

A high-temperature assembly for 1.91-cm (3/4-in.) piston-cylinder apparatus

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ABSTRACT

A 1.91-cm (3/4-in.) piston-cylinder assembly suitable for high-temperature experimentation has been designed. It can easily hold four capsules 3 mm in diameter encircling a thermocouple at the center of the graphite furnace. The overall design is simple in order to provide the samples and thermocouple a uniform, anhydrous environment poor in contaminants. The major components are made of NaCl, fused silica glass, and crushable alumina. No pressure correction is necessary at temperatures above 1400 °C, and experiments can be performed to 2100 °C. The vertical thermal gradient over the central 4.5 mm of the furnace in this assembly is <4 °C/mm below 1700 °C and reaches a maximum of 10 °C/mm at 2100 °C with either hot piston-out or hot piston-in pressurization techniques.

THE ASSEMBLY

The piston-cylinder apparatus (Boyd and England, 1960) is widely used to perform experiments at pressures and temperatures occurring in the lower crust and uppermost mantle. Phase equilibria studies at high pressures and at temperatures exceeding 1600 °C require a piston-cylinder assembly that is low in contaminants, anhydrous, frictionless, and capable of maintaining a large volume for multiple capsules and that generates a smooth thermal gradient. A 1.91-cm (3/4-in.) assembly containing no hydrous parts such as talc or pyrophyllite has been designed in order to fulfill these criteria.

The furnace assembly is illustrated in Figure 1. The pressure medium is made of three stacked NaCl cylinders whose total length is about 1 mm longer than the other parts of the assembly because of the high compressibility of salt. NaCl has the advantages of being inexpensive, being free of impurities, requiring no machining, and needing less electrical power than talc assemblies to reach the same temperature (Boettcher et al., 1981). The NaCl is separated from the graphite furnace by a fused silica sleeve; a Pyrex sleeve is used in experiments below 1400 °C. The inner part of the assembly consists of Norton AN900 crushable alumina (99.7 wt% Al₂O₃) with an axial hole for the thermocouple. Sample capsules are inserted in the assembly by cutting the Norton AN900 crushable alumina in two pieces and drilling cavities around the axial hole at the top of the bottom piece. The part of the axial hole adjacent to the sample capsules is slightly enlarged compared with that in the top piece of crushable alumina to avoid thermocouple breakage due to slight misalignment between the two crushable alumina pieces. To locate the thermocouple at the furnace center, the axial hole in the bottom crushable alumina piece is packed tightly with reagent-grade alumina powder or filled with a rod machined from AN900 crushable alumina topped with about 1 mm of reagent-grade alumina powder. Ther-

mocouple wires are insulated with McDanel 998 alumina (99.8 wt% Al₂O₃). Both alumina pieces, Norton AN900 and McDanel 998, provide an anhydrous environment low in contaminants and have virtually the same chemical composition and thermal conductivity and similar physical properties. This assembly design favors isotropic pressure distribution and a smooth thermal gradient. Also, thermocouple drift is minimized by use of high-purity alumina (Mao and Bell, 1971; Mao et al., 1971; Presnall et al., 1973). A rod of fused silica glass 5 mm long is necessary at the base of the furnace to prevent thermocouple breakage because of mechanical distortion; at temperatures below 1400 °C, a Pyrex rod 10 mm in length is used. The steel base plug at the top of the assembly is insulated from the pressure vessel with a Pyrex sleeve. Pyrex is preferred to conventional pyrophyllite sleeves because it is anhydrous, can be cut to size easily, and is cheaper. To lubricate the assembly, a Pb foil 0.05 mm thick (not shown in Fig. 1) is wrapped around the salt cell. No MoS₂ lubricant is used. This assembly design is free of most sources of H₂, H₂O, and S gases. Four capsules 3 mm in diameter that are 4 mm long may be easily accommodated. Alternatively, a single capsule of larger dimensions can be placed in the center of the assembly, and the thermocouple located slightly above the hot spot.

PRESSURE CALIBRATION AND MEASUREMENT OF THE THERMAL GRADIENT

Temperatures were measured with W₉₇Re₃-W₇₅Re₂₅ (type D) thermocouples made from wires calibrated by Engelhard Industries. This calibration is traceable to National Bureau of Standards test no. 243484 A and has an accuracy not exceeding ±0.7%. No pressure correction was applied to the emf of the thermocouples. Pressure calibration of this assembly at 1 GPa was performed using the melting temperature of diopside (1513 ± 3 °C) reported by Boettcher et al. (1982), which agrees to within

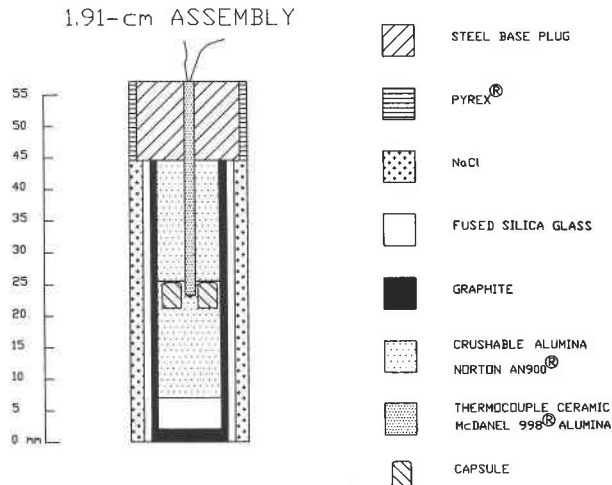


Fig. 1. Cross section of the 1.91-cm high-temperature assembly for the piston-cylinder apparatus.

10 °C with earlier data (Boyd and England, 1963; Williams and Kennedy, 1969). The pressurization and heating procedure for both hot piston-out and hot piston-in techniques was the same up to 1300 °C. A pressure of 0.15 GPa was first applied to ensure electrical contact between the piston, the graphite furnace, and the base plug. The assembly was then heated to 1300 °C at a rate of 300 °C/min; pressure was increased simultaneously such that, at 500, 1000, and 1300 °C, the pressure was approximately 0.4, 0.7, and 0.85 GPa. The temperature was then raised at 100 °C/min up to 1400 °C, and then at 50 °C/min to the experimental temperature. For the hot piston-out technique, pressure was increased to 1.2 GPa at 1400 °C; after reaching the experimental temperature, the pressure was decreased slowly to 1.0 GPa. For the hot piston-in technique, pressure was increased slowly while the assembly was heated from 1300 °C to the temperature of the experiment, in order to reach 1.0 GPa at the temperature desired. Between 1300 and 1400 °C, careful pumping must be performed for both techniques because the fused silica glass sleeve softens in this temperature range, resulting in a concomitant drop in pressure. Pressure was controlled within ± 0.008 GPa, and temperature within ± 1 °C. Results of the calibration indicate that no friction correction, within a precision of ± 0.04 GPa, is necessary at temperatures of 1400 °C and above for either hot piston-out or hot piston-in pressurization procedures.

The vertical thermal gradients in this assembly were measured at 1 GPa and temperatures between 1000 and 2100 °C. During the measurement of the thermal gradient, the temperature was increased at 300 °C/min to 950 °C and then raised at 50 °C/min for the duration of the experiment. Pressurization and heating of the assembly followed similar *P-T* paths, as described above, for pressure calibration. Thermal gradients were measured at 100 °C intervals between welded thermocouples located at the center of the furnace and 2.25 mm either above or below

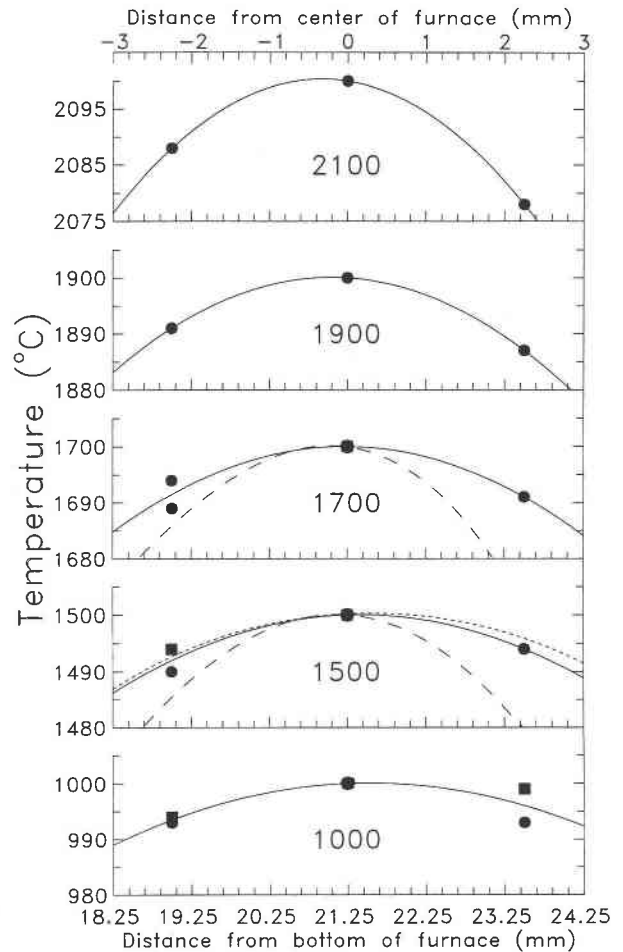


Fig. 2. Thermal gradients measured at 2100, 1900, 1700, 1500, and 1000 °C at 1.0 GPa over the central part of the furnace assembly. Squares represent data collected with four Pt capsules, and circles represent data collected with four Mo capsules. At 1000, 1500, and 1700 °C a circle is superimposed on a square at the distance of 21.25 mm from the bottom of the furnace. A second-degree polynomial has been used to fit the data points. The short-dashed line shows the thermal profiles reported by Cohen et al. (1967) whereas the long-dashed lines depict profiles measured by Boyd and England (1963), both in 1.27-cm assemblies. The thermal profiles of Boyd and England (1963) have been slightly shifted to bring the locations of maximum temperature into alignment for all three profiles.

the center. After the experiment, the location and the distance between the thermocouples were checked to make sure they did not move as a result of pressurization. A time interval of 90–240 s was required at each temperature for stabilization of the temperature readings from both thermocouples. All measurements were performed with loaded capsules to simulate actual experimental conditions in which Pt capsules are used at temperatures below 1700 °C and Mo capsules are used at higher temperatures. At 2100 °C the temperatures measured by both thermocouples fluctuated by ± 5 °C; however, the tem-

perature gradient between the thermocouples remained constant to within ± 1 °C.

Figure 2 shows the vertical thermal gradients measured over the central 4.5 mm of the graphite furnace in this assembly. At temperatures of 1700 °C and below, the gradient is < 4 °C/mm, and at 2100 °C, the maximum gradient is 10 °C/mm. This assembly has a zone 5.4 mm in length in which the temperature is no more than 10 °C below that of the hot spot, up to 1400 °C; at higher temperatures the length of this zone diminishes to 3.5 mm at 2100 °C. Vertical thermal gradients in our 1.91-cm assembly are similar to those measured in other 1.91-cm assemblies with straight-wall graphite furnaces (Leistner, 1979; Kushiro, 1976). Vertical thermal gradients in 1.27-cm (1/2-in.) assemblies are equal to or greater than those we have measured (Fig. 2). The gradient in the 1.27-cm assembly of Cohen et al. (1967) is similar to the ones we measured, whereas gradients reported by Boyd and England (1963) at 1500 and 1700 °C are steeper than ours (Fig. 2). Dunn's measurements (Dunn, 1993) at 1200 °C in his 1.27-cm assembly (similar in design to the standard Depths of the Earth 1.27-cm assembly) demonstrate that only the central 3.75 mm of his assembly are within 10 °C of the hot-spot temperature.

Radial temperature gradients appear similarly small, based on textural observations of cross sections through sample capsules. This is supported by radial temperature gradient determinations in other types of assemblies carried out by other investigators. In a 1.91-cm (3/4-in.) assembly made of NaCl, pyrophyllite, and graphite at 200–1000 °C and 1–3 GPa, there was a temperature difference of 1% between the center and inside wall of the graphite furnace, the maximum temperature being closest to the furnace wall (Leistner, 1979). In a 2.54-cm (1-in.) assembly made of NaCl and graphite the radial temperature difference between the center and a spot 1 mm away from the inside furnace wall was no larger than 1.5 °C at 1200 °C and 1.5 GPa (Bohlen and Boettcher, 1982). Additionally, alkali halide melting experiments carried out in a 2.54-cm (1-in.) assembly made of NaCl and graphite at 0.5 GPa showed that the thermal gradient across the sample was < 5 °C (Bohlen, 1984).

DISCUSSION

Assemblies of our design routinely operate to temperatures of 1900 °C for experiments of 60 min long and have been used in 20-min experiments at 2000 °C and in 5-min experiments at 2100 °C at 1 GPa. High-temperature experiments quench to 100 °C at a rate of about 1500 °C/min. At temperatures above 2100 °C at 1.0 GPa, the assembly undergoes gradual deterioration because of the melting of the alumina near 2200 °C, leading to failure of the experiment. Hot piston-in conditions are preferred at high temperatures because we observed a systematic in-

crease of the thermal gradient during the decompression step of the hot piston-out technique. This increase is probably the result of a change in the wall thickness of the graphite furnace in the vicinity of the four sample capsules that appears to occur when the assembly is decompressed, or to the stress effects on the two thermocouples (Mao and Bell, 1971; Mao et al., 1971).

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