[AMERICAN JOURNAL OF SCIENCE, VOL. 254, DECEMBER 1956, Pp. 722-735]

00

#66 Hall

A SIMPLE APPARATUS FOR HIGH PRESSURES AND TEMPERATURES

D. T. GRIGGS and G. C. KENNEDY



[American Journal of Science, Vol. 254, December 1956, P. 722-735]

A SIMPLE APPARATUS FOR HIGH PRESSURES AND TEMPERATURES*

D. T. GRIGGS and G. C. KENNEDY

ABSTRACT. A simple apparatus, based on the principle of Bridgman's shearing apparatus, provides pressures of 80 kilobars at 500°C, 50 kb at 800°C, and 20 kb at 1000°C. Pressure is known within approximately 5 percent, and temperature to 5°C. The sample, in powdered form, is compressed between two pistons which are externally heated and pressed together by a hydraulic jack. Under certain circumstances water vapor pressure in the sample may equal total pressure, even at high temperatures. The apparatus is extremely easy to use, and equilibrium seems to be attained more rapidly than in the case of pure hydrostatic pressure. Thus, it seems well adapted for study of metamorphic reactions within the range of pressure and temperature to be expected normally in the outer 50-100 kilometers of the Earth.

INTRODUCTION

Bridgman (1935) was the first to make quantitative experiments on a sample compressed between two flat piston faces. He showed theoretically (1937) that, to a first approximation, the stress system in such a compressed disk is hydrostatic except for a thin peripheral region (less than 5 percent of the radius in general). Hence the pressure over most of the sample is approximately equal to the force with which the pistons are pressed together, divided by the area of the piston face. Bridgman (1952, p. 177) later demonstrated that the pressure so calculated is equal to the actual pressure within "a few per cent" which was within the experimental error. This was done by measuring the electrical resistance of bismuth in an apparatus of this type. Its resistance changes sharply when bismuth undergoes a polymorphic transition at 24.9 kilobars at room temperature. The pressure at which this transition occurs had been previously determined by Bridgman in a conventional hydrostatic apparatus.

Larsen and Bridgman (1938) attempted to bring about mineral transitions in the shearing apparatus but encountered little success, as work was performed at room temperature. Griggs (1941) used apparatus of this type in experiments on metamorphic reactions at low pressures and moderate temperatures and had recently been using such an apparatus for experiments at 100 kb, room temperature. Kennedy suggested that the Bridgman apparatus might be adapted in such a way that mineral reactions might be explored at high temperatures and pressures and that water vapor might be retained. Hence, this cooperative project was undertaken. Experiments were started with a press on hand and pistons which had been acquired for work at room temperature, 100 kb. Later, apparatus more suitable to the purpose was constructed. The latest apparatus, familiarly known as the "simple squeezer," is described here.

* Publication no. 66, Institute of Geophysics, University of California, Los Angeles 24, California.

A report on research carried out under the auspices of the Office of Naval Research. Reproduction in whole or in part is permitted for any purpose of the United States Government.

D. T. Griggs and G. C. Kennedy

DESCRIPTION OF APPARATUS

The apparatus is shown in plate 1, and schematically in figure 1. A Blackhawk 20-ton ram pushes the pistons together in a homemade press. The ram is activated by a hand pump through a manifold valve which allows operation of five presses simultaneously. Each ram is fitted with a U. S. Gauge Company 10,000 lbs/in² gauge. A 700 bar Heise gauge is connected to the manifold valve and is used to check these gauges. Rudimentary measures are taken to provide coaxial alignment of the pistons. Alignment has not been found to be critical, fortunately, since thermal distortions make exact alignment very difficult.



Fig. 1. Schematic drawing of apparatus.

The pistons, holders, and pushers are heated by a Hevi duty Electric Company split furnace type 123-1 of 400 watts capacity. This furnace is run over-voltage for temperatures above 700°C by means of a variable transformer. Temperature is controlled by a Brown Pyrovane controller, operated by a thermocouple inserted in the furnace winding, to respond to heater element temperature.

Materials with the highest compressive strength are most desirable for the pistons. Such materials are brittle and must be subjected to confining pressure to prevent brittle fracture. This confining pressure is provided by making the pistons conical as shown in figure 2. Two cone angles have been used: 20°, and 45° half-angle. Neglecting friction, the normal stress on the cone surface is given by the force divided by the area of the cone surface

D. T. Griggs and G. C. Kennedy—A Simple

projected on a plane normal to the force. For .250" diameter piston faces in the designs illustrated, the normal stress is 29 percent of the sample pressure in both cases. The radial stress, normal to the applied force, is 27 percent and 20 percent of the sample pressure for the 20° and 45° cones, respectively. Higher confining pressures are desirable to achieve the highest sample pressures but have so far not been attained, due to insufficient strength in the material of the holders. Lubrication on the cone surface is provided by a thin copper foil, which has small strength at elevated temperatures. Even at 1000°C, this foil does not entirely squeeze out.



Δ

в Fig. 2. Pistons and holders: A. 20° cone, used only for cemented carbides. B. 45° cone in configuration used for high speed and stellite pistons. When using this cone angle for carbides, the upper and lower cylindrical sections are omitted, and the acute angle between the two cones is flush with the top of the holder. In both cases, .003" copper sheet was placed between the pistons and holders to serve as lubricant.

The highest pressures have been attained with cemented carbide pistons in the 20° cone shape (fig. 3). Kennametal grade K-6 was used to 800°C, where oxidation became excessive. Kentanium K-161B was used from 800°C to 1000°C. In these experiments, Carpenter 883 steel was used for holders to 500°C, and Inconel X from 500° to 1000°C. Due to the decrease of strength of the Inconel at high temperatures, the area of the piston face had to be diminished with successively higher pressures to prevent excessive deformation of the Inconel. At 1000°C, the diameter of the piston face was 0.10" for sample pressures of 21 kb. The normal stress on the cone face was only 4 percent of the sample pressure, or about 0.8 kb. With Stellite 98M2 holders, it is anticipated that .250" diameter piston faces could be used to 1000°C and that the sample pressures attained would be somewhat higher than those shown in figure 3, due to the beneficial effect of larger confining pressure.

Stellite 98M2 has been used in pistons with 45° cone (fig. 2). The pressures attained with these pistons is about 60 percent of that attained with the carbide pistons (fig. 3). The stellite 98M2 pistons have the advantage, however, of being less brittle than the carbide pistons and hence less subject to cracking.

All types of pistons, but most particularly cemented carbide, develop fractures long before their useful life is over. These fractures are typically of two types: (1) radial fractures extending up to but not entering the flat face; (2) spalling fractures roughly parallel to the upper, unsupported conical surface. In the case of carbide pistons, the former type of fractures almost

Apparatus for High Pressures and Temperatures



Fig. 3. Maximum working pressures that have been attained. In many of the points, no piston damage was observed. The Earth temperatures correspond to a surface heat flow of 1.2×10^{-6} cal/cm²sec, 2/3 to 3/4 originating in a 30 km crust, and a conductivity in the mantle of .008 cal/cm sec deg.

invariably appears after any run at 50-60 percent of the maximum pressure to which the pistons are usable. They are initially very fine radial cracks, and after repeated runs at higher pressures they gradually widen. Destructive fracture in carbide pistons of the type shown in figure 2-A occurs after very appreciable plastic flow has occurred and may occur in a test at considerably lower pressure than the piston has already withstood. Such fracture most commonly takes the form of shear on an inverted 45° cone, passing through the outer boundary of the piston face. This shear is typically associated with radial cracks external to the cone, and occasionally with spalls.

Stellite and High Speed Steel have much less tendency to crack and frequently their life is terminated simply by excessive flow. When destructive fracture does occur, it follows the pattern of the carbide pistons.

Both types of pistons show appreciable dishing after runs approaching the maximum pressure. Figure 4 shows the profile of one pair of Kennametal K-6 cemented tungsten carbide pistons after several runs at 500°C, at a maximum pressure of 80 kb. These pistons have made many more runs at high pressure.

This dishing has no deleterious effect so far as we have been able to learn. On the contrary, it has two beneficial effects: (1) the central pressure is more uniform due to steeper pressure gradients at the periphery; (2) the sample thickness is greater—reaching .015" in these pistons, independent of



Fig. 4. Profile of Kennametal K-6 piston faces after several runs at 500°C-maximum pressure 80 kb (vertical exaggeration 5:1). Depression in center of piston face: .005". Where pistons are not of same size, area of smaller one is used in calculating pressure.

pressure. With dished pistons an excess of sample is always used, to be sure of filling the space between the pistons at pressure.

For temperatures up to 600°C, pistons made of ordinary high speed steel provide respectable pressures.

Above 1000°C, pressures attainable with this type of apparatus may be expected to decrease to about 10 kb at 1200°C with the best materials available. For higher pressures at the higher temperatures, localized heating of the sample will be necessary, so that the pistons will be cool in regions of high stress. In principle, any desired temperature may thus be reached at 100 kb. Bridgman's (1952) resistance apparatus indicates one method by which electrical heating might be used.

Pushers are made of Inconel X. Transite was initially chosen for thermal insulation of the push rods after tests of other similar materials. At high temperature and pressure, transite deforms and must be frequently replaced. It has recently been found that the thermal insulation provided by the transite is unnecessary, and these parts are now made of stainless steel.

It is desirable to design the apparatus so that it undergoes large elastic strain at pressure, in order to reduce the pressure rise due to thermal expansion on heating. This is done principally by making the press tie-rods long and of minimum cross section. The apparatus shown in plate 1 increases in pressure about 60 percent on heating to 600°C, due to the expansion of the pushers and piston holders which would amount to about 1/16 of an inch at constant pressure. Approximately one-third of the yield of the apparatus is extension of the tie-rods, one-third is compression of the pushers and piston assembly, and the remainder is due to bending of the end plates, compression of oil in the ram, etc.

It is necessary to water-cool the plate at the top of the ram to prevent heating of the oil in the ram, which would cause a rise in pressure. With this water turned off, a pressure rise at an initial rate of 50 percent per hour is observed after attaining a stabilized temperature. With the water on, pressure remains constant to a few percent.

Apparatus for High Pressures and Temperatures





CALIBRATIONS

Due to the solid steel pushers there is substantial axial heat flow and consequently a moderately large temperature gradient away from the center of the furnace where the specimen is located. This could be mitigated by using a furnace wound much more heavily at the ends, or by the use of high-strength low-conductivity pusher material. These measures are expensive, however, and have been eliminated on finding that a reproducible sample temperature can be attained without them. The difference between sample temperature and reference thermocouple temperature is moderately sensitive to the position of the furnace. One-quarter of an inch difference in position of the furnace typically will change this difference by about 20°C. In practice, the furnace is positioned, by moving the hinges up or down, until the sample temperature as shown by a thermocouple between the pistons in the sample position is near the reference thermocouple temperature. A temperature calibration is then made, yielding a result like that in figure 5. This calibration is reproducible, so long as the apparatus is not changed. A new calibration is made after every change in the pistons, holders, or pushers. Thermocouple temperatures are recorded on a Foxboro six-point recorder which facilitates this calibration. It was found necessary to calibrate the recorder.

The force developed by the ram is determined by the bourdon gauge and the area of the ram. This is calibrated by inserting a Baldwin Southwark CXX precision load cell in place of the apparatus. It has been found that the U. S. Gauge Company gauges are initially within their stated tolerance of

D. T. Griggs and G. C. Kennedy—A Simple

0.5 percent of full scale, and that the friction on the Blackhawk rams is 1 percent. The Heise gauge is regularly used to check the U. S. gauges. It is desirable to measure the diameter of the piston faces to 1 percent or better, which we do with a cathetometer. One must be sure that there are no elements in the system which can introduce any undetermined friction or in any way bear any of the force which is thought to be applied to the specimen. In our apparatus, there are two such elements: the plate which aligns the ram (pl. 1), and the stainless steel ring. The alignment plate has been found by the above force calibration to introduce no measurable friction. The stainless steel ring clearly bears some load outside the piston face. This has been evaluated by measuring the deformation in the ring and roughly calculating the force required to produce this. The magnitude of this force varies with pressure, temperature, and sample size, but in our configuration it is always less than



PLATE 1

Apparatus, with furnace open to show piston assembly.

the force necessary to balance the pressure gradient at the periphery of the piston faces.

The corrections on central sample pressure with reference to the pressure calculated from force and initial piston area are approximately as follows:

Due to pressure gradient at periphery	+3%
Due to stainless steel ring	-2%
Due to elastic distortion of pistons	+1%

The net of these corrections appears to be within the uncertainty of pressure due to lack of precise knowledge of pressure distribution in the sample, so no correction is made. Near the limit of strength of the pistons, large plastic deformations can occur, resulting in increases of piston area by as much as 20 percent. The piston diameter must be measured after each run when in the region of flow. At very low pressures the correction due to the stainless ring can be much larger than 2 percent, and suitable precautions must be taken.

In assembling the pistons, sample, foil, and stainless ring, a split jig is used to insure alignment of all parts. This jig is removed only after several kilobars of pressure have been applied to the sample. From this point on there is no connecting member between the pistons save the sample and ring. There is thus no possibility that the force of the press can be borne by anything except the sample and ring.

SAMPLE PREPARATION

The sample is introduced in powder form. Platinum-10% rhodium foil .001" thick is placed between the sample and the pistons, to prevent reaction with the pistons and to facilitate removal of the sample. At temperatures above 500°C, Molykote (MoS_2) is applied to the piston faces to prevent adhesion of the foil. A stainless steel ring is used around the periphery of the piston faces to retain the sample and volatiles and to provide a thicker specimen. The part of this ring between the piston faces is .010" wide and .005" thick. The geometry of a typical ring and sample assembly at low pressure is shown in figure 6. At high pressure, of course, the ring is squeezed down and partially extruded.

If the initial amount of the sample is not too great to fill the void, then the platinum-rhodium foils and the stainless ring are in direct contact, and the pressure deforms them, making a metal-to-metal seal. This was initially thought to be necessary to retain water vapor, but subsequent experience has shown that it is not usually needed.

At moderate to high pressures, the amount of sample present is not critical. An excess of sample can be added, provided it is not so much in excess that it results in a blow-out of the stainless steel rings. In practice, this means that the sample is ladled in with a spatula so that it forms a shallow rounded pile above the ring. The upper platinum foil is emplaced, the upper piston put in, and the assembly placed in the press. We are unable to discover any difference in results correlated with initial amount of sample, so long as the stainless ring remains in position. With excess sample, some is extruded past the stainless ring, forming an annular sheet perhaps .001" thick. Diffusion of water



Fig. 6. Exploded assembly showing stainless ring, platinum foil, and sample geometry.

vapor through this extruded material is apparently so slow that it does not interfere with our experiments.

The sample comes out as a lenticular wafer .004"-.015" thick, weighing 1-10 milligrams. It is usually hard and coherent. Under the microscope its crystalline nature is usually evident. Grain size is usually 1-10 microns, so that some optical properties can be determined microscopically. Moderately good X-ray patterns can usually be obtained on a Norelco recording X-ray spectrometer. These X-ray determinations provide the easiest and most unequivocal means of identifying the crystalline phases present in the sample. It has been found that grinding the sample in a mortar before X-raying results in general in a better pattern. This is presumably due to the development of preferred orientation due to the shear stress and/or strain present in the sample under pressure.

PROCEDURE

Successful use of this apparatus requires appropriate quenching to preserve the sample in the crystal phase which it had attained at stabilized temperature and pressure. Quenching is normally done by swinging the furnace open and directing an air blast directly at the pistons. A cooling curve is shown in figure 7. Even this rapid rate of cooling is not sufficient to prevent recrystallization of some samples. Whenever the presence of water vapor or other volatiles is not necessary to preserve the crystal phase present during the run, the pistons and holders can be removed rapidly and water quenched. The sample in the stainless ring and platinum foil capsule usually separates readily from the piston, and quenching is essentially instantaneous on contact with water. The time to get the sample from test conditions into the water is less than 10 seconds.



Fig. 7. Typical cooling curve with air jet.

Any phase boundary may be followed only over a limited range of temperature. At low temperatures the rate of reaction is too low to achieve equilibrium in times available. At high temperature, the reaction rate may be so great that quenching becomes impossible. Frequently the role of water may be exploited to extend this range. In exploring the analcite-jadeite + water equilibrium, it was found that at temperatures in excess of 500°C air quenching was too slow, and analcite recrystallized in the quenching process. In this instance, the problem was solved by releasing pressure before air quenching. Jadeite and nepheline albite were unchanged by release of water vapor, and analcite retained its skeleton structure as anhydrous analcite. The rate of re-

action drops very rapidly when water vapor pressure is released, so this expedient is frequently helpful in quenching.

We have found that equilibrium is not readily attained when the initial material is composed of more than one crystalline phase. We had hoped that the shear strain imposed on the aggregate during loading would provide sufficiently intimate mixing so that all components would come to equilibrium. This is not the case. It may well be that rotation of the pistons with respect to each other would promote the attainment of equilibrium due to the resultant intense shearing strain. We shall shortly try this.

We have found three satisfactory methods of introducing water into the system:

(1) Starting material is a hydrate of the composition intended for study (e.g. analcite for the reaction jadeite \rightleftharpoons nepheline + albite).

(2) Starting material contains a hydrate whose anhydrous product does not take part in the reaction to be studied (e.g. to study the reaction jadeite + water \rightarrow analcite, start with diaspore + jadeite. The diaspore decomposes to corundum releasing water which combines with jadeite to form analcite. This will work only close to the diaspore-corundum boundary, in the corundum field.

(3) Starting material is glass with adsorbed water. Finely ground glass will absorb roughly 0.5 to 1 percent of water, which is bound to the glass even at elevated temperatures. This technique is not in general suitable for adding a known amount of water but is extremely useful in adding enough water to increase reaction rates. For example, glass of a basalt composition was run at 1000°C, 10 kb for one hour with no observable crystallization. This glass was wet but was not ground very fine. The same glass, with prior fine grinding under water, crystallizes completely in short times at temperatures as low as 800°C. It is presumed that this difference in reaction rate is due to the water adsorbed: the crystalline phases are anhydrous. Water vapor apparently also increases the reaction rate in certain solid-solid transitions.

Proof that equilibrium has been attained at a phase boundary is accomplished by standard techniques—e.g. demonstration that the reaction is reversible. In the case of dehydration boundaries, special techniques are required with this apparatus which are beyond the scope of this paper and will be reported in other papers dealing with such systems.

Experience to date indicates that at hydration-dehydration boundaries, the water vapor pressure closely approximates the total pressure. Such boundaries determined with this apparatus lie on a smooth extension of the boundaries determined at lower pressure in conventional hydrothermal apparatus.

We have the impression that reaction rates are faster in this apparatus than in a purely hydrostatic environment but do not yet have adequate information to prove this. MacDonald (in press), using our squeezer, found that the calcite \rightarrow aragonite transition went to completion in about 15 minutes at 500°C, whereas in a hydrostatic test at the same pressure and temperature no conversion to aragonite was observed in two hours in an experiment by Griggs.

In our experiments to date, it has been found that any reaction which will go at all will usually go in one or two hours. We have, however, insufficient experience with long-term tests. If shear stress or strain is important in promoting reaction, one would expect that short-term tests would achieve nearly the same result as long-term tests in the squeezer, since there is a relaxation of shear stress with time. This effect will be tested explicitly in our new shearing apparatus.

D. T. Griggs and G. C. Kennedy—A Simple

UTILITY OF THE APPARATUS

Figure 3 shows the temperatures and pressures attained thus far. It is reasonable to expect that somewhat higher pressures may be attained in this apparatus in the future. Throughout the range of figure 3 satisfactory samples and equilibrium results have been attained except at low pressures. Below 5 kb, erratic results have been obtained with hydrous systems, indicating leakage of water.

Exclusive of auxiliary instrumentation, the apparatus itself is cheap—a few hundred dollars—or much less if a machine shop is available. It is extremely easy to use and requires little skill. Over 600 runs were made in our laboratory in the first year of operation.

The apparatus has been used to date mainly in determining equilibrium relations in solid-solid transitions and in hydration-dehydration reactions. Figure 8 shows some boundaries that have been explored at the time of this writing. The quartz-coesite and calcite-aragonite transitions were done by MacDonald (in press, 1956) in our laboratory. The former has been slightly modified in figure 8 as a result of further work by Kennedy from 600° to 900°C. The work on jadeite-analcite was done by Griggs, Fyfe, and Kennedy (1955). The work on gibbsite, diaspore, corundum, pyrophyllite, sillimanite, and kyanite was done by Kennedy. These studies will be described separately in publications to follow. Figure 8 is preliminary and may be revised by further work but indicates types of reactions which may be studied with the apparatus.

Based on Bridgman's findings, the accuracy of the pressure calculated from the observed force on the ram should be about 5 percent. No rigorous check has yet been made in our work. Two comparisons with other work have been made: MacDonald (in press) found that the pressure for the calcitearagonite equilibrium as determined in our apparatus was about 1.5 kb lower than the value determined indirectly by Jamieson (1953). Kennedy's determination of the kyanite-sillimanite boundary (fig. 8) is almost identical with that found by Dr. Sydney Clark (personal communication) in Birch's hydrostatic apparatus.

Griggs, Fyfe, and Kennedy (1955) reported confirmation of the prior work of Robertson, Birch, and MacDonald (1955) on the jadeite = nepheline + albite equilibrium. Much subsequent work on this system by Kennedy indicates that our earlier results were in error owing to melting and that agreement can no longer be reported. Work on this is being continued and will be described later.

This apparatus is useful for rapid exploration of the stability fields of minerals at pressures and temperatures corresponding to those which are believed to exist in the outer 100-150 km of the Earth's crust and mantle in the normal Earth temperature gradient. The simplicity, ease of operation, and the short time required for each run should make it possible to expand greatly our knowledge of mineral stability at high pressure.

Apparatus for High Pressures and Temperatures

ACKNOWLEDGMENTS

This work was assisted by grants from the Office of Naval Research, U. S. Department of the Navy (Project grants N6onr-27511 project NR081-101 and Nonr 233(28)). For highly skilled technical assistance we are indebted to Mr. Donald Lyons, who conducted many of the experiments incorporated in figure 8; and to Mr. William Hoffman and Lester Emarine who built the apparatus. Our indebtedness to Professor Bridgman, who pioneered work with this type of apparatus, is obvious. William S. Fyfe and Gordon J. F. MacDonald did some of the experiments on which this account is based and provided much stimulating discussion of the problems and results encountered. Apparatus on loan from the U. S. Geological Survey was used in the early experiments.

References

Bridgman, P. W., 1935, Effects of high shearing stress combined with high hydrostatic pressure: Phys. Rev., v. 48, p. 825-847.

_____, 1937, Shearing phenomena at high pressures, particularly in inorganic compounds: Am. Acad. Arts Sci. Proc., v. 71, p. 387-460.

_____, 1952, The resistance of 72 elements, alloys, and compounds to 100,000 kg/cm²: Am. Acad. Arts Sci. Proc., v. 81, p. 165-251.

Griggs, D. T., 1941, An experimental approach to dynamic metamorphism: Am. Geophys. Union Trans., pt. 2, p. 526-528.

Griggs, D. T., Fyfe, W. S., and Kennedy, G. C., 1955, Jadeite, analcite, and nephelinealbite equilibrium (abs.): Geol. Soc. America Bull., v. 66, p. 1569.

Jamieson, J. C., 1953, Phase equilibrium in the system calcite—aragonite: Jour. Chem. Physics, v. 21, p. 1385-1390.

Kennedv, G. C., 1955, Pyrophyllite-sillimanite-mullite equilibrium relations to 20,000 bars and 800°C (abs.): Geol. Soc. America Bull., v. 66, p. 1584.

Larsen, E. S., and Bridgman, P. W., 1938, Shearing experiments on some selected minerals and mineral combinations: AM. JOUR. SCI., 5th ser., v. 36, p. 81-94.

MacDonald, G. J. F., in press, Experimental determination of calcite-aragonite equilibrium relations at elevated temperatures and pressures: Am. Mineralogist.

——, 1956, Quartz-coesite stability relations at high temperatures and pressures: AM. JOUR. Sci., v. 254, p. 713, 721.

Robertson, E. C., Birch, Francis, and MacDonald, G. J. F., 1955, Fields of stability of jadeite, kyanite, and pyrope (abs.): Geol. Soc. America Bull., v. 66, p. 1608.

INSTITUTE OF GEOPHYSICS

UNIVERSITY OF CALIFORNIA

LOS ANGELES, CALIFORNIA