



# Salt partitioning between water and high-pressure ices. Implication for the dynamics and habitability of icy moons and water-rich planetary bodies



Baptiste Journaux<sup>a,\*</sup>, Isabelle Daniel<sup>a</sup>, Sylvain Petitgirard<sup>b</sup>, Hervé Cardon<sup>a</sup>, Jean-Philippe Perrillat<sup>a</sup>, Razvan Caracas<sup>a</sup>, Mohamed Mezouar<sup>c</sup>

<sup>a</sup> Université de Lyon, Université Lyon 1, Ens de Lyon, CNRS, UMR 5276, Laboratoire de Géologie de Lyon, F-69622, Villeurbanne, France

<sup>b</sup> Bayerisches Geoinstitut (BGI), University of Bayreuth, 95444 Bayreuth, Germany

<sup>c</sup> European Synchrotron Radiation Facility, BP 220, F-38004 Grenoble Cedex, France

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## ABSTRACT

Water-rich planetary bodies including large icy moons and ocean exoplanets may host a deep liquid water ocean underlying a high-pressure icy mantle. The latter is often considered as a limitation to the habitability of the uppermost ocean because it would limit the availability of nutrients resulting from the hydrothermal alteration of the silicate mantle located beneath the deep ice layer. To assess the effects of salts on the physical properties of high-pressure ices and therefore the possible chemical exchanges and habitability inside H<sub>2</sub>O-rich planetary bodies, we measured partitioning coefficients and densities in the H<sub>2</sub>O–RbI system up to 450 K and 4 GPa; RbI standing as an experimentally amenable analog of NaCl in the H<sub>2</sub>O–salt solutions. We measured the partitioning coefficient of RbI between the aqueous fluid and ices VI and VII, using *in-situ* Synchrotron X-ray Fluorescence (XRF). With *in-situ* X-ray diffraction, we measured the unit-cell parameters and the densities of the high-pressure ice phases in equilibrium with the aqueous fluid, at pressures and temperatures relevant to the interior of planetary bodies. We conclude that RbI is strongly incompatible towards ice VI with a partitioning coefficient  $K_d^{(VI-L)} = 5.0(\pm 2.1) \cdot 10^{-3}$  and moderately incompatible towards ice VII,  $K_d^{(VII-L)} = 0.12(\pm 0.05)$ . RbI significantly increases the unit-cell volume of ice VI and VII by ca. 1%. This implies that RbI-poor ice VI is buoyant compared to H<sub>2</sub>O ice VI while RbI-enriched ice VII is denser than H<sub>2</sub>O ice VII. These new experimental results might profoundly impact the internal dynamics of water-rich planetary bodies. For instance, an icy mantle at moderate conditions of pressure and temperature will consist of buoyant ice VI with low concentration of salt, and would likely induce an upwelling current of solutes towards the above liquid ocean. In contrast, a deep and/or thick icy mantle of ice VII will be enriched in salt and hence would form a stable chemical boundary layer on top of the silicate mantle. Such a contrasted dynamics in the aqueous–ice VI–ice VII system would greatly influence the migration of nutrients towards the uppermost liquid ocean, thus controlling the habitability of moderate to large H<sub>2</sub>O-rich planetary bodies in our solar system (e.g., Ganymede, Titan, Calisto) and beyond.

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## 1. Introduction

H<sub>2</sub>O is one of the most abundant molecules in our galaxy and is present in a large variety of planetary environments. Its liquid phase is considered as mandatory for life, whether terrestrial or extraterrestrial (see review by Lammer et al., 2009). Habitability

therefore assumes the presence of liquid water at the surface of planetary bodies or in their interiors. Deep liquid oceans are predicted inside the icy moons of Saturn and Jupiter (see review by Sohl et al., 2010) and also in the recently discovered ‘ocean’ exoplanets beyond our solar system (Léger et al., 2004; Noack et al., 2016 and references therein). In large water-rich planetary bodies such as Ganymede, Titan and larger exoplanets, the habitability of subsurface oceans remains debated because of the predicted presence of a deeper high-pressure icy mantle, preventing chemical exchange between the rocky silicate mantle/core and the liquid ocean (Léger et al., 2004; Lammer et al., 2009; Fortes and Choukroun, 2010). This deep solid ice mantle may host different high-pressure

\* Corresponding author.

E-mail address: baptiste.journaux@gmail.com (B. Journaux).

<sup>1</sup> Now NASA Postdoctoral Program Fellow at NASA Astrobiology Institute, Earth and Space Sciences Department, University of Washington, Seattle, WA 98125, USA.

ice polymorphs, such as ice III, V, VI for icy moons, and up to ice VII and X for the largest ocean planets (Sotin and Grasset, 2007; Journaux et al., 2014; Noack et al., 2016). The interiors of icy satellites and ocean exoplanets are currently modeled using the phase diagram and equations of state of either pure H<sub>2</sub>O (Sotin and Tobie, 2004; Sotin and Grasset, 2007; Noack et al., 2016) or binary molecular systems H<sub>2</sub>O–NH<sub>3</sub>, H<sub>2</sub>O–CH<sub>4</sub>, H<sub>2</sub>O–CO<sub>2</sub> (Fortes and Choukroun, 2010 and references therein; Bollengier et al., 2013; Bezacier et al., 2014b) and H<sub>2</sub>O–MgSO<sub>4</sub> (Fortes and Choukroun, 2010; Vance and Brown, 2013 and references therein).

However, numerous evidences of dissolved salts in the liquid reservoirs of icy moons in our solar system have been gathered by space probes over the years. Interpretation of the magnetic field of large icy moons (Sohl et al., 2010 and references therein), of small oscillations of auroras on Ganymede (Saur et al., 2015) and of Schuman-like resonance in Titan's atmosphere (Béghin, 2015) requires a high electrical conductivity that is best explained by deep brines. In addition, remote spectroscopy evidenced the presence of sulfates on the surface of Europa and Ganymede (Dalton, 2010 and references therein), and potentially chlorides on Europa (Brown and Hand, 2013). Cassini also detected the emission signature of ice grains rich in sodium salt in Enceladus polar jets suggesting intense hydrothermal activity (Hsu et al., 2015). This is in good agreement with thermodynamic calculations that show that NaCl is one of the main solutes resulting from the aqueous alteration of chondritic material during the early accretion stages of water rich planetary bodies, just like on Earth (Zolotov, 2012). Because of its lack of vibrational spectroscopic signature (Brown and Hand, 2013), the remote sensing detection of halite remains challenging. Nevertheless, it is likely to be present beside the other salts such as MgSO<sub>4</sub>, KCl and the volatile organics NH<sub>3</sub>, CH<sub>4</sub>, CO<sub>2</sub> that have been proposed from both observations (Sohl et al., 2010 and references therein) and chemical models of the water/rock interactions in the early stages of icy moon formation (Zolotov, 2012).

Models of the interior of water-rich satellites and exoplanets assume ice phases composed of pure H<sub>2</sub>O. This is appropriate when considering ice Ih that does not incorporate chemical impurities (Gross and Svec, 1997). In the H<sub>2</sub>O–NaCl system, the partitioning coefficient of NaCl between ice Ih and the aqueous phase is as low as  $3.0(\pm 0.3) \cdot 10^{-3}$  (Gross and Svec, 1997 and references therein). There are only a few exceptions to this incompatible behavior of salts towards ice Ih, among which ammonium fluoride that forms a solid solution with water, by substitution of H<sub>2</sub>O molecules up to 5.2 mol% (Gross and Svec, 1997), due to the isomorphism between the crystal lattices of NH<sub>4</sub>F and ice Ih. In contrast to ice Ih, ice VII can incorporate at high pressure at least 1.6 mol% of NaCl, 5 mol% of CH<sub>3</sub>OH (Frank et al., 2006, 2013), and up to ca. 18 mol% of LiCl and LiBr (Klotz et al., 2009). Incorporation of large amount of solutes in ice would significantly affect the bulk physical and thermodynamic properties of high-pressure ices. The pioneering experimental work in the H<sub>2</sub>O–NaCl system (Adams, 1931) has recently been extended to *P–T* conditions relevant to water-rich planetary bodies and has shown, for instance, that NaCl: i) shifts the melting curves of high-pressure ice phases, ii) extends the stability of the liquid phase (Valenti et al., 2012; Journaux et al., 2013), and iii) induces a density cross-over between ice VI and NaCl-rich brines (Journaux et al., 2013).

A first-order understanding of the structure and dynamics of the interior of icy-moons and ocean exoplanets would be greatly improved from an estimation of the actual concentration of salt in the high-pressure ices, i.e. how it is partitioned between the fluid and ice phases and how salt alters the bulk properties of high-pressure ices. This is essential to model the cooling and subsequent freezing of a water-rich planetary body, i.e. the chemical evolution of its aqueous reservoir through time (Noack et al., 2016).

Since high-pressure ices cannot be quenched to ambient conditions, partitioning coefficients and densities can only be measured *in situ* at high-pressure in the diamond anvil cell (DAC) using synchrotron X-ray fluorescence (XRF) and X-ray diffraction (XRD) to probe the chemistry and the structure of high-pressure ices. Despite the high photon flux available at current synchrotron facilities, it is still highly challenging to measure fluorescence below 5 keV due to the strong absorption of diamond anvils in this spectral range (Schmidt et al., 2012). Sodium chloride has  $K\alpha$  fluorescence emission at 1.04 and 2.62 keV for Na and Cl, respectively, and diamond anvils of 2 mm thickness transmit less than  $10^{-30}$  at such a low energy (Haynes et al., 2012); therefore NaCl remains undetectable in a DAC even at very high concentration. Thus, we chose to investigate rubidium iodide (RbI) as a metal halide analogue to NaCl. RbI  $K\alpha$  fluorescence lines are at high energy,  $K\alpha_{\text{Rb}} = 13.39$  keV and  $K\alpha_1 = 28.61$  keV where diamond transmission is higher than 50%. NaCl and RbI have very close ionic radius ratios of 0.56 and 0.69, respectively and close electronegativity difference as well of 2.2 and 1.8 Pauling units, respectively. Such a similarity is essential when conducting partitioning experiments as it will greatly influence the possible incorporation or substitution sites for ions into the lattice of the high-pressure ice (Klotz et al., 2009; Bove et al., 2015). This study presents the first *in situ* measurements of the partitioning of a halide salt (RbI) between high-pressure ice VI, ice VII and the aqueous fluid, at (*P–T*) conditions relevant to the interior of large icy moons and the hydrospheres of the larger ocean exoplanets. The results also include the effects of RbI on the melting curve, volume and density of ice VI and ice VII, respectively.

## 2. Experimental and analytical methods

### 2.1. Sample and pressure set-up

The sample consisted of aqueous solutions of RbI prepared by dissolving rubidium iodide (99.9% ultra pure, Aldrich™) into pure Milli-Q™ water (18 MΩ cm). Solutions with concentrations of 0.5 and 1.0 mol kg<sup>-1</sup> were obtained by weighing RbI salt dried for 6 h at 400 K prior to dissolution. In order to prevent concentration change due to evaporation during loading the diamond-anvil cell (DAC), the solutions and the DAC were kept at 277 K. A pre-indented T-301 stainless steel gasket of 70 μm thickness drilled with a 200 μm hole and lined with platinum served as sample chamber. A droplet of the cold solution was loaded into the compression chamber, while the DAC was still cold, together with small ruby spheres (<10 μm) used as a pressure gauge. The DAC was closed immediately afterwards, ensuring no H<sub>2</sub>O evaporation.

Experiments were performed in a membrane-type diamond-anvil cell. The DAC was equipped with ultra-low fluorescence diamond anvils of 0.5 mm culet for the determination of the high-pressure ice melting curves and Raman spectroscopy. For the synchrotron experiments, we used an asymmetrical geometry for the diamond anvils with shorter anvils of 1.5 mm thickness, 0.6 mm culet on the upstream side and 1.2 mm thickness, 0.55 mm culet on the downstream side of the X-ray beam to collect the XRF and XRD signals. This asymmetrical geometry allowed collecting more XRF signal and less of the Rayleigh and Compton scattering.

Temperature was generated with a resistive coil around the DAC, and was insulated with ceramic fiber tape for high thermal stability. Temperature was controlled by a commercially calibrated K-type thermocouple glued on the side of one anvil, as close as possible to the culet. During experiments, temperature remained constant within ±0.5 K. Neither dissolution nor alteration of the ruby spheres was observed over the temperature and pressure range of the present study.

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