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# 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 $H_2O$ 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 mol percent KCl-bearing aqueous solution was studied up to $32.89 \pm 0.19$ 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 $24.7 \pm 0.9$ GPa, $4.44 \pm 0.09$, and $39.2 \pm 0.2$ Å$^3$, respectively. The impurity-laden ice was found to be 6–8% denser than ice VII formed from pure $H_2O$. 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 $10.2 \pm 0.4$ 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 $H_2O$ 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 $H_2O$-rich planets, and we speculate that this could supply an additional source of heat through the radioactive decay of $^{40}$K. 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.
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## 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, 1997, 1998, 2001; Kivelson et al., 1996; Schubert et al., 1996; Khurana et al., 1998; McCord et al., 1998, 2001, 2002; Greeley et al., 2000; 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 and Choukroun, 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

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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 system, as it is only stable at pressures greater than ~2 GPa, the processes observed on smaller planetary bodies, such as Enceladus and Ganymede, are also likely on larger $H_2O$-rich planets which have maintained a greater proportion of accretionary heat. This raises questions as to if the deep ices at the base of the subsurface oceans, ice VI in small to moderate sized bodies and ice VII in moderate to large bodies, have formed in contact with the same impurities observed at the surface through interactions with either the subsurface ocean or the deeper rock layers (Hsu et al., 2015). These solutes are well known to affect the density and freezing point of liquid $H_2O$, but their impacts on solid $H_2O$-ice are not well constrained. Numerous studies have explored the pure $H_2O$-ice system (Hemley et al., 1987; Wolanin et al., 1997; Loubeyre et al., 1999; Frank et al., 2004; Asahara et al., 2010; Fortes et al., 2011; Ahart et al., 2011; Ahart et al., 2014; Hirai et al., 2014), but only a few studies have been conducted in binary $H_2O$-rich systems. Frank et al. (2006) hypothesized that ice VII could hold ionic impurities and tested the hypothesis in the NaCl–$H_2O$ system. They noted that up to 2.4 mol percent NaCl could be incorporated into ice VII as $Na^+$ and $Cl^-$ which decreased the unit cell volume and increased the density of the ice relative to pure ice VII. Subsequently, numerous studies have verified that impurities, such as NaCl (Frank et al., 2008, 2012; Journaux et al., 2013), LiCl (Klotz et al., 2009), and $CH_3OH$ (Frank et al., 2012) could be incorporated into ice VII. Ice VII formed in the NaCl–$H_2O$ system has been shown to be denser than pure ice and has also been noted to lower the melting curve relative to pure ice (Frank et al., 2008; Journaux et al., 2013). This study explored ice VII formed in the KCl–$H_2O$ system to constrain the phase stability, *PVT* equation of state, melting curve, and 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–$H_2O$ solutions in a diamond anvil cell (DAC). Aqueous solutions containing KCl were prepared by dissolving KCl (assay, anhydrous basis ⩾99.0%) in distilled and deionized $H_2O$. All solutions contained 1.60 mol percent KCl, and this concentration was chosen because it fell below the estimated maximum solubility of NaCl in ice VII of approximately 2.4 mol 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 and 10 μm in diameter, to be used as a pressure indicator, were placed in the sample chamber. A drop of the KCl–$H_2O$ 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° 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

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