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# Salt Distribution from Freezing Intrusions in Ice Shells on Ocean Worlds: Application to Europa

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# Abstract

Several icy moons and dwarf planets appear to have hosted subsurface liquid water. Liquid water intruding upwards into the icy outer shells of these worlds freezes, forming ice and (from ocean solutes) non-ice solids. Here, we model concentrated aqueous solutions below 273 K to simulate the compositional evolution of freezing spherical intrusions. Starting solutions are based on five previously reported compositional end members for Europa's ocean. For moderate-pH end members dominated by chloride, sulfate, and/or carbonate, the solids formed include Ca-, Mg-, and Na-sulfates and -carbonates, as well as Na- and K-chlorides. For silica-rich, highpH end members, abundant amorphous silica forms with, potentially, similarly abundant NaOH and KOH. We further develop a new numerical model to compute the spatial distribution of the formed solids and residual brine as freezing progresses. If non-ice solids settle to the bottom, their deposits tend to have stacked hourglass shapes, widening each time the crystallization temperature of a new solid is reached. We discuss the applicability of this model to vertical fractures and global freezing of a subsurface ocean. These results inform (i) how compositional heterogeneities may affect the thermophysical properties of ice shells, which in turn influence convective and cryovolcanic transport, (ii) the compatibility of brine pockets with physicochemical conditions suitable for microbial life, and (iii) possible measurements of compositional heterogeneities within ice shells by spacecraft such as NASA's Europa Clipper and ESA's JUICE missions. The methodology developed here is applicable to other ice-covered ocean worlds.

*Unified Astronomy Thesaurus concepts:* Planetary structure (1256); Planetary interior (1248); Hydrosphere (770); Natural satellite evolution (2297); Geological processes (2289); Planetary mineralogy (2304); Europa (2189); Ceres (219); Ganymede (2188)

# 1. Introduction

Several icy solar system moons and dwarf planets appear to harbor past or present bodies of regional or global subsurface liquid water beneath icy shells (Hendrix et al. 2019, and references therein). This subsurface liquid material may be expressed at the surface or ejected into space, e.g., as endogenic non-H<sub>2</sub>O components (Table 1). Conveying material from the subsurface liquid bodies to the surface and to space requires mechanisms of material transport through the ice shells such as solid-state overturn (e.g., Kargel et al. 2000; Rubin et al. 2014), a geodynamically active shell (e.g., Kattenhorn & Prockter 2014; Allu Peddinti & McNamara 2015; Howell & Pappalardo 2018), and fluid ascent triggered by freezing-, exsolution-, or mechanically (e.g., tidally) induced pressurization of local and/or global subsurface liquid reservoirs (e.g., Crawford & Stevenson 1988; Fagents 2003; Manga & Wang 2007; Kite & Rubin 2016; Castillo-Rogez et al. 2018; Vilella et al. 2020; Lesage et al. 2020). All of these processes can involve intrusions of fluids bearing chemical species such as salts and dissolved gases into the ice shell (Buffo et al. 2020; Soderlund et al. 2020).

Transport processes, although influenced by the properties of the world on which they occur (e.g., gravity and ice shell thickness), are largely governed by the ice shell's mechanical

Original content from this work may be used under the terms of the Creative Commons Attribution 4.0 licence. Any further distribution of this work must maintain attribution to the author(s) and the title of the work, journal citation and DOI. properties (e.g., density, strength, and viscosity) and its thermal properties (e.g., conductivity and heat capacity; e.g., Durham et al. 2010; Howell and Pappalardo 2019; Carnahan et al. 2021). In turn, these properties depend on the ice shell composition (Vance et al. 2021a; Wolfenbarger et al. 2022b). Given the difference in temperature between cold surfaces and the  $\approx$ 273 K base of ice shells, these properties vary with depth. They also likely vary along directions parallel to these interfaces due to compositional heterogeneities.

Only recently have studies of transport begun to consider ice shell compositions other than pure water ice or spatial heterogeneities in this composition. The encounter between ascending warm ice and perched salt-bearing ice has been proposed (Schmidt et al. 2011) as a cause for generating perched melt lenses to explain surface chaos features on Europa. The formation and evolution of Europa's ice shell, basal fractures, and shallower intrusions of liquid have been simulated using a model informed by observations of saline ice formation and composition on Earth (Buffo et al. 2020, 2023), and assuming a starting ocean composition from Zolotov & Shock (2001). These simulations have suggested that the solidification of introduced fluids could result in compositional variations within the ice shell substantial enough to affect its thermophysical properties. High contents of MgSO<sub>4</sub> or NH<sub>3</sub> antifreeze were found to inhibit melt generation within ice shells due to localized heating from tidal dissipation (Vilella et al. 2020). The effect of physical conditions on the salinitydepth profile of a thickening ice shell has been investigated

 Table 1

 Examples of Endogenic Non-H<sub>2</sub>O Compounds Detected on Airless Icy World Surfaces

Icy world	Europa	Ceres	Charon
Endogenic non-H <sub>2</sub> O compounds observed	Red material: chloride/sulfate salt? Organic compounds? Fe? (Carlson et al. 2009; McCord et al. 2010; Hand & Carlson 2015)	Na/NH <sub>4</sub> -carbonate; NH <sub>4</sub> -Cl; NaCl•2H <sub>2</sub> O (De Sanctis et al. 2016; Carrozzo et al. 2018; De Sanctis et al. 2020)	NH <sub>3</sub> ; CH <sub>4</sub> ? (Cook et al. 2007; Dalle Ore et al. 2018; Menten et al. 2022)
Observed transport processes	Convection (mobile-lid?); cryovolcanism?; tectonics (Pappalardo & Barr 2004; Katten- horn & Prockter 2014; Roth et al. 2014; Sparks et al. 2016; Quick et al. 2017; Howell & Pappalardo 2018)	Cryovolcanism (Ruesch et al. 2016, 2019; Bucz- kowski et al. 2016; Sori et al. 2017; Scully et al. 2019; Quick et al. 2019)	Cryovolcanism? (Desch & Neveu 2017; Beyer et al. 2019; Menten et al. 2022)

Note. Other relevant icy worlds include Ganymede (e.g., Howell & Pappalardo 2018), Enceladus (Postberg et al. 2018 and references therein), Titan (e.g., Mitri et al. 2008), Uranian moons such as Ariel (Schenk 1991; Cartwright et al. 2020), Neptune's moon Triton (Schenk et al. 2021), and Pluto (Singer et al. 2022).

(Buffo et al. 2021b), as has the thermal and chemical evolution of kilometer-scale spheroidal sills in Europa's ice shell with tracking of the heterogeneous distribution of anhydrous  $MgSO_{4}$ (Chivers et al. 2021). The effect of antifreeze components on local brine reservoir pressurization and ability to trigger eruptions has been modeled (Lesage et al. 2020; Lesage et al. 2022), as well as the percolation of NaCl-H<sub>2</sub>O brine from near the surface down to the base of the ice shell as a means to transport oxidants (Hesse et al. 2022). A framework for modeling the trapped brine content of an ice shell formed from freezing of a salty ocean as a function of this ocean's NaCl and MgSO<sub>4</sub> content has been developed (Wolfenbarger et al. 2022b), and is applicable to other compositions. Although these studies provided significant physical detail on the ice shell processes involved, compositional detail was limited to one or two non-ice variables (bulk salinity, MgSO<sub>4</sub>, NH<sub>3</sub>, and/ or NaCl). As a result, the effect of spatial heterogeneities in composition on transport processes remains largely unexplored.

The study of intrusion compositions also bears on assessing their potential as near-surface habitable environments in ice shells (Chyba & Phillips 2001), shielded from exogenic radiation and with a higher propensity for material exchange with the surface. Unlike subsurface oceans, liquid intruded in ice shells is transient (in thermal disequilibrium), more concentrated, and colder, providing a greater challenge for the physicochemical tolerance range of microbial communities. Investigating compositions as a function of subzero degrees Celsius temperature provides a means to quantify these stresses.

To enable detailed investigation of ice shell compositions, we seek to determine the possible spatial distributions of a broader chemical set of impurities in ice shells resulting from the freezing of liquid intrusions. Leveraging recent improvements in geochemical models for freezing solutions, improved thermodynamic data, and new information about the possible compositions of Europa's ocean, we develop a numerical modeling approach for determining the spatial distribution of multiple different solid species formed as intruded liquid freezes. The model encompasses a freezing routine that adapts the capabilities of the FREZCHEM software (Marion & Kargel 2008), with additional thermodynamic data, to the widely used aqueous geochemical modeling software PHREEQC (Parkhurst & Appelo 2013). It also comprises a numerical routine distributing the ice, non-ice solids, and brine within a spherical intrusion according to assumptions on the

relative timescales of freezing, settling, mixing, and chemical equilibration.

This modeling approach is detailed in Section 2. An application to the spatial distributions of ice, non-ice solids, and residual brine as a function of temperature, using recent end-member estimates of Europa's ocean chemistry (Melwani Daswani et al. 2021), is presented in Section 3. In Section 4, we discuss implications of these results for heterogeneities in ice shell thermophysical properties, characterization using upcoming spacecraft measurements, and the extent to which briny solutions overlap with known tolerance ranges for microbial life. We conclude in Section 5.

### 2. Methods

The spatial distribution of ice, salts, and liquid in a freezing fluid intrusion within an ice shell is determined in two major steps. First, we compute the chemical sequence of forming species as a function of decreasing temperature. Second, we distribute the formed solids according to their density, the shape of the intrusion, and assumptions about the relative rates of crystallization, settling, and mixing.

For the chemical calculations, we use the PHREEQC v3 code (Parkhurst & Appelo 2013) with thermodynamic data either derived by Toner & Catling (2017a, 2017b) or converted by Toner & Sletten (2013) from prior work (Marion 2001; Marion et al. 2005, 2011 and references therein). These chemical calculations are independent of time; i.e., the time evolution of intrusion temperatures is ignored, and it is simply assumed that temperatures decrease with time (Section 2.1). Spatial distributions are obtained by converting molar amounts of formed chemical species to volumes of ice, salts, and solution (Section 2.1.1).

#### 2.1. Chemical Calculations

### 2.1.1. Thermodynamic Data and Software Considerations

In planetary science, the most widely used code to compute compositions of freezing salty solutions is FREZCHEM (Marion & Kargel 2008). FREZCHEM implements the Pitzer equations (Pitzer 1973) that include fitting parameters describing how interactions between ions depend on temperature, composition (especially ionic strength), and pressure to constitute an empirical model of concentrated solutions. The Pitzer model is empirical in that its parameters are fitted to experimental data, making their derived expressions unreliable outside the range of experimental pressures, temperatures, and compositions. This fundamental limitation affects applications to situations outside conditions investigated experimentally, such as carbon-bearing solutions below 0°C, as well as more complex chemical systems such as those included in this work. Many chemical species were added to FREZCHEM over the years (Marion & Kargel 2008; Marion et al. 2015 and references therein). Although this improved the versatility of FREZCHEM, thermodynamic consistency was reduced because parameters were not re-derived using the expanded data sets. Another limitation of FREZCHEM is that thermodynamic data are hard-coded, such that modifying them requires recompiling the FORTRAN code. The code also appears to generate floating point over/under-run in many scenarios, with these errors being compiler-dependent. In our experience, using the same version of FREZCHEM compiled either on two different machines or with different compilers (gfortran and ifort) yielded different results on the same test input, e.g., with one simulation proceeding further down in temperature than the other.

Previous work has sought to mitigate the limited range of accurate applicability, potentially inconsistent thermodynamic data, and computational unwieldiness by re-deriving Pitzer fits for combined chemistries (Toner & Catling 2017a, 2017b) and porting the thermodynamic data to a more modular software, PHREEQC (Toner & Sletten 2013). In particular, Toner & Catling (2017b) re-derived Pitzer model fits for Na-K-Mg-Ca-Cl-SO<sub>4</sub> chemistries, performing new experiments at conditions for which additional data were needed. They provided these data in a PHREEQC thermodynamic database called ColdChem.dat. ColdChem comprises eight solutes, 32 salts or hydrates, and water ice. To this database file, we added molar volumes so as to be able to vary pressures in simulations. Solute molar volumes are from Appelo et al. (2014) and are identical to those included in PHREEQC's default database, phreeqc.dat. Molar volumes for solids are taken from Marion et al. (2005). Importantly, the molar volume expressions of Appelo et al. (2014) capture dependence on both temperature and salinity (ionic strength) at the level of individual ions, whereas in FREZCHEM the dependence on ion concentrations is captured at the level of interactions between ions through volumetric Pitzer parameters (e.g., Marion et al. 2005, 2011). The molar volume (i.e., density) of ice depends perceptibly on pressure and temperature, but although this dependence is captured in FREZCHEM, it is not in PHREEOC. Finally, the pressure dependence of molar volumes of solutes at infinite dilution is linear in pressure for FREZCHEM (Marion et al. 2005), limiting its validity to pressures below 2000 bar due to a decrease in the pressure derivative (compressibility) at increasing pressures (Vance & Brown 2013). In PHREEQC, the pressure dependence is calculated using the semiempirical Helgeson–Kirkham–Flowers formulation (Appelo et al. 2014, and references therein), which is applicable at pressures up to 5000 bar (Helgeson et al. 1981). At higher pressures relevant to larger ocean worlds such as Ganymede, alternative expressions derived from experiments could be implemented (Vance & Brown 2013).

The *ColdChem* database does not include carbonate species, which can dominate starting fluid compositions (Section 3.1). Furthermore, carbonate equilibria depend on pH and therefore require treatment of acidity (equilibria with and between  $H^+$ ,  $OH^-$ , oxidized carbon species, and the above chemistries) that is lacking from *ColdChem*. Thus, for simulations that

involve chemistries beyond chloride and sulfates, such as carbonate species, we use the *frezchem.dat* database (Toner & Sletten 2013), also included by default in the PHREEQC distribution, and which is a direct conversion of FREZCHEM sulfate, chloride, carbonate, and proton-hydroxide data. Unfortunately, no experiments involving carbonate equilibria have been reported below 0°C (Marion 2001; Marion et al. 2011; J. Toner, private communication), so the use of experimental fits in the present work relies on extrapolations that are likely increasingly inaccurate as temperature decreases.

Starting fluid compositions can also be rich in aqueous methane and silica (Section 3.1). To account for the effect of these species on the nature and distribution of formed solids, we added solubility and Pitzer parameter fits to experimental data obtained at  $>0^{\circ}$ C from previous work. These additions, described below, are validated in Section 2.1.3.

We added methane as a redox-uncoupled species under the assumption that during freezing, methane does not get oxidized to CO<sub>2</sub> or carbonate species, and vice versa. For reduction, this is a reasonable assumption because the abiotic reduction of oxidized carbon to methane can take billions of years (Sherwood Lollar et al. 2002, 2021), much longer than the freezing timescale of local liquid reservoirs (Lesage et al. 2020, Lesage et al. 2022; see also Section 2.1.2). Thus, reduced carbon is only partitioned between aqueous methane, methane gas, or methane hydrate. The parameterization of methane gas solubility in pure water as a function of temperature and pressure is copied directly from PHREEQC's pitzer.dat database, in which it is indicated that this fit is for solubilities between 25°C and 100°C. We derive a parameterization for methane (clathrate) hydrate solubility in pure water as a function of temperature T (in kelvin) based on Equations (24), (25), and (28) of Tishchenko et al. (2005) evaluated at zero salinity, and as a function of pressure based on a molar volume of 136.112  $\text{cm}^3 \text{ mol}^{-1}$  provided in their work. The solubility is given by:

$$\log K(T) = \log m_{\text{CH4(aq)}}(T) = -10.654 + 0.042897 T - 3.0649 \times 10^{-5} T^2.$$
(1)

Here, *K* is the temperature-dependent equilibrium constant for the reaction  $CH_{4(g)} = CH_{4(aq)}$ , and  $m_{CH4(aq)}$  is formally the chemical activity of aqueous  $CH_4$ , here equated to the amount of dissolved  $CH_4$  in moles per kilogram of  $H_2O$  (molality) in the approximation of infinite dilution. To evaluate the solubility of methane gas and hydrate in saline solutions, we add empirical fitting parameters  $\lambda$  and  $\zeta$  from Duan et al. (1992), approximated as constants because of their small dependence on temperature (Duan et al. 1992). Marion et al. (2006) also adopted values for these parameters from Duan et al. (1992) but allowed some values to vary with temperature; using their values produces very similar computed solubilities.

We copied the data for aqueous silica species, amorphous silica, and other silicate solids from PHREEQC's *pitzer.dat* database. For silicate solids, analytical expressions for the dependence on the equilibrium constants for silicate dissolution were added from PHREEQC's *core10.dat* database, based on data from Helgeson et al. (1978) and valid from 0°C to 325°C (amorphous silica) or to 350°C (other silicates). Pitzer  $\lambda$  and  $\zeta$  parameters for silica are from Appelo (2015), obtained for the range 0°C–200°C. These parameters are therefore extrapolated when temperatures are below 273 K.

The dependence of thermodynamic properties on pressure is only captured through molar volumes of solutes and solids. Unlike FREZCHEM, PHREEQC does not capture the dependence on pressure of Pitzer parameters.

# 2.1.2. Freezing Routine

To perform FREZCHEM-like simulations using PHREEQC, we wrote an input file with instructions scripted in BASIC (Parkhurst & Appelo 2013) to loop calculations of solidsolution equilibria over temperature. If needed, calculations can also be looped concurrently or separately over pressure and water activity. As in FREZCHEM, two modes of crystallization are allowed to occur. In equilibrium crystallization, the formed solids can still participate in chemical reactions, i.e., dissolve and contribute to forming other products that become more stable at lower temperatures. In fractional crystallization, the formed solids are removed from the system, such that they accumulate without subsequently being allowed to react. In our BASIC input file, solid abundances are memorized for pathindependent equilibrium crystallization, and reset to zero for path-dependent fractional crystallization, in which case the amounts formed at each temperature step are cumulated in post-processing.

To allow the routine to proceed more smoothly (i.e., avoid runtime interruptions due to a lack of convergence of PHREEQC's solver), we added an inert neutral species with a concentration smaller than that of all other elements in the simulation, but whose concentration increases from negligible to dominant when the eutectic temperature is reached, keeping a small amount of solution unfrozen and allowing the program to proceed to determine the solid composition (J. Toner, private communication). We also decreased the step size for changing the activity of master solute species between iterations to a low factor, here 1.1 (J. Toner, private communication), decreased the step size for changing the activity of the electron to a factor 1 (i.e., constant electron activity because there are no redox equilibria among the species included in the calculation), and increased the number of allowed iterations to 1000 per temperature step (Parkhurst & Appelo 2013). Additionally, we forced the pH to be determined by charge balance.

We set a typical temperature step of 0.1–0.5 K, sufficient to achieve numerical convergence for fractional crystallization (equilibrium crystallization outcomes are independent of temperature step). The routine outputs solute molalities; solution density, pH, ionic strength, volume, and electrical conductivity; water activity, and molar amounts of solids formed (and, for equilibrium crystallization, redissolved) at each temperature step.

### 2.1.3. Validation of Chemical Calculations

To our knowledge, the most relevant calculations of detailed solid and solution compositions during freezing at various pressures are those of freezing ocean fluid as applied to Europa using FREZCHEM and reported in Figures 4 and 5 of Marion et al. (2005). Those calculations were carried out for a hypothetical Na–Mg–Ca–SO<sub>4</sub>–Cl–H<sub>2</sub>O system, and as such form a basis for comparison with results obtained with our PHREEQC freezing routine using both the *ColdChem.dat* and *frezchem.dat* databases.

A comparison of results obtained with the present freezing routine with those of Marion et al. (2005) is shown in Figure 1.

The starting fluid composition is the same in Figures 1(a), (b), and (c), but the pressures differ. In Figure 1(a), pressure and temperature co-vary (linearly between 243 bar/260 K and 209 bar/238 K at the eutectic); whereas in Figures 1(b) and (c), the pressures are set to 1 bar and 1460 bars, respectively.

In all three pressure-temperature cases, the solution compositions as a function of temperature computed with our PHREEOC implementation (Sections 2.1.1-2.1.2) are generally similar to those previously computed for the same initial composition (Marion et al. 2005; Vance et al. 2019). In Figure 1(a), irrespective of the PHREEQC database used (thin black lines for that of Toner & Sletten 2013 or thicker colored continuous lines for that of Toner & Catling 2017b), computed Cl molalities are indistinguishable, Mg and sulfate molalities slightly lower, and Na molalities slightly higher (increasingly so at lower temperatures) compared to Figure 4 of Marion et al. (2005). The increase in Ca molality with decreasing temperature and pressure is more pronounced with the PHREEQC routine, although the Ca profile obtained with PHREEQC/ frezchem.dat matches that computed by Vance et al. (2019) using FREZCHEM for the same temperatures, pressures, and initial fluid composition. In Figure 1(b) (1 bar), solute molalities show similar differences between PHREEQC and FREZCHEM outcomes. These differences are more pronounced in Figure 1(c) (1460 bar), in which at low temperatures the sulfate molality becomes much lower and Na becomes more abundant than Mg in the PHREEQC simulations, compared to Figure 5(b) of Marion et al. (2005).

The composition of the salts formed and their temperature of crystallization computed with our PHREEQC implementation (Sections 2.1.1-2.1.2) also generally match those computed by Marion et al. (2005). An exception is the formation of meridianiite (MgSO<sub>4</sub>•11H<sub>2</sub>O) instead of MgSO<sub>4</sub>•12H<sub>2</sub>O in Figure 5 of Marion et al. (2005); the dodecahydrate is absent from the PHREEQC databases because it is no longer thought to be the structure of meridianiite (Peterson et al. 2007). Another exception is the presence of gypsum ( $CaSO_4 \cdot 2H_2O$ ) at 1460 bars above the eutectic temperature (Figure 1(c)), which causes a depletion in aqueous Ca by a factor 2–3 relative to the results of Marion et al. (2005). The greater abundance of Na relative to Mg at low temperatures in Figure 1(c) implies the likely co-formation of hydrohalite (NaCl•2H2O) with MgCl<sub>2</sub>•12H<sub>2</sub>O. Hydrohalite formation at the eutectic was not noted by Marion et al. (2005), but the fate of Na is unclear from their case: the only Na salt indicated to form was NaSO<sub>4</sub>•10H<sub>2</sub>O, but at low temperature there is insufficient SO<sub>4</sub> to capture all of the remaining Na, part of which must form a Na-chloride salt (likely hydrohalite) given the high Cl abundance.

Overall, the differences between results obtained with *ColdChem.dat* and *frezchem.dat* are smaller than those between results obtained with either PHREEQC database and FREZ-CHEM by at least a factor of a few moles per kilogram in solute molalities (Figure 1). This is especially the case for aqueous sulfate at low temperature where the difference in molalities between PHREEQC and FREZCHEM simulations is at least an order of magnitude higher than that between PHREEQC simulations obtained with *ColdChem.dat* and *frezchem.dat*. Moreover, PHREEQC-FREZCHEM differences are greater in the 1460 bar case, indicating that the revised treatment of sulfate chemistries by Toner & Catling (2017a, 2017b) induces less of a change than the difference between



**Figure 1.** Inter-model comparisons for sulfates and chlorides at various pressures and pH 7. The starting fluid composition is the same in all three cases. (a) Comparison to Marion et al. (2005) Figure 4 (gray symbols) and Vance et al. (2019) Figure 4 (colored open symbols). Results obtained with the databases from Toner & Catling (2017b) and Toner & Sletten (2013) are shown with thick colored solid lines and thin black lines, respectively, and are seldom distinguishable except for Ca. Pressure is proportional to depth and is 243 bars at 20 km depth. (b) Comparison to Marion et al. (2005) Figure 5(a) (gray curves, symbols, text, and arrows; vertical dashed line indicates the eutectic temperature). Results obtained with the databases from Toner & Catling (2017b) and Toner & Sletten (2013) are shown with thick colored solid lines and thin black lines, respectively, and Toner & Sletten (2013) are shown with the databases from Toner & Catling (2017b) and Toner & Sletten (2013) are shown with the databases from Toner & Catling (2017b) and Toner & Sletten (2013) are shown with the databases from Toner & Catling (2017b) and Toner & Sletten (2013) are shown with the colored solid lines and thin dashed lines, respectively, and are seldom distinguishable except for Ca. The pressure is 1 bar. (c) Same as in panel b, but with the pressure set to 1460 bars. In the bottom part of panels (b) and (c), forming solids are indicated by vertical bars, equivalent to the arrows in Figure 5 of Marion et al. (2005), that denote presence rather than abundance. Brackets indicate that solids are present only in that temperature range.

PHREEQC and FREZCHEM in the treatment of pressure effects on ion interactions in concentrated solutions (lack of pressure dependence of Pitzer parameters in PHREEQC). At 1 bar (Figure 1(b)) the outputs of PHREEQC/frezchem.dat and FREZCHEM are essentially the same, save for small changes in  $Ca^{2+}$  and  $SO_4^{2-}$  molalities that increase as temperature decreases and may reflect growing numerical inaccuracies in one or both computer programs at later simulation steps. We thus attribute the higher differences in Ca and SO<sub>4</sub> molalities at 1460 bars to (1) the difference between PHREEQC and FREZCHEM in how solute molar volumes depend on pressure and ion concentrations (Section 2.1.1), which seems to favor gypsum formation in the PHREEQC cases, and (2) the lower abundance of Ca, which emphasizes small absolute differences on the figure's logarithmic scale. These differences also cause slight changes (a few kelvin) in the computed eutectic temperatures (end of curves in Figure 1). Finally, at 1460 bars, the temperature at which ice first forms is a few kelvin lower in the PHREEQC simulations. This difference cannot be attributed to the pressure dependence of ice density (molar volume), which is considered in FREZCHEM but not

PHREEQC, since this would result in a *higher* freezing point prediction in PHREEQC. Instead, it may be due to small differences in the water activity (e.g., as in Figure 1(a)) linked to other solute molality differences, possibly caused by the different treatments of solute molar volumes and Pitzer parameters as a function of pressure (Section 2.1.1).

These comparisons validate the freezing routine described in Section 2.1.2 and quantify differences with prior FREZCHEM calculations (Marion et al. 2005) due to different treatments of molar volumes and sulfate chemistries (*ColdChem.dat* case). The simulated case does not include carbonate species or non-neutral pH, but Toner & Sletten (2013) showed the applicability of their *frezchem.dat* database to such cases.

Regarding validation of data added to *frezchem.dat*, methane gas solubilities at 0°C and 60°C, pressures 1–500 bar, and NaCl molalities 0–6 mol (kg H<sub>2</sub>O)<sup>-1</sup> are compared to those calculated by Duan et al. (1992) in Figures 2(a)–(b). Among the conditions investigated, the agreement is closest at 60°C and high NaCl molality, suggesting that solubilities computed with the present model are increasingly inaccurate at lower temperatures. The inaccuracy at 0°C is on the order of 25%–



Figure 2. (a)–(b) Validation of methane gas solubility model. Solid lines: model from PHREEQC's *pitzer.dat* database, reportedly fitted to experimental data at 25°C–100°C. Dotted lines show calculations of Duan et al. (1992). (c)–(d) Validation of methane hydrate solubility model. Black lines show the model from PHREEQC's *pitzer.dat* database, and gray lines depict the calculations of Tishchenko et al. (2005).

50%. Methane hydrate solubilities at 0°C and 5°C, pressures 1–500 bar, and pure or seawater compositions with 1× and 2× the typical Earth ocean salinity ( $\approx 0.6$  and 1.2 mol (kg H<sub>2</sub>O)<sup>-1</sup> of Na, respectively) are compared to those calculated by Tishchenko et al. (2005) in Figures 2(c)-(d). Our model underestimates the decrease in hydrate solubility with increasing salinity and pressure in a way that skews the boundary of the stability field of hydrates (where hydrate and gas solubilities are equal; see Figures 4–6 of Duan & Sun 2006) to pressures lower by a few bars for a given temperature or, equivalently, to temperatures higher by a few kelvin for a given pressure. Additionally, PHREEQC spuriously computes CH<sub>4</sub> molalities  $\approx 10\%$  too high in pure water and at pressures 45–55 bar (Figure 2(c)) in what appears to be a numerical artifact. Despite these obvious inaccuracies, the present model is sufficient to capture to first order the possible conversion of aqueous methane to gas and/or hydrate during freezing. We confirmed that the model accurately reproduces silica solubility data from which parameters for silica were derived by Appelo (2015) in concentrated solutions at various temperatures (Figures 2-5 of Azaroual et al. 1997; data from Marshall & Chen 1982).

# 2.2. Spatial Distribution of Crystallized Salts

The spatial distribution of crystallized salts depends on the initial shape of the intrusion and on the relative timescales of chemical and physical processes such as precipitation/dissolution, freezing, settling, and mixing. If freezing or settling are

faster than precipitation/dissolution, then crystallization is assumed to be fractional. Otherwise, crystallization is assumed to take place in chemical equilibrium (the formed salts can still take part in the chemical reactions by redissolving).

We consider freezing in a spherical chamber within an ice shell. Although analogies with subsurface magma intrusions on Earth suggest intrusions likely have one axis whose length differs significantly from the other two, as in spheroidal sills and laccoliths or cylindrical dikes (Schmidt et al. 2011; Michaut & Manga 2014; Manga & Michaut 2017), assuming a sphere is a simpler first step that provides general insight into the spatial distribution of formed salts.

Cooling of the fluid intrusion is driven by heat conduction through the surrounding ice shell, such that freezing is expected to begin at the chamber walls and proceed from the outside in. Temperature gradients in the ice shell across the range of depths spanned by the reservoir are neglected in this model, which can cause deviations from a spherical geometry resulting from changes in freezing rate with depth. This assumption is valid if the chamber height is small relative to the ice shell thickness.

In our approach, we make the simplifying assumption that the ice-brine interface remains sharp, as opposed to mushy (Vance et al. 2019; Buffo et al. 2020, 2021a, 2021b, 2022, 2023). This notably neglects the typical mechanism for the entrainment of salt in ice, which involves the trapping of brine pockets at the ice-brine interface. We conceptually consider two end-member freezing cases: a fast-freezing case and a slow freezing case (Figure 3). In the fast-freezing case



Figure 3. Possible end-member distributions of materials in a freezing spherical chamber. (a) Fast freezing during which newly formed salts are incorporated into the forming ice wall where they can no longer equilibrate with the central brine (fractional crystallization). (b) Slow freezing during which newly formed salts are excluded from the ice and remain well mixed with the chamber fluid (equilibrium crystallization). (c) As in panel (b), but with salts settling rather than remaining well mixed (fractional crystallization). The spurious stepping pattern is overemphasized to illustrate the discretization of the calculation in temperature steps (compare to Figure 7). Top row: partially frozen chamber with a temperature below the onset of freezing ( $T_{\text{freeze}}$ ). Bottom row: fully frozen chamber below the eutectic temperature  $T_{\text{eutectic}}$ .

(Thomas et al. 2019; Vu et al. 2020; Fox-Powell & Cousins 2021), we assume that salts (solid or solute) are trapped directly into the ice at the ice-brine interface at 100% efficiency. In the slow freezing case, we assume salts are perfectly rejected from the ice and either remain well mixed in the chamber (equilibrium crystallization) or stratified (fractional crystallization).

If freezing is fast relative to precipitation, salts forming in the peripheral regions of the intrusion are thus assumed to be incorporated in the thickening ice wall (Figure 3(a)). Otherwise, the forming solids are assumed to be fully rejected from the ice and either remain suspended in the chamber if settling is slow relative to the chamber mixing timescale (Figure 3(b)) or otherwise sink to the bottom due to their higher density relative to the solution (Figure 3(c)) (methane clathrates, less dense than the solution, would float to the top). Observations of iceliquid interface properties in marine environments on Earth suggest that these scenarios may all be at play in different locations of the same ice shell (Wolfenbarger et al. 2022a). Ultimately, we apply our salt distribution model to the slow freezing case only (Figures 3(b)-(c)), since, as detailed in Section 3.1.1, the effect of salt entrainment is to enrich the outer ice wall in non-ice solids, and therefore deplete the chamber's central impurity-rich region without otherwise

significantly affecting the compositional evolution of the freezing fluid.

In the case of Figure 3(c), if settling is fast relative to precipitation, the formed salts remain well mixed in the sediment layer formed at that temperature, and the sediment layer is compositionally stratified based on how equilibria change as a function of temperature, with the compositions resulting from the lowest-temperature equilibria at the top. If instead settling is slow relative to precipitation, then salts forming over a range of temperatures sink and eventually settle together, such that the sediment layer is instead stratified by salt density.

Below, we estimate the timescales for precipitation/dissolution, freezing, settling, and mixing. We then use these estimates to identify key variables (intrusion and salt grain sizes) and determine regimes of salt distribution in this parameter space (Figure 4).

# 2.2.1. Timescales of Physicochemical Processes

*Precipitation*. Precipitation rate data are difficult to obtain experimentally owing to metastable reaction products and nucleation effects (Palandri & Kharaka 2004). Accordingly, we follow Palandri & Kharaka (2004) in assuming microscopic reversibility to obtain the precipitation rate  $k_{prec} = k_{diss}/K_{eq}$ .



**Figure 4.** Grain and chamber size regimes leading to well mixed versus nomixing conditions in Figure 3 in the absence of significant convective mixing. If convective mixing occurs, the well-mixed case applies across the full range of realistic grain and intrusion sizes.

This relation requires that both the forward and backward reactions proceed by a single reversible mechanism.

Dissolution rates  $k_{diss}$ , in mol m<sup>-2</sup> s<sup>-1</sup>, are given by:

$$\frac{dn}{dt} = -SA k_{\rm diss} \times \exp\left[-\frac{E}{R}\left(\frac{1}{T} - \frac{1}{298.15 \,\rm K}\right)\right] (1 - \Omega^p)^q, \quad (2)$$

(Palandri & Kharaka 2004), where dn/dt is the change in molar abundance per unit time, *SA* is the surface area of mineral being dissolved, *E* is the activation energy, *R* is the gas constant (8.314 J mol<sup>-1</sup> K<sup>-1</sup>),  $\Omega$  is the ratio of the product of activities (*Q*) to the equilibrium constant  $K_{eq}$ , and generally *p* and *q* are equated to 1 short of sufficiently detailed experimental data sets. Among relevant salts, Palandri & Kharaka (2004) compiled rate parameters for NaCl (log  $k_{diss} = -0.21$  at 25°C, E = 7.4 kJ mol<sup>-1</sup>), anhydrite (log  $k_{diss} = -0.39$  at 25°C, E = 14.3 kJ mol<sup>-1</sup>), and gypsum (log  $k_{diss} = -2.79$  at 25°C, E = 0).

The resulting precipitation timescales are given by:  $t_{precipitation} = n/(k_{prec} SA) = n K_{eq}/(k_{diss} SA)$  where *n* is the number of moles. For cubic grains of length *r*,  $SA = 6r^2$  and the molar volume is  $V_m = r^3/n$ . Thus,

$$t_{\text{precipitation}} = rK_{eq}/(6V_m k_{diss}).$$
 (3)

We use the analytical expressions from the *llnl.dat* database of PHREEQC (see Neveu et al. 2017 for validation of these expressions against other thermodynamic databases) to infer  $K_{eq}$  at mild subzero temperatures. For NaCl, given log  $K_{eq} \approx 1.50$  at 0°C and  $\approx 1.56 (\pm 0.02)$  at 25°C, we infer log  $K_{eq} \approx 1.44$  at -20°C. For anhydrite, given log  $K_{eq} \approx -4.07$  at 0°C and  $\approx -4.35 (\pm 0.05)$  at 25°C, we infer log  $K_{eq} \approx -3.85$  at -20°C. For gypsum, given log  $K_{eq} \approx -4.51$  at 0°C and  $\approx -4.53 (\pm 0.05)$  at 25°C, we infer log  $K_{eq} \approx -4.50$  at -20°C. For grain sizes  $r = 1 \mu m$ , the lower bounds (i.e., for  $\Omega = 0$ ) on

precipitation timescales range between a few microseconds for anhydrite and  $\approx 0.5\,s$  for NaCl.

*Freezing*. We approximate an order-of-magnitude freezing timescale by roughly discretizing the equation of heat transport by conduction:

$$t_{freezing} \sim (C_p \Delta T + L) \left(\frac{k}{\rho} \frac{\Delta T}{R \Delta r}\right)^{-1}$$
 (4)

where k = 567/T W m<sup>-1</sup> K<sup>-1</sup> (Klinger 1980) is the thermal conductivity of water ice,  $\rho \approx 918$  kg m<sup>-3</sup> is its density (here assumed constant with *T* and *P* for simplicity),  $C_p \approx$ 7.73 *T* J kg<sup>-1</sup> K<sup>-1</sup> (Desch et al. 2009) is its heat capacity, and L = 334 kJ kg<sup>-1</sup> is the enthalpy of freezing for water. Approximating the temperature gradient length scale  $\Delta r$  as the chamber radius *R*, and for  $\Delta T \sim 100$  K (the difference between intrusion and background ice shell temperatures, assumed close to the freezing temperature),

$$t_{freezing} \sim 10^4 \left(\frac{\Delta r}{1 \text{ km}}\right)^2 \text{ years.}$$
 (5)

Although this expression ignores the roughly linear decrease in  $\Delta r$  over time, this timescale is comparable to the computed  $\sim 10^6$  yr needed to freeze a 10 km scale chamber in detailed simulations (Hesse & Castillo-Rogez 2019). It is also within the range of freezing times ( $10^3-10^5$  yr) computed by Michaut & Manga (2014) and Chivers et al. (2021) for kilometer-scale spheroidal intrusions.

Settling. For a spherical grain, the Stokes flow settling velocity is given by  $v = 2/9 \ \Delta \rho_{grain-sol} g r^2/\mu$ , where  $\Delta \rho_{grain-sol}$  is the density difference between the salt and the solution, g is the gravitational acceleration, and  $\mu \sim 10^{-1}$  Pa s is the solution viscosity (Cox & Weeks 1975; Collins & Deming 2011; Quick et al. 2022). Salt densities are on the order of 1.5 kg m<sup>-3</sup> (see Table 3). For  $\Delta \rho_{grain-sol} \approx 500$  kg m<sup>-3</sup>, g = 1 m s<sup>-2</sup> (the gravity at Europa's surface), and  $r = 10^{-6}$  m, settling velocities are on the order of 1 nm s<sup>-1</sup>, such that settling takes:

$$t_{\text{settling}} = \frac{\Delta r}{v} = \frac{9}{2} \frac{\Delta r \,\mu}{\Delta \rho_{\text{grain-sol}} \,g \,r^2}$$
$$t_{\text{settling}} \sim 10^4 \,\text{yr} \left(\frac{1 \,\mu\text{m}}{r}\right)^2 \frac{\Delta r}{1 \,\text{km}} \,. \tag{6}$$

This is consistent with measured sinking velocities on the order of kilometers per day for millimeter-sized gypsum grains (Wollenburg et al. 2020).

Convective mixing. Mixing by convection induced by gradients in fluid density due to heterogeneities in temperature or composition (salinity) could offset salt settling for larger grains. A nonzero density gradient requires the intrusion to be large enough for there to be a vertical temperature gradient in the ice shell along its vertical dimension to induce differences in fluid temperature and salinity. The convection velocity is  $u \sim \Delta \rho ~ (\Delta r)^2 ~ g/\mu$ . For a seawater composition, density variations between -20°C and 5°C and 0–100 ppt salinity are largely driven by salinity (e.g., Fofonoff 1985), reaching a maximum  $\Delta \rho = 100 \text{ kg m}^{-3}$  across this range. The convective

mixing timescale is thus:

$$t_{conv\ mix} = \Delta r/u = \mu/(\Delta\rho\ \Delta r\ g)$$
  
$$t_{conv\ mix} \sim 10^{-6} \ s \ \frac{100 \ kg \ m^{-3}}{\Delta\rho} \frac{1 \ km}{\Delta r}.$$
 (7)

#### 2.2.2. Regimes of Salt Distribution

Settling and convective mixing timescales are equal for grain sizes  $r = (9/2 \ \Delta \rho / \Delta \rho_{grain-sol})^{1/2} \ \Delta r$ . Whole-reservoir convective mixing is efficient even for small density differences  $(\Delta \rho = 1 \text{ kg m}^{-3})$ , so if it occurs, there should be no settling unless grains are  $\ge 10\%$  of the chamber size  $\Delta r$ . On the other hand, chamber walls are isothermal at the freezing temperature, so there should not be a temperature gradient across it. Any temperature gradient in the surrounding ice shell would instead be reflected in a vertical flattening of the chamber shape due to preferential freezing of the colder areas (Michaut & Manga 2014). Brine rejected from ice walls should thus have approximately the same composition (density) as the rest of the intrusion, so whole-reservoir convection may not develop.

Freezing becomes the limiting factor for a lack of settling in the chamber if there is no convection. Settling and freezing have comparable timescales for  $r \sim 3 \times 10^{-5} \Delta r^{-1/2}$ , so for a kilometer-scale chamber, settling occurs only if grains are larger than  $\sim 1 \mu m$  (Figure 4). If so, case (c) of Figure 3 applies; if not, it is case (b) that applies according to the degree of brine entrapment (Section 4.2).

Precipitation is faster than settling for grain sizes  $\leq 1 \text{ cm}$ , although this upper bound depends sensitively on grain composition. These sizes encompass the 1–100  $\mu$ m salt grains observed in sea ice (Sinha 1977) and sea salt aerosols (e.g., Yang et al. 2008). Grains larger than 100  $\mu$ m can result from sublimation of ice with salinity >3.5% or temperature  $> -20^{\circ}C$ (Závacká et al. 2022) or evaporation of water in hypersaline lakes (e.g., Warren 1982). For millimeter-sized gypsum grains at subzero degrees Celsius temperatures, settling has been observed to compete with precipitation (Wollenburg et al. 2020). However, because non-ice solid densities are similar within a factor of 2 (see Table 3), non-ice solids are more likely to become stratified by temperature of formation than by density, irrespective of the relative timescales of precipitation and settling. Thus, the assumption we carry forward for poorly mixed chambers is that of stratification by temperature of formation.

# 2.2.3. Quantification of Salt Distribution in a Spherical Chamber

We assume that the chamber starts at the temperature at which ice first forms, because the intruding liquid is assumed to be sourced from the ice shell-ocean interface, which is at the freezing point. If the chamber is not sealed (i.e., remains connected to the underlying ocean), any non-ice solids formed sink back into the ocean. It is assumed that the intruding liquid remains well mixed with ocean water (e.g., fluid velocities of 1 m s<sup>-1</sup> postulated for Enceladus; Kite & Rubin 2016). The liquid composition is thus assumed to remain constant until the onset of freezing. Should a chamber arise instead from local melting of the ice shell due, e.g., to a rising warm plume (Schmidt et al. 2011) or tidal dissipation in the shell (Vilella et al. 2020), the assumption of a start at the freezing temperature holds, but the initial composition is presumably that of the local ice shell material.

Given our assumptions of an isothermal chamber losing heat by conduction through its walls, ice is assumed to form along the walls in a layer of uniform thickness. Initially, freezing may be fast enough for significant salt entrapment to occur (Figure 3(a)). The chamber remains spherical, and the spatial distribution of solids can be described by a single parameter, the ratio of the radius  $R_2$  of the central liquid pocket to the radius  $R_1$  that the chamber had prior to any freezing (Figure 3(a)). This ratio decreases with decreasing temperature.

As the chamber cools further, the fraction of forming salt that is trapped in the ice wall becomes < 10% (see Section 4.2) and is neglected here given our assumption of a sharp ice–liquid interface (Section 2.2). If the chamber is well mixed (either because convective mixing is faster than settling or because the chamber fully freezes before solids settle), the spatial distribution of solids can still be described by  $R_2/R_1$ , with pure ice outside  $R_2$  and a mixture of residual brine and non-ice solids within it (Figure 3(b)).

If the chamber is poorly mixed (Figure 3(c)), salts settle to the bottom, likely in the order in which they crystallize due to small density differences across salts (Section 2.2.2). The incremental height h of the volume  $V_{\text{sediment}}$  of sediment precipitated and settled at the bottom during a temperature step is the height of a spherical segment, obtained by solving:

$$V_{sediment} = [(R_2^2 - b^2)h + bh^2 - h^3/3]\pi$$
(8)

where  $V_{sediment} = \sum_{i=1}^{N} n_i V_{m,i}$  is the sum of the products of moles  $n_i$  of the *N* newly precipitated salts (computed with PHREEQC) by their respective molar volumes  $V_{m,i}$ , and *b* is the distance between the chamber center and the top of the salt deposit. Assuming for now that the deposit is entirely made of salt,  $b = R_1 - H$  with *H* the cumulative height of the salt deposit.

In addition to salts, ice forms at each temperature step and is assumed, as above, to crystallize along the walls in a layer of uniform thickness. However, it is assumed that no ice forms where salt settles at a given temperature step; i.e., salt displaces the location of ice crystallization. This allows us to compute the spatial distribution end member with the least mixing between ice and salts. The radius  $R_2$  of the residual brine pocket is thus obtained from:

$$\frac{V_{solution}}{\pi} - \frac{2R_2^3}{3} + (R_2^2 + R_1H)(H - R_1) + \frac{R_1^3 - H^3}{3} = 0$$
(9)

If the volume of salt formed during a temperature step is small enough, and the volume of ice is high enough, ice may fully cover the salt deposited at the previous time step. Numerically, Equations (8) and (9) can still be used with the variables defined as above (e.g., H as the sum of h values for all previous steps) if  $R_1$  and  $R_2$  are reset to the  $R_2$  value of the previous temperature step. That is, the chamber is returned to its initial spherical shape, except with a new initial radius set to the smaller radius of the brine pocket at the current temperature. This is illustrated in Figure 3(c) where  $R_1$  is shown as the radius of the chamber at the step of first non-ice solid formation.

For all three cases of Figure 3, the calculation of spatial distribution is independent of the initial chamber size as long as parameters are ratioed to  $R_1$ . We have implemented the scale-independent calculation of solution and solid compositions,

 $R_2/R_1$ , and (for Figure 3(c))  $h/R_1$  in two freely available numerical routines (see Acknowledgments). The first is a spreadsheet implementation, which can be used on any operating system, but requires copy-paste import of a PHREEOC selected output, manual identification of the formed salts, and separate solving of the cubic Equations (8) and (9) (for which we coded a binary search algorithm using the free software SciLab). This spreadsheet implementation does not handle the occasional case of ice fully covering the salt deposited at the previous time step. The second is a C language implementation called *IceShellXtal* that automatically executes PHREEQC as a subroutine at each temperature step (foregoing use of the above-mentioned BASIC language temperature loop in the PHREEQC input; Section 2.1.2). IceShellXtal then carries out the spatial distribution calculations by solving first Equation (8), then Equation (9) at each temperature step. Finally, *IceShellXtal* graphically displays the resulting spatial distribution of ice, individual non-ice solids, and residual brine. This implementation was used to make Figures 5 and 7 below. Regardless of the chosen implementation, PHREEQC input file templates and thermodynamic databases modified from those of Toner & Sletten (2013) and Toner & Catling (2017b) are provided along with the code.

# 3. Results

# 3.1. Crystallization of Europa Ocean End-member Compositions

We simulate solid compositions resulting from freezing of end-member compositions for Europa's ocean obtained by Melwani Daswani et al. (2021) and summarized in Table 2. Melwani Daswani et al. (2021) simulated the devolatilization of the underlying rocky (mainly silicate) core, driving expulsion of water with a composition resulting from fluid-rock chemical equilibrium at each core depth. Their final ocean compositions were obtained by aggregating and mixing liquid expelled from all core depths.

Melwani Daswani et al. (2021) named these end members based on the starting core composition: "EM-CM" for a core with the elemental composition of CM carbonaceous chondrites, "EM-CI" with that of CI chondrites, and "MC-Scale" as resulting from accretion of material from weighed randomized heliocentric distances and corresponding compositions. We also consider two compositions from their Supporting Information: "EM CI FMQ-2" with the elemental composition of EM-CI but with the oxygen fugacity set two log units below the fayalite-magnetite-quartz mineral buffer (which roughly represents the redox state of the upper mantle on present-day Earth), and "MC-Scale+comet" with the composition of MC-Scale plus cometary amounts of volatiles such as carbon. For this last composition, silica was supersaturated, so for these freezing calculations we used its solubility as its initial concentration.

The EM-CM, EM-CI, and MC-Scale scenarios are investigated with both the Toner & Sletten (2013, "TS13") and Toner & Catling (2017b, "TC17") PHREEQC databases, whereas the EM-CI FMQ-2 and MC-Scale+comet cases are only run with the TS13 database due to their high initial dissolved silica content (silica is absent from TC17 data). We aggregated the detailed compositional information from Melwani Daswani et al. (2021) into total elemental concentrations (molalities), which is how PHREEQC input solution compositions are specified. These elemental molalities are re-speciated by

PHREEQC into the relevant species included in the TS13 and TC17 databases. This step resulted in neglecting abundances of elements Fe and Al, not included in these databases, and redox information beyond relative oxidized carbon versus inert methane abundances (namely, sulfide abundances). Abundances of Fe and Al were negligible (below  $10^{-7}$  M where M denotes mol per kg of H<sub>2</sub>O) in all cases owing to their general insolubility at the conditions simulated by Melwani Daswani et al. (2021). Sulfide too was generally negligible (below  $10^{-4}$  M) except in the reducing EM CI FMQ-2 case, where its molality was  $4.4 \times 10^{-2}$  M; as such, the PHREEQC input for this case, which neglects sulfide, does not accurately reflect the EM-CI FMQ-2 composition. Nitrogen species were not considered either by Melwani Daswani et al. (2021) or in this work owing to their current lack of implementation in PHREEOC.

The starting compositions of Melwani Daswani et al. (2021) are relatively insensitive to pressure. We opt to select compositions and set the PHREEQC simulation pressure to 100 bar, which corresponds roughly to a 7.5 km depth on Europa. This is within Europa's  $\sim$ 25 km thick ice shell (Howell 2021), provides an upper bound for the 1–5 km depths of intrusions inferred for Europa's ice shell (Schmidt et al. 2011; Manga & Michaut 2017), and is within the range of pressures for which the PHREEQC model is benchmarked against prior work (Section 2).

#### 3.1.1. Equilibrium Crystallization Simulations

Results of equilibrium crystallization simulations, assumed to pertain to slow freezing in a well-mixed chamber, are shown in Table 2 (central spherical pocket composition) and Figure 5 (composition as a function of temperature). The ice is assumed to form along the chamber walls in a uniformly thick layer, whereas the crystallized salts are assumed to remain in the central briny pocket and can continue to participate in chemical reactions. Initial fast freezing, which would partially trap salt in ice, is ignored here but can be inferred from redistribution of the salts formed early in fractional simulations (see Figure 7 below) along the outer chamber wall. Since the compositional evolution of the solutions due to fractional crystallization (Section 3.1.2) is quite similar to that due to equilibrium crystallization as described below, we do not expect fast freezing to significantly affect the compositional evolution of chambers for the end-member solutions simulated here. Rather, we only expect a slight enrichment of the outer ice wall (and, therefore, depletion of the chamber's central impurity-rich region) in the first non-ice solids to precipitate.

A constant chamber size is assumed once salts start to precipitate; actual volume variations are on the order of a few percent due to the changes in molar volumes (densities) between liquid (largely water, but also solutes) and solids (largely water ice). Simulations tend to proceed to temperatures where there remain only a few percent (<12%) of the initial solution mass, corresponding to the central pocket having <50% of the initial chamber radius. The exception to this is the case EM-CI FMQ-2, for which 60% of the solution remains at the end of the simulation.

Unlike the benchmark simulation of freezing of the pHneutral solution of Marion et al. (2005; see Figure 1), most simulations in this section were interrupted before reaching the eutectic temperature, except for the "MC-Scale" case using the



**Figure 5.** Fluid physicochemical properties and amounts of solids formed in equilibrium crystallization simulations as a function of decreasing temperature. In solution plots, the ordinate axis represents the quantities shown in the legend (various units; total element abundances in mol (kg  $H_2O$ )<sup>-1</sup>). In solid abundance plots, the ordinate axis represents solution volume in L or solid volumes in cm<sup>3</sup> for a starting mass of water of 1 kg. Except for the {MC-Scale, TC17} case, simulations stopped before the eutectic temperature was reached due to a lack of convergence of PHREEQC calculations at low temperatures (see the text for details). Conductivity does not always monotonically increase with decreasing temperature, likely due to the changing relative proportions of singly and doubly charged ions.

Table 2

Compositional Makeup of Spherical Intrusions with End-member Compositions at 273 K from Melwani Daswani et al. (2021; columns) under the "Well-mixed" Assumption, from Equilibrium Simulations Using Either the PHREEQC Thermodynamic Database of Toner & Sletten (2013, "TS13") or That of Toner & Catling (2017b, "TC17")

Europa Ocean Compositional End-member	EM-CM		EM-CI		MC-Scale		EM-CI FMQ-2	MC-Scale+comet
PHREEQC Database	TS13	TC17	TS13	TC17	TS13	TC17	TS13	TS13
	]	Initial concentrations	s (molalities in mol (kg	H <sub>2</sub> O) <sup>-1</sup> ; Melwani Da	swani et al. 2021)			
pH <sup>a</sup>	6.05	N/A	5.93	N/A	6.89	N/A	13.34	12.81
Na <sub>(aq)</sub>	$9.19 \times 10^{-2}$		$3.05 \times 10^{-2}$		$1.37 \times 10^{-1}$		3.18	$5.59 \times 10^{-1}$
Mg <sub>(aq)</sub>	2.83 ×	$2.83 \times 10^{-2}$		$5.17 \times 10^{-3}$		$8.75   imes  10^{-4}$		$2.65 \times 10^{-11}$ b
K <sub>(aq)</sub>	5.85 ×	$10^{-3}$	$2.64 \times 10^{-3}$		$6.89 \times 10^{-3}$		$9.19  imes 10^{-2}$	$1.62 \times 10^{-2}$
Ca <sub>(aq)</sub>	$2.76 \times 10^{-3}$		$1.78 \times 10^{-2}$		$3.26 \times 10^{-3}$		$1.42 \times 10^{-7 b}$	$3.02  imes 10^{-6}$
$H_2SO_{4(aq)} + HSO_{(aq)}^{-} + SO_{(aq)}^{2-}$	$4.47 \times 10^{-2}$	$9.51 \times 10^{-2}$	$1.46 \times 10^{-2}$	$4.93 \times 10^{-2}$	$2.25 \times 10^{-2}$	$4.95\times10^{-2}$	$9.16 \times 10^{-16 \ b}$	$6.19 \times 10^{-12}$ b
Cl <sub>(aq)</sub>	2.00 ×	$10^{-2}$	1.52 ×	$10^{-2}$	8.03 ×	10 <sup>-2</sup>	$4.11 \times 10^{-2}$	$4.07\times 10^{-2}$
$CO_{2(aq)} + HCO^{-}_{(aq)} + CO^{2-}_{(aq)}$	$5.04  imes 10^{-2}$	None	$3.47 \times 10^{-2}$	None	$2.70 \times 10^{-2}$	None	$1.50 \times 10^{-8}$	$1.51 \times 10^{-2}$
Si <sub>(aq)</sub>	$2.86\times10^{-5}$	None	$9.44 \times 10^{-9 \ b}$	None	$2.91\times10^{-7}$	None	3.12	$4.89  imes 10^{-1}$
CH <sub>4(aq)</sub>	$5.27 \times 10^{-12 \ b}$	None	$3.71 \times 10^{-12 \ b}$	None	$4.45 \times 10^{-11}$	None	$9.92 \times 10^{-4}$	$1.10 \times 10^{-3}$
Lowest temperature simulated (K)	269.15	248.80	268.23	264.95	258.99	230.90	259.35	259.15
Central pocket radial fraction	0.396	0.269	0.297	0.269	0.314	0.242	0.843	0.480
			Composition of centra	l pocket (vol.%)				
Residual briny solution	93.1	28.4	96.3	82.7	82.6	10.2	98.6	98.5
Amorphous silica (SiO <sub>2</sub> )	None	None	None	None	None	None	1.4	1.5
Gypsum (CaSO <sub>4</sub> •2H <sub>2</sub> O)	None	0.84	1.8	6.7	None	0.19	None	None
Meridianiite (MgSO <sub>4</sub> •11H <sub>2</sub> O)	None	23.8	None	None	None	1.3	None	None
Mirabilite (Na <sub>2</sub> SO <sub>4</sub> •10H <sub>2</sub> O)	5.9	44.9	None	10.5	14.2	64.8	None	None
Picromerite (K <sub>2</sub> SO <sub>4</sub> •MgSO <sub>4</sub> •6H <sub>2</sub> O)	None	2.0	None	None	None	None	None	None
Calcite (CaCO <sub>3</sub> )	None	None	1.0	None	None	None	None	None
Dolomite (CaMg(CO <sub>3</sub> ) <sub>2</sub> )	0.21	None	0.89	None	None	None	None	None
Magnesite (MgCO <sub>3</sub> )	0.71	None	None	None	None	None	None	None
Ikaite (CaCO <sub>3</sub> •6H <sub>2</sub> O)	None	None	None	None	1.0	None	None	None
Nahcolite (NaHCO <sub>3</sub> )	None	None	None	None	2.1	None	None	None
Hydrohalite (NaCl•2H <sub>2</sub> O)	None <sup>c</sup>	None <sup>c</sup>	None <sup>c</sup>	None <sup>c</sup>	None <sup>c</sup>	21.7	None <sup>c</sup>	None <sup>c</sup>
Sylvite (KCl)	None <sup>c</sup>	None <sup>c</sup>	None <sup>c</sup>	None <sup>c</sup>	None <sup>c</sup>	1.8	None <sup>c</sup>	None <sup>c</sup>

Notes. Intrusions are all assumed to comprise a pure ice rim (spherical shell) enclosing a central pocket composed of the rejected precipitated solids and residual briny solution.

<sup>a</sup> Value of pH obtained by Melwani Daswani et al. (2021). The pH computed by PHREEQC tends to differ by a few tenths of units from this value at 273.15 K and match it instead a few kelvin below. <sup>b</sup> Neglected in the PHREEQC calculation due to low abundance and in order to facilitate convergence. <sup>c</sup> Simulation final temperature above temperature of formation. N/A: Not applicable.

TC17 database. This is due to limitations of the PHREEQC software, which below a certain temperature (different for each simulation) could not converge toward compositions satisfying mass balance and chemical activity ratios consistent with temperature-dependent thermodynamic equilibrium constants. All simulations proceeded to lower temperatures when adding a neutral inert species whose initial concentration is lower than all other solutes, as well as by decreasing the numerical solver's step size and increasing its number of iterations (J. Toner, private communication; Parkhurst & Appelo 2013; see Section 2.1.2). Excluding chemical elements with low initial abundance from simulations (Table 2) also helped by shrinking the system of equations to be solved. Successful attempts were made at restarting equilibrium simulations at temperatures lower than those of interruption. The lowest temperatures simulated shown in Table 2 and Figure 7 are those below which none of the above workarounds helped simulations proceed any further.

The solids formed include amorphous silica; Ca-, Mg-, and Na-sulfates (respectively, gypsum, meridianiite, and mirabilite) and -carbonates (respectively, calcite and ikaite, dolomite and magnesite, and nahcolite); and sodium and potassium chloride. Potassium does not seem to form sulfates (except picromerite in one case) or carbonates. Calcium and magnesium do not seem to form chlorides, although this could occur at temperatures lower than those simulated.

Initial carbonate-to-sulfate ratios are on the order of 1 across the EM-CI, EM-CM, and MC-Scale compositions (Table 2). In this context, sodium carbonate (nahcolite) seems to form only if sodium is initially much more abundant than calcium and magnesium (MC-Scale case; Na:Ca ratio of 42; no sodium carbonate in the other cases where min(Na:Mg, Na:Ca) < 4). Instead, Na readily combines with sulfate to form mirabilite (Table 2). Ca and Mg preferentially form carbonates; Casulfate (gypsum) is scarce even if Ca dominates the solution composition along with Na, SO<sub>4</sub>, and CO<sub>3</sub> (EM-CI case), and Mg-sulfate (meridianiite) forms only in carbonate-free simulations with the TC17 database. Thus, in these silica-poor fluids, the divalent cations Ca and Mg appear to preferentially bind to divalent anions (sulfate and carbonate), presumably leaving monovalent cations Na and K (and, at the lowest temperatures, H; see Section 3.2) to combine with monovalent Cl (and, at the lowest temperatures, OH).

For the silica-rich, high-pH fluid end members EM-CM FMQ-2 and MC-Scale+comet, there is comparatively little freezing and abundant amorphous silica forms at the exclusion of salts. Further insight into the salts that would form as temperatures keep decreasing could not be obtained from the simulations, interrupted around 260 K. However, the Na-rich, sulfate-free solution compositions at 260 K suggest the potential for forming mole-percent level, relative to silica, of NaCl and/or KCl and (for the MC-Scale+comet case) Na- or K- carbonate(s), with a high excess of sodium and (for the EM-CM FMQ-2 case) excess potassium forming NaOH and KOH at the lowest temperatures (see Section 3.2) at molar abundances similar to silica. Since NaOH, KOH, and amorphous silica have similar molar volumes (18.8, 27.5, and 27.5-29 cm<sup>3</sup> mol<sup>-1</sup>, respectively), the volume ratio of hydroxide salts to silica is also expected to be close to 1 in fully frozen intrusions.



**Figure 6.** Generic properties of salt intrusion resulting from freezing of a putative spherical chamber of salty ocean water within an ice shell, as suggested by the simulation results shown in Figure 7. The color-coding of solids is similar to that of Figure 7.

#### 3.1.2. Fractional Crystallization Simulations

In fractional crystallization simulations, the non-ice solids are assumed to settle as in Figure 3(c). The aspect (width-toheight) ratio of the salt layer reflects the relative degrees of non-ice solid versus ice formation as a function of temperature. For each non-ice solid type, the largest volume formed at a given temperature step tends to occur at the temperature of the onset of precipitation. As the brine cools, the extent of salt formation decreases relative to that of freezing and the accumulating salt deposit grows narrower. This tends to make salt deposits in the shape of stacked hourglasses (Figure 6). Extrapolation of these results suggests that for an oblate spheroid chamber, a more realistic intrusion shape (Michaut & Manga 2014; Chivers et al. 2021), the general shape of salt deposits might remain the same, albeit with an aspect ratio changed to an extent roughly proportional to the spheroid's axis ratio.

The non-ice solid precipitation sequence tends to be silica, followed by carbonates and/or sulfates, with chlorides forming last owing to their high solubility and ability to keep brine liquid at low temperatures. The volume of these solids relative to chamber volume tends to be higher for initially more concentrated solutions. When substituting sulfate for carbonate (TC17 runs), because sulfate dissociates much more readily than carbonate (carbonic acid being weaker than sulfuric acid), the pH of the solution is much lower.

Results of fractional crystallization simulations, run with a -0.05 K temperature step from the temperature at which ice first forms, are shown in Figure 7. We checked that this temperature step ensures numerical convergence. Prior to ice formation, any formed salt is assumed to drain back to the ocean. Generally these simulations proceed to a temperature similar to the final temperature of equilibrium crystallization simulations, and the solids formed are qualitatively the same, except that meridianiite does not form in the MC-Scale case simulated with the TC17 database. As for equilibrium



**Figure 7.** Compositional makeup of spherical intrusions with end-member compositions at 273 K from Melwani Daswani et al. (2021; rows) under the "no-mixing" assumption, simulated using either the PHREEQC thermodynamic database of Toner & Sletten (2013) or that of Toner & Catling (2017b; columns). The spatial distribution of ice and salts within the chamber is shown at the temperature at which the simulation stopped (indicated near the chamber center), which is higher than the eutectic temperature. Where more than one salt co-precipitates, volume proportions of each salt are shown as the corresponding fraction of the width of the salt layer. The ice is colored from cyan to white to gray, depending on its crystallization temperature. The space occupied by the remaining fluid is shown in blue. Fluid physicochemical properties as a function of decreasing temperature are shown to the left of each chamber (the volume corresponds to a starting mass of water of 1 kg). Kinks in these curves correspond to the onset of the precipitation of solids. Except for the {MC-Scale, TC17} case, simulations stopped before the eutectic temperature was reached due to a lack of convergence of PHREEQC calculations at low temperatures (see the text for details).

simulations, a constant chamber size is assumed once salts start to precipitate; actual volume variations are on the order of a few percent. Interestingly, the case where freezing progress is the most limited (EM-CI FMQ-2) is also the one for which the highest volumetric proportion of non-ice solids form.

# 3.2. Extrapolating to the Eutectic: The Effect of Nonneutral pH

Compositions of salts formed at colder conditions might be extrapolated from the compositions of solutions obtained at the lowermost simulated temperatures, with significant caveats. First, such extrapolations pertain only to the final, fully solidified state; they cannot provide compositions at a variety of temperatures at which solids and brine still coexist. Second, the salts formed have to be guessed from a shortlist compatible with what is left in solution. Despite inevitable inaccuracies inherent in this exercise, we illustrate its value through the following example (MC-Scale/TS13 database, equilibrium crystallization).

At the lowest temperature simulated, 259 K, the solution (24.00 g of water left of the initial 1 kg, pH 6.58, electrically neutral) contains 29 mM Ca, 37 mM Mg, 3.35 M Na, 0.29 M K, 3.36 M Cl, 0.10 M SO<sub>4</sub>, 0.32 M CO<sub>3</sub>, and negligible amounts of Si and CH<sub>4</sub>. Some mirabilite (Na<sub>2</sub>SO<sub>4</sub>•10H<sub>2</sub>O), nahcolite (NaHCO<sub>3</sub>), and ikaite (CaCO<sub>3</sub>•6H<sub>2</sub>O) have previously formed. Let us assume that the solutes able to form these minerals continue to form them as the temperature keeps decreasing. With this assumption, once everything is solid, an additional 2.4 mmol of mirabilite will have formed. This zeros out dissolved sulfate and stoichiometrically removes twice as much sodium from solution, decreasing its dissolved amount from 80.4 to 75.6 mmol. Since mirabilite is a decahydrate, the mass of liquid water (18 g mol<sup>-1</sup>) removed is 0.43 g. Below the eutectic temperature and with the above assumption, all calcium is precipitated as ikaite. This decreases the amount of dissolved carbonate from 7.7 to 7.0 mmol. Ikaite is a hexahydrate, so 0.075 g of water is removed from solution. The rest of the carbonate could precipitate as nahcolite, removing another 7.0 mmol of sodium from solution (68.6 mmol left) and the same amount of H<sup>+</sup>, but for the sake of not affecting pH (yet) let us assume that natron (Na<sub>2</sub>CO<sub>3</sub>•10H<sub>2</sub>O) forms instead, which removes 14.0 mmol of sodium and 70 mmol of water. Left in solution are Mg, Na, K, and Cl, which must precipitate as MgCl<sub>2</sub>, NaCl, and KCl or, more likely, their hydrates (e.g., hydrohalite NaCl•2H2O). This leaves an excess of 10 mmol of Cl, which must combine with the only cation left, H<sup>+</sup>. H<sup>+</sup> ions are available in exactly matching amounts because the solution and all formed solids are electrically neutral (the pH of neutrality increases above 7 with decreasing temperature, so the pH 6.58 solution is quite acidic). HCl or its tri- or hexahydrate are formed (Marion 2002), and the rest of the water (roughly 20 g) freezes as ice.

The above exercise illustrates the role of  $H^+$  or  $OH^-$  (depending on pH relative to its temperature-dependent neutrality value) in forming salts. To our knowledge, the effect of H- or OH-bearing solids such as HCl, H<sub>2</sub>SO<sub>4</sub>, KOH, and NaOH in depressing the freezing point of brines has not been extensively discussed in the context of planetary environments. The eutectic temperatures of binary mixtures of these solids with water are, respectively,  $\leq 200$  K (Marion 2002), 211 K (Linke 1965; Marion 2002), 230 K (Pickering 1893), and 241 K (Pickering 1893). In contrast, Ca- and Mg-hydroxides

are poorly soluble in water, conferring them negligible antifreeze capability (Guthrie 1878; Lambert et al. 1992). In any freezing non-pH-neutral solution of the chemical systems investigated here, one of HCl,  $H_2SO_4$ , KOH, or NaOH is likely the last non-ice solid to form. Thus, small amounts of briny liquid could persist down to 200–210 K in solutions of even mild acidity, as in the example above.

# 4. Discussion

# 4.1. Applications to Cylindrical Crack and Global-scale Ocean Freezing

The case of solid partitioning in an open fracture in an ice shell is a simplification of the spherical chamber case in that the crack is still communicating with the ocean; i.e., only a single temperature corresponding to the onset of ice formation needs to be considered. In the crack, we assume that mixing is faster than freezing, such that liquid has a constant composition and onset-of-ice-formation temperature. For the above fluid velocity estimate of 1 m s<sup>-1</sup> (Section 2.2.3), this assumption of constantly mixed fluid requires freezing to take place more slowly than  $\sim(100 \text{ km}/[1 \text{ m s}^{-1}]) \approx 1 \text{ day}$ . For simple cylindrical or parallel vertical plane shapes, the distribution of salts is independent of crack height.

For 100% salt entrapment (fast-freezing end member), for a fluid with the starting composition of Marion et al. (2005; see Figure 1), the solid wall composition is 67 vol.% ice, 26 vol.% meridianiite, 6 vol.% mirabilite, and 0.1 vol.% gypsum (the same composition as for the outermost layer of a fast-freezing spherical chamber). If no salt is trapped, the thickening wall is pure water ice and any salts formed are rejected. Unlike in a chamber, the salty water drains into the ocean below and the fluid is maintained at the ocean composition and salinity. Intermediate cases have been investigated in more physical detail by Buffo et al. (2020), and for NaCl- or MgSO<sub>4</sub>-bearing fluid by Buffo et al. (2023). In the latter study, partial brine entrapment and rejection leads to finer-scale, complex compositional structure that is not captured by our analysis, with chemical zonation patterns reminiscent of metallurgic analogs (Buffo et al. 2023).

The case of a global ocean freezing is similar to that of a spherical chamber in terms of compositional evolution. If the ocean is well mixed, the non-ice solids are distributed throughout the liquid similarly to the well-mixed chamber case, with the exception of the presence of a rocky core surrounded by the ocean. The 1-10 S m<sup>-1</sup> conductivities of the partially frozen solutions considered here (Figures 5 and 7) suggest that global partially frozen oceans with these compositions would be detectable with existing remote magnetometry sensing at, e.g., the moons of ice giants (Cochrane et al. 2021, 2022; Castillo-Rogez et al. 2023), even without considering additional contributions to solution conductivities from nitrogen-bearing species (Castillo-Rogez et al. 2022).

If mixing is much slower than settling, the non-ice solids could settle into a global layer surrounding the core at the base of the ocean. Based on the X = 0.3-11 vol.% solid volume fractions of non-ice solids resulting from our simulations (with 88%-98% of the initial solution volume having frozen, except for 40% in the case EM-CI FMQ-2), we estimate global non-

ice solid layer thicknesses  $d_{salt}$  as:

$$d_{salt} = [X(R_p^3 - R_{shell}^3) + R_c^3]^{1/3} - R_c$$
(10)

where  $R_p$  is the icy world's outer radius,  $R_c$  is the radius of its core, and  $R_{shell}$  is the radius at the base of its ice shell. We set  $R_c = R_p/1.2$  for a body with density  $\approx 2000 \text{ kg m}^{-3}$  (about half-water, half-rock by volume), and adjust  $R_{shell} > R_c + d_{salt}$  to match the volume fractions of residual solution in Table 2. The resulting non-ice solid layer thicknesses are  $d_{salt} = [0.03\%-0.8\%]R_p$ , i.e., on the order of a few kilometers.

The direct application of Section 3 results to the case of a global ocean is limited by two factors. First, even a vigorously convecting ocean is not isothermal, with adiabatic gradients resulting in temperature contrasts on the order of a few kelvin across the convective layer due to heat transfer from the radioactive core and into the overlying ice (e.g., Bire et al. 2022). Second, although thick oceans are expected to be efficiently mixed (Soderlund et al. 2014), heterogeneities in temperature and composition with depth (stratification) and/or latitude may arise due to, e.g., the icy world's spin (Zhu et al. 2017; Soderlund 2019; Zeng & Jansen 2021), latitudinal variations in ice shell thickness and distribution of tidal dissipation (Kang et al. 2022a, 2022b), and competing effects of temperature and salinity on density, which result in doublediffusive convection (Vance & Brown 2005; Travis et al. 2012; Wong et al. 2022).

### 4.2. Implications of Neglecting Brine Entrapment in Ice

Brine entrapment may occur to an extent that depends on freezing rate (Cox & Weeks 1988), and therefore especially in the early freezing stages when the cooling rate is highest due to the high temperature contrast between the new warm intrusion into the colder ice shell. The ice salinity  $S_i$  can be represented by  $S_i = k_{eff}(V) S_b$ , where  $k_{eff}$  is the effective solute distribution coefficient,  $S_b$  is the fluid (brine) salinity, and V is the velocity of the freezing front. Based on Equation (5),  $V \approx \Delta r/t_{freezing} \sim 10 \ (\Delta r/1 \text{ km})^{-1} \text{ cm year}^{-1}$ . The effective solute distribution coefficient varies widely over the range of observed sea ice thickening rates (Table 2 of Wolfenbarger et al. 2022a). As the freezing rate approaches zero,  $k_{eff}$  approaches a constant value that has been referred to as the effective equilibrium solute distribution coefficient (Wolfenbarger et al. 2022a), here  $k_{eff,eq}$ . The freezing front in a partially frozen intrusion is 1–3 orders of magnitude slower than the  $10^{-6}$ – $10^{-4}$  cm s<sup>-1</sup> rates of sea ice formation (Wolfenbarger et al. 2022a), such that we assume that the ice salinity is governed by  $k_{eff,eq}$ . Based on Figure 4 of Wolfenbarger et al. (2022a),  $k_{eff,eq} \approx 0.1$  and  $k_{eff,eq} = 0$  are, respectively, reasonable upper and lower limits (no brine entrapment; Figures 3(b)-(c)). Entrapment may lead to chemical fractionation, e.g., enriching the ice in chloride relative to other solutes (Wolfenbarger et al. 2022a). In addition to freezing rate,  $k_{eff}$  also depends on the composition of the brine and is higher for brines with lower eutectic temperatures (Wolfenbarger et al. 2022b). These compositional effects are neglected here.

Entrapped brine, if any, is partially redistributed as the temperature decreases due to the processes of brine expulsion and brine migration (Steinbrügge et al. 2020). The combination of this process and gravity drainage (Notz & Worster 2009; Vance et al. 2019; Buffo et al. 2021a, 2021b; Hesse et al. 2022; Wolfenbarger et al. 2022a) is not considered in the present

model, but is expected to result in a general downward migration of brine, either as a partial loss from the upper chamber wall back into the central pocket of remaining liquid (e.g., Buffo et al. 2020), or within the chamber sidewalls. Indeed, two-dimensional freezing simulations of sills with upper and lower ice walls indicate downward brine migration out of the upper wall, but no brine migration from the lower wall (Buffo et al. 2023).

Brine entrapment may thus be expected to affect the results obtained for an idealized spherical chamber in three ways. First, while freezing is ongoing, incorporation of brine in the ice is likely to result in a thicker wall and hence, a smaller inner chamber. Second, brine entrapment may fractionate solutes such as chlorides preferentially into the ice wall, altering the composition of the chamber fluid and that of the non-ice solids that form within the chamber. Third, the downward migration of the brine trapped in the ice wall is expected to break its spherical symmetry, resulting in a brine-depleted, potentially thinner chamber ice roof relative to the ice floor at the chamber bottom, and perhaps a salinity gradient in the sidewalls from brine-poor near the roof to brine-rich near the floor. By returning some of the trapped brine to the chamber, this downward migration may partly offset the other two effects of brine entrapment.

# 4.3. Implications for Ice Shell Thermophysical Properties

A summary of the known physical properties of the non-ice solids formed in the above simulations (Table 2), compared to those of water ice, is shown in Table 3. These properties determine the effect of non-ice deposits on transport of material through the ice shell by convection and cryovolcanism (Buffo et al. 2020; Morrison et al. 2023) as discussed below.

The density contrast between a solution and the surrounding ice shell is a key factor in determining the ease of eruption (e.g., Lesage et al. 2020). The density contrast between pure water ice and liquid is about  $65-82 \text{ kg m}^{-3}$  (increasing with increasing temperature). This can be overcome with  $\leq 5$  vol.% up to 12.5 vol.% salt in the ice shell, depending on whether the liquid is pure water or has the densities of the EM-CM, EM-CI, or MC-Scale solutions at the onset of ice formation  $(1009-1014 \text{ kg m}^{-3})$ . The silica-rich solutions of scenarios EM-CI FMQ-2 and MC-Scale+comet have respective computed densities of 1275 and 1054 kg m<sup>-3</sup> at the onset of freezing, likely requiring additional pressurization mechanisms for ascent. For comparison, the density of ocean world shells or crusts is expected to vary between about  $920 \text{ kg m}^{-3}$  for Enceladus (Hemingway & Mittal 2019)-plume fallout porosity could lower this number significantly (Neveu et al. 2022)—and 1200–1350 kg m<sup>-3</sup> for Ceres (Ermakov et al. 2017; Park et al. 2020). Among simulation results, the composition of residual brine as a function of temperature (Figures 5 and 7) provides a qualitative estimate of the composition and density of fluid erupted from such chambers. The (temperature-dependent) thermal expansivities of ice and salts result in modest density variations within ocean world ice shells over the relevant temperature ranges of  $\sim$ 50–273 K (Johnson et al. 2017; Howell & Pappalardo 2019).

The thermal conductivities of hydrated salts (largely from the data set of González Díaz et al. 2022) and silica are lower than that of water ice, conferring insulating properties to salt deposits, but not as much as might be inferred from thermal conductivities of less hydrated species (e.g., Prieto-Ballesteros & Kargel 2005).

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Table 3	
Known Physical Properties of the Non-ice Solids Formed in the Simulations of This Study,	Compared to Those of Water Ice

Salt	Water Ice	Amorph. Silica	Gypsum	Meridianiite	Mirabilite	Calcite	Dolomite	Magnesite	Hydrohalite	Sylvite
Formula	$H_2O$	SiO <sub>2</sub>	CaSO <sub>4</sub> •2H <sub>2</sub> O	MgSO <sub>4</sub> •11H <sub>2</sub> O	Na <sub>2</sub> SO <sub>4</sub> •10H <sub>2</sub> O	CaCO <sub>3</sub>	CaMg(CO <sub>3</sub> ) <sub>2</sub>	MgCO <sub>3</sub>	NaCl•2H <sub>2</sub> O	KCl
Density (kg m <sup>-3</sup> )	918 to 935 $^{\rm a}$	2100 to 2300 b	2310 $^{\rm c}$ ; 2350 $^{\rm d}$	1530 °	1470—1490 <sup>e</sup>	2710 <sup>c,d</sup>	2870 <sup>c,d</sup>	3010 °	1630 <sup>c</sup>	1990 <sup>c</sup> ; 1860 <sup>d</sup>
Thermal conductivity (W m <sup>-1</sup> K <sup>-1</sup> )	$567/T^{ m f}$	1.3*log( <i>T</i> )–1.872 <sup>g</sup>	1.30 to 3.40 $^{\rm h,i}$	- 0.0077* <i>T</i> +3.38 <sup>j</sup>	$-0.0119^{*}T$ +5.15 <sup>j</sup>	-3e-8*T <sup>3</sup> +6e-5*T <sup>2</sup> -0.036*T+9.78 <sup>k</sup>	4.78 to 5.51 <sup>h</sup>	5.84 to 7.59 <sup>h,i</sup>	i -0.00641*T +3.5 <sup>j</sup>	6.4 to 6.95 <sup>h</sup>
at 250 K	2.27	1.25	1.30 to 3.40 $^{\rm h,i}$	1.46	2.18	4.06	4.78 to 5.51 <sup>h</sup>	5.84 to 7.59 h,i	i 1.90	6.4 to 6.95 $^{\rm h}$
Heat capacity (J kg <sup>-1</sup> K <sup>-1</sup> )	7.73 <sup>*</sup> T <sup>1</sup>	9.1* <i>T</i> -1624 <sup>(250-260 K) g</sup> 412.95+3.287* <i>T</i> + 1.586e8* <i>T</i> <sup>-2 m</sup>	$\frac{1000^{(183-212 \text{ K})} 403}{2.75^* T^{(212-293 \text{ K})} n} + \frac{2.75^* T^{(212-293 \text{ K})} n}{530.75+1.847^* T^{\circ}}$	1879 <sup>p</sup> <sup>(298 K)</sup>	4.9* <i>T</i> +268 <sup>q</sup> 5.0* <i>T</i> +319 <sup>r</sup>	$9.1^{*}T - 1526^{(250 - 260 \text{ K})\text{g}}$ $1\ 044.2 + 0.219^{*}T +$ $2.592e8^{*}T^{-2 \text{ m,s}}$	$1\ 869.1 + \ 0.743^*T + \ 4.577e8^*T^{-2}$	$ \begin{array}{c} \overset{\text{m,t}}{} & 824.8 + \\ & 0.524^{*}T + \\ & 1.985 \text{e8}^{*}T^{-2} \end{array} $	2099–12.06*74 + 1 0.037 7*7 <sup>2 u</sup>	$13.4 + 0.217^*T - 3.219e7^*T^{-2}$ m
at 250 K	1933	651 $^{\rm g}$ ; 2265 $^{\rm m}$	992 <sup>1</sup> ; 1091 <sup>n</sup>	1879 <sup>(298 K)</sup>	1493 <sup>q</sup> ; 1569 <sup>r</sup>	749 <sup>g</sup> ; 1514 <sup>m,s</sup>	2787	1273	1445	416
Thermal diffusivity at 250 K (m <sup>2</sup> s <sup>-1</sup> )	1.28e-6	0.25 to 0.87e-6	0.52 to 1.48e-6	0.51e-6	0.97e-6	0.99 or 2e-6	0.60 to 0.69e-6	1.52 to 1.98e-6	0.81e-6	7.73 to 8.40e-6
Enthalpy of crystal- lization (kJ kg <sup>-1</sup> ) at 298 K and 1 bar	334 (freezing at 273 K) <sup>v</sup>	-333 <sup>m</sup>	9.9 <sup>w</sup>	753 (anhydrous MgSO <sub>4</sub> ) <sup>x</sup>	-660 <sup>w</sup>	257 <sup>m</sup> (add $-147$ if pH > $10)^{y}$	325 $^{\rm m}$ (add –159 if pH $>$ 10) $^{\rm y}$	528 <sup>m</sup> (add – 174 if pH > 10) <sup>y</sup>	–63 <sup>z</sup> (anhy- drous NaCl)	-233 <sup>m</sup>
Viscosity (Pa s) for a stress of 1 MPa	$10^{14} \exp[25^*]$ (273 K/T – 1)] <sup>aa</sup>	Depends on densification <sub>ab,ac</sub>	Not available <sup>ad,ae</sup>	$10^{9.1} \exp(6700/T)^{af}$	$(10^{-6.4} \text{ exp})$ (15400/T) <sup>ag</sup>	$2e10 \exp(24000/T)^{ah}$	1e-15 exp $(44000/T)^{ai}$	$3.9e-6 \exp(25000/T)^{aj}$	Not available	Not available
at 250 K, 1 MPa	1.1e14	N/A (brittle) ab,ac	N/A (brittle) ad	5.1e20	2.2e20	N/A (brittle)	N/A (brittle)	N/A (brittle)	Not available	Not available
Yield strength (MPa)	10 <sup>af</sup>	7000 <sup>ab</sup> - 9050 <sup>ac</sup>	10-20 <sup>ad</sup>	6 <sup>af,ak</sup>	Not available	1000-3500 <sup>ah</sup>	Similar to calcite? <sup>ai</sup>	Higher than calcite? aj	Not available	Not available
Bulk modulus (GPa)	$(-1.20e-3^{*}T)$ +1.19) *10 <sup>al</sup>	12 <sup>am</sup>	45 <sup>an</sup>	19.9 <sup>ao</sup>	19.6 <sup>ap</sup>	67 <sup>(298 K)</sup> aq	94 <sup>ar</sup> ; 91 <sup>as</sup>	107 <sup>(298 K)</sup> aq	Not available	17.5 <sup>at</sup>
Thermal expansivity (× $10^{-6}$ , K <sup>-1</sup> )	$(0.027^*T - 17.2)^{au}$	0.5 to 0.8 <sup>av</sup>	$69.6^* (1 + 322/T)^{\text{aw}}$	$T/2 - (T/47)^2 - 18$ e,ax	$3T/2 - (T/47)^2 - 5$	22 to 25 <sup>ay</sup>	41 <sup>as</sup>	40+0.0049*T	53 to 84 ba	111 <sup>at</sup>

Notes. Picromerite, ikaite, and nahcolite are absent from this table because, to our knowledge, only their densities (respectively 2100, 1770, and 2160 kg m<sup>-3</sup>; Marion et al. 2005 and references therein) are known. The notation "cN" implies "× 10<sup>N</sup>," N/A: Not applicable. <sup>a</sup> Haynes et al. (2010), <sup>b</sup> Calculated as the ratio of molar mass and molar volumes taken from PHREEQC's *pitzer.dat* (Appelo 2015) and Helgeson et al. (2010), <sup>c</sup> Urai et al. (2008). <sup>c</sup> Brand et al. (2009); the thermal expansivity expression is a rough fit to their Figure 8 in the range 75–275 K. <sup>f</sup> Klinger (1980). <sup>g</sup> Durham et al. (2010), <sup>cling</sup> Didate et al. (2022). <sup>k</sup> Third-order polynomial fit to data reported by Clauser and Huenges (1995) and references therein. <sup>1</sup> González Díaz et al. (2022). <sup>k</sup> Third-order polynomial fit to data reported by Clauser and Huenges (1995) and references therein. <sup>1</sup> González Díaz et al. (2010), <sup>cling</sup> Thi-order polynomial fit to data reported by Clauser and Huenges (1995), and references therein. <sup>1</sup> González Díaz et al. (2010), <sup>cling</sup> Thi-order polynomial fit to data reported by Clauser and Huenges (1995), and references therein). <sup>1</sup> Approximation of Desch et al. (2009). <sup>m</sup> Helgeson et al. (1978), <sup>n</sup> Durham et al. (2010), <sup>cling</sup> Brodale and Giauque (1958), <sup>T</sup> Durham et al. (2010) citing prieto-Ballesteros and Kargel (2005), <sup>s</sup> Plummer and Busenberg (1982), <sup>cl</sup> Shock and Helgeson (1988), <sup>u</sup> Drebushchak & Ogienko (2020), <sup>v</sup> Kee et al. (1987), <sup>w</sup> Approximation of Thomas et al. (1974), <sup>acl</sup> action of HCO<sub>3</sub><sup>-</sup> = CO<sub>3</sub><sup>-</sup> + H<sup>+</sup>; HCO<sub>3</sub> predominates at roughly 6 < pH < 10 at 298 K and 1 bar and CO<sub>3</sub><sup>-</sup> = predominates at pH > 10. <sup>z</sup> Svrijensky et al. (2005), <sup>eutericic composition, coarse colony size case; viscosity is proportional to stress<sup>-1,2</sup>, <sup>ag</sup> Durham et al. (2005), <sup>eutericic composition, viscosity is proportional to stress<sup>-4,4</sup>, <sup>ah</sup> Sly et al. (2011), <sup>aff</sup> McCarthy et al. (2008), <sup>ad</sup> Jense et al. (2008), <sup>ad</sup> Fort 1 µm grains. At a given grain size, magnesite is stronger </sup></sup>

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This could be because the higher hydration states of the salts formed in our simulations make the properties of the anhydrous salts tend more toward those of water ice. Some minerals in Table 3 (e.g., anhydrous Ca- and Mg-carbonates) are more conductive than ice at 250 K.

The heat capacities of the solids in Table 3 are generally lower than that of water ice but remain within a factor of 2-3 of that value, except for sylvite (KCl) which has a heat capacity 4-5 times lower than ice. Similarly, thermal diffusivities (the ratio of thermal conductivity to the product of density and heat capacity), which determine the propensity of a material for conductive heat transfer, are all between 0.5 and  $2 \times 10^{-6}$  m<sup>2</sup> s<sup>-1</sup> across water ice, salts, and silica, except again for sylvite. This might suffice for salt deposits to generate thermal anomalies within ice shells, e.g., with higher temperatures (and/or thinner ice) below areas of lesser thermal diffusivities (i.e., insulating). Pileup of salts at the bottom of an intrusion is also likely to generate asymmetries (neglected in our simulations) in the intrusion's thermal evolution that compound with asymmetries arising from vertical temperature gradients in the surrounding ice shell (e.g., Hesse & Castillo-Rogez 2019).

Specific enthalpies of solid formation can differ widely from those of ice. Like ice, the formation of some solid salts is exothermic; for others, it is endothermic. Enthalpy absolute values do not exceed  $10^3$  kJ kg<sup>-1</sup> across all solids of Table 3. Based on the amounts of forming salts reported in Table 2, non-ice solid formation or dissolution may affect the heat of phase change of impure ice by a few percent relative to that of pure ice.

The viscosities of salts and silica are orders of magnitude higher than that of water ice, especially above 200 K. The viscosity of ice-salt mixtures tends to be dominated by that of the lower-viscosity end member (ice) unless the high-viscosity end member is abundant enough (volume fraction  $\approx 0.6-0.7$ ) for its grains to be adjoined (e.g., Durham et al. 2010). Thus, salt deposits from poorly mixed chambers or, perhaps, smaller central mixed ice-salt pockets below the eutectic temperature may significantly influence the local mechanical behavior of the ice shell, e.g., by impeding local convective motion (Durham et al. 2010), or by facilitating failure (decreasing the strength) of intimate ice-salt mixtures (McCarthy et al. 2011). It may be that unless salt deposits have a spatial extent comparable to the ice shell thickness, they are carried along by the rest of the mobile ice shell.

Many non-ice solids in Table 3 exhibit brittle behavior at the MPa-level stresses relevant to ice shells. Some hydrated salts (gypsum, meridianiite) seem to have similar yield strengths as water ice; other non-ice solids (amorphous silica, anhydrous carbonates) are 2–3 orders of magnitude stronger. This may bear on the ability of fractures to propagate through heterogeneous ice shells. Piled-up salt deposits might prevent further fluid intrusion, forcing ascending fluids to find alternative paths.

The bulk modulus (inverse of compressibility) increases with pressure; we have aimed to report values applicable to pressures on the order of a few megapascals or less. All nonice solids are less compressible than water ice with its bulk modulus of  $\approx 9$  GPa, but generally tend to have similar thermal expansivities. Indeed, the thermal expansivity of sea ice has been shown to be equal to that of pure water ice within experimental uncertainty (Cox 1983; Johnson & Metzner 1990). Solid solutions of NaCl-KCl can have lower bulk modulus and higher thermal expansivity than either end member (Walker et al. 2004). Thus, the mechanical properties of salt mixtures such as those obtained in our simulations (e.g., Figure 5) need not be within the ranges delineated by the end members of Table 3.

Nonetheless, viscosity appears to be the mechanical property that varies the most across solids relevant to ice shells. Therefore, material viscosity is likely to dominate the influence of composition on the propensity for convective transport, quantified by the Rayleigh number, which also involves density, thermal expansivity, and thermal diffusivity. These latter three parameters are all within the same order of magnitude across ice and non-ice solids. The propensity for cryovolcanic transport appears to be higher in a denser shell, provided fracture propagation is not impeded by stronger dehydrated solids. Thus, first-order information about the nonice content of the underlying ice shell may be obtained by investigating morphologically heterogeneous icy world surfaces bearing regional, but not global, evidence of convection or cryovolcanism, such as Ceres, Europa, Enceladus, Triton, Pluto, and Charon (Table 1).

# 4.4. Ice Shell Characterization by Upcoming Missions

The solid distributions shown in Figures 5 and 7 may lend themselves to remote detection by several sensing methods (Marusiak et al. 2021). First, the difference in their mechanical properties (density, bulk modulus, and viscosity) relative to pure water ice may affect the response to tidal forcing of the ice shell of moons. This might lead to a difference in tidal displacement or fracturing detectable by imaging or altimetry (e.g., Steinbrügge et al. 2015). Second, subsurface intrusions or the frozen remains of former intrusions, and some of their characteristics (e.g., shape) could be detectable by radar sounding (e.g., Schroeder et al. 2016), gravimetry (Ermakov et al. 2017; Park et al. 2020; Raymond et al. 2020), or from the surface using electromagnetic sounding (Grimm et al. 2021; Biersteker et al. 2023) or seismometry (Vance et al. 2018: Marusiak et al. 2022). Third, indirectly, an intrusion could be detected by how the spatial variations that it induces in thermal diffusivity changes the local thickness of the icy lithosphere and full ice shell. Such heterogeneities may persist over timescales much longer than that of reservoir formation and freezing.

Irrespective of the technique, the detectability of heterogeneities likely primarily depends on their size; the larger, the easier. Intrusions into Europa's ice shell may be kilometers wide (Schmidt et al. 2011; Manga & Michaut 2017). The 1–10 S m<sup>-1</sup> conductivity range of the modeled solutions (Figures 5 and 7), quantified using the methodology described in Parkhurst & Appelo (2013), indicates that kilometer-sized intrusions with such compositions are detectable with existing electromagnetic sounding instrumentation on board a landed mission, and that constraints on the shape and salinity of these intrusions can be obtained (Grimm et al. 2021).

Recent exploration of Ceres by the Dawn mission has shown the ability to identify subsurface heterogeneities in morphological, compositional, and gravimetric data sets acquired from orbit (e.g., Bland et al. 2016; Scully et al. 2017). In particular, radio tracking data acquired at Ceres during  $\sim$ 140 orbits with periapsis at 35 km altitude allowed for retrieval of a subsurface chamber size on the order of tens of kilometers under Occator crater, with an inferred density

 Table 4

 Activity of H<sub>2</sub>O and Solution Salinity at the Lowest Temperature Simulated

Europa Ocean Compositional End-member		EM-CM		EM-CI		Scale	EM-CI FMQ-2	MC-Scale +comet
PHREEQC database	TS13	TC17	TS13	TC17	TS13	TC17	TS13	TS13
Lowest temperature simulated (equilibrium or fractional) (K)	269.15	247.30	267.83	264.95	251.15	228.60	259.35	259.15
Activity of $H_2O(a_{H2O})$ at lowest temperature simulated	0.969	0.781	0.958	0.930	0.813	0.647	0.881	0.880
Salinity at lowest temperature simulated (mass %)	6.4	28.1	9.1	10.4	34.2	43.9	27.4	27.7

Note. Water activities are found to be the same for equilibrium and fractional crystallization if the temperature is the same. Therefore, activities corresponding to the minimum temperature simulated across the equilibrium and fractional crystallization of each solution (shown in Table 2 and Figure 7) are shown. Salinity is expressed as the mass of non-H, non-O elements divided by the mass of water; i.e., the mass of O in SO<sub>4</sub> and CO<sub>3</sub> is ignored.

 $45-200 \text{ kg m}^{-3}$  lower than the surrounding ice-silicate crust indicating a higher brine and lower silicate content (Raymond et al. 2020). The detectability of subsurface chambers by gravimetry at icy moons may be complicated by perturbations from the rest of the giant planet system.

In the coming decade, the JUpiter ICy moons Explorer (JUICE; Grasset et al. 2013) and Europa Clipper missions (Howell & Pappalardo 2020) are set to characterize the ice shells of Jupiter's moons Europa and Ganymede to understand the habitability of their oceans. At Europa, sites of interest have been identified in imaging and spectral data returned by the Galileo spacecraft (e.g., chaos regions; Schmidt et al. 2011). These regions may retain altered electrical conductivity (e.g., Grimm et al. 2015) that might be detected by radar (e.g., Culha et al. 2020; Culberg et al. 2022) or as localized magnetic induction features (Vance et al. 2021b). Subsurface radar sounding of ocean world ice shells by the Europa Clipper REASON and JUICE RIME instruments might therefore find variations in thickness and electrical properties associated with fossil reservoirs. For example, the REASON very high frequency band will use 60 MHz signals to identify reflective contrasts (Bayer et al. 2017) at scales relevant to the size of the reservoirs and resulting brine deposits described here.

More compositional detail likely hinges on analysis of surface material sourced from the subsurface. The timedependence of reservoir composition during freezing can create sequences of erupted compositions determined by the conditions of the eruption (Johnson & Vu 2022), which can be analyzed by Europa Clipper's MISE instrument in the 1–5  $\mu$ m spectral range (Bayer et al. 2017). Compositionally dependent insulating effects, eruption volumes, and eruption timescales may also influence the surface heat balance, transporting heat conductively or by the upward advection, intrusion, and eruption of liquid water in ways that might be detectable by Europa Clipper's E-THEMIS thermal infrared instrument.

Beyond sensing by multi-flyby and orbiting spacecraft, information on heterogeneities in the subsurface structure also bears on reconnaissance for surface and subsurface exploration. Salty intrusions or deposits are important targets for in situ missions because they may preserve biosignature materials (Hand et al. 2022). Non-ice solids may also impede the ability of melt probes to descend into the ice shell (Oleson et al. 2019). Understanding their provenance is thus key to planning in situ mission operations.

# 4.5. Compatibility of Physicochemical Conditions in Brine Pockets with Ranges Tolerable by Microbial Extremophiles on Earth

The presence of liquid water reservoirs in ice shells brings about the question of the extent to which their physicochemical conditions are within the tolerance range for microbial growth and reproduction, as understood from extremophile communities on Earth. Under otherwise favorable conditions (e.g., temperature above a few degrees Celsius), the pH tolerance range of life is 1-13 (Harrison et al. 2013). On the basis of pH alone, only solutions resulting from partial freezing of EM-CM, EM-CI, and MC-Scale have a pH tolerable by life. On the basis of water activity alone, microbial communities have been reported in environments with water activity as low as  $\approx 0.4$ (Merino et al. 2019 and references therein) but more commonly  $\approx 0.6$  (Benison et al. 2021 and references therein). In the solutions simulated here, water activity decreases with decreasing temperature (Figures 5 and 7) to values that remain above these minima at 250-270 K (Table 4). Considering a 248 K minimum temperature for microbial survival (Merino et al. 2019), the combined stresses due to salinity and pH may not preclude microbial population growth in partially frozen solutions EM-CM and EM-CI, with the MC-Scale solution at the limit of the tolerance range for growth of microbial extremophile communities on Earth at the end of the simulation (see Figure 1 of Harrison et al. 2013). The addition of thermal stress may preclude this latter solution from being suitable for life (Harrison et al. 2013; Merino et al. 2019).

Thus, only two of the end-member solutions of Melwani Daswani et al. (2021), when partially frozen, appear to retain physicochemical conditions at which microbial growth is possible. A more quantitative assessment of the habitability of fluid intrusions with these compositions requires considering fluxes of chemical (oxidation-reduction) energy and nutrients to these intrusions. Redox energy fluxes might arise from gradients associated with disequilibrium (fractional) crystallization, but the PHREEQC modeling framework used in this study does not include redox reactions (Section 2.1.2), precluding identification of such gradients. Additional fluxes may arise from advection of ice shell material due to, e.g., thermal gradients or tectonism (Vance et al. 2016), brine percolation (Hesse et al. 2022), or plume deposition (Ray et al. 2021). The degree of brine entrapment (Section 4.2), although not quantified in this study, bears on the connectivity between brine reservoirs and the associated

potential for delivery of nutrients to these potential habitats (Wolfenbarger et al. 2022c).

# 5. Conclusions

In this work, we have used an implementation of a model of concentrated aqueous solutions at temperatures below 273 K (Toner & Sletten 2013; Toner & Catling 2017b) to simulate the compositional evolution of freezing intrusions within an ice shell. Starting solution compositions were taken from a recent geochemical modeling effort of compositional end members for the subsurface ocean of Jupiter's icy moon Europa (Melwani Daswani et al. 2021). The results of our simulations thus inform the nature and properties of compositional heterogeneities within Europa's ice shell in the context of these end members. For moderate-pH end members dominated by chloride, sulfate, and/or carbonate, the solids formed include Ca-, Mg-, and Na-sulfates and -carbonates; and Na- and K-chlorides. For silica-rich, high-pH end members, abundant amorphous silica forms with, potentially, similarly abundant NaOH and KOH. Although the end members of Melwani Daswani et al. (2021) encompass a broad range of possibilities for the composition of Europa's ocean, the methodology described herein can be applied to other ocean chemistries that may be found to be more relevant in the future. The model can also be applied to worlds other than Europa (Table 1) once the chemical space of PHREEQC thermodynamic data for concentrated solutions is expanded to, e.g., nitrogen-bearing species.

Beyond compositional evolution, we have developed a numerical model tracking the spatial distribution of solids (water ice, minerals, and other precipitated solids such as gas hydrates and amorphous silica) and dissolved species. Using this model, we have computed the shape and composition of solids formed within intrusions of ocean material into an ice shell as a function of their frozen fraction. If non-ice solids settle to the bottom, their deposits tend to have stacked hourglass shapes, widening each time the crystallization temperature of a new solid is reached in the precipitation sequence of silica, sulfates-carbonates, and finally chlorides.

We have discussed the applicability of this model to situations other than intrusions, such as fractures and global freezing of a subsurface ocean. The results of this work could help to evaluate the detectability and characterization of compositional heterogeneities within Europa's ice shell. Observations of these compositional heterogeneities by spacecraft can elucidate their role in governing transport processes and habitable niches within ice shells.

Follow-up work could simulate the progressive decrease in salt trapping efficiency as freezing slows, by keeping track of the composition (as Wolfenbarger et al. 2022b did for bulk salinity) and thermal evolution of the reservoir (Buffo et al. 2020, 2021a, 2021b; Chivers et al. 2021). Tracking both salt trapping and chamber compositional evolution would require reinitializing the composition of the chemical system simulated with PHREEQC at each temperature step based on results of the previous step, thus intertwining geometry and PHREEQC calculations. Another avenue for improvement is the investigation of nonspherical chambers and nonisothermal ice shells (Michaut & Manga 2014; Chivers et al. 2021) by interfacing PHREEQC with numerical models setting the physical environment.

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