

Characterization of the NaCl-H₂O System at High Pressure

M. Frank¹, C. Runge¹, S. Maglio¹, J. Olson, H. Scott², G. Shen³, V. Prakapenka³

¹Northern Illinois University, DeKalb, IL, U.S.A.

²Indiana University South Bend, South Bend, IN, U.S.A.

³University of Chicago, Chicago, IL, U.S.A.

Introduction

Recent studies have hypothesized that high-pressure H₂O polymorphs (figure 1), specifically Ice VI and Ice VII, make up a significant portion of the interiors of both Ganymede and Callisto. Several of Jupiter's satellites have been conjectured to contain subsurface salty H₂O waters; therefore, any potential "warm" ice phases in the interiors of these satellites could have interacted extensively with either the salty oceans or rocky interiors. Whereas numerous studies have been conducted previously to study the bonding structure and unit cell parameters of pure Ice VII; little data exist on the effects of salts on solid H₂O at high pressures. To obtain more realistic data for use in planetary physics, it is important to understand the influences of impurities on H₂O at high pressures. We have chosen the NaCl-H₂O system as an analogue for more complicated "dirty" ice systems. This study measured the unit cell volumes of "dirty" Ice VII formed from 5 and 10 wt. % NaCl-H₂O solutions, addresses volumetric effects of impurities on Ice VII, and quantifies the freezing point depression of Ice VII by 5 wt. % NaCl.

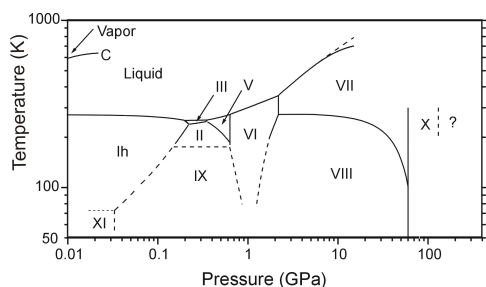


Figure 1. Phase relations in the H₂O system up to 100 GPa and 1000 Kelvin (modified from S. Gramsch). Experiments in this study were conducted in the NaCl-H₂O system rather than pure H₂O. Even though > 85 mole % H₂O, phase stability fields of Ice VI and Ice VII formed in "dirty" systems have been shown to vary slightly from those formed from pure H₂O.

Methods and Materials

This study measured the unit cell volumes of Ice VII formed from a 5 wt. % NaCl-H₂O solution up to 25 GPa and 800 K by using a Bassett style hydrothermal diamond anvil cell and synchrotron X-ray radiation. For simple compression experiments, we used symmetric diamond anvil cells with diamonds with 450 micrometer culets. The NaCl-H₂O solution and a pressure indicator

(gold; Anderson et al., 1989) were loaded into a sample chamber (100-150 micrometers) drilled in the Re-gasket material. Select experiments contained small grains of ruby so that pressures obtained by ruby fluorescence could be compared to those from the unit cell parameters of gold. For experiments at elevated temperatures, hydrothermal diamond anvil cells (HDAC) with 350 micrometer culets and two external heaters were utilized. Each HDAC was heated using a set of chromel wires wrapped around each diamond. Temperatures were monitored by placing a type-K thermocouple (Chromel-Alumel) directly against the surface of each diamond. Temperatures were kept within a precision of ± 3 K during data collection. The experiments were conducted at the GSECARS 13-BM-D beamline (Advanced Photon Source, Argonne National Laboratory), using monochromatic X-ray radiation and an online imaging system. The unit cells of Ice VII, NaCl, and gold were monitored during the experiment with gold being used as an internal pressure calibrant. Data were analyzed using the FIT2D software (Hammersley, 1997). CeO₂ was used to calibrate the sample to detector distance, coordinates of the directed beam on the detector, and the angle and tilt of the detector.

Results

The formation of Ice VII, at 298 Kelvin, from a dilute NaCl-H₂O solution has been shown to produce a single homogenous solid phase (Figure 2). The diffraction data indicate that Ice VII formed from a 5 wt. % NaCl-H₂O solution does not display diffraction lines for NaCl, however, NaCl is observed as an independent phase in experiments with an initial starting composition of 10 wt. % NaCl-H₂O (Figure 3). Additionally, as pressure is increased, NaCl diffraction lines become more pronounced in samples where the Ice VII formed from a 10 wt. % NaCl-H₂O solution.

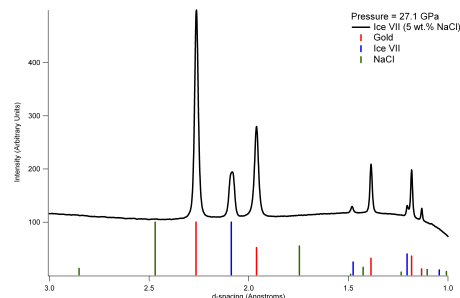


Figure 2. Representative diffraction pattern of Ice VII (formed from a 5 wt.% NaCl-H₂O solution) and gold at 298 K and 27.1 GPa. Diffraction lines representative of NaCl are not observed at any location within the sample chamber.

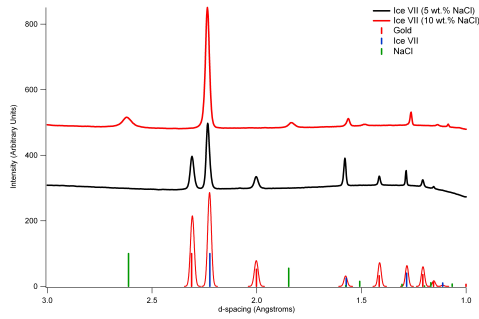


Figure 3. The black and red diffraction patterns are at 11.5 and 4.5 GPa, respectively. The patterns are stacked to illustrate the absence of NaCl in Ice VII formed from a 5 wt.% NaCl-H₂O solution.

Discussion

The {110}, {200}, and {310} diffraction lines of Ice VII were used to calculate unit cell volumes of Ice VII. The 300 K compression data were collected up to 32 GPa and fit to a third-order Birch-Murnaghan equation of state (Birch, 1978):

$$P \text{ (GPa)} = \frac{3}{2} K_{T0} \left[\left(\frac{V_0}{V} \right)^{\frac{7}{3}} - \left(\frac{V_0}{V} \right)^{\frac{5}{3}} \right] \times \left[1 - \frac{3}{4} (4 - K'_{T0}) \left(\left(\frac{V_0}{V} \right)^{\frac{2}{3}} - 1 \right) \right]$$

where K_{T0} , K'_{T0} and V_0 are the isothermal bulk modulus, its pressure derivative and the volume at zero pressure, respectively (figure 4).

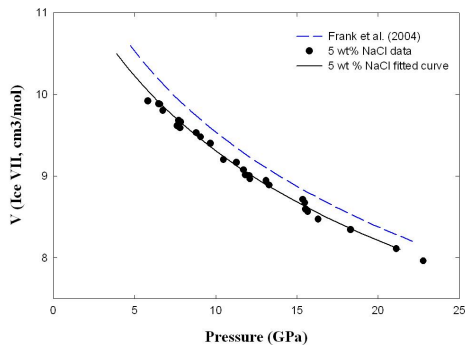


Figure 4. The PVT relations of Ice VII formed from a 5 wt.% NaCl solution and pure H₂O indicate that the "dirty" Ice VII has a greater molar volume by approximately 5 percent. This increase in molar density will change the calculated thickness of the ice layers (and proportion of ice to rock) in select planetary bodies.

The diffraction lines of Ice VII and NaCl, where applicable, were monitored as a function of pressure and temperature up to the melting temperature at any given pressure (figure 5). The methodology employed in this study was to use the disappearance of the diffraction pattern of Ice VII along with the appearance of diffuse

scattering to monitor the melting of Ice VII. The melting curve for Ice VII (formed from a 5 wt.% NaCl-H₂O solution) was defined in this study by the midpoint between Ice VII present and absent points in pressure-temperature space. These results, when compared to melting of "pure" Ice VII, suggest that the presence of NaCl depresses the melting curve by approximately 40 Kelvin at any given pressure.

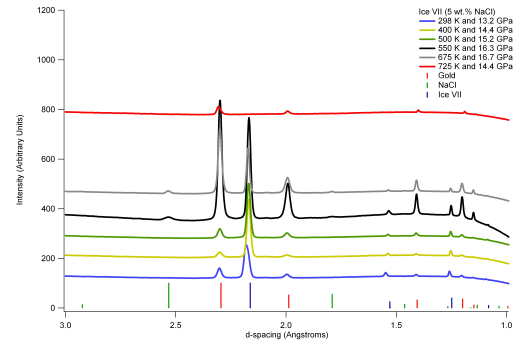


Figure 5. Diffraction data of NaCl, gold and Ice VII (formed from a 5 wt.% NaCl-H₂O solution) are presented here by d-spacing. These data are stacked as a function of temperature; and indicate that NaCl becomes a separate phase in this sample between 500 and 550 K. Further, melting is observed between 675 and 725 K with a noticeable shift in the gold diffraction lines at 725 K due to a pressure decrease associated with melting.

Conclusions

This study has shown that the solubility of NaCl in Ice VII is greater than 5 weight percent at 298 K. Ice VII formed from a 5 wt.% NaCl-H₂O solution has a molar density that is systematically higher at any given pressure relative to the molar density of Ice VII formed from pure H₂O. "Dirty" ice in the interior of an icy body will have a greater molar density than pure ice and effect stratification models. The melting curve of Ice VII (formed from a 5 wt.% NaCl-H₂O solution), when compared to the Datchi et al. (2000) study of pure H₂O systems, are consistent with a systematic depression of the melting curve of Ice VII by approximately 40 Kelvin. This depression increases the stability field of Ice VI (at low temperatures and pressures) and fluid H₂O (at elevated pressures). These data will allow for more precise and accurate density profile modeling of H₂O-rich bodies.

References

- Anderson et al. (1989), *J. Appl. Phys.*, 65, 1534-1543; Birch (1947), *Phys. Rev.*, 71, 809-824; Datchi et al. (2000), *Phy. Rev. B*, 61, 6535-6546; Frank et al. (2004), *Geochim. Cosmo. Acta*, 68, 2781-2790; Hammersley (1997), ESRF Internal Report

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