Volume and ionic conductivity measurements of H_2O ice at high pressure and temperature

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We examined isothermal volume (V) compression of H_2O ice based on *in situ* x-ray diffraction measurements at 33-79 GPa and 873 K, and its ionic conductivity at 20-60 GPa up to 920 K using impedance spectroscopy (IS) technique. High pressure (P) and temperature (T) conditions were generated by using an externally-heated diamond anvil cell. The anomalous volume reduction likely due to the hydrogen bond symmetrization was observed at 50-53 GPa and 873 K, while the previous study at room temperature reported that the highly compressible phase associated with the symmetrization is present at 40-60 GPa. There is no volume discontinuity in the isothermal compression, which contadicts the proposed first order P-T boundary between ice VII and superionic ice [2, 3]. In addition, *in situ* IS measurements shows that the ionic conductivity of ice monotonically increases with increasing T, and exhibits superionic conduction (>10^{-1} S/cm) above 580-720 K at 20-60 GPa, which is the first experimental evidence of the superionic conduction in H_2O ice at high pressure. This suggests that superionic ice appears at sufficiently lower P-T than the proposed triple point.

Combining above results with the existing planetary isentropes [4], superionic H_2O ice is stable at P-T conditions corresponding to the interiors of Neptune and Uranus, the ice giants. The presence of superionic ice in these planets possibly accounts for the non-dipolar and non-axis symmetric structure of their magnetic fields.

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The system SiO_2-H_2O revisited: Equation of state to very high temperatures and pressures including critical behavior

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The system SiO_2-H_2O represents a simple model for metasomatism and hydrous melting in the lower crust and upper mantle. In this binary, the upper critical end point (UCEP), where complete miscibility between concentrated aqueous fluids and hydrous silicate melts occurs, is located at 1100 °C and 9.5 kbar [1], near the geothermal subduction gradient with important consequences for aqueous devolatilization *vs*. melt generation in the subducting slab. We have derived a new equation of state for aqueous silica, which combines intrinsic thermal properties of SiO_2 units with volumetric contributions resulting from solvent compression in the hydration sphere. The concentration scale is mole fraction, which enables the difference between standard states at infinite dilution and pure substance to be linked *via* excess energy of mixing represented by symmetric Margules term (W). In addition, the pressure-temperature locus of the UCEP provides two additional constraints on energy-composition relationships, thus reducing the effective number of independent parameters of the equation of state. The Gibbs energy of SiO_2 (aq) has the form: $\Delta G = a + bT + cT\ln T + dP + eT\ln\rho_w$, where ρ_w is the density of aqueous solvent at pressure and temperature of interest. The thermal part is assembled from constant enthalpy, entropy, and heat capacity, whereas the pressure term employs constant volume of the unhydrated species. Additional contribution arises from the pressure-volume work necessary to compress solvent molecules from bulk density to the density in hydration shell due to electrostriction, and it is related to solvent volumetric properties only [2]. The model was calibrated by 342 experimental quartz solubilities at 25-1100 °C and 0.001-20 kbar and ranging from 9 ppm to 70 wt.%, yielding $a = -963.5$ kJ mol^{-1}, $b = 844.3$ J K^{-1} mol^{-1}, $c = -124.1$ J K^{-1} mol^{-1}, $d = 2.26$ J bar^{-1} mol^{-1}, $e = -16.65$ J K^{-1} mol^{-1}, and $W = 29.1$ kJ mol^{-1}, with overall accuracy of 1.3 kJ mol^{-1}. In contrast to previous studies, our new model is capable of addressing SiO_2 behavior in dilute aqueous fluids and hydrous melts, including their supercritical mixtures.

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