

Supporting Information for “Compositional Controls on the Distribution of Brine in Europa’s Ice Shell”

N. S. Wolfenbarger¹, M. G. Fox-Powell², J. J. Buffo³, K. M. Soderlund¹, D.

D. Blankenship¹

¹Institute for Geophysics, Jackson School of Geosciences, University of Texas at Austin, Austin, Texas, USA

²AstrobiologyOU, The Open University, Walton Hall, Milton Keynes, UK

³Dartmouth College, Hanover, New Hampshire, USA

Contents of this file

1. Derivations 1.1 to 1.3
2. Figures S1 to S3
3. Table S1 to S7

Introduction This supporting information includes derivations, figures, and tables that provide important background and context for the published manuscript. Derivations 1.1 – 1.3 represent equations which are incorporated into the code base used to obtain the results published in the main text. The derivations presented here illustrate: (1.1) how to obtain our expression for brine volume fraction from the work of Cox and Weeks (1983), (1.2) how the density of solid salts is calculated from the output of FREZCHEM, and (1.3) how the solid salt volume fraction is estimated for temperatures below the eutectic. Figures S1 and S2 demonstrate the sensitivity of the phase behavior functions

to the ocean salinity specified in the FREZCHEM v15.1 input file for our analog end-member ocean compositions. Figure S3 is a reproduction of the bottom row of Fig. 8 where only brine volume fraction is shown. Table S1 presents the temperature at which each salt mineral starts to precipitate in the FREZCHEM v13.3 simulations of terrestrial seawater shown in Fig. 2. Tables S2 – S5 provide the best fit coefficients for the phase behavior functions used to estimate brine volume fraction for terrestrial seawater, our binary endmember compositions, and our analog endmember compositions, respectively. Table S6 presents the temperature at which each salt mineral starts to precipitate in the FREZCHEM v15.1 simulations of our analog endmember compositions shown in Fig. S1 and S2. Table S7 presents a comparison of salt precipitation sequences from PHREEQC (using the ColdChem and frezchem databases) and FREZCHEM (v13.3 and v15.1).

1. Derivations

1.1. Brine Volume Fraction, $\frac{V_b}{V}(T)$

Cox and Weeks (1983) derive an expression (Eq. 5 in Cox and Weeks (1983)) for the brine volume fraction of sea ice as a function of temperature, T , given by

$$\frac{V_b}{V}(T) = \frac{\rho S}{F_1(T)} \quad (1)$$

where ρ is the bulk density of sea ice in units of g/cm³ and S is the bulk ice salinity in ppt. Their expression for the sea ice bulk density (Eq. 15 in Cox and Weeks (1983)) is given by

$$\rho = \left(1 - \frac{V_a}{V}\right) \frac{\rho_i F_1(T)}{F_1(T) - \rho_i S F_2(T)} \quad (2)$$

where ρ_i is the pure ice density in units of g/cm³ and $F_1(T)$ and $F_2(T)$ are the phase behavior functions. If we substitute Eq. (2) into Eq. (1) we obtain

$$\frac{V_b}{V}(T) = \left(1 - \frac{V_a}{V}\right) \frac{\rho_i S}{F_1(T) - \rho_i S F_2(T)} \quad (3)$$

which is equivalent to the form of the brine volume equation provided as (1.8) in Petrich and Eicken (2017).

1.2. Density of Solid Salts, $\rho_{ss}(T)$

The density of solid salts at a given temperature is given by

$$\rho_{ss}(T) = \frac{m_{ss}(T)}{V_{ss}(T)} \quad (4)$$

where $m_{ss}(T)$ is the total mass of solid salts present and $V_{ss}(T)$ is the total volume of solid salts present at the same temperature. The total mass of solid salts can be expressed as

$$m_{ss}(T) = \sum_{n=1}^N m_{ss,n}(T) \quad (5)$$

where $m_{ss,n}(T)$ represents the total mass of the n th solid salt of N solid salts present at a given temperature. This quantity can be calculated from the “Moles” column of the “Solid SPECIES” section in FREZCHEM output file or “Final Moles in assemblage” column of the PHREEQC output file. The total volume of solid salts can be similarly expressed as

$$V_{ss}(T) = \sum_{n=1}^N V_{ss,n}(T) \quad (6)$$

where $V_{ss,n}(T)$ represents the total volume of the n th solid salt present at a given temperature. $V_{ss,n}(T)$ can be equivalently expressed as

$$V_{ss,n}(T) = \sum_{n=1}^N \frac{m_{ss,n}(T)}{\rho_{ss,n}} \quad (7)$$

where $\rho_{ss,n}$ represents the density of the n th solid salt, assumed to be temperature invariant. Although $\rho_{ss,n}$ cannot be obtained from the FREZCHEM output file, we adopt the molar volumes specified in the relevant documentation (Marion et al., 2005, 2012). Molar volumes can also be found in the frezchem database file in PHREEQC, although we note that they are not present in the ColdChem database file. The total density of solids salts can thus be expressed as

$$\rho_{ss}(T) = \frac{\sum_{n=1}^N m_{ss,n}}{\sum_{n=1}^N \frac{m_{ss,n}}{\rho_{ss,n}}}. \quad (8)$$

1.3. Solid Salt Volume Fraction Below the Eutectic, $\frac{V_{ss}}{V}(T \leq T_{eut})$

The solid salt volume fraction below the eutectic temperature is governed by the total mass fraction of solid salts that forms once the solution solidifies completely and the density of the solid salt and ice phases. We can express this as

$$\frac{V_{ss}}{V}(T \leq T_{eut}) = \frac{x_{ss}(T = T_{eut})}{x_{ss}(T = T_{eut}) + (1 - x_{ss}(T = T_{eut})) \frac{\rho_{ss}(T=T_{eut})}{\rho_i(T)}} \quad (9)$$

where $x_{ss}(T = T_{eut})$ represents the total mass fraction of solid salts which precipitate at/beyond the eutectic and $\rho_{ss}(T = T_{eut})$ represents the total salt density at/beyond the eutectic. Although in this work we define the eutectic temperature as the last convergent temperature step, because brine is remaining at this temperature step, additionally salt precipitation occurs below this temperature up through the “true” eutectic. Note that although FREZCHEM specifies which minerals are precipitating at/beyond the eutectic, it does not calculate the amount of each mineral precipitating¹. As such, we must estimate the mass of solid salts precipitating beyond the final temperature step. To do this, we define a linear system

$$\mathbf{d} = \mathbf{C}\mathbf{x} + \epsilon \quad (10)$$

where \mathbf{d} is a column vector containing the moles of ionic species present at the final convergent temperature step, \mathbf{C} is a matrix which maps the ionic species present at the final convergent temperature step to the solid salts precipitating beyond the final convergent temperature, and \mathbf{x} represents the number of moles of each solid species which forms beyond the final convergent temperature. We want to find \mathbf{x} such that concentration of dissolved ions remaining beyond the eutectic, ϵ , is minimized. Because we are only allowing for precipitation beyond the final temperature step (and not dissolution), we must also impose the constraint that \mathbf{x} is greater than

zero. Therefore, the solution to this problem is obtained via constrained least squares (`lsqlin` in MATLAB). For both of the analog endmember compositions assumed in this work, the linear system is represented by

$$\mathbf{d} = \begin{bmatrix} [\text{Cl}^-] \\ [\text{Mg}^{2+}] \\ [\text{Na}^+] \\ [\text{SO}_4^{2-}] \end{bmatrix} \quad (11)$$

$$\mathbf{x} = \begin{bmatrix} [\text{NaCl} \cdot 2\text{H}_2\text{O}] \\ [\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}] \\ [\text{MgSO}_4 \cdot 11\text{H}_2\text{O}] \end{bmatrix} \quad (12)$$

$$\mathbf{C} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 1 & 2 & 0 \\ 0 & 1 & 1 \end{bmatrix} \quad (13)$$

subject to the constraint $\mathbf{Ax} \leq \mathbf{b}$, where $\mathbf{A} = -\mathbf{I}$ and $\mathbf{b} = \vec{0}$. We can obtain $m_{ss}(T \leq T_{eut})$ by summing the mass obtained from solving the constrained least squares problem above, $m_{ss}(T = T_{eut})$, to the cumulative mass present at the eutectic temperature, $m_{ss}(T > T_{eut})$. This can be expressed by the following:

$$m_{ss}(T \leq T_{eut}) = m_{ss}(T > T_{eut}) + m_{ss}(T = T_{eut}). \quad (14)$$

However, this specifically represents the mass of solid salts for the initial brine salinity specified in the FREZCHEM (or PHREEQC) input file. We need to scale this mass for a bulk ice salinity of interest, S . This can be done by multiplying $m_{ss}(T \leq T_{eut})$ by the ratio of the mass of salt in a system of bulk salinity S , defined as $m_s^b(T = T_0, S)$, to the mass of salt used to derive $m_{ss}(T \leq T_{eut})$ (i.e., the mass of salt specified in the input file, defined as $m_s^b(T = T_0)$). This yields an expression for the mass fraction of solid salts at the eutectic of

$$x_{ss}(T = T_{eut}) = \left(\frac{m_s^b(T = T_0, S)}{m_s^b(T = T_0)} \right) \left(\frac{m_{ss}(T \leq T_{eut})}{M + m_s^b(T = T_0, S)} \right) \quad (15)$$

where $m_s^b(T = T_0, S)$ is given by

$$m_s^b(T = T_0, S) = \frac{1000S}{1000 - S} \quad (16)$$

which represents a conversion of the bulk ice salinity, S from units of grams of salt per kg solution (ppt) to grams of salt per kg of water. Substituting Eq. (16) into Eq. (15) yields

$$x_{ss}(T = T_{eut}) = \left(\frac{\frac{1000S}{1000-S}}{m_s^b(T = T_0)} \right) \left(\frac{m_{ss}(T \leq T_{eut})}{M + \frac{1000S}{1000-S}} \right) \quad (17)$$

where M is the total mass of water (always 1000 g in our simulations). Taking $M = 1000$ g, this simplifies to

$$x_{ss}(T = T_{eut}) = \frac{Sm_{ss}(T \leq T_{eut})}{1000m_s^b(T = T_0)} \quad (18)$$

We define a scale factor, k^* , as

$$k^* = \frac{m_{ss}(T \leq T_{eut})}{m_s^b(T = T_0)} \quad (19)$$

which effectively represents the increase in the mass of solid salts at/beyond the eutectic relative to the initial mass of dissolved salts, resulting from the hydration of salts as the solution freezes. Substituting Eq. (18) and Eq. (19) into Eq. (9) yields

$$\frac{V_{ss}}{V}(T \leq T_{eut}) = \frac{Sk^*}{Sk^* + (1000 - Sk^*) \frac{\rho_{ss}(T=T_{eut})}{\rho_i(T)}}. \quad (20)$$

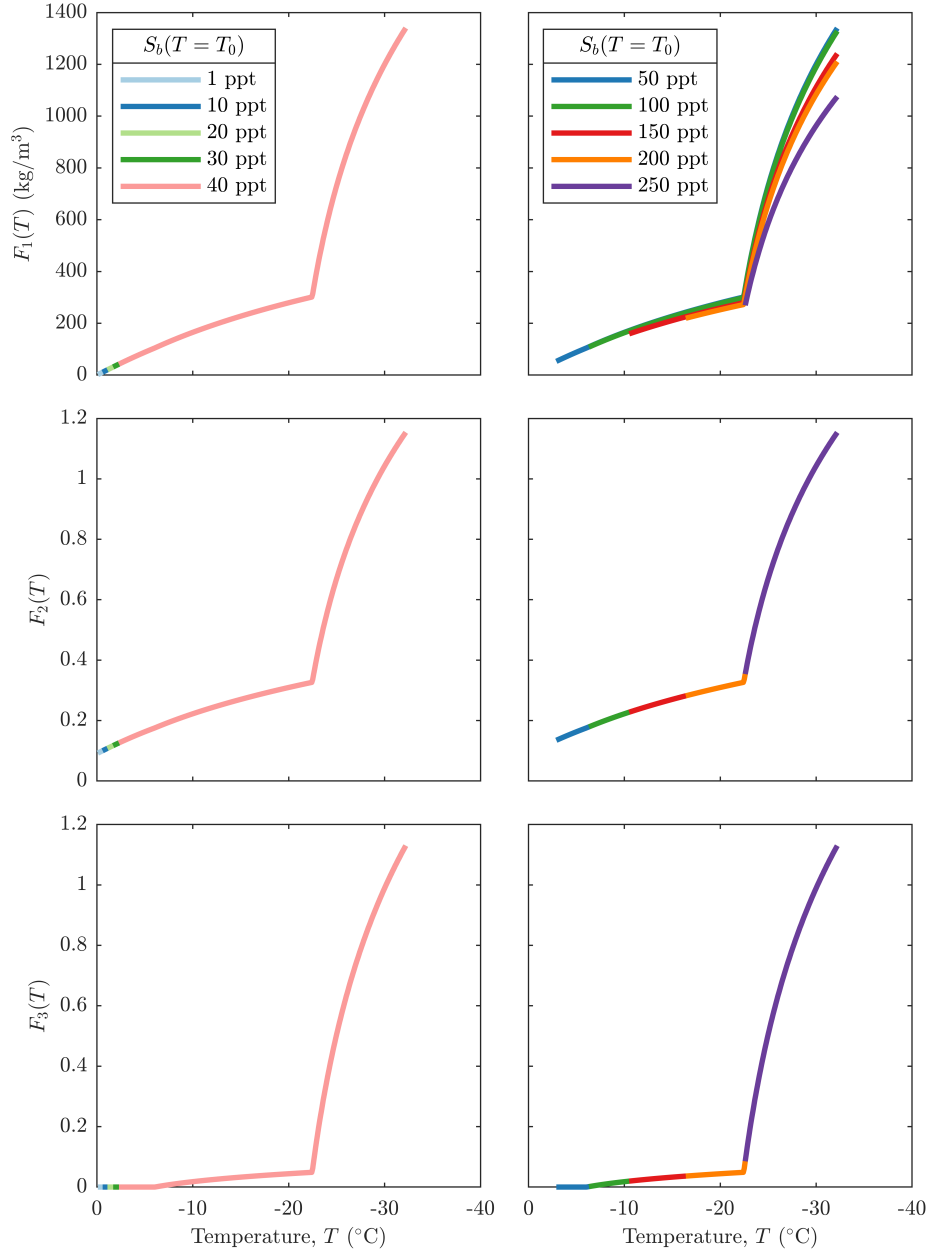


Figure S1. Phase behavior functions derived from FREZCHEM simulations of our Cl-dominated European ocean, assuming a range of ocean salinities $S_b(T = T_0)$.

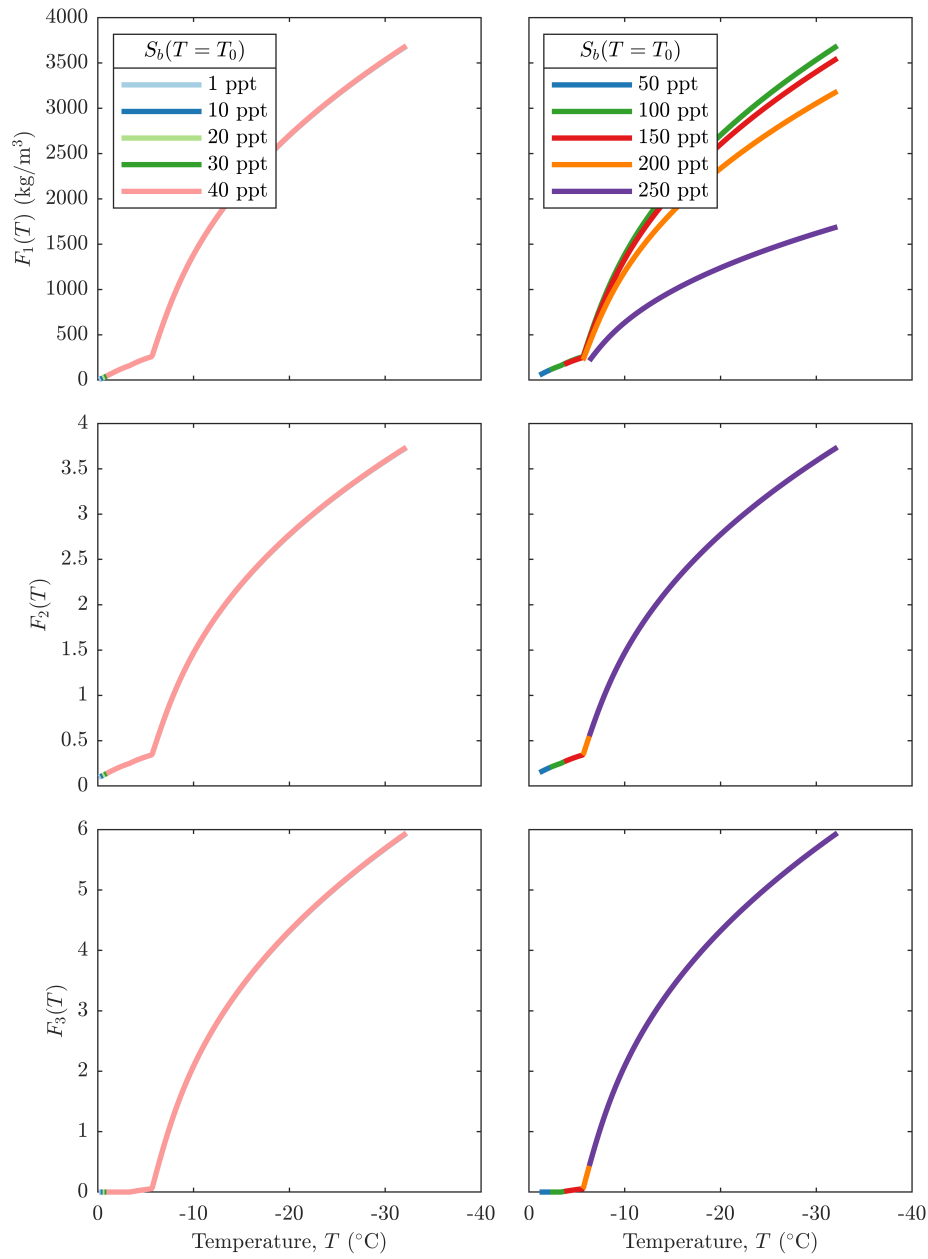


Figure S2. Phase behavior functions derived from FREZCHEM simulations of our SO_4 -dominated European ocean, assuming a range of ocean salinities $S_b(T = T_0)$.

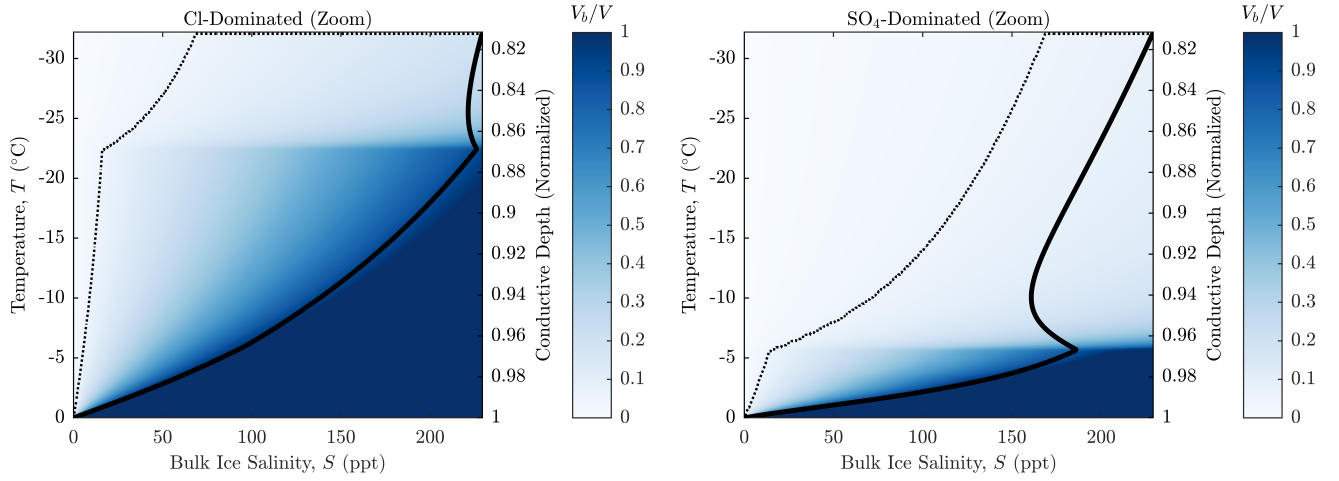


Figure S3. Brine volume fraction for the bottom $\sim 20\%$ of a conductive ice layer at Europa assuming analog endmember compositions for the ocean and a fixed pressure of 1 atm. The vertical axis corresponds to the temperature at a given depth within the ice shell. The thick solid curve represents the brine salinity as a function of temperature, whereas the thin dotted curve corresponds to a brine volume fraction of 0.05.

Table S1. The temperature at which a specified salt starts precipitating for terrestrial seawater of salinity, $S_b(T = T_0)$ at a pressure of 1 atm, predicted by FREZCHEM v13.3. Note that for a seawater salinity greater than 100 ppt certain salts begin precipitating at higher temperatures, influencing the phase behavior functions shown in Fig. 2.

$S_b(T = T_0)$ (ppt)	1	10	20	30	40	50	100	150	200	250
	Temperature, T ($^{\circ}\text{C}$)									
<i>Ikaite</i> $\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$	-4.9	-4.9	-4.9	-4.9	-4.9	-4.9	≥ 0.0	≥ 0.0	≥ 0.0	≥ 0.0
<i>Gypsum</i> $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	-6.2	-6.2	-6.2	-6.2	-6.2	-6.2	-6.2	≥ 0.0	≥ 0.0	≥ 0.0
<i>Mirabilite</i> $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$	-6.4	-6.4	-6.4	-6.4	-6.4	-6.4	-6.4	-3.4	-1.0	≥ 0.0
<i>Hydrohalite</i> $\text{NaCl} \cdot 2\text{H}_2\text{O}$	-22.9	-22.9	-22.9	-22.9	-22.9	-22.9	-22.9	-22.9	-22.9	-22.9
NaBr	-22.9	-22.9	-22.9	-22.9	-22.9	-22.9	-22.9	-22.9	-22.9	-22.9
<i>Meridianiite</i> $\text{MgSO}_4 \cdot 11\text{H}_2\text{O}$	-33.3	-33.3	-33.3	-33.3	-33.3	-33.3	-33.3	-33.3	-33.3	-33.3
<i>Sylvite</i> KCl	-33.4	-33.4	-33.4	-33.4	-33.4	-33.4	-33.4	-33.4	-33.4	-33.4
$\text{MgCl}_2 \cdot 12\text{H}_2\text{O}^a$	-	-	-	-	-	-	-	-	-	-

^aOur version of FREZCHEM v13.3 fails to display text that $\text{MgCl}_2 \cdot 12\text{H}_2\text{O}$ is precipitating at/beyond the eutectic, possibly due to a compiler issue; however this is known from previous works (Marion et al., 1999; Vancoppenolle et al., 2019). We also note that this text appears to be absent in the FREZCHEM v13.3 output files of some other authors (see Vancoppenolle et al. (2019)).

Table S2. Phase behavior functions for seawater (Marion et al., 2009) derived from a best fit to the output of FREZCHEM v13.3. The piecewise polynomial functions were optimized to ensure that they were continuous across the temperature domain from 0 °C to −33 °C and that $F_1(0) = 0$ and $F_2(0) = \frac{\rho_w(T=T_m)}{\rho_i(T=T_m)} - 1$. The temperature breakpoints precede major precipitation events that occur along the freezing pathway (i.e., the formation of hydrohalite at −22.9 °C and meridianiite at −33.3 °C). F_3 is zero above −6.4 °C, where mirabilite begins to form, since a negligible amount of salt precipitates above this temperature. Brine is no longer stable below the eutectic temperature of −36.2 °C.

$F_1(T) = a_1T^3 + b_1T^2 + c_1T + d_1$				
Temperature (°C)	a_1	b_1	c_1	d_1
$0 \geq T \geq -22.8$	-1.2639×10^{-3}	-2.8711×10^{-1}	-1.9451×10^1	0
$-22.8 \geq T \geq -33.3$	-4.3760×10^{-1}	-4.2299×10^1	-1.4294×10^3	-1.5479×10^4
$-33.3 > T \geq -36.2$	-2.1724×10^{-1}	-2.6462×10^1	-1.1510×10^3	-1.4946×10^4
$F_2(T) = a_2T^3 + b_2T^2 + c_2T + d_2$				
Temperature (°C)	a_2	b_2	c_2	d_2
$0 \geq T \geq -22.8$	-3.2209×10^{-6}	-3.1992×10^{-4}	-1.6257×10^{-2}	9.0673×10^{-2}
$-22.8 \geq T \geq -33.3$	-3.4364×10^{-4}	-3.3285×10^{-2}	−1.1263	-1.2116×10^1
$-33.3 > T \geq -36.2$	-1.7424×10^{-4}	-2.1228×10^{-2}	-9.2188×10^{-1}	-1.1881×10^1
$F_3(T) = a_3T^3 + b_3T^2 + c_3T + d_3$				
Temperature (°C)	a_3	b_3	c_3	d_3
$-6.4 \geq T \geq -22.8$	-5.5615×10^{-6}	-3.4648×10^{-4}	-9.3360×10^{-3}	-4.6587×10^{-2}
$-22.8 \geq T \geq -33.3$	-4.4404×10^{-4}	-4.3059×10^{-2}	−1.4537	-1.5972×10^1
$-33.3 > T \geq -36.2$	-2.2481×10^{-4}	-2.7533×10^{-2}	−1.1977	-1.5854×10^1

Table S3. Phase behavior functions for the binary solutions NaCl and MgSO₄ derived from a best fit to the output of FREZCHEM v15.1. The piecewise polynomial functions were optimized to ensure that they were continuous across the temperature domain and that $F_1(0) = 0$ and $F_2(0) = \frac{\rho_w(T=T_m)}{\rho_i(T=T_m)} - 1$. Note that because no salts precipitate at temperatures higher than the eutectic temperature, F_3 is zero. Brine is no longer stable below the eutectic temperature (-21.3 °C for NaCl and -3.5 °C for MgSO₄).

$F_1(T) = a_1T^3 + b_1T^2 + c_1T + d_1$					
Species	Temperature (°C)	a_1	b_1	c_1	d_1
NaCl	$0 \geq T \geq -21.3^a$	-7.0940×10^{-4}	-2.4083×10^{-1}	-1.7786×10^1	4.4811×10^{-2}
MgSO ₄	$0 \geq T \geq -3.5^a$	1.8483	1.6781×10^{-1}	-7.8748×10^1	1.9840×10^{-1}
$F_2(T) = a_2T^3 + b_2T^2 + c_2T + d_2$					
Species	Temperature (°C)	a_2	b_2	c_2	d_2
NaCl	$0 \geq T \geq -21.3^a$	-2.8790×10^{-6}	-2.8102×10^{-4}	-1.4350×10^{-2}	9.0709×10^{-2}
MgSO ₄	$0 \geq T \geq -3.5^a$	1.3459×10^{-3}	-3.8949×10^{-3}	-8.8293×10^{-2}	9.0895×10^{-2}

^aWe note that the eutectic temperatures obtained from FREZCHEM v15.1 differ slightly from those published in the literature.

Estimated eutectic temperatures for NaCl range from -21 °C to -22.4 °C (Drebushchak et al., 2019), although recent works adopt a eutectic temperature of -21.1 ± 0.1 °C (Drebushchak et al., 2017; Light et al., 2009; Bode et al., 2015). The eutectic temperature for MgSO₄ is estimated to be -3.9 °C (Genceli et al., 2007; Fortes et al., 2008). PHREEQC predicts eutectic temperatures of -21.1 °C for NaCl and -3.8 °C for MgSO₄, using the ColdChem database, and eutectic temperatures of -21.1 °C for NaCl and -3.4 °C for MgSO₄, using the frezchem database.

Table S4. Phase behavior functions for chloride analog endmember composition for Europa's ocean derived from FREZCHEM v15.1. The temperature breakpoint precedes a major precipitation event that occurs along the freezing pathway (i.e., the formation of hydrohalite at -22.5 °C). F_3 is zero above -6.1 °C (i.e., where mirabilite begins to form) since salt does not precipitate above this temperature. Brine is no longer stable below the eutectic temperature of -32.2 °C. The piecewise polynomial functions were optimized to ensure that they were continuous across their domain and that $F_1(0) = 0$ and $F_2(0) = \frac{\rho_w(T=T_m)}{\rho_i(T=T_m)} - 1$.

$F_1(T) = a_1T^3 + b_1T^2 + c_1T + d_1$				
Temperature (°C)	a_1	b_1	c_1	d_1
$0 \geq T \geq -22.4$	-1.1294×10^{-3}	-2.8149×10^{-1}	-1.9146×10^1	0
$-22.4 \geq T \geq -32.2$	-6.0432×10^{-1}	-5.6265×10^1	-1.8131×10^3	-1.8873×10^4
$F_2(T) = a_2T^3 + b_2T^2 + c_2T + d_2$				
Temperature (°C)	a_2	b_2	c_2	d_2
$0 \geq T \geq -22.4$	-3.2037×10^{-6}	-3.1727×10^{-4}	-1.6009×10^{-2}	9.0673×10^{-2}
$-22.4 \geq T \geq -32.2$	-4.8362×10^{-4}	-4.5048×10^{-2}	-1.4516	-1.5023×10^1
$F_3(T) = a_3T^3 + b_3T^2 + c_3T + d_3$				
Temperature (°C)	a_3	b_3	c_3	d_3
$-6.1 \geq T \geq -22.4$	-5.5705×10^{-6}	-3.3455×10^{-4}	-8.7581×10^{-3}	-4.1939×10^{-2}
$-22.4 \geq T \geq -32.2$	-6.5682×10^{-4}	-6.1217×10^{-2}	-1.9691	-2.0724×10^1

Table S5. Phase behavior functions for sulfate analog endmember composition for Europa's ocean derived from FREZCHEM v15.1. The temperature breakpoint precedes a major precipitation event that occurs along the freezing pathway (i.e., the formation of meridianiite at -5.7 °C). F_3 is zero above -3.4 °C in the SO_4 -dominated case (i.e., where mirabilite begins to form) since salt does not precipitate above this temperature. Brine is no longer stable below the eutectic temperature of -32.2 °C. The piecewise polynomial functions were optimized to ensure that they were continuous across their domain and that $F_1(0) = 0$ and $F_2(0) = \frac{\rho_w(T=T_m)}{\rho_i(T=T_m)} - 1$.

$F_1(T) = a_1T^3 + b_1T^2 + c_1T + d_1$				
Temperature (°C)	a_1	b_1	c_1	d_1
$0 \geq T \geq -5.6$	1.8370×10^{-1}	3.3590×10^{-1}	-5.0106×10^1	0
$-5.6 \geq T \geq -32.2$	-1.9041×10^{-1}	-1.4282×10^1	-4.3325×10^2	-1.7529×10^3
$F_2(T) = a_2T^3 + b_2T^2 + c_2T + d_2$				
Temperature (°C)	a_2	b_2	c_2	d_2
$0 \geq T \geq -5.6$	2.4977×10^{-5}	-1.4689×10^{-3}	-5.4060×10^{-2}	9.0673×10^{-2}
$-5.6 \geq T \geq -32.2$	-1.9265×10^{-4}	-1.4447×10^{-2}	-4.3544×10^{-1}	-1.6763
$F_3(T) = a_3T^3 + b_3T^2 + c_3T + d_3$				
Temperature (°C)	a_3	b_3	c_3	d_3
$-3.4 \geq T \geq -5.6$	1.2940×10^{-3}	1.5725×10^{-2}	3.8278×10^{-2}	2.1866×10^{-3}
$-5.6 \geq T \geq -32.2$	-3.7263×10^{-4}	-2.7554×10^{-2}	-8.0217×10^{-1}	-3.6398

Table S6. Salt minerals precipitating in FREZCHEM v15.1 simulations of our analog endmember compositions for Europa's ocean. The temperature at which a given salt mineral first begins precipitating (i.e., the highest temperature of occurrence) is provided for different simulated ocean salinities $S_b(T = T_0)$ assuming a pressure of 1 atm. Note that for $S_b \geq 100$ ppt certain salts begin precipitating at higher temperatures, influencing the phase behavior functions shown in Fig. S1 and Fig. S2.

$S_b(T = T_0)$ (ppt)	1	10	20	30	40	50	100	150	200	250
Cl-Dominated	Temperature (°C)									
<i>Mirabilite</i> $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$	-6.1	-6.1	-6.1	-6.1	-6.1	-6.1	-5.7	-0.2	≥ 0.0	≥ 0.0
<i>Hydrohalite</i> $\text{NaCl} \cdot 2\text{H}_2\text{O}$	-22.5	-22.5	-22.5	-22.5	-22.5	-22.5	-22.5	-22.5	-22.5	-13.8
<i>Meridianiite</i> $\text{MgSO}_4 \cdot 11\text{H}_2\text{O}^a$	-32.3	-32.3	-32.3	-32.3	-32.3	-32.3	-32.3	-32.3	-32.3	-32.3
SO₄-Dominated	Temperature (°C)									
<i>Mirabilite</i> $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$	-3.4	-3.4	-3.4	-3.4	-3.4	-3.4	-3.4	-2.0	≥ 0.0	≥ 0.0
<i>Meridianiite</i> $\text{MgSO}_4 \cdot 11\text{H}_2\text{O}$	-5.7	-5.7	-5.7	-5.7	-5.7	-5.7	-5.7	-5.7	-5.7	≥ 0.0
<i>Hydrohalite</i> $\text{NaCl} \cdot 2\text{H}_2\text{O}^a$	-32.3	-32.3	-32.3	-32.3	-32.3	-32.3	-32.3	-32.3	-32.3	-32.3

^aFREZCHEM predicts this salt will precipitate beyond the final convergent temperature step, so we estimate this

temperature as 0.1 °C below the eutectic temperature.

Table S7. Salt precipitation sequences obtained by freezing simulations of our analog end-member compositions for Europa’s ocean, using PHREEQC and FREZCHEM. In FREZCHEM we define the eutectic temperature as the final convergent temperature step in the simulation; however in PHREEQC, we define it as the temperature where the final moles in assemblage is no longer increasing. Note that for the PHREEQC simulation of the Cl-Dominated composition, both the ColdChem and frezchem databases predict the dissolution of mirabilite once meridianiite starts to form. Because our FREZCHEM simulation does not converge where meridianiite begins to form, this is not represented in our results.

	Temperature, T (°C)			
	Cl-Dominated			
	FREZCHEM		PHREEQC	
	v13.3	v15.1	ColdChem	frezchem
<i>Mirabilite</i>				
$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$	−6.1	−6.1	−6.3	−6.0
<i>Hydrohalite</i>				
$\text{NaCl} \cdot 2\text{H}_2\text{O}$	−22.5	−22.5	−22.3	−22.4
<i>Meridianiite</i>				
$\text{MgSO}_4 \cdot 11\text{H}_2\text{O}$	-	−32.3 ^a	−31.3	−31.9
$\text{MgCl}_2 \cdot 12\text{H}_2\text{O}$	-	-	*	−34.9
Eutectic Temperature	−32.2	−32.2	−35.3	−35.3
	SO4-Dominated			
	FREZCHEM		PHREEQC	
	v13.3	v15.1	ColdChem	frezchem
<i>Mirabilite</i>				
$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$	−3.4	−3.4	−3.4	−3.3
<i>Meridianiite</i>				
$\text{MgSO}_4 \cdot 11\text{H}_2\text{O}$	−5.7	−5.7	−5.7	−5.6
<i>Hydrohalite</i>				
$\text{NaCl} \cdot 2\text{H}_2\text{O}$	-	−32.3 ^a	*	*
Eutectic Temperature	−32.2	−32.2	−31.2	−31.3

^aFREZCHEM predicts this salt will precipitate beyond the final convergent

temperature step, so we estimate this temperature as 0.1 °C below the eutectic temperature of −32.2 °C.

*Although this salt does not precipitate in the simulation, at the final convergent temperature step the saturation index is near zero, suggesting precipitation is likely imminent.

References

- Bode, A. A., Pulles, P. G., Lutz, M., Poullisse, W. J., Jiang, S., Meijer, J. A., . . . Vlieg, E. (2015). Sodium chloride dihydrate crystals: morphology, nucleation, growth, and inhibition. *Crystal Growth & Design*, 15(7), 3166–3174.
- Cox, G. F., & Weeks, W. F. (1983). Equations for determining the gas and brine volumes in sea-ice samples. *Journal of Glaciology*, 29(102), 306–316.
- Drebushchak, V., Drebushchak, T., Ogienko, A., & Yunoshev, A. (2019). Crystallization of sodium chloride dihydrate (hydrohalite). *Journal of Crystal Growth*, 517, 17–23.
- Drebushchak, V., Ogienko, A., & Yunoshev, A. (2017). Metastable eutectic melting in the nacl-h₂o system. *Thermochimica acta*, 647, 94–100.
- Fortes, A., Wood, I., & Knight, K. (2008). The crystal structure and thermal expansion tensor of mgso₄·11d₂o (meridianiite) determined by neutron powder diffraction. *Physics and Chemistry of Minerals*, 35(4), 207–221.
- Genceli, F. E., Lutz, M., Spek, A. L., & Witkamp, G.-J. (2007). Crystallization and characterization of a new magnesium sulfate hydrate mgso₄· 11h₂o. *Crystal Growth and Design*, 7(12), 2460–2466.
- Light, B., Brandt, R. E., & Warren, S. G. (2009). Hydrohalite in cold sea ice: Laboratory observations of single crystals, surface accumulations, and migration rates under a temperature gradient, with application to “snowball earth”. *Journal of Geophysical Research: Oceans*, 114(C7).
- Marion, G., Farren, R., & Komrowski, A. (1999). Alternative pathways for seawater freezing. *Cold Regions Science and Technology*, 29(3), 259–266.
- Marion, G., Kargel, J., Catling, D., & Lunine, J. (2012). Modeling ammonia–ammonium

- aqueous chemistries in the solar system's icy bodies. *Icarus*, *220*(2), 932–946.
- Marion, G., Kargel, J. S., Catling, D. C., & Jakubowski, S. D. (2005). Effects of pressure on aqueous chemical equilibria at subzero temperatures with applications to europa. *Geochimica et Cosmochimica Acta*, *69*(2), 259–274.
- Marion, G., Millero, F., & Feistel, R. (2009). Precipitation of solid phase calcium carbonates and their effect on application of seawater s a–t–p models. *Ocean Science*, *5*(3), 285–291.
- Petrich, C., & Eicken, H. (2017). Overview of sea ice growth and properties. *Sea ice*, 1–41.
- Vancoppenolle, M., Madec, G., Thomas, M., & McDougall, T. J. (2019). Thermodynamics of sea ice phase composition revisited. *Journal of Geophysical Research: Oceans*, *124*(1), 615–634.