MODELS FOR THE VOLUME FRACTION OF BRINE IN EQUILIBRIUM WITH ICE ON EARTH AND ACROSS THE SOLAR SYSTEM.

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Introduction: The stability of brine in ice represents an important factor governing the bulk thermophysical properties, the bulk dielectric properties, and the distribution of potential habitats [1]. We present a framework for generating models representing the brine volume fraction in impure water ice as a function of temperature and bulk ice salinity. This framework decouples bulk ice salinity from composition, allowing a single model for impure ice of a specified composition to be applied over a range of possible bulk ice salinity. A major motivation for the development of the proposed framework is to facilitate the incorporation of more complex chemical species in geophysical investigations of ocean worlds; however, the framework is applicable to impure water ice anywhere in the solar system.

Methods: The amount of brine stable in ice is governed by the bulk salinity of the ice, the temperature, and the composition of the impurities. Through knowledge of the phase behavior, defined here as the solution properties as a function of temperature, models for the brine volume fraction in ice can be obtained. This approach was inspired by models originally developed for application to sea ice [2]; however, we extend the application to impure water ice of any composition. Figure 1 illustrates the proposed framework.
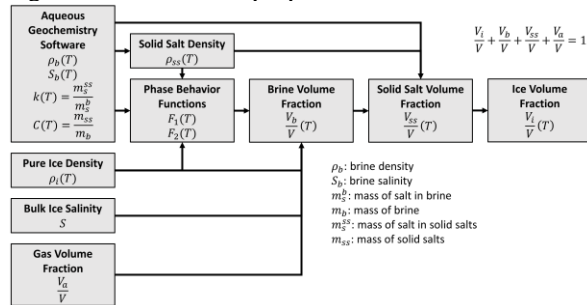

Figure 1. Framework for modeling the volume fraction of brine and solid salts in equilibrium with ice.

Obtaining Phase Behavior Functions. We employ the opensource aqueous geochemistry program FREZCHEM to obtain the phase behavior for the impure water ice assuming equilibrium crystallization. The solution composition is specified in the input file such that the *relative* concentration of chemical species is equivalent to that of the impure ice. Note that in this approach only a single FREZCHEM simulation is needed to represent a range of possible bulk ice salinity as opposed to needing to run a simulation for each bulk ice salinity of interest. The phase behavior can be extracted from the FREZCHEM output files and used to generate the phase behavior functions, $F_1(T)$ and $F_2(T)$. The phase behavior functions are derived in [2] and defined as

$$F_1(T) = \rho_b(T)S_b(T)(1 + k(T))$$

where ρ_b is the brine density (g/cm^3), S_b is the brine salinity (ppt), and k is the ratio of mass of salts in the form of solid salts to the mass of salt in the brine, and

$$F_2(T) = \left(1 + C(T)\right)\frac{\rho_b(T)}{\rho_i(T)} - \frac{C(T)\rho_b(T)}{\rho_{ss}(T)} - 1$$

where C is the ratio of mass of solid salts to the mass of brine, ρ_b is the brine density (g/cm^3), ρ_i is the pure ice density (g/cm^3), and ρ_{ss} is the density of solid salts (g/cm^3). These phase behavior functions can then be represented as a function of temperature, T, by fitting the data extracted from the model to a set of piecewise third order polynomial functions. The brine volume fraction can be obtained using

$$\frac{V_b}{V}(T) = \frac{\rho_i(T)S}{F_1(T) - SF_2(T)}$$

where ρ_i is the ice density (g/cm^3) and S is the bulk ice salinity (ppt).

Validation of the Proposed Framework through Comparison to Sea Ice. We validate our proposed framework through application to sea ice. We compare the phase behavior functions in our model, derived from the output of a FREZCHEM v13.3 simulation for standard mean ocean water [3], to the phase behavior functions originally obtained by [2] and augmented by [4]. Figure 2 presents a comparison of the brine salinity, brine density, and phase behavior functions between the two models. The circles reflect the original dataset of [5], from which the phase behavior functions of [2] were derived. The models agree with each other, although our brine density and phase behavior functions are slightly higher at temperatures below -22.9 °C, where hydrohalite begins to precipitate. This translates to a lower brine volume fraction for a given bulk ice salinity. We argue that our model represents an improvement to the contemporary model by (i) extending the temperature range where sea ice brine volume fraction can be estimated down to the eutectic temperature and (ii) reflecting the Gitterman freezing pathway, thought to be more representative of natural sea ice [6].
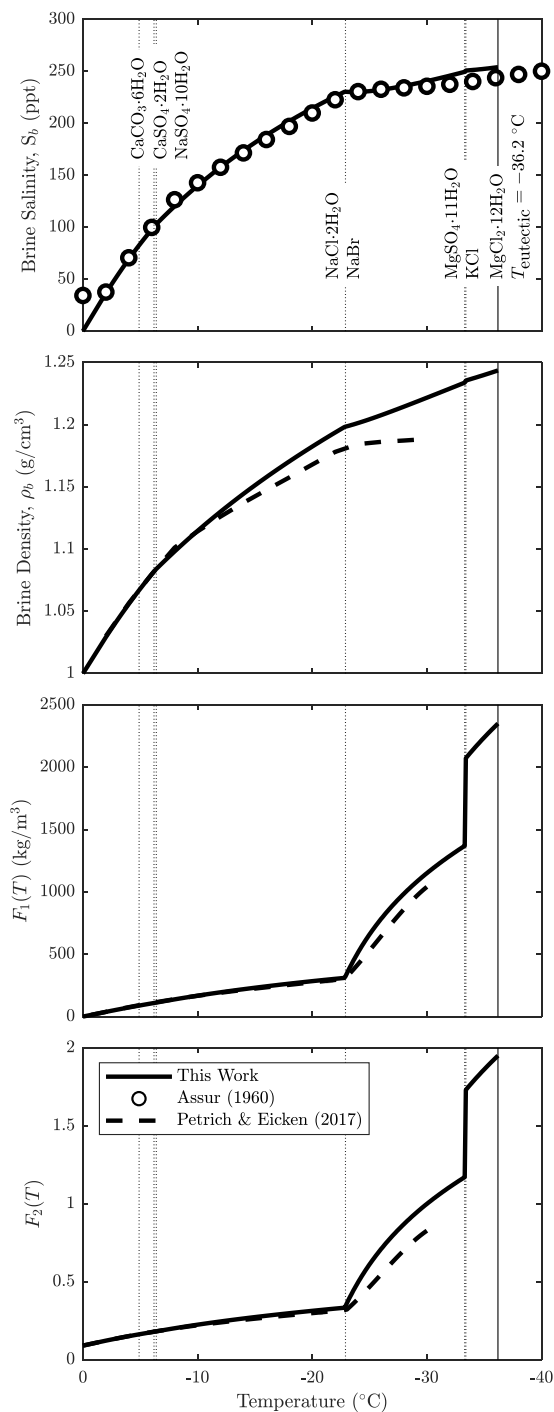
Figure 2. Validation of our framework through application to sea ice. The solid line represents our model whereas the dashed line represents the contemporary model presented in [1].

Representing Phase Behavior Functions as Surfaces to Account for the Influence of Pressure.

For application to other worlds, including the ice shells of ocean worlds like Europa and Enceladus, the influence of pressure on the phase behavior is an important consideration. To robustly account for the influence of pressure on the phase behavior for any solution, the phase behavior functions must be represented as a surface instead of a curve (i.e., a function of both temperature and pressure instead of temperature alone). Figure 3 is a graphical representation of the phase behavior surface, $F_1(T, P)$, for seawater. Note that for a pressure of 1 atm, the surface would collapse to the curve in Fig. 2.
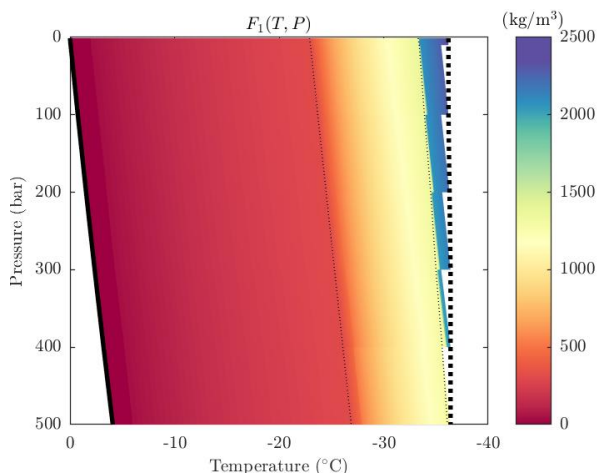

Figure 3. An example of a phase behavior surface for seawater.

Results & Discussion: We apply this framework to examine the distribution of brine within Europa's ice shell considering binary (NaCl and $MgSO_4$) and analog (Cl-dominated and SO_4-dominated) endmember compositions for the ice shell. We find that the vertical extent of brine in an ice shell where impurities are composed of binary species is more sensitive to composition than an ice shell where impurities are composed of multiple species. We selected our analog endmember compositions such that they shared a eutectic temperature (i.e., the vertical extent of brine in an ice shell was the same) and found that the brine volume fraction was consistently higher for the Cl-dominated ice shell than the SO_4-dominated ice shell. Ice thickness (i.e., pressure) was found to have only a minor effect on the distribution of brine within an ice shell relative to temperature and bulk salinity.

References:

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