**ION FRACTIONATION IN PLANETARY ANALOG ICES.** J. J. Buffo<sup>1</sup>, A. Murdza<sup>1</sup>, M. G. Fox-Powell<sup>2</sup>, C. R. Meyer<sup>1</sup>, and B. E. Schmidt<sup>3</sup>. <sup>1</sup>Thayer School of Engineering, Dartmouth College, Hanover, NH, USA. (jacob.j.buffo@dartmouth.edu), <sup>2</sup>The Open University, Milton Keynes, UK. <sup>3</sup>Cornell University, Ithaca, NY, USA.

Introduction: There is a growing consensus that ocean-derived impurities, and particularly salts, likely play a key role in both the geophysical evolution and habitability of planetary ice shells [1]. This is bolstered by several observations including 1) the association of endogenic material with geologically young surface features [2, 3], 2) the ability of salts to depress the freezing temperature and thereby extend the longevity of liquids within planetary ice shells [4], 3) the critical role salts play in governing the material properties, biogeochemistry, and habitability of salt-rich ice on Earth [5-8], and 4) the fundamental role small melt fractions and impurity levels play in the terrestrial mantle-lithosphere system [9, 10] (an analog of ice shell brittle lids and ductile solid-state convection regions [11]). Moreover, as the primary vehicle and medium for the transport and expression of observable signatures from any underlying oceans these impurity enriched ices provide a geological record of subsurface ocean properties and processes as well [12, 13].

Given these significant geophysical and astrobiological implications, there has been a recent effort to constrain the material entrainment rates occurring at the ice-ocean and ice-brine interfaces (the latter distinguishing freezing fronts of hydrological features within ice shells - e.g., sills, lenses) of icy satellites across the solar system [12, 14, 15]. Bred from the multiphase physical models of analogous terrestrial systems (sea ice [5, 6], magma chamber dynamics [16], solidifying metal alloys [17]), these investigations have successfully produced parameterizations linking interface conditions to material entrainment rates and resultant ice properties [12, 14]. Moreover, they have been validated against bulk salinity profiles and material entrainment rates observed in natural and laboratory grown sea ice cores [14, 18].

However, it is likely that the ocean compositions of other ocean worlds in the solar system may differ from that of the Earth [3, 19]. If this is the case, it bodes the question, are all salts species entrained at an equal rate? Furthermore, how do diverse mixtures of salt species impact ice-ocean/brine interface properties, dynamics, and entrainment rates? Recent research has suggested that ion fractionation, the preferential entrainment/rejection of salt species into/out of the forming ice, could be prevalent under ice-ocean world thermodynamic conditions [20]. If so, ionic speciation within planetary ices may not be directly representative

of the progenitor fluid reservoir from whence they came.

While there exists extensive ionic composition measurements for ice cores derived from our own NaCldominated ocean [21], there currently exists a dearth of empirical data related to the ionic composition of ices formed from alternate ocean chemistries. A small sample set of ice cores from hypersaline lakes exist [8, 22], but their exposure to significant diurnal temperature variations during their growth makes it difficult to constrain relationships between thermal driving at the ice-brine interface and resultant ice properties. Additionally, surface melting and flushing of the interstitial brine within the ice can occur, further obscuring these relationships.

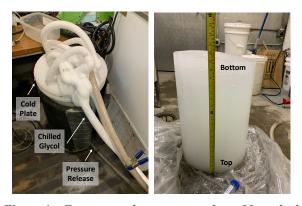
As such, there remains a large gap in our understanding of the entrainment rates of various salt species in ices formed from planetary relevant brines. These are likely critical processes operating within the ice shells of ocean worlds, controlling their geochemistry, geophysics, and habitability. Moreover, a well constrained dataset of salt entrainment rates in compositionally diverse ices is needed to benchmark predictive models of planetary ice-ocean and ice-brine systems to guarantee their accuracy and optimize their utility for upcoming missions (e.g., Europa Clipper, Dragonfly).

**Methods:** To bridge this knowledge gap we are establishing a database of physical, thermal, chemical, and material properties of compositionally diverse saline ices grown from putative ice-ocean world brine compositions (e.g., [3, 19]).

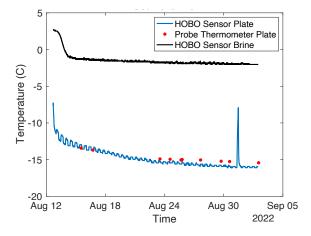
Ices are generated using a custom experimental setup (Figure 1) that enables controlled top-down solidification rates. The apparatus consists of an insulated 57L Nalgene tank with a pressure release line at the base to guarantee that the brine does not become over pressurized during experiments. The tank resides in a 2C cold room and freezing is driven by a glycol cooled plate (range -40C - +20C) placed atop the tank. Throughout the experiment we measure both the cold plate temperature and the underlying brine temperature (e.g., Figure 2) to track thermal driving magnitudes (assuming a linear thermal profile within the ice the icebrine interface thermal gradient can be calculated) and freezing point depression in the underlying brine (which can be used to track cryoconcentration rate).

We sample the initial brine before the experiment begins. At the end of an experimental run, we sample the sub-ice brine, and the ice is extracted (Figure 1) and immediately stored in a -30C freezer to prevent any brine loss until the ice is processes and analyzed.

For ionic composition analysis the ice core is vertically partitioned at 2 cm intervals, melted, filtered through 0.2  $\mu$ m PES filters, and analyzed for ionic species concentrations via ion chromatography and inductively coupled plasma-optical emission spectrometry. The initial and final brine samples are analyzed in the same fashion.



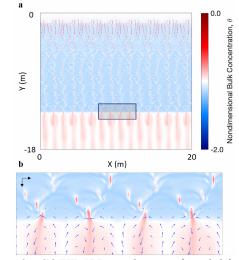
**Figure 1** – *Experimental apparatus and an* ~50 cm thick ice layer produced by freezing a MgSO<sub>4</sub>-dominated putative Europa ocean chemistry [3].



**Figure 2** – Cold plate (blue line and red dots) and underlying brine (black line) temperatures during an experiment run. The spike in plate temperature was cause by a brief loss of power to the facility.

**Results:** Here we present preliminary ionic composition profiles of ices grown from two potential Europa ocean compositions (NaCl-dominated/Earth-like [2] and MgSO<sub>4</sub>-dominated [3]). We compare their salt entrainment rates and test whether ionic fractionation occurs in either of these compositional systems. Additionally, we investigate whether the 2D

multiphase reactive transport model SOFTBALL [23], which has been used to simulate salt entrainment in planetary ices (Figure 3) [12], can accurately reproduce the ionic composition profiles observed in these laboratory grown ices – a critical benchmark test for such models.



**Figure 3** – SOFTBALL simulations of a solidifying icy satellite shell – Bulk salinity profiles [12].

We describe additional ocean compositions and concentrations being tested and describe microstructural (porosity, permeability) and mechanical property (ice strength, rheology) testing that is currently underway. Finally, we discuss the important implications this database of planetary ice analog physicochemical properties has for our understanding of ice-ocean world geophysics, habitability, and mission science interpretation.

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