings, 3 inches thick, 9 inches in diameter.

Upper Closure (*D*, Figure 2).
Mushroom plug made of steel, hardness RC 52–54. Stem of mushroom is $^5/_{16}$ inch in diameter; seal is $^1/_{16}$ inch neoprene washer; Third component is an Omega steel washer, behind packing. Hard steel thrust block completes assembly. Thrust block made from either high-speed tool steel of 18-4-1 variety or Teton, Allegheny-Ludlum's ball-bearing steel.

Bottom Closure (Figure 3).
Plug is high-speed steel, hardened to RC 65. Electrical leads are soldered to steel cones insulated with 0.010 inch massive pyrophilite made by American Lava Corp.

Furnace (*F*, Figure 2).
Resistance winding is Kanthal or platinum—10% rhodium on $^1/_4$ inch diameter ceramic core. Winding is 3 inches long. All open spaces in furnace are filled with a refractory material to reduce flow of gas.

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end. Thus the transverse failure is of the nature of a pinch-off.

To combat these failures, different types of steel have been tried at different hardnesses, and the outside diameter of the piece has been changed. In use, the tapered cylinder is stressed far beyond its yield point, and permanent distortion is inevitable. Steels harder than about RC 50 or with a carbon content of more than about 0.60% will not withstand sufficient elongation, and fail by rupture after a short life. If the hardness is below RC 40, the bore enlarges rapidly in service, and must be refinished after a few exposures to high pressure. Most of the tapered cylinders have been made of Omega steel, and no superior alloy has yet been found. AISI 4340 steel performs about as well, and some of the new "ultra-high strength" alloys are being tested.

Most of the tapered cylinders are about 2 inches in diameter at the upper, small end and $2^3/_4$ inches in diameter at the base. Results to date with cylinders about $^5/_8$ inch larger in diameter have not been encouraging, but this may be due to inadequate control of hardness. Experiments are being continued.

The tapered cylinders are subjected to nearly the maximum stress which they can withstand, and failure may be initiated by minor imperfections which would ordinarily be negligible. This would account for their capricious behavior. Fine cracks may develop during grinding of the hardened piece; special care is required in this operation. There is also a vague correlation between failure and the use of commercial nitrogen as a pressure medium. Bridgman (*3*, p. 97) has noted that air shows a slight tendency to attack steel under high pressures, and nitrogen may produce a similar effect. Impurities in the gas may corrode the steel at a rate accelerated by pressure. Unfortunately, it is difficult to avoid the use of nitrogen, as it is the only inert gas which is readily available and does not freeze under the conditions of use.

The hot furnace inside the pressure vessel does not make an important contribution to failure. From the power supplied to the furnace and the thermal conductivity of steel, it is estimated that the temperature of the bore of the tapered cylinder does not exceed 120° C. opposite the furnace. This temperature is too low to affect the mechanical properties of the steel appreciably, although it might increase the corrosion rate. The breaks have shown no tendency to occur opposite the furnace, however.

Limiting Pressures and Temperatures

The limit to the pressure which can be obtained in this apparatus is at present set by the strength of the steel parts in the upper closure; 30,000 bars has been reached with pentane as the pressure medium, but deformation of the packings was considerable. It has been found best to restrict maximum pressure to about 27,000 bars. There is no obvious connection between the life of a tapered cylinder and the maximum pressure to which it is exposed, and failure of the component may not be a limiting factor, once its tendency to fail at low pressures is corrected. Eventually the maximum pressure will be determined by the freezing point of nitrogen, which lies between 28,000 and 29,000 bars at 20° C.

The maximum temperature attainable is determined by the melting point of the furnace material, and by the requirement that the power to the furnace not exceed about 1 kw. The maximum temperature can be made extremely high if the size of the furnace is reduced. There has been no reason to do so, and 1400° C. is the highest temperature that the authors have attempted to reach.

Accuracy of Measurements of Pressure and Temperature

Pressure is measured with a Manganin coil which has a resistance of about 50 ohms. It is mounted at the top of the bottom plug, between leads of thermocouple wire. Measurement of the thermal electromotive force in this circuit enables the temperature of the coil to be determined; it rarely exceeds 50° C., but this change of temperature introduces a correction to the measured pressure. The temperature coefficient of resistance of Manganin is negative above room temperature, and hence an increase in temperature of the coil has the same effect as a decrease in pressure. The pressure coefficient of the wire increases by about 3% between 25° and 125° C. This second-order correction is probably not the same for different spools of wire, so that individual calibration is necessary.

An accuracy of 100 bars seems adequate in measurement of pressure. There is no reason why the correction for the effect of temperature on the resistance of the coil and of the wires leading to the coil could not be determined to a higher accuracy; an accuracy of 20 bars is certainly attainable.

The temperature of the charge is measured with platinum-platinum–10% rhodium thermocouples at each end. The thermocouple circuits consist entirely of thermocouple wire except for a distance of $^3/_{16}$ inch, which is in the hardened steel cone forming the pressure-tight seal. This cone introduces an error of about 3° C., and the effect of pressure on the thermal e.m.f., as found by extrapolation of Birch's (*1*) data, amounts to about 12° C. at 20,000 bars. Hence the temperature of the junction is known within 10° C.

The temperature of the charge is subjected to greater uncertainty because of thermal gradients. At the ends of the furnace core it is probably less than 300° C. Near the center of the winding, 1.5 inches away, it is perhaps 1000° C.; the mean gradient in the furnace is then about 500° C. per inch. Evidently the region of uniform temperature is short, and precise location of the charges is necessary to avoid large gradients. The uncertainty due to gradients can be as low as 10° C. in favorable circumstances, but it occasionally may be two or three times this.

Platinum-platinum–10% rhodium thermocouples are used instead of Chromel-Alumel because of deterioration of the latter type of couple in high-pressure nitrogen. This effect revealed itself as an apparent decrease in temperature at constant pressure and power input. It disappeared when platinum-rhodium couples were introduced.

Use

The equipment has been used in the study of solid-solid transitions in systems of geochemical and geophysical interest. High-pressure forms synthesized to date include jadeite, $NaAlSi_2O_6$; kyanite, Al_2SiO_5; aragonite, $CaCO_3$; and pyrope, $Mg_3Al_2Si_3O_{12}$. The stability fields of the first three substances have been determined, and results described by Robertson, Birch, and Macdonald (*7*), Clark, Robertson, and Birch (*6*), and Clark (*5*). Further details about the apparatus have been published (*2*, *7*). This apparatus is well suited for determining melting relations under pressure, and for studying physical properties of solids at high pressure.

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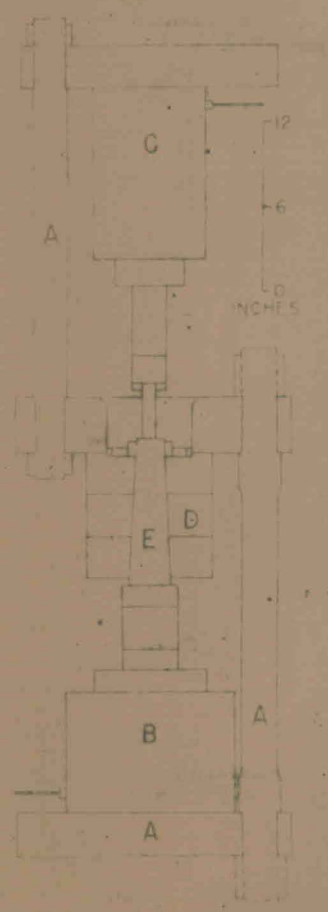
Birch's design with beefed up tie bars -

Apparatus

A
~30,000 incl gas charger + furnace + gage
Don Newhall ~4 mo. delivery
Harwood Eng., Walpole Mass.



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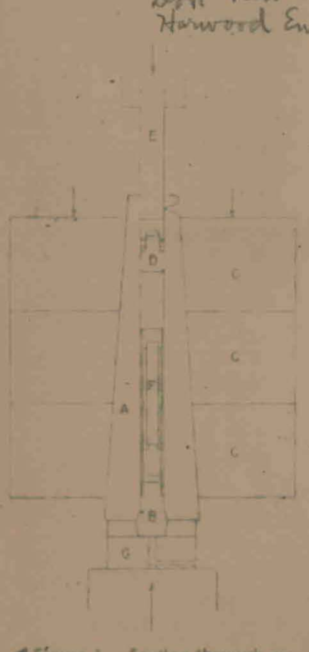

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