

INFLUENCE OF NaCl ON ICE VI AND ICE VII PHASE RELATIONS AND PROPERTIES: IMPLICATIONS FOR SOLAR SYSTEM ICES.

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Introduction: Ice VI and ice VII may be important in the interiors of Europa, Ganymede, Callisto and Titan. Oceans and interior pore waters in these bodies likely contain dissolved salts [1-4]; however, the influence of salts on the stability, composition and physical properties of ice VI and ice VII is poorly known. To address this, we investigated phase equilibria in the system H₂O-NaCl at 1 molal (5.5 wt%) NaCl in a diamond-anvil cell (DAC) to 150°C and 5 GPa.

Previous Work: Previous experimental studies of salt-H₂O systems at high pressure have focused chiefly on lower density H₂O ices (ice Ih to ice V) in the presence of MgSO₄ or NH₃ [e.g., 5-8]. The abundant terrestrial salt NaCl is probably strongly partitioned into planetary fluid reservoirs, and will therefore be an important constituent in the interiors of icy satellites. However, this salt has received little attention. Early work at room temperature [9] suggested that NaCl had a relatively minor effect on the formation of ice VI, but assumed that the ice phase contained no NaCl. Frank et al. [10] showed that at room temperature, ice VII could contain significant NaCl. However, the system H₂O-NaCl does not appear to have been studied at high temperature.

Methods: Experiments were conducted in a gas-membrane high-temperature diamond-anvil cell fitted with ultra-low-fluorescence diamonds. A 5.5 wt% NaCl solution was used in all experiments. The cell was loaded by placing a 93- μ m thick Pt-lined steel gasket with a 150- μ m-diameter hole on one of the diamond culets, adding three ruby spheres, and then dispensing a drop of salt solution into the hole with a syringe. The cell was closed immediately, ensuring no H₂O loss by evaporation. The DAC was heated externally; a thermocouple in the gas chamber was constantly monitored, and cell temperature (T) was calculated using a calibration curve.

Phase identifications were made by optical microscopy combined with Raman spectroscopy. Raman spectra were collected using an argon laser (200 mW), Jobin-Yvon/Horiba spectrometer with a Mitutoyo long-working-distance 50x objective, 1800 grating, and 100 μ m hole size. Pressure (P) in the cell was calculated using the ruby R_1 frequency shift [11]. Estimated pressure uncertainty is ± 0.05 GPa.

Experiments were conducted at 22-150°C and up to 5 GPa by allowing the cell to thermally equilibrate at a

given temperature and then varying pressure isothermally while observing phase changes. A key advantage of the gas-membrane DAC for this work is that it maintains nearly constant volume near phase transitions involving the liquid phase, which permits precise determination of liquidus and solidus pressures.

Results and Discussion: The liquidus curves of ice VI and ice VII in a 5.5 wt% NaCl solution were determined at stable and metastable conditions. Significant metastable persistence of each polymorph improved precision of the determinations. Melting was observed at ten discrete temperatures for each polymorph, from 22 to 80°C (ice VI) and from 35 to 150°C (ice VII). A fit to the ice VI data gave $P_m = 0.00415 \cdot \exp(0.0190T_m)$, where P_m is melting pressure (in GPa), T_m is melting temperature (in Kelvins) and $R = 0.999$; similar fitting of the ice VII data yielded $P_m = 0.234 \cdot \exp(0.00700T_m)$ ($R = 0.997$). Both curves are steeper than the respective NaCl-free melting curves [12,13], indicating that the freezing-point depression at this bulk composition increases with increasing pressure. At 4.4 GPa, ice VII crystallizes from a 5.5 wt% NaCl solution at 150°C, 90°C below the crystallization temperature of this ice from in the pure H₂O system at 240°C [13]. This effect is significantly greater than is observed for ice Ih at 1 bar.

The intersection of the two liquidus curves indicates that VI-VII-liquid triple point lies at 67 ± 2 °C and 2.57 ± 0.1 GPa at the studied bulk composition. The addition of 1 molal NaCl to H₂O thus results in a shift in the triple point of approximately -13 °C and $+0.5$ GPa relative to the pure H₂O system.

The 5.5 wt% NaCl bulk composition crystallizes completely to a single solid phase of NaCl-bearing ice VI or ice VII solid solution over the investigated temperature range. Raman scattering in the OH-stretching region of both ices shows elevated intensity of the higher frequency components relative to pure H₂O forms. At 22°C, complete crystallization to ice VI_{ss} (where the subscript 'ss' indicates solid solution) was observed at ~ 1.55 GPa, indicating that ice VI_{ss} coexists with liquid over a ~ 0.5 GPa interval at this T . As T increases, this P interval decreases significantly, such that at 150°C it is < 0.1 GPa.

It proved possible to grow large single crystals of ice VI_{ss} or ice VII_{ss} by slow compression of the cell from near-liquidus conditions to the solidus. Raman

spectra of the last-formed portions of these crystals (grown from NaCl-rich brine) indicated significantly greater scattering in the high-frequency portion of the OH-stretching region than in the cores (grown from ~5.5 wt% NaCl solution). These differences are consistent with zoning in the crystal. The zoning persists for hours to days at 22°C, indicating relatively slow Na⁺ and Cl⁻ diffusivity in the ice structures.

At any temperature, increasing P eventually leads to exsolution of a NaCl phase from ice VI_{ss} or ice VII_{ss}. At >30°C, cubic crystals that are not Raman active exsolve from the ice solid solutions. These crystals are interpreted to be halite. At 22 and 30°C, an unidentified Raman-active phase forms at 1.75±0.1 and 1.9±0.1 GPa, respectively, and persists to higher P . Raman spectra of the unknown phase yield peaks at positions expected for hydrohalite (NaCl·2H₂O). If the phase is hydrohalite, it is stable to higher P and T than previously inferred [9].

Implications: The large depression of the freezing point in a relatively dilute, 1 molal NaCl solution has important implications for the oceans and interiors of the icy satellites of Jupiter and Saturn. Stabilization of the liquid phase to lower T than would be predicted from low- P phase relations means that salt-bearing fluids remain stable to much greater depth expected. This would promote more extensive metamorphism of the silicate interiors due to interaction with mobile fluids. Such fluids would more efficiently strip salts from the silicates and transport them to fluid and ice reservoirs. If this behavior is also characteristic of the other ice polymorphs, it would suppress formation of ices at the bottoms of deep oceans in Titan and the Galilean satellites.

The observation that ice VI and VII form solid solutions with NaCl from 22 to 150°C is also important. The qualitative inference of low Na⁺ and Cl⁻ diffusivity suggests that compositional gradients could persist over at least modest time scales in these ices. Moreover, the presence of NaCl in ice VI and VII will likely reduce their viscosity and increase electrical conductivity.

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