

Temperature gradients in rapid-quench cold-seal pressure vessels

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Abstract

Temperature gradients existing inside horizontal cold-seal pressure vessels have been measured at a variety of pressures up to 2 kbar using water, argon, and CO₂ as pressure media. Conventional vessels of 20.3 cm (8") length give acceptable results (temperature gradients of no more than 5°C) for sample lengths of 30 mm or less, provided a filler rod is used. Attaching a rapid-quench water jacket (Wellman, 1970) causes gradients to increase dramatically. For a 20.3 cm vessel, all pressure media give unacceptable results. On the other hand, a 30.5 cm vessel with a rapid-quench attachment and pressurized to 2 kbar by argon produces gradients of less than 5°C over a distance of 50 mm.

Introduction

The temperature gradients which exist within conventional cold-seal pressure vessels (Tuttle, 1949) are of particular concern to experimental petrologists. Boettcher and Kerrick (1971) measured gradients between a thermocouple placed inside the vessel pressurized by water to 1 kbar and an external couple placed in a well in the vessel wall. The effects of orientation of the vessel and of the presence or absence of a filler rod were evaluated as a function of the depth of immersion of the vessel into the furnace. The most satisfactory results were obtained by placing a closely fitting filler rod inside the pressure vessel. All vessels had an overall length of 20.3 cm (8") and a maximum immersion depth of 17 cm.

Recently Wellman (1970), following a suggestion made by Greenwood, modified the conventional vessel by attaching a water jacket to the cool end of the bomb. At the conclusion of the experiment the charge was quenched simply by tipping the bomb and letting the charge capsule slide at pressure to the cold head of the bomb. Rapid quenching is particularly important when the composition of the solution in equilibrium with a mineral assemblage is to be investigated. In this manner, the effects of reactions during quench can be minimized. Rapid-quench bombs have been used extensively for studies of metamorphic solutions using the acid-base buffers developed by Frantz and

Eugster (1973). Preliminary data on a number of reactions were reported by Gunter *et al.* (1973, 1974). Filler rods were used in all of these experiments.

In simple hydrothermal runs, charges are contained in noble metal capsules up to 20 mm in length, while in acid-buffered experiments, the length had to be increased to 38 mm to allow space for the Ag + AgCl buffer and for enough solution to be extracted after an experiment. In buffered experiments, the outer capsule which encloses the hydrogen buffer had a length of 57 mm. Preliminary tests using the melting point of halite as an indicator at 2 kbar helium and methane pressure convinced us that temperature gradients for these long tubes were still acceptable, that is no more than 5°C, and the calibration of the HCl buffer (Frantz and Eugster, 1973) was carried out under this assumption. Recently, however, some discrepancies were discovered, and it was found necessary to measure the temperature gradients existing in rapid-quench bombs directly by placing thermocouples inside the pressure vessel. The results were sufficiently surprising that anyone using this type of equipment should be aware of them.

Experimental procedures.

Figure 1 shows the type of rapid-quench bomb used in the experiments. A conventional 20.3 cm or 30.5 cm (8" or 12") pressure vessel *P* made of Stellite 25 or René 41 is connected with a double cone and nut *C* to an extension *E*, 20.5 cm long and made of the same material or a good quality stainless steel. The extension has the same diameter (25 or 32 mm) as the

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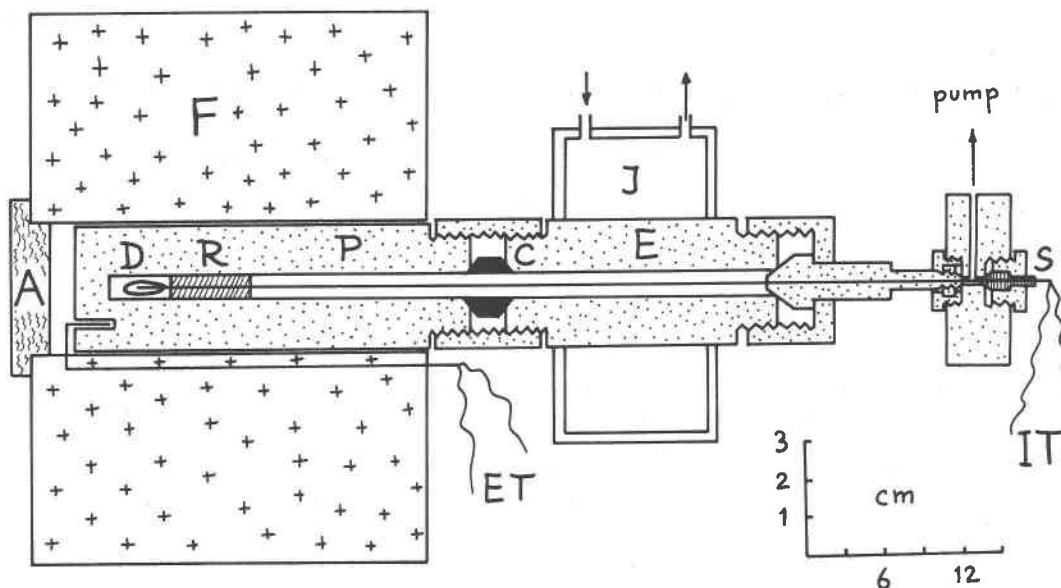


FIG. 1: Pressure assembly with rapid quench attachment. The pressure vessel *P* is connected by a double cone *C* to the extension *E* which is surrounded by cooling jacket *J*. Temperatures are measured with an external (*ET*) and internal (*IT*) thermocouple. The internal couple is soldered to cone *S*, and passes through a filler rod *R* into a dummy charge *D*. The open end of the furnace *F* is closed with an asbestos plug *A*. Note that the vertical scale is exaggerated three-fold.

pressure vessel and the same bore (6.4 mm). It is surrounded by a water jacket *J* made of lucite and sealed with *O* rings against the extension. The open end of the extension is closed by a conventional cone-and-nut assembly. The pressure vessel is then placed horizontally in a split furnace with a short filler rod resting against the charge to minimize convection. The length of the filler rod is governed by the length of the water jacket. After each experiment the assembly is removed from the furnace and quickly tipped to a near-vertical position, so that filler rod and charge fall into the cold end of the extension. A rap with a hammer insures that the charge does not get hung up inside the bomb. After tipping, the charge is at pressure and near room temperature and can be removed at leisure. There are two advantages in using an extension over the use of a 60 cm pressure vessel as suggested by Wellman (1970). Pressure vessels of conventional length can be used, and the double-cone-nut assembly *C* acts as a partial heat shield for the cooling jacket.

In order to measure temperatures, a sheathed thermocouple (*IT*) was calibrated against the melting point of NaCl at 1 atm. This is accomplished most conveniently by constructing a reentrant sample tube with a pocket to accommodate the thermocouple. A gold or platinum tube, 2.6 mm in diameter, 1.2 cm long, is welded shut at one end. It is placed inside

another gold or platinum tube, 4.0 mm in diameter, 2.5 cm long, so that two of the rims are flush. These two rims are then welded to each other, so that the inner tube forms the pocket. The large tube is filled from the other end with NaCl and crimped or welded shut. Melting and crystallization of NaCl can readily be observed by the arrest of the galvanometer during heating and cooling cycles.

The thermocouple calibrated in this manner was placed inside the pressure assembly, and the vessel was pressurized. In this mock-up, the filler rod *R* (see Fig. 1) was drilled along its axis to allow the thermocouple to pass through. The tip of the couple was inserted in a dummy charge capsule *D* in order to duplicate the actual run conditions as closely as possible. The pressure assembly was then heated, with the cooling water circulating, and temperatures were recorded for the internal couple (*IT*) and an external couple (*ET*), making sure that thermal equilibrium was reached before each measurement. Next, the position of the thermocouple within the pressure vessel was changed in order to explore the temperature gradient along the bomb axis. This can be achieved most easily by changing the length of the cone which connects the extension *E* to the *T*-junction at the end of the assembly. Results were obtained for the three pressure media H₂O, CO₂, and argon, and for several pressures, and they are shown in Figure 2. Because

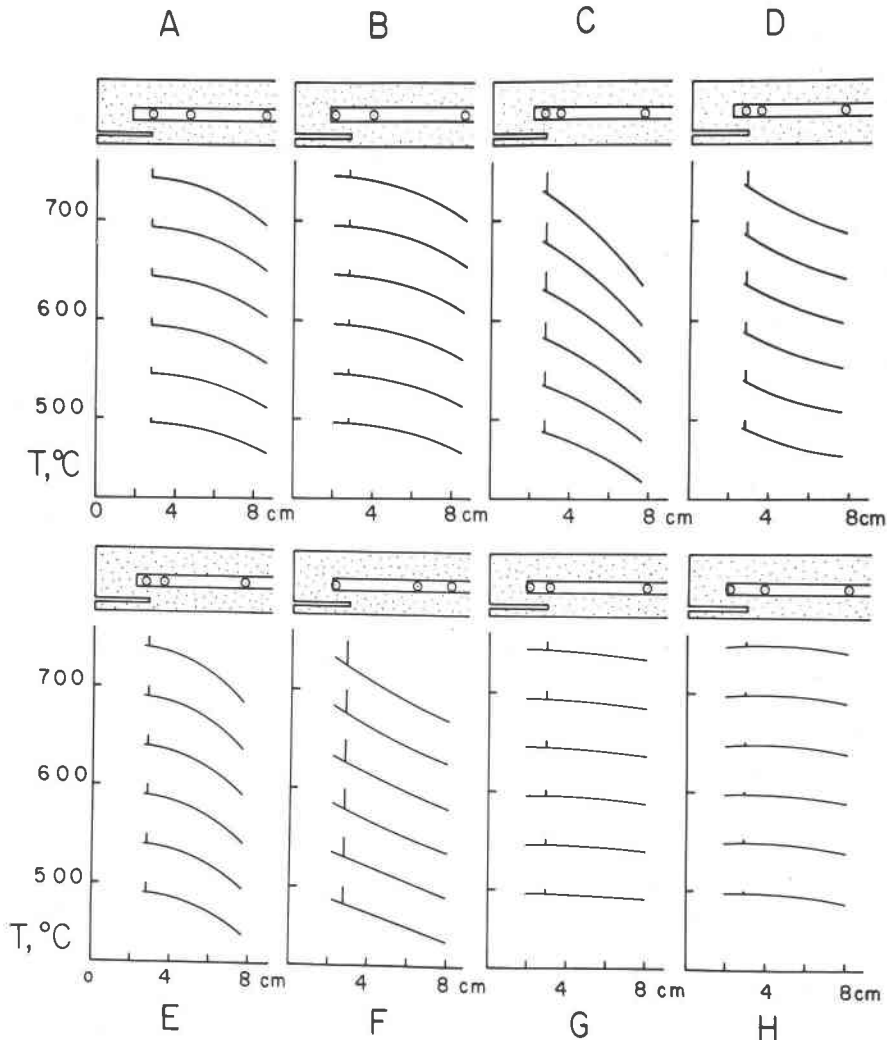


FIG. 2. Temperature gradients for a variety of experimental conditions. (A) H₂O at 2 kbar, 20.3 cm vessel, no rapid-quench attachment; (B) argon at 2 kbar, 20.3 cm vessel, no rapid-quench attachment; (C) H₂O at 1 kbar, 20.3 cm vessel, rapid-quench attachment; (D) H₂O at 2 kbar, 20.3 cm vessel, rapid-quench attachment; (E) argon at 2 kbar, 20.3 cm vessel, rapid-quench attachment; (F) CO₂ at 2 kbar, 20.3 cm vessel, rapid-quench attachment; (G) H₂O at 2 kbar, 30.5 cm vessel, rapid-quench attachment; (H) argon at 2 kbar, 30.5 cm vessel, rapid-quench attachment. The measuring points, three internal and one external, are indicated in the sketches of the pressure vessels above each set of gradients. The three internal temperatures are connected by a curve, and the external temperature is shown as the upper end of the short, vertical line segment connected to the curve.

bombs and thermocouples had to be disassembled after each set of measurements, the gradients cannot be exactly duplicated by subsequent measurements, but the gradients shown in Figure 2 are representative.

The first two sets (A and B) refer to conventional 20.3 cm vessels of 32 mm diameter *without* a rapid-quench attachment, using water and argon, respectively, at 2 kbar as pressure media. For samples of up

to 3 cm in length, acceptable gradients are less than 10°C. However, there is an additional difference of 5–8°C between the externally measured temperature and the internal temperature at a corresponding point. Beyond 3 cm, temperatures fall off rapidly. Simple hydrothermal experiments are often carried out in sealed metal tubes 20 mm (3/4") in length. For these, once the discrepancy between external thermocouple and sample temperature has been calibrated,

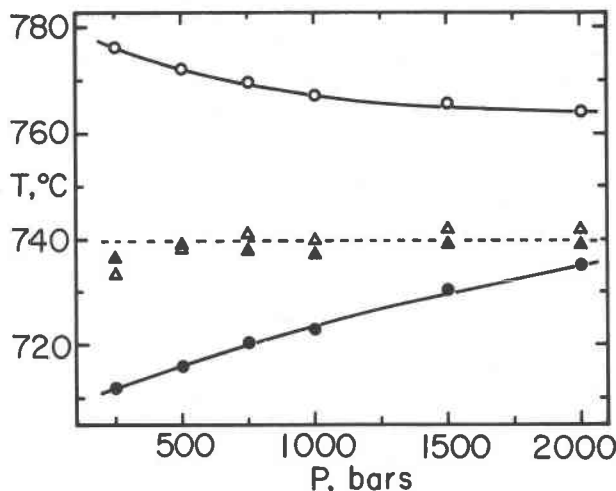


FIG. 3: Effect of pressure on temperature gradient for H₂O and argon in a 30.5 cm vessel with a rapid-quench attachment. Circles are for water and triangles for argon. Open symbols refer to the external thermocouple, closed symbols to an internal couple placed 8 cm from the end of the pressure vessel. Measurements made by decompression from 2 kbar, keeping the furnace temperature constant.

gradient uncertainties are less than 10°C using either water or argon in conjunction with a filler rod. For conventional buffered runs (Eugster and Wones, 1962), however, the outer tube containing the buffer is often 38 mm (1 1/2") long. In this case, gradients are greater than 10°C. Longer sample tubes are undesirable.

The next four sets of Figure 2 (C, D, E, and F) refer to measurements made with short (20.3 cm) vessels of 32 mm diameter in conjunction with a rapid-quench attachment, using water at 1 kbar (C) and 2 kbar (D), argon at 2 kbar (E) and CO₂ at 2 kbar (F). In all cases, temperature gradients are unacceptable. For a charge of 38 mm length (a normal buffered charge), the following gradients would have to be tolerated: up to 62°C for water at 1 kbar, up to 47°C for water at 2 kbar, up to 45°C for CO₂ at 2 kbar, and up to 28°C for argon at 2 kbar. Argon is obviously the most desirable medium, but the gradients are still too large. As a comparison between Figures 2C and 2D shows, pressure has a considerable effect on the temperature gradients.

Results using a 30.5 cm pressure vessel in conjunction with rapid quench attachments, on the other hand, give satisfactory results. Figures 2G and 2H show the data for 2 kbar H₂O and argon, respectively. Again, argon is distinctly better, maintaining a 5°C gradient over some 50 mm, while with water the same gradient can be maintained only over 35 mm.

To investigate the pressure effect further, a 30.5 cm vessel with rapid-quench attachment was pressurized with H₂O to 2 kbar. An internal thermocouple was placed 8 cm from the end of the vessel, and its temperature was recorded as well as that of the external couple. The vessel was then decompressed in steps to 250 bars, and the corresponding equilibrium temperatures were recorded. This procedure was repeated with argon, and the results are given in Figure 3. Obviously, there is no effect with argon, whereas there is a pronounced divergence between *IT* and *ET* with lowering of the water pressure. For this particular set-up, the initial difference was larger than it was for Figure 2G. Nevertheless, the measurements indicate a marked increase of heat loss as the density of the aqueous fluid decreases. Because of this strong pressure effect when water is used, argon is the preferred pressure medium. With the latter, samples of up to 50 mm length can be used, which should be adequate for most hydrothermal experiments. Further improvements can be achieved by attaching longer extensions, which also allows space for longer filler rods.

In conclusion, we recommend that buffered experiments using rapid-quench attachments should be carried out only in pressure vessels at least 30 cm in length and pressurized by argon.

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