Experimental determination of PVTX relations of fluids in the diamond-anvil cell

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Introduction

PVTX relations of geological fluids are of primary importance to many geological applications. However, accurate experiments performed above 6 kbar and 800°C are scarce, and therefore, uncertainties arise when different versions of equation of state (EOS) are used to extrapolate. During the past few years, we have developed a method to determine fluid PVTX relations at high pressures and temperatures using a gasketed diamond-anvil cell (Bassett *et al.*, 1993) and have studied the pure H_2O system as well as the NaCl-H_2O system up to 850°C and 12 kbar.

Experimental methods

Our method relies on one important observation of the behaviour of the sample chamber (formed by compressing a rhenium gasket with a drilled hole between two diamond anvils) in the diamond-anvil cells. The volume of the sample chamber does not change significantly during cooling from the highest temperature and does not change significantly during heating and cooling once the heating cycle has been repeated two or three times.

FIG. 1.

This was confirmed by the behaviour of the laser interference fringes and planimetric measurement in an air-filled sample chamber. Once the nearly isochoric behaviour of the sample chamber has been established, the PVTX properties of fluids can be determined by accurate measurements of the homogenization temperatures of the fluid phases, the α-β transition temperatures in a quartz platelet loaded in the sample chamber together with the fluid sample, and the melting temperature of ice polymorphs or dissolution temperature of salts (Shen *et al.*, 1992). All measured temperatures were corrected according to calibration based on the melting points of NaCl (800.75°C) and $NaNO_3$ (306.8°C) and triple points of water-ice I-vapor (0.01°C) and ice I-ice III-water(-21.98°C). We have also used detailed statistical analyses of the uncertainties in the temperatures arising from both measurement and correction procedures. The PVTX properties of a salt solution such as the NaCl-H_2O system can be calculated from these corrected temperatures as follows: the densities of the homogenized fluid can be calculated from the homogenization temperatures based on the saturation properties of fluids; the pressures at the α-β quartz transition can be calculated from the observed transition temperatures based on the published α-β quartz boundary (Mirwald and Massonne, 1980; Shen *et al.*, 1993); and the compositions of the homogenized fluids can be calculated from either the melting temperatures of ice or the dissolution temperatures of salt based on the solubility data.

Results

We have established the internal consistency of the EOS of H_2O formulated by Haar *et al.* (1984, NBS/NRC Steam Tables) and the α-β quartz transition (Mirwald and Massonne, 1980). Figure 1 depicts the H_2O isochores calculated from different versions of EOS for H_2O having the same density. Clearly, there is good agreement
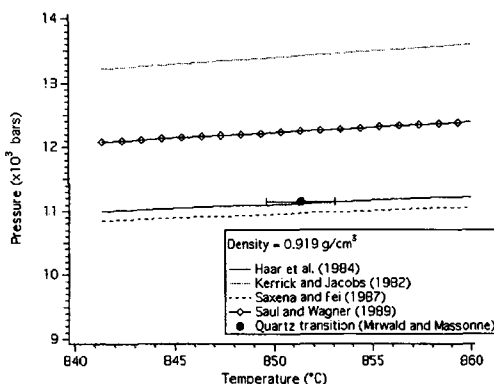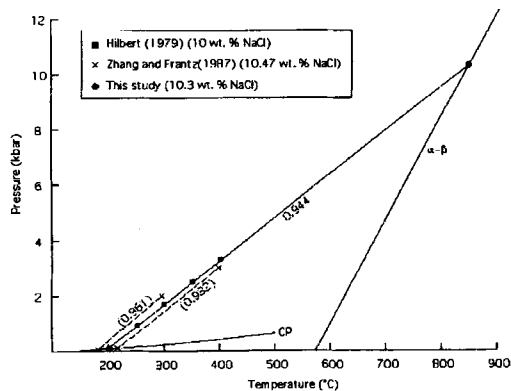
FIG. 2.

between our data and those of Haar *et al.* (1984). Figure 2 depicts our recent results on the PVTX relations in the NaCl–H_2O system. Isochores of 10 wt.% NaCl solutions are shown. The solid circles represent our data points and the solid squares are from Hilbert (1979). It is apparent that they are in excellent agreement. The crosses are data points from Zhang and Frantz (1987). The slopes of their isochores (dashed lines) are comparable to ours but slightly different. The number beside each isochore is the density calculated from homogenization temperatures using the density formulation in Zhang and Frantz (1987). This technique has provided an efficient way of determining the fluid PVTX relations and has extended current knowledge of such relations to higher pressures and temperatures.

Discussion

Dissolution of quartz and its effect on the PVTX relations are of concern. However, this uncertainty should be very small, because only a very small amount of SiO_2 is involved (molar H_2O/SiO_2 > 50), the effect on the molar volume of H_2O should be very small. Assuming 10 wt.% SiO_2 solubility in pure H_2O, the resulting maximum variation in

the H_2O molar volume is $\sim$ 1–3%. In addition, in practical geological applications such as the fluid-inclusion studies, dissolution of the host mineral (usually quartz) into the fluid is inevitable.

Another concern is the possible existence of the curvature of fluid isochores. At present, our method can construct the true isochore only at two P-T points. However, recent developments in pressure calibrants such as $PbTiO_3$ (Chou and Haselton, in press) and $BaTiO_3$ (Chou *et al.*, 1993) will provide additional intermediate P-T points to establish the curvature of the isochore.

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