A reliable high-temperature setup for internally heated pressure vessels: Applications to silicate melt studies

JACQUES ROUX, FRANÇOIS HOLTZ, ANDRÉ LEFÈVRE

Centre de Recherches sur la Synthèse et la Chimie des Minéraux, CNRS, 1A rue de la Férollerie, 45071 Orléans, France

FRANK SCHULZE

Institut für Mineralogie, Universität Hannover, Welfengarten 1, 30167 Hanover, Germany

ABSTRACT

A reliable, vertically operated furnace assembly has been designed for high temperatures (up to 1400 °C) and long-duration experiments of several days or weeks in internally heated, Ar-medium pressure vessels (IHPV) working up to 10 kbar. Useful volumes with vertical temperature gradients $< \pm 10$ °C over 3.5–4 cm (o.d. = 1 cm) are available at high pressures.

This goal has been achieved by using a two-stage furnace consisting of (1) a low gradient, Kanthal A-1 primary furnace and (2) a high-temperature secondary furnace made of either Kanthal A-1 for operation up to 1200 °C or Pt_{90}-Rh_{10} for operation up to 1400 °C. This design reduces current overloads and hot spots that are common in more conventional single-stage furnaces using high-temperature Pt or Mo heating wires.

The high-temperature secondary furnace, the most fragile part of the setup, can be installed and removed readily. However, this proved unnecessary after more than 1350 h of operation between 1200 and 1400 °C using a Pt_{90}-Rh_{10} high-temperature winding in one pressure vessel (pressures up to 4 kbar). Temperatures up to 1200 °C have been obtained using a Kanthal A-1 high-temperature element (up to 10 kbar).

The high-temperature furnace design described here has been used to study H_2O solubility in granitic and SiO_2 melts, and to measure the viscosity of hydrous granitic melts under controlled temperature, pressure, and H_2O content. It is also intended to permit experimental studies of high-temperature equilibria and phase relationships in andesitic to basaltic systems.

INTRODUCTION

Experimental investigations of the physical properties of hydrous or volatile-bearing aluminosilicate melts and phase relationships in magmatic systems require an accurate control of pressure and temperature for relatively long durations (up to 10 kbar, 1500 °C, and several days). Such conditions can be attained in a piston cylinder apparatus (e.g., Boyd and England, 1960; Johannes, 1973), but only very small samples can be used (typically 20 mg), and larger P and T uncertainties are obtained than in an internally heated pressure vessel (IHPV). A detailed description of IHPVs was given by Holloway (1971). In spite of a working volume several orders of magnitude larger than that available in a piston cylinder apparatus, the operation of IHPVs has been plagued by large and ill-controlled temperature gradients and quick furnace failures at high temperatures. Isothermal conditions in large volumes can be attained at $T \le 1000$ °C (e.g., Roux and Lefèvre, 1992; Scaillet et al., 1992), but achieving low temperature gradients is increasingly difficult at temperatures above 1000 °C and a pressure of several kilobars. Holloway et al. (1992) reported temperature gradients of

about 20 °C across a capsule 1 cm long at 1300 °C and 1500 bars. This work describes the design of an improved high-temperature furnace and high-pressure ports, along with typical applications in several fields of high-pressure and -temperature experimental work.

THE FURNACE

The wires suitable to make high-T furnaces, such as Pt, Pt-Rh, Mo, or W, have temperature coefficients about a hundred times larger than that of the specially designed alloy, Kanthal A-1, which, however, has a melting temperature of about 1330 °C, several hundred degrees lower than that of Pt or Mo.

Because of the strong positive temperature dependence of the resistivity, temperature gradients are amplified by the resistivity change of the Pt or Mo heating wires. Hot spots typically occur using these materials in hand-made, conventionally wound furnaces. In addition, the power load required for high operating temperatures often exceeds that recommended in the manufacturer's technical specifications, resulting in significant overheating of the wires and subsequent failures.
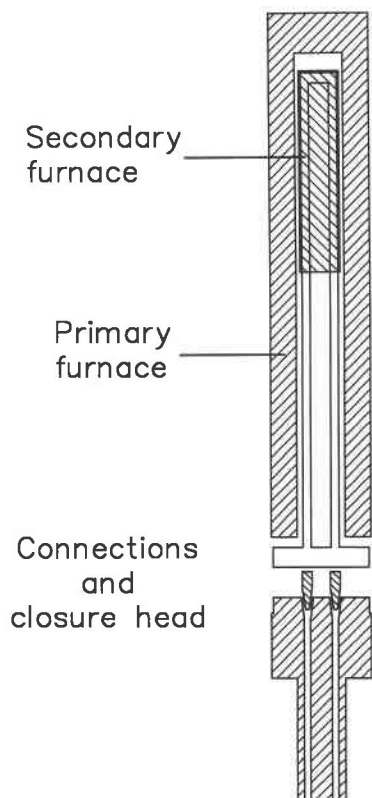
Fig. 1.   Schematic cross section of the closure head, primary furnace (1000 °C) and secondary furnace (1400 °C).
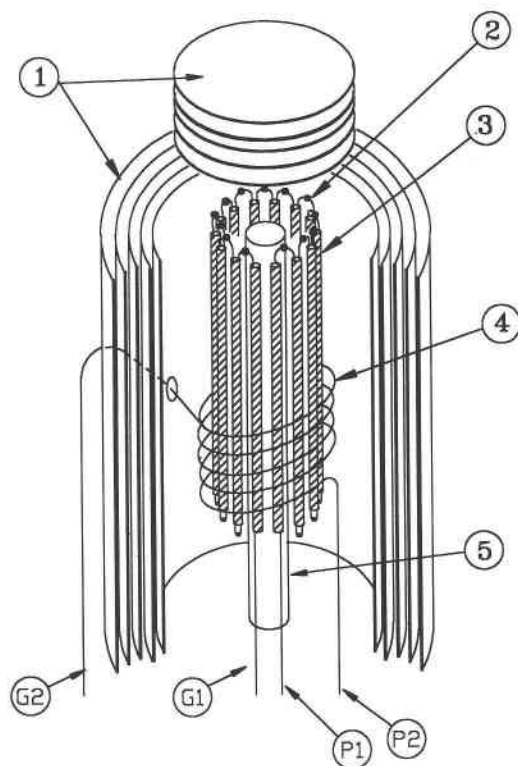

Fig. 2.   Details of the primary furnace: (1) thermal insulation made of Ni or stainless steel foils and ceramic paper (Fiberfrax); (2) main Kanthal A-1 resistor with Ar arc-welded elements in (3) alumina capillary tubes; (4) external Kanthal A-1 resistor; (5) Inconel muffle. G1 and G2 connected to ground; P1 and P2 connected to power electrodes.

The design described below addresses both problems. The starting point was the successful operation of a vertical Kanthal A-1 furnace providing a very large isothermal volume at temperatures up to 1000 °C, as quoted in Roux and Lefèvre (1992). The workspace available in this primary furnace is sufficient to accommodate a high-temperature auxiliary winding with a ceramic sample holder of about 1 cm i.d. and a temperature shield. Most of the power is provided by the primary furnace, so that only a moderate current needs to be applied to the preheated high-temperature winding. The current limiting device needed to accommodate the low value of the resistance, at room temperature, of Pt or Mo wires is not required. The temperature shield protects the Kanthal A-1 low-temperature winding from overheating.

The high temperature furnace assemblage described here (Fig. 1) has been designed for one IHPV currently used at the CRSCM (Centre de Recherches sur la Synthèse et la Chimie des Minéraux), with a 5-cm internal diameter and a 35-cm working length operated up to 4 kbar. All figures presented in this study refer to this specific IHPV. A similar setup has been operated in a smaller IHPV (i.d. = 3.5 cm and a 20-cm working length) used up to 10 kbar.

THE PRIMARY FURNACE, 1000 °C

The primary, low-*T* furnace, working vertically, is similar to that described by Roux and Lefèvre (1992) and detailed in Figure 2. It is composed of a sealed Inconel muffle (o.d. = 2 cm) and two separately controlled resistors made of thick Kanthal A-1 wires (o.d. = 1.4 mm) all of which are surrounded by thermal insulation and a stainless steel protection tube.

The first winding is the main internal Kanthal wire, which covers the entire length of the muffle and is tightened parallel to the symmetry axis of the furnace. This unusual setup offers several advantages: the difficulty of regularly spacing the windings is avoided, and therefore the probability of developing hot spots is lessened. The electrical connections are straightforward since the ends of both leads are conveniently located at the bottom of the furnace. The wire is mechanically protected and electrically isolated by straight alumina tubes (length = 18 cm).

The second resistor is wound around the lower half of the first winding. This second winding helps control the temperature gradient in the furnace. Spacing of the wire
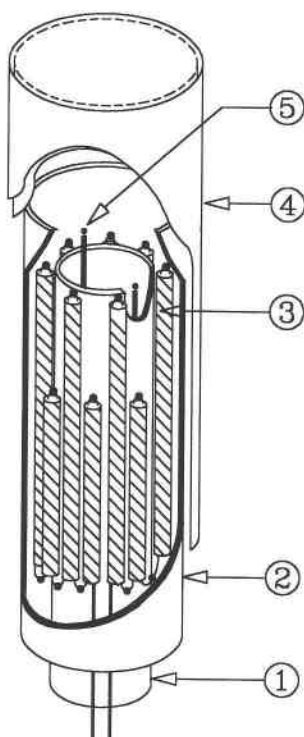
Fig. 3. Details of the secondary furnace: (1) internal alumina tube (o.d. = 10 mm); (2) external alumina tube (o.d. = 20 mm); (3) Pt-Rh$_{10}$ resistor in twin bore alumina capillaries: long and short elements are required to improve the temperature gradient; (4) thermal shield, which slides over the external alumina tube, made with Ni foil and Fiberfrax ceramic paper; (5) thermocouple.
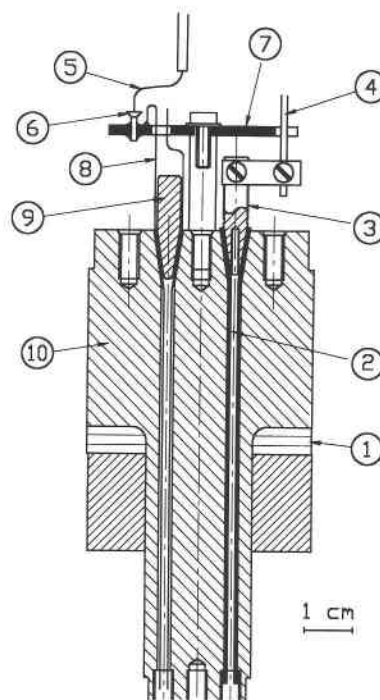

Fig. 4. Closure plug: (1) Bridgman seal; (2) insulated brass power electrode screwed into (3) a steel cone (machined plastic insulator) connected to (4) the primary furnace power leads. (5) Thermocouple wire plugged into (6) a tulip integrated-circuit connector soft-soldered to (7) a glass-epoxy printed-circuit board. (8) Thin insulated Cu wires squeezed between (9) a steel plug and (10) the closure head body, embedded in cast epoxy (six wires per plug).

is not critical because it is located in the low-temperature area of the furnace. For the same reason, the reduction of available space for insulation is not critical in this part. The return wire from this resistor is grounded and need not be insulated from the thermal shield (see below).

The thermal insulation along and at the top of the furnace is made of several tightly packed Ni or stainless steel foils and ceramic paper (Fiberfrax from Carborundum). Electrical insulations, where needed (e.g., location 2 in Fig. 2), are made with scintered alumina and high-temperature cement. The primary furnace is the most time-consuming and expensive part to make of the setup.

THE SECONDARY FURNACE, 1400 °C

This high-temperature part (see Fig. 3) is made of an inner, scintered alumina tube, o.d. = 1.1 cm, a Pt$_{90}$-Rh$_{10}$ wire, and an outer ceramic tube, o.d. = 2.0 cm. The inner alumina tube is long enough to be fixed on the closure head. The Pt$_{90}$-Rh$_{10}$ wire, o.d. = 9 mm, runs parallel to the axis of the furnace and is placed in alumina capillaries (twin holes normally used for thermocouples). Long and short alumina capillaries (10 and 6 cm) are alternatively placed along the inner ceramic tube to improve the tem-

perature distribution. This geometry is again preferred, as pointed out previously, to minimize hot spots, and it provides easier electrical connections at the bottom of the furnace.

The heat shield, a finger made of Ni foils (thickness 0.1 mm) separated by ceramic paper, slides over the outer alumina tube of the Pt furnace, and provides a thermal insulation to the primary furnace (at 1 atm Inconel starts to melt between 1260 and 1350 °C, depending on the composition of the alloy). This part of the furnace can be made and quickly replaced at a moderate cost.

CLOSURE HEAD

The high-pressure closure heads (Fig. 4) of both pressure vessels used have a maximum of six ports. All pressure plugs are steel cones with an angle of 14°. They can be easily removed and replaced.

Power electrodes are obtained by screwing a brass rod into the bottom of the steel cone. Electrical insulation from the closure head and from the high-pressure Ar tight seal is made of a machined or cast plastic material. Three power ports are needed to control the three windings of the furnaces.
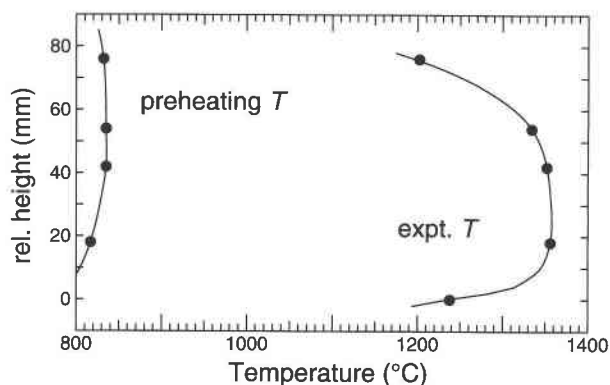
Fig. 5. Temperatures recorded during a typical experiment: preheating *T* was obtained during the first heating period using the primary furnace (about 830 °C); the experiment *T* was reached after powering the secondary furnace and reaching the set point at about 1350 °C.

Above 1200 °C, sheath thermocouples have been found to fail fairly rapidly. It is therefore impractical costwise to use these devices in the required *P* and *T* conditions. Standard type B ($PtRh_6$-$PtRh_{30}$) thermocouple wires were used instead. They are particularly suitable at high temperature and have a negligible cold-seal correction, up to 50 °C, allowing the connections to be made to thin Cu wires in the cold bottom part of the furnace. They are protected by scintered alumina capillaries with two holes. Up to six thermocouples have been used simultaneously. Only three ports are available for the thermocouples, which are connected to thin Cu wires (o.d. = 0.15 mm, 600 V, 6-μm polyurethane insulator) squeezed between the three available plugs and their plastic pressure seal. Each port is fitted with six wires, which are soft-soldered to tulip microelectronic connectors (normally used for electronic integrated circuits) on a small glass-epoxy printed circuit board. Thermocouple wires (o.d. = 0.6 mm) are plugged directly into these Au-plated connectors. The thermocouples can therefore be quickly changed from experiment to experiment, to help investigate temperature distributions. Because of the large number of wires available (up to 18), it is not necessary to share a common negative lead between thermocouples, which improves the reliability of the setup.

OPERATION

The vessel is first brought to a starting pressure of approximately 60% of the desired final experimental pressure. In all high-*T* experiments, heating takes place in two steps. The first step (about 20 min) consists of heating the area in which the Pt furnace is located using the primary furnace (up to 800–850 °C). The power is then applied to the Pt_{90}-Rh_{10} winding, and the set point is reached at temperatures up to 1400 °C after 5–10 min. The total power consumed at 2.5 kbar and 1350 °C is about 1000 W. The distribution of power between the windings is about 15–25% for the Pt element and 75–85% for the

Kanthal A-1 elements, when experiments between 1100 and 1400 °C are performed. A typical power distribution, measured at 1300 °C and 2 kbar, is 490 W for the main low-temperature winding, 320 W for the second (external) low-temperature winding, and only 220 W for the Pt_{90}-Rh_{10} winding.

In these conditions, the current is maintained below the recommended maximum value for Kanthal A-1 at 1000 °C in the primary furnace (about 14 A, at 1000 °C, for 1.4-mm wires, i.e., corresponding to 4 W/cm², with ρ = 1.46 × 10^{-6} Ω/m).

The temperatures recorded on five thermocouples during an experiment in the Pt furnace at 2.5 kbar for a set point of 1350 °C are shown on Figure 5. Temperature oscillations are about ±1 °C.

Another thermocouple, located between the Pt furnace and the Inconel muffle, was used to optimize the power balance between the primary and the secondary furnace. In normal operation, it is removed, leaving space to the heat shield on the secondary furnace (location 4 in Fig. 4).

Quenching is performed by turning off the power supply. Samples cool after approximately 5 min from 1400 to 800 °C and after another 10 min from 800 to 300 °C, depending on pressure. A drop quench device (Holloway et al., 1992; Roux and Lefèvre, 1992) can be adapted if necessary.

APPLICATIONS

Synthesis of hydrous glasses

The high-*T* furnace has been successfully used to synthesize large samples (250–500 mg) of bubble-free hydrous aluminosilicate glasses, which can be used for spectroscopic investigations or as starting material to determine the properties of hydrous aluminosilicate melts. In particular, samples with very low amounts of H_2O (<1 wt% H_2O) and high liquidus *T* can be easily synthesized. The best method for obtaining bubble-free glass with a homogeneous distribution of H_2O consists of sealing a dry bubble-free glass block and the desired amount of H_2O in a noble metal capsule. The capsule is then heated under pressure and kept at *P-T* conditions above the liquidus for sufficient time to allow complete homogenization by diffusion of H_2O through the sample. The experimental duration must be relatively long, considering diffusion coefficients of H_2O of 10^{-7} cm²/s at 850 °C in haplogranitic melts (Lapham et al., 1984). Typical durations used to hydrate natural leucogranite samples or synthetic Fe-free andesitic and granitic samples were 4 d at 1300–1400 °C (Lejeune, 1994; Schulze et al., 1994). The experimental products were hydrous bubble-free glass blocks.

The homogeneous distribution of H_2O was checked by Karl Fischer titration (for analytical details, see Holtz et al., 1992) and infrared spectroscopy (Behrens, unpublished manuscript; Nowak and Behrens, 1994). As an example, the analysis by Karl Fischer titration of several

slices along a glass cylinder (1.5 cm) of leucogranitic composition, placed at 1300 °C and 2.1 kbar for 4 d with 4 wt% added H_2O, yielded values of 4.14, 4.18, and 4.22 wt% H_2O (uncertainty: ±0.15 wt% H_2O).

H_2O solubility determinations

Experiments using dry bubble-free glass blocks and H_2O as starting materials also allow the determination of H_2O solubility in aluminosilicate melts (if excess H_2O is present in the charge) by measuring the H_2O content of the quenched glass (Tuttle and Bowen, 1958, p. 14; Holtz et al., 1992). Typical experimental durations at 1400 °C for samples of 30–60 mg are 3–4 d. Recent experiments showed that the use of the furnace assemblage described above also allows the H_2O solubility in SiO_2-H_2O melts to be determined. H_2O solubility at 2.5 kbar was found to be 4.4 ± 0.15 wt% between 1200 and 1400 °C (not temperature-dependent in these conditions: Holtz, unpublished data).

Viscosity measurements of hydrous melts

Another application of the high-*T* furnace assemblage described above is the determination of viscosities of hydrous melts up to 1400 °C (Schulze et al., 1994). Using prehydrated glass samples (1.5–2 cm length) with known amounts of H_2O (see technique above) and containing small Pt spheres, melt viscosities have been successfully determined using the falling-sphere method (as described by Bacon, 1936, and Shaw, 1963a). Schulze et al. (1994) investigated the viscosity of melts with a haplogranitic composition at 3 kbar, in the temperature range 900–1300 °C, and for H_2O contents of the melt between 1 and 8 wt%.

The viscosity of a melt with a normative composition of $Qz_{28}/Ab_{38}/Or_{34}$ has been measured as a function of H_2O content. The viscosity decreased from $10^{4.8}$ to $10^{3.9}$ while the H_2O content of the melt increased from 1 to 3.2 wt% H_2O. Depending on *T* and the size of the Pt sphere, the experimental durations were between 6 h and 3 d. The short heating duration (<4 min between 800 and 1300 °C) is particularly helpful for viscosity measurements using the falling-sphere method (in case of a low heating period, the sphere starts to fall over a significant height before reaching the equilibrium temperature).

CONCLUSIONS

The furnace assemblage described in this study allows experiments of long duration in IHPVs at temperatures up to 1400 °C and pressures up to 10 kbar, depending on the characteristics of the IHPV. The high-temperature furnace assemblage tested at the CRSCM has been used for more than 60 experiments and for a total duration of >1350 h. The large isothermal volume, 3 cm³, is sufficient for several charges to be placed together or for performing experiments with large capsules. Because experimental durations of several days (or weeks) are possible,

this new design is particularly helpful in attaining equilibrium conditions in the investigation of phase relationships of andesitic to basaltic systems. The large volume can also be employed in the in-situ determination of the physical properties of silicate melts, such as viscosity measurements using the falling-sphere method. The overall assembly time is about one week, and the cost of the materials is less than $1000.

Further improvements of the assemblage are possible. In particular, a rapid quench device (Holloway et al., 1992; Roux and Lefèvre, 1992) or a Shaw membrane for the control of f_{H_2} (Shaw, 1963b; Scaillet et al., 1992) can be adapted to the furnace assemblage described here.

REFERENCES CITED

Bacon, L.R. (1936) Measurements of absolute viscosity by the falling sphere method. Journal of the Franklin Institution, 221, 251–273.

Boyd, F.R., and England, J.L. (1960) Apparatus for phase equilibrium measurements at pressures up to 50 kilobars and temperatures up to 1750 °C. Journal of Geophysical Research, 65, 741–748.

Holloway, J.R. (1971) Internally heated pressure vessels. In G.C. Ulmer, Ed., Research techniques for high temperature and pressure, p. 217–258. Springer Verlag, New York.

Holloway, J.R., Dixon, J.E., and Pawley, A.R. (1992) An internally heated, rapid-quench, high-pressure vessel. American Mineralogist, 77, 643–646.

Holtz, F., Behrens, H., Dingwell, D.B., and Taylor, R.P. (1992) Water solubility in aluminosilicate melts of haplogranite composition at 2 kbar. Chemical Geology, 96, 289–302.

Johannes, W. (1973) Eine vereinfachte Piston-Zylinder-Apparatur hoher Genauigkeit. Neues Jahrbuch für Mineralogie Monatshefte, 337–351.

Lapham, K.E., Holloway, J.R., and Delaney, J.R. (1984) Diffusion of H_2O and D_2O in obsidian at elevated temperatures and pressures. Journal of Non-Crystalline Solids, 67, 179–191.

Lejeune, A.M. (1994) Rhéologie des magmas: Influence des cristaux et des bulles en suspension, 312 p. Thesis, University of Paris VII, France.

Nowak, M., and Behrens, H. (1994) Characterization of the OH-incorporation in silicate glasses by IR-spectroscopy. Terra Abstracts, 6, 36.

Roux, J., and Lefèvre, A. (1992) A fast-quench device for internally heated pressure vessels. European Journal of Mineralogy, 4, 279–281.

Scaillet, B., Pichavant, M., Roux, J., Humbert, G., and Lefèvre, A. (1992) Improvements of the Shaw membrane technique for measurements and control of f_{H_2} at high temperatures and pressures. American Mineralogist, 77, 647–655.

Schulze, F., Behrens, H., Holtz, F., Roux, J., and Johannes, W. (1994) The influence of water on the viscosity of a haplogranitic melt. Terra Abstracts, 6, 43.

Shaw, H.R. (1963a) Obsidian-H_2O viscosities at 1000 and 2000 bars in the temperature range 700 to 900 °C. Journal of Geophysical Research, 68, 6337–6343.

——— (1963b) Hydrogen-water vapor mixtures: Control of hydrothermal experiments by hydrogen osmosis. Science, 139, 1220–1222.

Tuttle, O.F., and Bowen, N.L. (1958) Origin of granites in the light of experimental studies in the system $NaAlSi_3O_8$-$KAlSi_3O_8$-SiO_2-H_2O. Geological Society of America Memoir, 74, 145 p.