A miniclave for experiments up to 4 kbar and 1200 °C used to study *REE*-carbonate glasses

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Abstract

Glasses quenched from synthetic *REE*-carbonatite liquids in recent Tuttle bomb experiments require fast cooling rates. To study these glasses further, an internally-heated miniclave has been developed to increase quench rates and extend the operating P–T range of standard Tuttle bombs. The Haskel miniclave can achieve simultaneous P and T of up to 1200 °C at 4 kbar for small diameter (1–2 mm) samples. Gas (Argon) pressure is supplied by a small intensifier unit and heating by an internal platinum-wound furnace. Because of the relatively small thermal mass, run temperatures can be reached within a few minutes and quench rates approach those of solid media apparatus.

KEYWORDS: experimental apparatus, high pressure, Haskel miniclave, *REE*-carbonatite, glass.

Introduction

EXPERIMENTS by Jones and Wyllie (1983) designed to study rare earth element (*REE*) behaviour in carbonatite magmas encountered some liquid compositions capable of being quenched to clear glass. An initial bulk composition *E* was chosen to synthesise the *REE*-carbonatite at Mountain Pass in California, where the *REE*-fluorcarbonate mineral bastnäsite (Glass and Smalley, 1945; Donnay and Donnay, 1953) forms between 5 and 15 modal percent of the *REE* ore body (Olson *et al.*, 1954) and up to 30 modal percent of associated carbonatite dykes. To mixture *E*, estimated to be close to the quaternary eutectic in the system $CaCO_3$–$Ca(OH)_2$–$BaSO_4$–CaF_2, was added *REE* in the form of $La(OH)_3$. Results for the join *E*–$La(OH)_3$ were given in Wyllie and Jones (1985) and yielded bubble-free volatile-rich glass from runs above or just below the liquidus (Fig. 1) with a few anomalies, for the studied compositions. The glasses were analysed by electron probe which confirmed their starting compositions and high volatile contents. These experimental runs were all made in standard Tuttle bombs at 1 kbar pressure, using the fastest practical quench rates with compressed air and water cooling. Small proportions of glass were often restricted to axial regions of charges and some could easily have been overlooked. Pure compositions in the related simple system $CaCO_3$–$Ca(OH)_2$–$La(OH)_3$ did not reveal glasses (Jones and Wyllie, 1986) and no other glasses in carbonatite systems have been recorded. A desire to facilitate production of further carbonate glasses was a primary motivation in designing the miniclave described in this paper.

The use of static high-pressure and high-temperature apparatus for experiments in the Earth Sciences has proliferated mostly since the 1950s and several systematic reviews are available (Roy and Tuttle, 1956; Wyllie, 1966). Excluding recent developments with large and expensive uniaxial presses and small diamond anvils, three of the four major ways of combining high pressure (hydrostatic or uniaxial) with high temperature (externally or internally heated) have yielded the most widespread experimental tools in petrology. These have undergone many refinements but essentially little change since their inception. The designs have necessarily been related to the availability of specialist materials, primarily metals, and their associated machining capabilities. The

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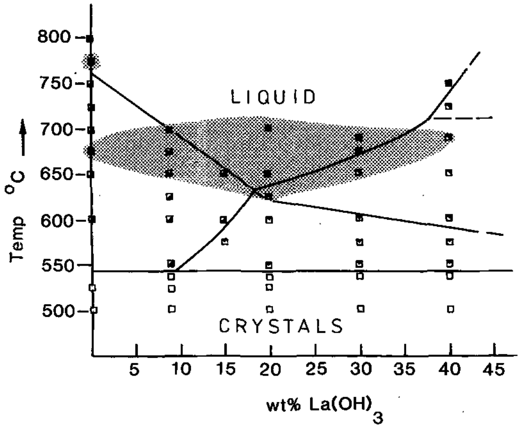

FIG. 1. Stippled zone outlines experimental runs which produced glass in the system E-La(OH)$_3$, using conventional Tuttle bombs (phase fields omitted for clarity; further details in Wyllie and Jones, 1985). Bulk composition E was chosen to be close to the quaternary eutectic in the system $CaCO_3$-$Ca(OH)_2$-$BaSO_4$-CaF_2 and to simulate the bulk composition of the *REE*-carbonatite at Mountain Pass, California (Jones and Wyllie, 1983). Small amounts of glass in some runs may have been overlooked; they were produced near non-destructive quench rate limits for Tuttle bombs.

popular experimental equipment used in petrology is, in increasing order of pressure limits: (1) Tuttle bombs (hydrostatic, externally heated, see esp. Luth and Tuttle, 1963) standard maximum pressures of approximately 4 kbar but a severe trade off with temperature (less than about 500 °C at this pressure). (2) Internally heated pressure vessels (hydrostatic, internally heated) capable of approximately 10 kbar pressure routinely at high temperatures (up to 1600 °C). (3) Piston cylinder (uniaxial, internally heated, see esp. Boyd and England, 1960), pressures normally up to 45–50 kbar at high temperatures. For all these methods towards their practical maxima, time in terms of run duration becomes important since the confining materials become weaker. Of these, only Tuttle bombs can be considered as inexpensive, while (2) and (3) are also much larger. The new apparatus described below was designed to extend the pressures and temperatures beyond the range of (1) but at a fraction of the costs of (2) and (3). As a trade off for these attributes there are some limitations, which are described later.

Miniclave

General. Development of the miniclave has been fully supported from the outset by Haskel Inc. (Burbank, USA) and it is now called a 'Haskel Miniclave'. Some refinements are still in progress, but the essential features are embodied in this paper.

The miniclave is machined from similar high tensile alloy (1 inch diameter rod) as that commonly used for Tuttle bombs (e.g. Rene 41), retaining a similar internal radius (a) to external radius (b) ratio of 1:4. A line drawing of the miniclave is given in Fig. 2. The resultant 'thick-walled tube' of approximately 20 cm in length is terminated at both ends with conventional 59/60° cone in cone seals and large threaded locking nuts similar to a Tuttle bomb. This is, however, where the similarity ends, for instead of being externally heated, a small platinum wound furnace provides internal heating. An alumina tube acts as the former for the furnace windings, which are wound spaced by grooves in the tube and secured with Zircar alumina cement cured at 400 °C. Two electrical power leads are taken through new purpose-built double cone in cone high-pressure electrical connections (Fig. 3), in a Y-shaped stainless steel housing (not shown). Temperature is monitored by a thermocouple, silver soldered or otherwise sealed at the other end of the miniclave. The furnace is insulated from the miniclave body by a silica sleeve, ground to loose fit, allowing for differential thermal expansion. The main portion of the miniclave is surrounded by a removable aluminium cooling jacket connected to a low-pressure water supply.

Stresses. Consideration of the different stresses produced in response to pressure and temperature is useful both for safety and operational purposes. Stress calculations have been made assuming that the miniclave can be modelled to a first approximation as a thick-walled cylinder of infinite length, internal radius a and external radius b. Although the ends of the cylinder might concentrate stresses, these can be ignored for temperature, because they remain cool. Stresses were calculated using the solutions of Timoshenko (1970) and are illustrated graphically in Fig. 4 (A and B), for a temperature of 1000 °C and a pressure of 4 kbar respectively. The thermal stresses (Fig. 4A) are significant and compressive inside the miniclave (negative at radius a), becoming tensional at the outside (positive at radius b). Thus, an internal temperature of 1000 °C could cause internal stresses on the order of 3 to 4 kbar. These peak stresses are reduced by approximately a half through the thermal insulation provided by the silica sleeve around the furnace. The internal compressive stress can be usefully offset by the tensional stresses of gas pressure, and the life of the miniclave can be extended by step-wise increasing of temperature and pressure combined. The maximum stress pro-

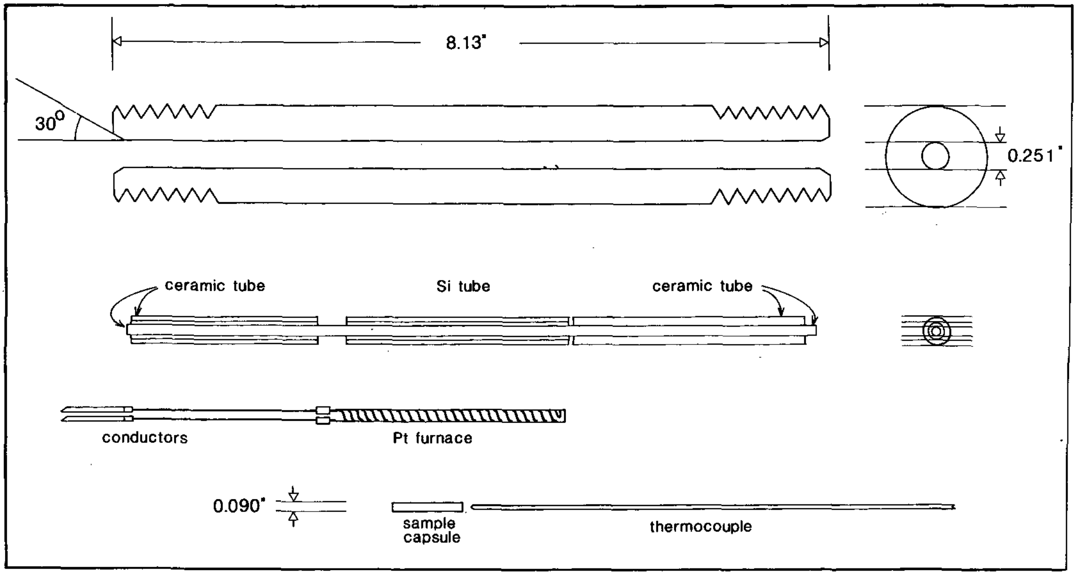

FIG. 2. A line drawing of the Haskel Miniclave showing essential features (see text). Note overall size is approximately 20 cm in length, similar to a Tuttle bomb. The Pt furnace is space-wound onto ceramic (alumina) tube and electrical power provided through copper conductors with gold connectors.

duced in response to pressure (Fig. 4B) always slightly exceeds the applied gas pressure and is greatest on the internal wall. It is a consequence that because the sum of σ_r and σ_θ is constant, increase in pressure will produce a uniform extension of the miniclave along its axis. The end nuts and seals are identical in format to those successfully proven with Tuttle bombs to be safe for routine pressures to at least 4 kbar and have not so far been tested under run conditions beyond this pressure.

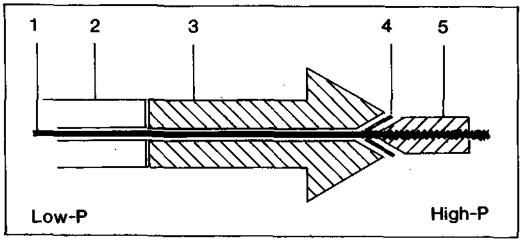

FIG. 3. Sketch of the double cone-in-cone electrical connection (one per conductor). Low-P and high-P sides indicated, Y-shaped housing not shown. All components have circular cross sections: 1 = conductor, 2 = nylon insulator, 3 = stainless steel plug, 4 = plastic insulator, 5 = brass threaded locking sphincter nut with reverse cone. Overall length about 7.5 cm.

Operation. The complete miniclave system is small and is operated on a bench. It comprises three units; the miniclave itself, a pressure control unit and a temperature control unit.

A sample is prepared conventionally in the form of a capsule, usually made from platinum or gold tubing of approximately 2.0 mm diameter. The completed capsule of desired length is then cold formed by tamping in a die to ensure ease of loading into the centre of the furnace assembly inside the miniclave. The furnace assembly is removed periodically to inspect for cracking of the silica insulating sleeve, and electrical connections are made by soft soldering and/or crimping to power leads. Thermocouple and power end nuts are attached to the miniclave assembly, which is connected to the high-pressure line. The thermocouple (usually $\frac{1}{16}''$ stainless steel sheathed with Cr-Alumel) is in near contact with the sample capsule, located in the hot zone of the furnace. The hot zone is long in comparison to sample capsules and with a separation between capsule and thermocouple of less than 0.5 mm; deviations in temperature are estimated to be less than 5 °C. Argon gas is flushed through the lines and assembly before final tightening of the end nuts. High argon gas pressure is achieved with a special small 100 000 psi intensifier unit (Haskel) and driven with compressed air. Argon is taken from a standard gas cylinder

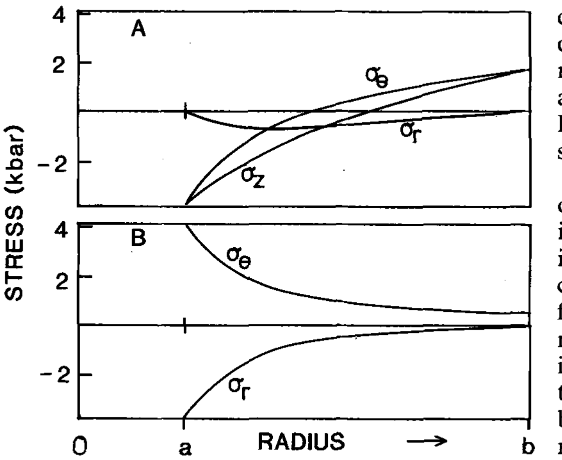

FIG. 4. (A) Calculated stresses for 1000 °C internal temperature. Stresses are high and negative (compressive) on the inner surface (*a*) but are tensional on the outer surface (*b*). Actual temperature-induced stresses across the miniclave are reduced significantly by thermal insulation (see text). (B) Calculate stresses for 4 kbar internal pressure. Note σ_θ is positive (tensile) and greatest at the inner surface of the miniclave, where it slightly exceeds the applied gas pressure. O is origin at centre of miniclave.

at pressures usually below a few thousand psi, and charged into the intensifier by a small air-driven hydraulic pump. Depending on the pressure desired, the pressure is boosted by recharging and recycling the single stroke intensifier through a series of valves. Because of the small internal volumes of both the lines and miniclave unit, pressure can be increased rapidly. An initial problem with temperature control was experienced due to the small thermal mass and thermocouple delay. This was overcome with a fast thyristor-based temperature control system borrowed from piston cylinder technology (Eurotherm) and the system also works well under manual temperature control, using a variac. Heating is very fast, and application of pressure is the rate-limiting part of setting up a run, though this can usually be achieved in about ten minutes. Pressure is monitored by an in-line Bourdon type gauge and also by a digital millivolt-type output transducer coupled to a computer. Both temperature and pressure are monitored simultaneously by computer, where a graphics display facilitates incremental increase in *T* and *P* until the desired run conditions are achieved. The miniclave is protected with a steel shielding assembly, made from approximately 35 cm diameter thick steel pipe, whose open ends allow 'directional failure predictability' and access for wiring and pipe connections. Where controlled cooling is not desired, quenching is achieved by disconnecting the power supply, giving cooling rates several times faster than a Tuttle bomb and approaching those available with a piston cylinder. Fast quenching is a successful result of the designed small thermal mass and water cooling.

Advantages and limitations. The main advantages of the miniclave are as follows: it is small and inexpensive, allowing several to be run side by side; it provides very good temperature and pressure control beyond standard Tuttle bombs in a *P*–*T* field of significant interest for magmatic experiments at crustal pressures up to 1200 °C at 4.0 kbar; it has a rapid quench rate that is several times faster than a Tuttle bomb. Some of these features can only be achieved by accepting certain limitations, the most obvious of which are the restriction to small sample diameters, and the absolute limits of *P* and *T*.

The miniclave is obviously attractive for limited budgets, and can be very effectively improved with the availability of a supervisory minicomputer. The miniclave system at Kingston is run with an IBM-PC compatible computer equipped with 15-bit analogue/digital convertors (CIL Electronics LTD, Worthing) and matching software from Norfolk Microsystems, details of which are available on request.

Applications

The miniclave has been used successfully to produce carbonate glasses, and, until recently, studies have been devoted to duplicating previous results and calibrating the apparatus. A series of new carbonate-glass experiments has started, with characterization of volatile species by infrared spectroscopy.

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