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A new type of high-temperature, high-pressure cell for spectroscopic studies of hydrous silicate melts

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Abstract

A novel type of high-temperature, high-pressure cell has been designed for near-infrared and optical spectroscopy of hydrous silicate melts at pressures up to 3 kbar and temperatures up to 800 °C. It consists of an externally heated cell with a disk-shaped sample chamber (4 mm in diameter and 0.2 mm in height) that is compressed between a tungsten carbide piston and a cylindrical sapphire window. A platinum ring surrounding the sample prevents loss of melt or water during the experiment.

The new spectroscopic cell was used for direct measurement of H_2O species in aluminosilicate melts by near-infrared spectroscopy. Other possible applications of the cell include the study of silicate melts doped with transition metal ions in the UV-VIS-NIR and the observation of the crystallization and dissolution of minerals in hydrous silicate melts under in situ conditions.

Introduction

The interaction of dissolved H_2O and silicate melts is of considerable interest for earth scientists because H_2O is the most important volatile component of natural magmatic systems. Our present understanding of the interaction of H_2O and the silicate network is based mainly on indirect methods, e.g., infrared spectroscopy of hydrous glasses at room temperature and 1 bar (e.g., Scholze 1959, 1960; Frantz and Kelen 1967; Bartholomew et al. 1980; Stolper 1982a, 1982b, 1989; Newman et al. 1986; Silver and Stolper 1989; Silver et al. 1990; Zhang et al. 1995) and interpretation of thermodynamic and kinetic properties of glasses and melts (e.g., Burnham 1975; Burnham and Davis 1971, 1974; Shaw 1974; Lapham et al. 1984; Zhang et al. 1991). The main problem in the investigation of silicate melts with high H_2O contents at high temperatures is outgassing of dissolved H_2O at 1 atm. To prevent loss of H_2O during the spectroscopic measurements the samples must remain pressurized. Also the measurements must be performed in the P-T range of H_2O undersaturation to avoid formation of fluid bubbles in the melt.

Numerous optical high-pressure and high-temperature cells were described by Sherman and Stadtmuller (1987). Diamond-anvil cells are used for high- and ultra-high-pressure investigations of fluids and solid materials (Piermarini and Block 1975). The advantage of the diamond-anvil cell is its small size, which allows the adjustments to be made on a microscope stage. Recently, Shen and Keppler (1995) applied such a device for near-infrared spectroscopic measurements of the incorporation of H_2O into a peraluminous melt up to 1000 °C and 10 kbar. However, a disadvantage of the diamond-anvil cell for measuring hydrous silicate melts is that a fluid serving as a pressure medium must surround the sample. Controlled variation of pressure during the experiment is difficult to achieve because the volume of the sample chamber is almost fixed by the gasket. Furthermore, interaction of the melt and the pressure-medium fluid, which may be water or an inert gas, can result in compositional changes of the melt and fluid during the experiment.

Takano and Wakatsuki (1991) developed a sapphire-anvil cell with a sample diameter of 2.5 mm. But it has not been demonstrated that this cell can be heated. Numerous optical high-pressure, high-temperature cells designed for the investigation of fluids are limited to maximum P-T conditions of 7 kbar and 625 °C (Franck and Roth 1967; Lindner 1970; Von Tapavicza et al. 1975; Le Noble and Schlott 1976; Heym 1979; Eckel et al. 1981; Buback 1977, 1981, 1991; Frantz et al. 1993). Again, the fluids to be measured are at the same time the pressure medium. Thus, these cells are also not suitable for high-P, high-T measurements of hydrous silicate melts. Therefore, we developed a new type of cell for in situ spectroscopic studies of hydrous melts. The new cell fulfills the following requirements: (1) For measuring the H_2O speciation in haplogranitic melts containing 1–6 wt% H_2O_{tot}, temperatures up to 800 °C and pressures up to 2000 bars are necessary (Holtz et al. 1995); (2) to obtain sufficient absorbances of the H_2O- and the OH-combination modes at 5230 and 4500 cm^{-1}, respectively, a sample thickness of 300 μm for a glass or melt with 1 wt% dissolved H_2O_{tot} is required; (3) the sample diameter should be 3–4 mm if conventional optical lenses are used for the near-infrared optics because the focus diameter is about 2 mm; and

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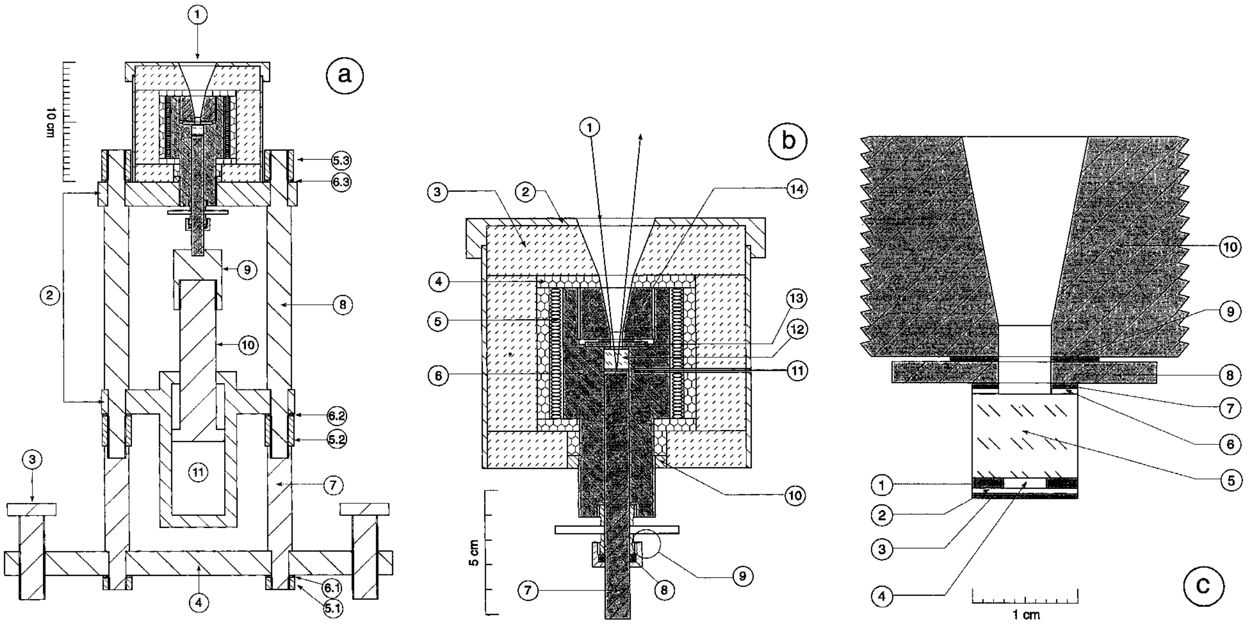

Figure 1. (**a**) Schematic drawing of the new cell assemblage: 1 = the cell, 2 = flanges, 3 = adjustable screw, 4 = base plate, 5.1–5.3 = nuts, 6.1–6.3 = washers, 7 and 8 = steel poles, 9 = coupling, 10 = oil hydraulic piston, and 11 = oil hydraulic cylinder. (**b**) Details of the cell: 1 = near-infrared beam, 2 = aluminum pot, 3 = isolation made of mullite wool, 4 = pyrophyllite box, 5 = heating coil, 6 = cell cylinder, 7 = hard metal piston, 8 = teflon seal, 9 = argon gas supply, 10 = stop ring, 11 = thermocouple, 12 = sapphire window, 13 = pressure ring, and 14 = sealing screw. (**c**) Details of the sample chamber: 1 = platinum ring, 2 = gold disk, 3 = platinum disk, 4 = sample, 5 = sapphire window, 6 = gold ring, 7 = platinum ring, 8 = pressure ring, 9 = platinum ring, and 10 = sealing screw.

(4) the material of the cell window must be temperature, pressure, and chemically resistant and transparent for near-infrared light.

The cell

The new cell consists of an externally heated superalloy cylinder. In this cylinder the disk-shaped sample, 4 mm in diameter and 0.2 mm in height, is squeezed between a sapphire window and a piston for pressurization. Figure 1 shows schematic drawings of the cell assemblage.

Cylinders made of sapphire and measuring 10 mm in diameter and 8 mm thick were used as spectroscopic windows. This material is transparent between 50000 and 2000 cm^{-1}. The cylindrical sapphire windows were cut from single crystals so that the crystallographic *c* axis is perpendicular to the polished window surfaces. Thus, maximum strength and optical isotropy is maintained. The rims of the sapphire window are beveled at an angle of 66° to prevent cracking during pressurization.

The cell cylinder, the sealing screw, and the pressure ring are made of a superalloy (Vakumelt 2.4888). A coupling made of D22S (1.6850) connects the piston of the oil hydraulic cylinder with the piston made of hard metal (tungsten carbide in cobalt matrix, 10 mm in diameter and 100 mm long). The piston is flushed with a flow of argon to prevent oxidation of the hard metal at temperatures above 300 °C. The flange of the oil hydraulic cylinder and the flange of the cell are connected by four steel poles. The whole assemblage is mounted on a massive base plate of aluminum, which is seated on three adjustable screws.

Oil pressure is increased with the use of an electrical piston pump that is connected to the oil hydraulic cylinder. A hydraulic hand pump positioned between the oil pump and the hydraulic cylinder is used for precise adjustment of the oil pressure, which is controlled by a strain-gauge manometer with a precision of ±1 bar. The hard metal piston increases the oil pressure generated by the pump by a factor of 42.3.

An annealed gold disk, 50 μm thick and 10 mm in diameter, placed between the sample and the hard metal piston is used as a mirror for beam reflection. A 50 μm thick platinum disk is placed between the hard metal piston and the gold disk to prevent the alloying of both. The disk-shaped sample (4 mm in diameter and ~180 μm thick) is seated in an annealed platinum ring (outer diameter of 10 mm and inner diameter of 4 mm) of the same thickness that is positioned between the sapphire window and the gold disk. The platinum ring surrounding the sample prevents loss of melt or water during the experiment. To minimize pressure spikes, an annealed gold ring and a platinum ring (outer diameter of 10 mm, inner diameter of 5 mm, and thickness of 50 μm) is sandwiched between the sapphire window and the pressure ring. The platinum ring prevents alloy formation between the gold ring and the pressure ring. A sealing screw holds the pressure ring in the cell cylinder. Finally, a 100 μm thick platinum ring (outer diameter of 14 mm and inner diameter of 5 mm) buffers small deviations in the position of the sapphire window and the pressure ring that may occur during pressurization. This cell is believed to be nearly free of frictional pressure loss.

The cell cylinder is heated externally by a heating coil contained in a pyrophyllite box. The heating coil is made of Kanthal wire, 7 m long and 0.7 mm in diameter. For thermal isolation, the resistance-furnace box is surrounded by a layer of 20 mm thick mullite wool that is fixed in an aluminum pot. The experimental temperature is measured with a calibrated Ni-CrNi-thermocouple (Heraeus Sensor) in a hole in the cell cylinder very close to the sample. A Eurotherm controller and programmer (type 818) provides the required temperature program.

NEAR-INFRARED OPTICS

Near-infrared spectra were measured with a Bruker IFS88 FTIR spectrometer with a spectral resolution of 4 cm^{-1} and using a tungsten lamp as the light source, a CaF_2 beam splitter, and an InSb detector.

The Bruker IFS88 spectrometer has an external port with an almost parallel measurement beam. The optical bench hanging in a robust metal frame consists of two near-infrared transparent Infrasil lenses (Steeg and Reuter), a pair of gold-coated mirrors with variable angle adjustment, an iris aperture, and an InSb detector. The position of each optical component can be shifted manually, and the whole optical bench is adjustable in three dimensions with fine thread screws. This suspension of the optical components allows an easy adjustment of the incident near-infrared beam to optimize the intensity of the light that passes the sample and reaches the detector (Fig. 2).

The modulated near-infrared beam is focused by a plain convex lens (focal length of 300 mm and diameter of 50 mm) and is reflected into the cell with the use of the first gold mirror. The beam passes the sapphire window and the sample and is reflected by the gold disk that is positioned between the sample and the hard metal piston. Thus, the beam passes the sample twice. Finally, the beam is reflected by the second gold mirror through a biconvex lens (focal length of 150 mm and diameter of 50 mm) onto the detector. The iris aperture between the biconvex lens and the detector fades, jamming scattering light. During the entire experiment the temperature-sensitive gold mirrors were cooled by a flow of air.

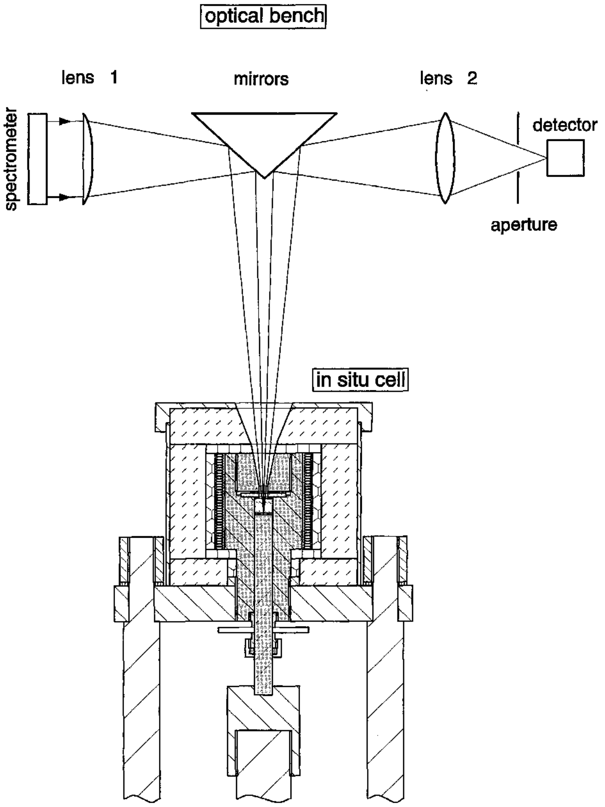

FIGURE 2. Scheme of the near-infrared optics.

IN SITU MEASUREMENTS AT HIGH TEMPERATURES AND PRESSURES

The hydrated glass disk was pressurized to the required pressure before heating the cell. The cell was then heated by ramps of 5 °C/min to 400 °C and of 2.5 °C/min to 800 °C dwelling time. These ramps were slow enough to let the whole pressure assemblage relax, so that there was minimum stress on the sapphire window. Higher heating ramps often resulted in cracking of the brittle sapphire window. A cooling rate of 5 °C/min was adjusted by the heating-cooling program. Below 200 °C the cooling rate decreased because of the exponentially decreasing heat flow. Constant oil pressure was maintained manually by using the hydraulic hand pump. Near-infrared spectra were measured during the heating and cooling cycle, accumulating 100 scans for each spectrum. This means that the near-infrared spectra were measured in a temperature interval of 2 °C for the heating ramp of 2.5 °C/min and of 4 °C for the heating and cooling ramp of 5 °C/min.

To test the influence of radiation emission from the cell at high temperatures, temperature measurements were performed at 800 °C with the tungsten lamp switched off. No radiation intensity was measured by the detector. This is attributed to the modulation of the beam by the Michelson interferometer (Keppler and Bagdassarov 1993). The intensity of the beam is a periodical function of time, and the spectra were calculated only with the modulated portion of the near-infrared signal. Unmodulated light like heat radiation does not affect the measurements.

Absorption spectra of the samples were calculated using reference spectra measured at the same temperatures. The reference spectra were collected at 1000 bars in 25–50 °C steps from 25 to 800 °C in the wavenumber region

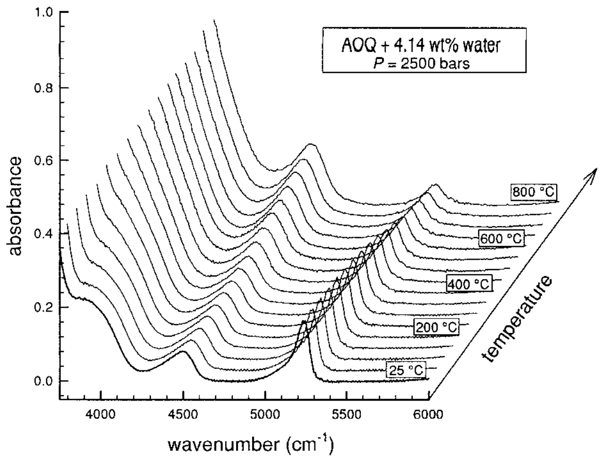

FIGURE 3. Near-infrared spectra of a haplogranitic sample (labeled AOQ) with normalized anhydrous composition of 4.65 wt% Na_2O, 5.68 wt% K_2O, 13.53 wt% Al_2O_3, and 76.14 wt% SiO_2, containing 4.14 wt% H_2O_{tot} from 800 to 25 °C at 2500 bars collected during the cooling period.

from 3800 to 8000 cm^{-1} using an Infrasil glass chip that is essentially free of H_2O. The ratios of reference spectra measured at different temperatures vary linearly with temperature. Hence, there is a parallel shift of the background of the absorption spectra with increasing temperature. Pressurization of the Infrasil glass up to 3 kbar had no influence on the reference spectra. Figure 3 shows near-infrared spectra from 800 to 25 °C at 2500 bars of a sample with haplogranitic composition ($Qz_{28}Ab_{38}Or_{34}$, in weight percent) containing 4.14 wt% H_2O_{tot}.

The room-temperature spectra measured by the high-*P*, high-*T* equipment gave slightly smaller intensities of the absorption bands than spectra of the same sample measured by standard techniques. We attribute this effect to a small portion of the beam that was reflected from parts of the sealing screw and reached the detector without passing through the sample. Raw spectra of the high-*P*, high-*T* equipment were corrected by

$$A_r = -\log\left[\frac{1}{F}(F - 1 + 10^{-A_m})\right] \qquad (1)$$

where A_r is the real absorbance of the sample and A_m is the absorbance measured at the detector. The portion *F* of the beam that passed through the sample was calculated from the height of the band at 5230 cm^{-1} measured by the high-*P*, high-*T* equipment (A_{m,H_2O}) and by standard techniques (A_{st,H_2O}):

$$F = \frac{10^{-A_{m,H_2O}} - 1}{10^{-A_{st,H_2O}} - 1}. \qquad (2)$$

For all experiments *F* was in the range of 0.90.

The thickness of a sample with 4.14 wt% H_2O_{tot} decreased during the heating period from 172 to 165 μm at 800 °C. This decrease is due to the viscous flow of the hydrous melt above the transformation temperature because the glass plate that was inserted at the beginning of the experiment is slightly smaller than the hole of the platinum ring. The sample was held for 60 min at 800 °C and 2500 bars, and no additional changes in the spectra were observed. Therefore, the spectra measured after mechanical relaxation and temperature equilibration and during the following cooling and heating periods were not affected by a change in thickness. More details about the evaluation of the spectra are given elsewhere (Nowak 1995; Nowak and Behrens 1995).

RELIABILITY OF TEMPERATURE AND PRESSURE DETERMINATION

Several temperature measurements at 800 °C yielded a slight deviation of 10 °C between the temperature at the thermocouple position of the cell and that at the outer surface of the sapphire window. Thus, at 800 °C the error in the temperature of the sample at thermally equilibrated conditions is believed to be less than ±10 °C.

Deformation of the sample beyond the glass transition clearly shows that the cell assemblage is flexible to pressure. The pressure of the oil reservoir increased 42.3 times by the ratio of the area of the hydraulic cylinder to that of the hard metal piston. This determines the maximum pressure on the sample. Minimum pressures can be estimated from H_2O solubility data for haplogranitic melts (Holtz et al. 1995). If the pressure is below the saturation pressure for a given H_2O content, bubbles are formed in the melt, H_2O is lost from the melt, or both, depending on the viscosity of the melt.

Careful decompression of a melt containing 4.14 wt% H_2O_{tot} at 800 °C and pressure of 3000 bars in steps of 2 bars of oil pressure leads to bubble formation in the melt if the maximum H_2O solubility is exceeded. The bubble formation was observed indirectly as a considerable shift of the background at 8000 cm^{-1} of the near-infrared spectra at approximately 500 bars. This shift is attributed to diffuse scattering of light. The scattering of light can be observed if the diameter of the bubbles is equal to or greater than the wavelength of the incident light. This means that the bubbles must be >1.25 μm to cause a shift of the background at 8000 cm^{-1}. Repressurization of the bubble-bearing melt from 500 to 1500 bars resulted in dissolution of the bubbles into the melt. When the bubbles dissolved in the melt, the background shifted back to the value before decompression. The sample containing 4.14 wt% H_2O was stored at 800 °C at a pressure of 1500 bars for 30 min without loss of H_2O or bubble formation. On the basis of H_2O solubility data (Holtz et al. 1995) the minimum pressure of the sample must have been above 1000 bars. At pressures below the saturation limit of the melt, H_2O can be lost from the melt if the viscosity is low enough. This was demonstrated by a decompression experiment with a melt containing 6.05 wt% H_2O_{tot}. The decompression from a pressure of 2500 to 1050 bars caused bubble formation and a loss of 0.9 wt% H_2O. After repressurization to 2000 bars, the bubbles dissolved and H_2O content remained constant at 5.15 wt%.

On the basis of these observations the maximum deviation in pressure is <500 bars. It must be noted that this technique is not very sensitive to pressure. Therefore, the use of more suitable pressure calibrants, e.g., quartz embedded in hydrous glass (α-β transition) (Shen et al. 1993) or ^{13}C-diamond (Frantz and Mysen 1996), is required to ascertain whether the reported pressures are the real pressures and what pressure uncertainties might actually be involved.

OTHER POSSIBLE APPLICATIONS FOR THE HIGH-*T*, HIGH-*P* CELL

The sapphire window is transparent over a wide frequency range. Thus, spectroscopic measurements on hydrous silicate melts can also be performed in the visible and ultraviolet regions. This makes it possible to study the incorporation of transition-metal ions into hydrous melts under in situ conditions. Another application might be in situ Raman spectroscopy of silicate melts. If the cell is combined with a microscope or a video system, direct observation of kinetic processes, e.g., crystallization or dissolution of minerals, might be possible. This can give new insights into the mechanisms of reactions involving melts.

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