Potassium Chloride-Bearing Ice VII and Ice Planet Dynamics

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ABSTRACT

Accurate modeling of planetary interiors requires that the pressure-volume-temperature (*PVT*) properties of phases present within the body be well understood. The high-pressure polymorphs of H₂O have been studied extensively due to the abundance of ice phases in icy moons and, likely, vast number of extra-solar planetary bodies, with only select studies evaluating impurity-laden ices. In this study, ice formed from a 1.6 mole percent KCl-bearing aqueous solution was studied up to 32.89±0.19 GPa and 625 K, and the incorporation of K⁺ and Cl⁻ ionic impurities into the ice VII structure was documented. The compression data at 295 K were fit with a third order Birch-Murnaghan equation of state and yielded a bulk modulus (K_{T0}), its pressure derivative (K'_{T0}), and zero pressure volume (V_0) of 24.7±0.9 GPa, 4.44±0.09, and 39.2±0.2 Å³, respectively. The impurity-laden ice was found to be 6-8% denser than ice VII formed from pure H₂O. Thermal expansion coefficients were also determined for several isothermal compression curves at elevated temperatures, and a *PVT* equation of state was obtained. The melting curve of ice VII with incorporated K⁺ and Cl⁻ was estimated by fitting experimental data up to 10.2±0.4 GPa, where melting occurred at 625 K, to the Simon-Glatzel equation. The melting curve of this impurity-laden ice is systematically depressed relative to that of pure H₂O by approximately 45 K and 80 K at 4 and 11 GPa, respectively. A portion of the K⁺ and Cl⁻ contained within the ice VII structure was observed to exsolve with increasing temperature. This suggests that an internal differentiating process could concentrate a K-rich phase deep within H₂O-rich planets, and we speculate that this could supply an additional source of heat through the radioactive decay of ⁴⁰K. Our data illustrate ice VII can incorporate significant

concentrations of K^+ and Cl^- and increasing the possibility of deep-sourced and solute-rich plumes in moderate to large sized H_2O -rich planetary bodies.

1. INTRODUCTION

The abundance of volatile elements in the universe resulted in a large number of ice-rich planetary bodies clustering in the outer portions of any given solar system due to the low temperatures required for the condensation of ices, such as H_2O , CO_2 , CO , etc (Anderson et al., 1996; Kivelson et al., 1996; Schubert et al., 1996; Anderson et al., 1997; Anderson et al., 1998; Khurana et al., 1998; McCord et al., 1998; Greeley et al., 2000; Anderson et al., 2001; McCord et al., 2001; McCord et al., 2002; Head et al., 2002; Butler et al., 2004; Kuskov and Kronrod, 2005; Gillon et al., 2007). H_2O is an important component in these domains with it dominating the outer layer of ice in many planetary bodies and taking on different structural configurations within those bodies with ice VI, VII and X being the relevant high-pressure polymorphs (e.g., Hemley et al., 1987; Pruzan et al., 1997; Fortes, A.D. and Choukroun, M., 2010; Men et al., 2014). The presence of active geysers or emanations of H_2O , salts, and other compounds on Europa (Roth et al., 2014), Callisto (Lebofsky, 1977), Ganymede (Saur et al., 2015), and Enceladus (Hansen et al., 2006; Waite et al., 2006; Hsu et al., 2015) suggest subsurface oceans rich in dissolved solutes exist below the outer ice layers (Kargel, 1991; Kargel et al., 1991; Khurana et al., 1998; Kivelson et al., 2000; Zimmer et al., 2000; Ruiz, 2001; Baland and Van Hooist, 2010; Fortes, 2012). The subsurface oceans on these moons are thought to exist between the surface ice, ice Ih, and a higher-pressure form of ice, likely ice V or VI, at depth. Although ice VII is not thought to exist within many of the moons of our solar

70 system, as it is only stable at pressures greater than ~2 GPa, the processes observed on
71 smaller planetary bodies, such as Enceladus and Ganymede, are also likely on larger
72 H₂O-rich planets which have maintained a greater proportion of accretionary heat. This
73 raises questions as to if the deep ices at the base of the subsurface oceans, ice VI in small
74 to moderate sized bodies and ice VII in moderate to large bodies, have formed in contact
75 with the same impurities observed at the surface through interactions with either the
76 subsurface ocean or the deeper rock layers (Hsu et al., 2015). These solutes are well
77 known to affect the density and freezing point of liquid H₂O, but their impacts on solid
78 H₂O-ice are not well constrained. Numerous studies have explored the pure H₂O-ice
79 system (Hemley et al., 1987; Wolanin et al., 1997; Loubeyre et al., 1999; Frank et al.,
80 2004, Fortes et al., 2011; Asahara et al., 2010; Ahart et al., 2011; Hirai et al., 2014), but
81 only a few studies have been conducted in binary H₂O-rich systems. Frank et al. (2006)
82 hypothesized that ice VII could hold ionic impurities and tested the hypothesis in the
83 NaCl-H₂O system. They noted that up to 2.4 mole percent NaCl could be incorporated
84 into ice VII as Na⁺ and Cl⁻ which decreased the unit cell volume and increased the
85 density of the ice relative to pure ice VII. Subsequently, numerous studies have verified
86 that impurities, such as NaCl (Frank et al., 2008; Frank et al., 2012; Journaux et al.,
87 2013), LiCl (Klotz et al., 2009), and CH₃OH (Frank et al., 2012) could be incorporated
88 into ice VII. Ice VII formed in the NaCl-H₂O system has been shown to be denser than
89 pure ice and has also been noted to lower the melting curve relative to pure ice (Frank et
90 al., 2008; Journaux et al., 2013). This study explored ice VII formed in the KCl-H₂O
91 system to constrain the phase stability, *PVT* equation of state, melting curve, and
92 potential heat flow from the ice up to 32.9 GPa at 300 K and 650 K at 10.6 GPa. The

incorporation of KCl into ice VII would also add ^{40}K , a long lived radioactive isotope of potassium, and produce radiogenic heat from within ice-rich planets. The implications for potential planetary dynamics are profound as the inclusion of K^+ and Cl^- into ice VII could help to drive exchange between deep ice layers, subsurface oceans, and near-surface ice layers and, perhaps, the tenuous atmosphere of these planetary bodies.

2. EXPERIMENTAL AND ANALYTICAL METHODS

2.1. Experimental Methods

Ice samples containing K^+ and Cl^- were produced by compressing KCl-H₂O solutions in a diamond anvil cell (DAC). Aqueous solutions containing KCl were prepared by dissolving KCl (assay, anhydrous basis $\geq 99.0\%$) in distilled and deionized H₂O. All solutions contained 1.60 mole percent KCl, and this concentration was chosen because it fell below the estimated maximum solubility of NaCl in ice VII of approximately 2.4 mole percent (Frank et al., 2006), matched the mole percent of NaCl used in the high-temperature study of ice VII by Frank et al. (2008) and allowed for a direct comparison of the ice VII melting curve and thermal expansion.

Room-temperature compression experiments were conducted in symmetric diamond anvil cells (DACs), with the diamond anvils having 350 μm culets. Inconel 625 gaskets were compressed between the anvils to generate a pre-indented area, and sample chambers of approximately 150 μm in diameter were drilled in the center of the indentation using an electric discharge machine (EDM). Three to four gold flakes (purity $>99.95\%$) between 5-10 μm in diameter, to be used as a pressure indicator, were placed in the sample chamber. A drop of the KCl-H₂O solution was added to the sample

chamber and immediately sealed by compressing the anvils together to generate pressures greater than 1 GPa. The samples were compressed at increments of approximately 0.5 GPa up to approximately 13 GPa and at increased increments up to 32.89 ± 0.19 GPa.

High-temperature and high-pressure runs were conducted by using an externally heated Hydrothermal Diamond Anvil Cell (HDAC; Bassett et al., 1993). The diamond anvils had 350 μm culets and were mounted on tungsten carbide seats wrapped with chromel wire. The gasket material was Inconel 625 for runs with target pressures below 6 GPa and rhenium for experiments at higher pressures. Gaskets were pre-indented to a thickness of 30-45 μm and sample chambers were compressed and loaded as for the room-temperature experiments described above.

For each heating step, samples were first compressed to a target pressure while at room temperature. High-temperatures were reached by passing current through the chromel wires wrapped around the tungsten carbide seats of each diamond. The HDAC is designed with an external casing around the cell so that a reducing atmosphere of argon-hydrogen (1% hydrogen) would prevent oxidation of the diamonds and heaters during high-temperature operation. Temperatures were monitored with type-K thermocouples placed directly against the surface of each diamond and were kept within 2 K of the set temperature during data collection with an overall uncertainty of less than 5 K. Data were collected at 50 degree increments at low temperatures and smaller increments near the expected melting point for a given pressure. The actual pressure upon reaching a desired temperature was determined from *in situ* X-ray diffraction of the gold flakes, as described below.

2.2. Analytical Method

Experiments were conducted at the GSECARS 13-BM-D beamline of the Advanced Photon Source, Argonne National Laboratory. X-ray radiation with a wavelength of 0.3344 Å was focused on the sample for *in situ* powder diffraction analysis. The X-ray beam was 14 and 7 µm in the horizontal and vertical directions, respectively, and was scanned across the sample chamber to search for all phases present in the chamber and to minimize the effects of ice-grain coarsening. An angle dispersive X-ray diffraction technique with a MAR345 online imaging system was used to maximize accuracy and precision. The sample-to-detector distance, coordinates of the directed beam on the detector, and the angle and tilt of the detector were calibrated with CeO₂ positioned in the same location as the DAC samples. Data were analyzed by using the FIT2D software package (Hammersley, 1997).

X-ray diffraction lines of the ice sample and pressure calibrant (gold) were obtained as a function of temperature as measured by the thermocouples and with pressure calculated from gold diffraction by using its *PVT* equation of state. The Anderson et al. (1989) model was used to determine pressure rather than newer models (e.g., Fei et al., 2007) to maintain an internal consistency with earlier studies (Frank et al., 2006; Frank et al., 2008). Exposure times of 5 minutes were used for most runs and multiple replicate patterns were taken with increasing time to demonstrate that a steady state had been reached. Variations in the gold unit-cell volume calculated from the (111), (200), (220), (311), and (222) diffraction lines were used to assess deviatoric stresses in the non-hydrostatic DAC (Meng et al., 1993). The uncertainty in the unit cell parameter for gold, and thus the calculated pressure, was determined by taking the 2 σ standard deviation from the mean of the lattice parameters for gold determined from each of the

five diffraction lines as the minimum uncertainty. This uncertainty was propagated through the pressure calculation to provide a minimum pressure uncertainty as well. Each of the four diffraction lines for ice VII was used to calculate a unit cell parameter and a volume at a given pressure and temperature. The uncertainty in the calculated values is the 2σ standard deviation from the mean (table 1). Diffraction patterns were monitored for the presence of crystalline KCl - sylvite (Campbell and Heinz, 1991; Mashimo et al., 2002). There was little overlap of the KCl and ice VII diffraction lines as at least two independent lines for KCl and four for ice VII could be observed over the entire range of temperatures and pressures studied.

Diffraction patterns were stacked as a function of pressure and temperature so that phase changes and melting could be easily discerned. Melting was noted upon the disappearance of ice VII diffraction lines and the presence of diffuse scattering while at elevated pressures. Further, after the confirmation of melting, the samples were cooled until diffraction lines indicative of ice VII reappeared. Large ice VII grains sometimes formed during cooling after the melting point had been reached and were difficult to observe with the powder diffraction method. The stage was rotated to help detect the grains in these cases with a success rate of approximately 50%. The midpoint in pressure and temperature space between ice present and ice absent points was taken to be the melting point for ice VII.

3. RESULTS

3.1. X-ray diffraction of KCl-bearing Ice VII at 295 K

X-ray diffraction patterns of ice VII formed from an aqueous solution with 1.60 mole percent K^+ and Cl^- were obtained at room temperature, 295 K, from 2.49 ± 0.04 to 32.89 ± 0.19 GPa (table 1). The (110), (200) and (211) diffraction lines for ice VII were observed in the majority of the patterns and were used to calculate a unit cell parameter. Gold diffraction lines could be ascribed to (111), (200), (220), (311), and (222) and were present in all patterns (figure 1). Variations in the calculated unit cell parameter for gold from each diffraction line were small and suggested minimal stress in the sample chamber. Diffraction lines indicative of a solid KCl phase were not observed in any diffraction pattern at 295 K; notably, the X-ray beam was scanned across the majority of the sample chamber to ensure that all phases present were documented. No visual evidence or X-ray diffraction data indicated any phase other than ice VII was present in the sample chamber at 295 K. These data suggest that K^+ and Cl^- were incorporated into the ice VII structure in a manner similar to that of Na^+ and Cl^- (Frank et al., 2006; 2008; 2012; Journaux et al., 2013) and Li^+ and Cl^- (Klotz et al., 2009).

Ice samples were compressed from 2.49 ± 0.04 to 32.89 ± 0.19 at 295 K (figure 2). The ice VII diffraction lines were monitored for phase changes throughout the compression sequence and no changes were observed as ice VII remained in a body-centered cubic structure. Although others have noted peak splitting and suggested that ice VII becomes tetragonal at pressures above approximately 11-14 GPa (Goncharov et al., 1999; Somayazulu et al., 2008; Hirai et al., 2014), no peak splitting was observed over the entire range of pressure-temperature conditions studied and, thus, ice VII was fit as a cubic phase as has been done in the majority of studies (e.g., Hemley et al., 1987; Fei

et al., 1993; Frank et al., 2004; Frank et al., 2012; Bezacier et al., 2014). The compression data at 295 K were fit to a third-order Birch-Murnaghan equation of state (EoS):

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

where K_{T0} , K'_{T0} and V_0 are the isothermal bulk modulus, its pressure derivative and the volume at zero pressure, respectively (Birch, 1978; table 2). K_{T0} , K'_{T0} and V_0 were found to be 24.7 ± 0.9 GPa, 4.44 ± 0.09 , and $39.2 \pm 0.2 \text{ \AA}^3$, respectively. The data indicate that ice VII formed from a 1.60 mole percent KCl aqueous solution has a unit cell volume which is depressed systematically relative to ice VII formed from H_2O , but roughly equivalent to ice formed from a 1.6 mole percent NaCl aqueous solution. Further, the compression data and fit parameters are approximately the same as those noted by Frank et al. (2006) for ice VII doped with the same molar concentration of Na^+ and Cl^- (table 2).

3.2. X-ray diffraction of KCl-bearing Ice VII at High-temperatures

High-temperature X-ray diffraction data were collected up to 625 K and 12.24 ± 0.12 GPa (table 1). These data were monitored for d-spacing values, phase transformations, and melting at increments of 50 or 25 K, depending on proximity to the expected melting point (figure 3). The observed diffraction lines were used to calculate unit cell parameters for gold (pressure indicator), ice VII, and KCl (if present). Ice VII was determined to be the only H_2O -rich phase over the entire pressure-temperature range investigated. The lattice parameters and unit cell volume were calculated assuming a body-centered cubic structure. Calculated volumes of ice VII at elevated pressure and temperature were used to determine thermal expansion by using the volume coefficient of thermal expansion, α (P, T), as defined by:

$$\alpha(P, T) = \alpha_0(T) \left[1 + \left(\frac{K'_{T0}}{K_{T0}} \times P \right)^{-n} \right] \quad (2).$$

The $\alpha_0(T)$ term is the thermal expansion coefficient at zero pressure and can be expressed as:

$$\alpha_0 = a_0 + a_1 T \quad (3)$$

where the empirical coefficients a_0 and a_1 were determined to be -2.93×10^{-4} and 1.27×10^{-6} /K, respectively. The pressure effect on the measured volume, η , was calculated to be 0.77. The *Pressure-Volume-Temperature* equation of state model developed here for KCl-enriched ice VII matched closely the data from the experiments (figure 4) and is compared to those for ice VII formed from pure H₂O systems (e.g., Fei et al., 1993; Frank et al., 2004) and the NaCl-H₂O system (Frank et al., 2008) in table 3.

3.3. Melting Curve of KCl-bearing Ice VII

The absence of ice VII diffraction lines and the presence of diffuse scattering upon increasing temperature or decreasing pressure at a given temperature were assumed to be the result of ice VII melting. The midpoint between ice-present and ice-absent pressure-temperature data were defined as the melting point with the uncertainty on the midpoint being half the difference in pressure and temperature space between the adjacent data (table 4; figure 5). The estimated melting-point data were fit with a Simon-Glatzel equation (Simon and Glatzel, 1929):

$$P = \left[P_c \times \left\{ \left(\frac{T}{T_t} \right)^c - 1 \right\} \right] - P_t \quad (4)$$

where P , P_t , P_c , T , T_t , and c are the pressure along the melting curve, pressure at the ice VII-ice VI-fluid triple point, the pressure best-fit parameter, the temperature along the

melting point, temperature at the triple point, and another best-fit parameter, respectively (table 4). The P_t and P_c values used in this study were derived from the melting point data presented here rather than the values established for pure ice VII. The calculated melting curve closely matches the experimental data that were previously determined for ice VII formed from a 1.6 mole percent NaCl-H₂O aqueous solution (Frank et al., 2008), except at pressures less than 3 GPa and greater than 12 GPa. The melting point of ice VII formed from a 1.60 mole percent KCl-H₂O solution is systematically depressed relative to pure ice VII (Lin et al., 2004; Datchi et al., 2000) at all pressures; the observed depression is approximately 45 K and 80 K at 4 and 11 GPa, respectively.

4. DISCUSSION

4.1. Pressure-Volume-Temperature Equation of State

The volume of ice VII formed from a 1.60 mole percent KCl-H₂O solution was monitored up to 32.9 GPa at 295 K. The diffraction patterns collected at 295 K showed no evidence of a solid KCl phase, which is consistent with previous work and suggests that the ice VII structure can accommodate significant ionic impurities (Frank et al., 2006; Frank et al., 2012; Klotz et al., 2009). Equation of state data from this and earlier studies were used to compare modelled P - V curves for pure ice VII (Hemley et al., 1987; Fei et al., 1993; Frank et al., 2012; Bezacier et al., 2014), ice VII with impurities of Na⁺ and Cl⁻ (Frank et al., 2006; Frank et al., 2012) and now ice VII with impurities of K⁺ and Cl⁻. The volume of ice VII with included K⁺ and Cl⁻ as a function of pressure at 295 K is consistent with ice formed with Na⁺ and Cl⁻, but it is systematically less than that of pure ice VII (figure 2). This suggests that the difference in ionic radii of Na⁺ and K⁺ were less

important than the size of Cl^- in controlling the volumetric properties of solute-bearing ice VII.

The K_{T0} and K'_{T0} values for ice VII with included K^+ and Cl^- are broadly consistent with values determined by previous workers in both pure and impurity-rich system (table 2 for studies that reported a 3rd order Birch-Murnaghan equation of state). The data support the hypothesis of Frank et al. (2006) who suggested that ionic impurities will decrease the volume of ice VII while molecular impurities cause an increase in volume (Frank et al., 2012).

Experiments were conducted at elevated temperatures to measure the thermal expansion of the ice samples as well as to determine the melting curve. Samples were heated initially at increments of 50 K and smaller increments near the estimated melting curve (figure 5). Although efforts were made to heat the sample isobarically, there was often a change in pressure during heating, thus, great care was taken in measuring the diffraction patterns with increasing temperature to constrain pressure variations (figure 3). Two diffraction lines indicative of crystalline KCl were observed to form during the heating cycle in all experimental runs (figure 3). This newly observed KCl is thought to form as a result of exsolution of the K^+ and Cl^- that was contained within the ice VII initially; a similar phenomenon was observed in the $\text{NaCl-H}_2\text{O}$ system (Frank et al., 2008). Frank et al. (2008) hypothesized that such exsolution could be driven by an entropic effect, as increasing temperature would likely decrease the ordering within impurity-laden ice, and thus exsolution to form a separate, but pure, ionic salt phase may be favored thermodynamically.

The thermal expansion coefficient data are broadly consistent with previous studies on ice VII (Fei et al., 1993, Frank et al., 2004, Frank et al., 2008; and Bezacier et al., 2014) suggesting that an increase in temperature has a similar effect on the volume of both pure and impurity laden ice VII (table 3). The minimal variation in the thermal expansion suggests that the exsolution of KCl was minor at elevated temperatures as it did not substantially impact the observed volume, although it is difficult to estimate the actual amount of exsolved KCl.

4.2. Melting Curve of Ice VII formed from a KCl-H₂O aqueous solution

The melting of ice VII with incorporated K⁺ and Cl⁻ was determined up to 625 K and 10.6 GPa and was fit by using a Simon-Glatzel equation. Melting of the impurity-laden ice occurred at lower temperatures (45 K and 80 K at 4 and 11 GPa, respectively) than pure ice VII (e.g., Lin et al., 2004; Datchi et al., 2000). The depression of the melting curve at any given pressure is due to either the presence of the included K⁺ and Cl⁻ or the solid KCl that exsolved from the KCl-doped ice (figure 5). Frank et al. (2008) documented the melting curve of ice VII formed from a 1.6 mole percent NaCl-H₂O aqueous solution. Their melting curve closely matches that observed in this study with a noted deviation at 2.2-3.5 GPa where they had no data and used the triple point of pure ice VII, ice VI and fluid. The data presented here indicate that the melting curve is depressed at these pressures as well which will increase the fluid stability field in pressure-temperature space. This has also been documented by Journaux et al. (2013) for the NaCl-H₂O system. These data, when consider in totality, indicate that ionic

impurities, such as Na^+ , K^+ , and Cl^- , can be incorporated into ice VII and will lower the melting curve substantially.

5. IMPLICATIONS

The formation of ice VII from an ionic aqueous solution results in an impurity-laden ice VII phase, and such ionic impurities have been shown to decrease the volume of ice VII at any given pressures (Frank et al., 2006, Frank et al., 2008, Frank et al., 2012; this study). The increase in atomic mass within the unit cell, along with the reduction in unit cell volume, results in a density increase for the KCl-rich ice by approximately 8% and 6% at 3 and 30 GPa, respectively, relative to pure ice VII (figure 6). The calculated density of pure ice from Bezacier et al. (2014), Frank et al. (2012), Frank et al., (2004), Fei et al. (1993) was found to be within 1-2% of that of Hemley et al. (1987), indicating that while there is variability between every study, the density difference for ice in the KCl-H₂O system was much greater than would be expected from only experimental uncertainty.

The potassium included within the ice will also provide a source of radiogenic heat as the decay of ⁴⁰K contributes 2.7 $\mu\text{cal/g}\cdot\text{year}$ for each wt.% of K (Birch, 1951). The results presented here suggest up to at least 3.33 wt.% can be incorporated into the structure of ice VII which can provide a notable source of heat. Thus, the ice VII layers of large, extra-solar H₂O-rich planetary bodies may also be a source of radiogenic heat.

Ice VII is stable at pressures greater than ~2 GPa and is not likely a major phase within the Galilean satellites, with the possible exception of Callisto, however, the surface features observed on those moons and the deeper ice-fluid interactions that

produce those features indicate H₂O-rich planetary bodies that have internal heat sources can be dynamic and may have convective deep ice layers. These data also suggest that ionic impurities in ice VII will increase the vigor of convective motions through ice VII-bearing mantles by increasing the density contrast between pure and impurity laden ice and also by promoting internal melting of ice. The hypothetical extra-solar planet depicted in figure 7 has a geothermal gradient that crosses from low-pressure ice Ih through the fluid phase field and directly into the ice VII stability field. This scenario allows for impurity-laden ice VII to form directly from a fluid which would subduct or sink below pure ice due to its greater density. This hypothetical process could bring impurity-laden ice deep into the planet where temperatures and pressures are elevated. Although the rheology of the solute-bearing ice is not well constrained, ice VI is thought to deform through dislocation creep (Durham et al., 1996), and it seems likely that ice VII may deform similarly. The addition of impurities, and the presence of solid KCl, which can also deform through dislocation and point defects (Kobayashi et al., 1995; Shuldiner and Zakrevskii, 2002) at elevated temperatures should increase the deformation and flow within such ice layers. The greater ductility and lower melting point of KCl-bearing ice VII, relative to pure ice VII, could produce plumes of fluid that rise towards the surface of the planet. The ice-fluid convection could also recycle materials from deep within the body and provide deep-sourced solutes and heat to the subsurface ocean. A large density difference between the rising plume and surrounding material could allow for the plume to broach the deeper ice layers and initiate currents in the subsurface oceans that contribute to surficial geyser-like activity. Geysers have been observed on many H₂O-rich moons (e.g., Lebofsky, 1977; McCord et al., 2001; McCord et al., 2002; Baland and

Van Hooist, 2010; Roth et al., 2014; Saur et al., 2015) and have been linked to ice “overturn” on Enceladus, Ganymede and other H₂O-rich moons (McKinnon, 1999; O’Neill and Nimmo, 2010) and could possibly lead to surface flooding as observed on Ganymede (Schenk et al., 2001). Therefore, the presence of solutes within ice VII increases the density of the ice, lowers the melting curve relative to pure ice VII, increases the possibility of ice convection, and makes plumes of solute-rich fluids possible.

6. CONCLUSIONS

The phase relations and volumetric properties of high-pressure phases of H₂O are important in planetary physics as a large number of planets and moons exist at great enough distances from stars to have formed at temperatures below ice condensation temperatures. This study examined ice VII formed in the KCl-H₂O system to ascertain if K⁺ and Cl⁻ could be included into the structure of ice VII and to constrain the volumetric properties and behavior of this impurity-laden ice. 1.6 mole percent of K⁺ and Cl⁻ were incorporated into the structure of ice VII which: 1) increased the density relative to pure ice VII by 6-8% (compared to the model from Hemley et al., 1987); 2) induced exsolution of a KCl solid phase from the impurity-laden ice VII with increasing temperature; 3) lowered the melting curve by up to 80 K at 12 GPa relative to pure ice VII; 4) increased the likelihood that the ice layer produced heat through the decay of ⁴⁰K; 5) provides a possible mechanism for ice convection driven by subduction-like processes and deep ice plume generation, and 7) a source of deep material for subsurface oceans and their surface manifestations.

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FIGURE CAPTIONS

Figure 1. Diffraction pattern of gold, the pressure indicator, and ice VII formed from a 1.60 mole percent KCl-H₂O aqueous solution at 295 K and 5.41 ± 0.29 GPa. The Miller indices (hkl) of diffraction peaks for gold and ice VII are in gray and black, respectively. No peaks indicative of a solid KCl phase were observed in any diffraction pattern at 295 K.

Figure 2. The pressure-volume relationship of ice VII formed from a 1.60 mole percent KCl-H₂O aqueous solution at 295 K. The data were fit with a 3rd order Birch-Murnaghan equation of state and compared to previous data for pure ice VII (Hemley et al., 1987).

Figure 3. Diffraction patterns showing peaks for gold (gray labels) and ice VII (bolded, black labels) are stacked in order of increasing temperature. Diffraction lines indicative of the B2 phase of KCl (black labels) are first observed at temperatures of 400 K and increase in intensity with increasing pressure. These KCl B2 peaks disappear entirely at 475 K and 4.34 GPa as the ice began to melt and, presumably, the KCl dissolved into the high-temperature fluid H₂O. The ice peaks at these conditions sharpen considerably and the ice melts completely during the exposure as a subsequent diffraction pattern has no discernable ice peaks. These patterns suggest melting occurred between 450 K (4.21 GPa) and 475 K (4.34 GPa); hence, the melting point was estimated as the midpoint of 463 ± 0.12 K and 4.28 ± 0.07 GPa.

Figure 4. The volume of ice as a function of pressure at high-temperatures is plotted relative to the calculated volume at the same pressure and 295 K. The isotherms were calculated using procedures outlined in the text. Whereas all high-temperature data were used to calculate a *PVT* equation of state, for the sake of clarity, only data collected at increments of 50 K are displayed in the figure.

Figure 5. The melting curve of ice VII formed from a 1.60 mole percent KCl-H₂O aqueous solution is plotted as a function of pressure. The ice VII, ice VII + KCl, and fluid phase fields represent the phase(s) observed by using *in situ* X-ray diffraction at any given pressure and temperature. Melting curves for pure ice VII (Lin et al., 2004) and ice VII formed from a 1.6 mole percent NaCl-H₂O solution (Frank et al., 2008) are presented for comparison.

Figure 6. The density of ice VII formed from pure H₂O (Hemley et al., 1987; Frank et al., 2012) is compared to ice VII formed from 1.60 mole percent aqueous solutions of KCl-H₂O (this study) and NaCl-H₂O (Frank et al., 2012) at 295 K and as a function of pressure. Ice VII with K⁺ and Cl⁻ ionic impurities was found to be approximately 7% and 5% denser than pure ice VII (Hemley et al., 1987) at 2 and 40 GPa, respectively.

Figure 7 a.) A schematic diagram of a hypothetical extra-solar H₂O-rich planet. b.) The formation of ice VII from a solute-rich fluid will produce a denser phase of ice that may sink below the less dense pure ice VII. As the impurity-laden ice moves to deeper portions of the planet, a portion of the K⁺ and Cl⁻ will exsolve forming solid KCl. The

666 impurities also depress the melting curve of ice VII and would result in the production of
667 a KCl-bearing H₂O-rich fluid that could then rise back to the subsurface ocean. c.) The
668 proposed pressure-temperature path for this hypothetical extra-solar planet starts in the
669 ice Ih phase field before passing through the fluid H₂O field and crossing into the
670 stability field of ice VII (diagram modified from one courtesy of Stephen A. Gramsch,
671 Carnegie Institution of Washington).
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674 Figure 1

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676 Figure 2

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680 Figure 4

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682 Figure 5

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684 Figure 6

Figure 7

Temperature (K)	Pressure (GPa)	Volume ($\text{\AA}^3$)	Temperature (K)	Pressure (GPa)	Volume ($\text{\AA}^3$)	Notes
295	2.49±0.04	36.03±0.08	350	1.91±0.07		Fluid
295	3.97±0.34	34.62±0.06	350	5.06±0.05	33.89±0.04	
295	4.25±0.22	34.35±0.05	400	4.56±0.19	34.53±0.03	KCl
295	4.54±0.19	34.19±0.02	450	4.21±0.07	35.10±0.02	KCl
295	4.70±0.13	34.09±0.01	475	4.34±0.13	35.11±0.04	Melting
295	5.05±0.19	33.82±0.01	500	3.66±0.05	NA	Fluid
295	5.29±0.15	33.66±0.05	350	5.96±0.42	33.21±0.03	
295	5.41±0.29	33.57±0.03	400	6.05±0.21	33.34±0.01	
295	5.50±0.20	33.46±0.01	450	6.69±0.09	33.17±0.01	KCl
295	5.84±0.14	33.20±0.01	500	6.73±0.29	33.49±0.01	KCl
295	6.17±0.12	32.95±0.12	550	6.99±0.33	33.54±0.06	KCl
295	6.57±0.38	32.73±0.09	550	6.37±0.33	NA	Fluid
295	6.97±0.15	32.62±0.05	350	6.10±0.17	33.15±0.02	
295	7.57±0.26	32.28±0.01	400	6.52±0.30	33.07±0.03	
295	7.89±0.02	31.97±0.01	450	6.82±0.30	33.09±0.03	KCl
295	8.17±0.40	31.77±0.09	475	6.81±0.13	33.29±0.01	KCl
295	8.50±0.40	31.65±0.04	500	6.98±0.16	33.29±0.02	KCl
295	8.85±0.41	31.41±0.13	500	7.28±0.31	33.08±0.01	
295	9.51±0.28	31.03±0.04	350	10.07±0.16	30.91±0.03	
295	9.79±0.23	30.90±0.10	400	9.77±0.12	31.15±0.02	
295	9.85±0.16	30.86±0.08	450	9.58±0.10	31.48±0.01	KCl
295	10.18±0.09	30.75±0.11	500	9.01±0.18	32.00±0.02	KCl
295	10.63±0.18	30.53±0.10	525	9.00±0.18	32.10±0.02	KCl
295	11.28±0.10	30.29±0.01	550	8.57±0.19	32.54±0.01	KCl
295	11.36±0.40	30.19±0.03	550	7.32±0.19	33.36±0.12	KCl
295	11.61±0.39	30.12±0.06	550	6.53±0.12	NA	Fluid
295	13.00±0.62	29.56±0.03	350	6.22±0.33	33.06±0.05	
295	15.41±0.37	28.76±0.08	400	6.81±0.26	32.86±0.04	
295	15.59±0.40	28.64±0.04	450	7.47±0.05	32.74±0.03	KCl
295	16.97±0.33	28.24±0.03	500	7.70±0.23	32.83±0.02	KCl
295	18.34±0.20	27.88±0.05	550	7.99±0.13	33.00±0.04	KCl
295	19.60±0.57	27.44±0.05	575	8.11±0.13	33.09±0.03	KCl
295	22.11±0.25	26.79±0.06	350	12.59±0.24	29.76±0.02	
295	22.76±0.38	26.63±0.10	400	13.44±0.21	29.58±0.02	
295	23.89±0.15	26.32±0.06	450	13.57±0.17	29.60±0.02	
295	24.15±0.10	26.28±0.03	500	13.93±0.28	29.71±0.03	KCl
295	25.60±0.45	25.99±0.08	550	13.34±0.40	30.16±0.03	KCl
295	27.49±0.52	25.49±0.07	600	12.68±0.21	30.76±0.02	KCl
295	30.21±0.25	25.06±0.10	625	12.24±0.12	31.02±0.03	KCl
295	32.89±0.19	24.56±0.04	625	10.59±0.22	31.92±0.08	KCl
			625	9.80±0.05	NA	Melting

	625	6.57±0.28	Fluid

687 Table 1. Pressure-volume data for ice VII collected at 295 K. The uncertainties are 2σ
688 standard deviations from the means. Fluid = aqueous KCl-bearing fluid; KCl = an ice
689 VII and solid phase of KCl mixture; Melting = a pressure and temperature point at which
690 melting was observed during analysis by X-ray diffraction; NA = not applicable or not
691 observed.
692

Ice VII Pressure-Volume Fit Parameters at 295 K			
	K_{T0} (GPa)	K'_{T0}	V_0 (Å ³)
1.60 mole % KCl-H ₂ O (This Study)	24.7±0.9	4.44±0.09	39.2±0.2
1.60 mole % NaCl-H ₂ O (Frank et al., 2012)	26.47±0.46	4.27±0.03	38.96±0.08
1.60 mole % CH ₃ OH-H ₂ O (Frank et al., 2012)	21.53±0.68	4.37±0.04	41.0±0.19
One-component, H ₂ O (Hemley et al., 1987)	23.7±0.9	4.15±0.07	40.9±0.9
One-component, H ₂ O (Fei et al., 1993)	23.9±0.7	4.2±0.5	40.9±0.7
One-component, H ₂ O (Frank et al., 2004)	21.3±1.3	4.4±0.1	41.2±0.1
One-component, H ₂ O (Frank et al., 2012)	20.14±1.11	4.62±0.07	40.8±0.33
One-component, H ₂ O (Bezacier et al., 2014)	20.77±0.26	4	41.2±0.1

Table 2. A comparison of the zero-pressure volume (V_0), bulk modulus (K_{T0}), and pressure derivative (K'_{T0}) of pure ice VII and ice VII formed from 1.60 mole percent aqueous solutions of KCl-H₂O, NaCl-H₂O, and CH₃OH-H₂O.

698

Ice VII Pressure-Volume-Temperature Fit Parameters			
	η	a_0	a_1
1.60 mole % KCl-H ₂ O (This Study)	0.77	-2.93×10^{-4}	1.27×10^{-6}
1.60 mole % NaCl-H ₂ O (Frank et al., 2008)	0.9	-4.1×10^{-4}	1.54×10^{-6}
One-component, H ₂ O (Frank et al., 2004)	1.1	-4.2×10^{-4}	1.56×10^{-6}
One-component, H ₂ O (Fei et al., 1993)	0.9	-3.9×10^{-4}	1.5×10^{-6}

699

700 Table 3. The pressure-volume-temperature fit parameters for the KCl-bearing ice VII of
 701 this study are compared to those of pure ice VII and that formed from a NaCl-H₂O
 702 solution.
 703

Ice VII Melting Curve Data	
Temperature (K)	Pressure (GPa)
323±27	2.20±0.29
463±12	4.28±0.07
550±5	6.68±0.31
550±5	6.93±0.40
625±5	10.2±0.40
Simon fit of Melting Point Data	
c	3.72
P_C	0.759
T_t	324
P_t	2.2

Table 4. The melting curve of ice VII was determined by using the Simon-Glatzel equation and the melting point data presented here. Some of the data represent midpoints in P - T space between ice-absent and ice-present diffraction patterns whereas others are from experiments where ice was observed to melt in successive patterns.