Modeling Interfacial Liquid Layers in Environmental Ices

SUPPLEMENTARY MATERIAL

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Derivation of BL Model

Additional symbols not listed in Table 1

Symbol	***Quantity***
f_w^{ice}	Fugacity of pure ice
$\hat{f}_w^{brine}$	Fugacity of water in brine layer
f_w^{vap}	Fugacity of water in vapor space above ice
f_w	Fugacity of pure liquid water
x_w	Mole fraction of water in brine layer
H_w^{ice}	Enthalpy of ice at T, P
$H_w^{ice,0}$	Enthalpy of ice at reference state
$\overline{H}_w^{brine}$	Partial molar enthalpy of water in brine layer
$H_w^{liq,0}$	Enthalpy of water in unfrozen liquid solution at reference state
$\Delta\overline{H}_w^{brine}$	Enthalpy change upon formation of brine layer
ΔH_w^{vap}	Enthalpy change upon vaporization
V_w^{ice}	Volume of ice at T, P
$\overline{V}_w^{brine}$	Partial molar volume of water in brine layer
ΔV_w^{fus}	Volume change of fusion
$\Delta\overline{V}_w^{brine}$	Volume change upon formation of brine layer
ΔV_w^{vap}	Volume change upon vaporization
γ_w	Activity coefficient of water in brine
m_s	Molality of solute in brine layer [=] mole/kg water
M_w	Molar mass of water

Derivation

At equilibrium (Tester and Modell, 1996),

$$d\ln f_w^{ice} = d\ln \hat{f}_w^{brine} \tag{S1}$$

Expanding,

$$\left(\frac{\partial \ln f_w^{ice}}{\partial T}\right)_P dT + \left(\frac{\partial \ln f_w^{ice}}{\partial P}\right)_T dP = \left(\frac{\partial \ln \hat{f}_w^{brine}}{\partial T}\right)_{P,x_w} dT + \left(\frac{\partial \ln \hat{f}_w^{brine}}{\partial P}\right)_{T,x_w} dP + \left(\frac{\partial \ln \hat{f}_w^{brine}}{\partial x_w}\right)_{T,P} dx_w \tag{S2}$$

Substituting for the partial derivatives of fugacity,

$$\left(\frac{H_w^{ice} - H_w^{ice,0}}{RT^2}\right) dT + \frac{V_w^{ice}}{RT} dP = \left(\frac{\bar{H}_w^{brine} - H_w^{liq,0}}{RT^2}\right) dT + \frac{\bar{V}_w^{brine}}{RT} dP + \left(\frac{\partial \ln \hat{f}_w^{brine}}{\partial x}\right)_{T,P} dx_w \tag{S3}$$

Collecting terms,

$$\left(\frac{\partial \ln \hat{f}_w^{brine}}{\partial x_w}\right)_{T,P} \frac{dx_w}{dT} = \left(\frac{H_w^{ice} - \bar{H}_w^{brine}}{RT^2}\right) + \frac{V_w^{ice} - \bar{V}_w^{brine}}{RT} \frac{dP}{dT} \tag{S4}$$

$$\left(\frac{\partial \ln \hat{f}_w^{brine}}{\partial x_w}\right)_{T,P} \frac{dx_w}{dT} = \left(\frac{\Delta H_w^{fus} - \Delta \bar{H}_w^{brine}}{RT^2}\right) + \left(\frac{\Delta V_w^{fus} - \Delta \bar{V}_w^{brine}}{RT}\right) \frac{dP}{dT} \tag{S5}$$

we know

$$\hat{f}_w^{brine} = \gamma_w f_w x_w \tag{S6}$$

therefore,

$$\left(\frac{\partial \ln \hat{f}_w^{brine}}{\partial x_w}\right)_{T,P} = \frac{1}{\gamma_w}\left(\frac{\partial \gamma_w}{\partial x_w}\right)\Big|_{T,P} + \frac{1}{x_w} = \left(\frac{\partial \ln \gamma_w}{\partial x_w}\right)_{T,P} + \frac{1}{x_w} \tag{S7}$$

Substituting into eq (S5) yields

$$\left[\left(\frac{\partial \ln \gamma_w}{\partial x_w}\right)_{T,P} + \frac{1}{x_w}\right] \frac{dx_w}{dT} = \left(\frac{\Delta H_w^{fus} - \Delta \bar{H}_w^{brine}}{RT^2}\right) + \left(\frac{\Delta V_w^{fus} - \Delta \bar{V}_w^{brine}}{RT}\right) \frac{dP}{dT} \tag{S8}$$

Also,

$$d\ln f_w^{vap} = d\ln \hat{f}_w^{brine} \tag{S9}$$

$$\left(\frac{\partial \ln \hat{f}_w^{brine}}{\partial x_w}\right)_{T,P} \frac{dx_w}{dT} = \left(\frac{\Delta H_w^{vap} - \Delta \bar{H}_w^{brine}}{RT^2}\right) + \left(\frac{\Delta V_w^{vap} - \Delta \bar{V}_w^{brine}}{RT}\right) \frac{dP}{dT} \tag{S10}$$

Equating eqs (S5) and (S10),

$$\frac{dP}{dT} = \frac{-1}{T}\left(\frac{\Delta H_w^{vap} - \Delta H_w^{fus}}{\Delta V_w^{vap} - \Delta V_w^{fus}}\right) \tag{S11}$$

Substituting eq (S11) into eq (S8),

$$\left[\left(\frac{\partial \ln \gamma_w}{\partial x_w}\right)_{T,P} + \frac{1}{x_w}\right]\frac{dx_w}{dT} = -\left(\frac{\Delta H_w^{fus} - \Delta \bar{H}_w^{brine}}{RT^2}\right) + \left(\frac{\Delta V_w^{fus} - \Delta \bar{V}_w^{brine}}{RT}\right)\left(\frac{\Delta H_w^{vap} - \Delta H_w^{fus}}{T\left(\Delta V_w^{vap} - \Delta V_w^{fus}\right)}\right) \tag{S12}$$

Neglect the partial molar enthalpy and volume of mixing, and simplify.

$$\left[\left(\frac{\partial \ln \gamma_w}{\partial x_w}\right)_{T,P} + \frac{1}{x_w}\right]\frac{dx_w}{dT} = \frac{\Delta V_w^{fus}\Delta H_w^{vap} - \Delta H_w^{fus}\Delta V_w^{vap}}{RT^2\left(\Delta V_w^{vap} - \Delta V_w^{fus}\right)} \tag{S13}$$

Dividing through on top & bottom by ΔV_w^{vap} and using the fact that $\Delta V_w^{fus} << \Delta V_w^{vap}$, eq (S13) simplifies to:

$$\left[\left(\frac{\partial \ln \gamma_w}{\partial x_w}\right)_{T,P} + \frac{1}{x_w}\right]\frac{dx_w}{dT} = \frac{-\Delta H_w^{fus}}{RT^2} \tag{S14}$$

Eq (S14) can be rewritten in terms of solute mole fraction x_s using the Gibbs-Duhem equation

$$\left(x_w \frac{\partial \ln \gamma_w}{\partial x_w}\right)_{T,P} = \left(x_s \frac{\partial \ln \gamma_s}{\partial x_s}\right)_{T,P} \tag{S15}$$

and the fact that $x_w = 1 - x_s$:

$$\frac{1}{1-x_s}\left[x_s\left(\frac{\partial ln\gamma_s}{\partial x_s}\right)_{T,P} + 1\right]\frac{dx_s}{dT} = \frac{-\Delta H_w^{fus}}{RT^2} \tag{S16}$$

For systems with non-volatile solutes, the concentration and activity coefficient equations are often expressed in terms of molality rather than mole fraction. Equations S16 can be written in terms of solute molality using the substitution:

$$m_s = \frac{1000}{M_w}\left(\frac{x_s}{1-x_s}\right) \tag{S17}$$

where m_s has the units of (mole solute/kg H_2O) and M_w is the molar mass of water.

For example, eq (S16) can be rewritten as:

$$\left[\frac{m_s M_w}{1000}\left(\frac{\partial ln\gamma_s}{\partial m_s}\right)_{T,P} + \frac{1}{1000/_{M_w} + m_s}\right]\frac{dm_s}{dT} = \frac{\Delta H_w^{fus}}{RT^2} \tag{S18}$$

REFERENCES

Tester, J.W. and Modell, M. Thermodynamics and its Applications, 3rd Ed. Prentice Hall, Upper Saddle River, N.J. (1996)

FIGURES

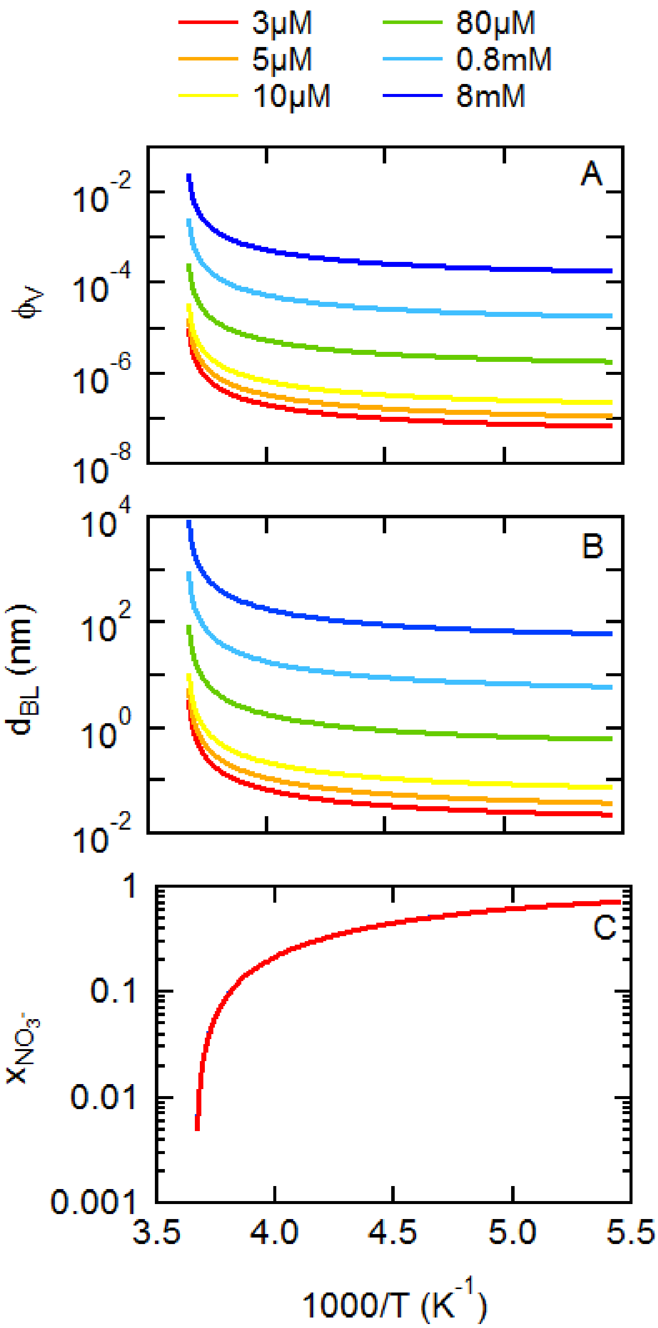

Figure S1: Model prediction based on non-volatile solute scenario of A) brine volume fraction, B) brine thickness calculated assuming spherical ice crystals, 1 mm in radius and C) nitrate mole fraction in the brine at different nitrate concentrations in the melt and at a range of temperatures assuming ideal behavior

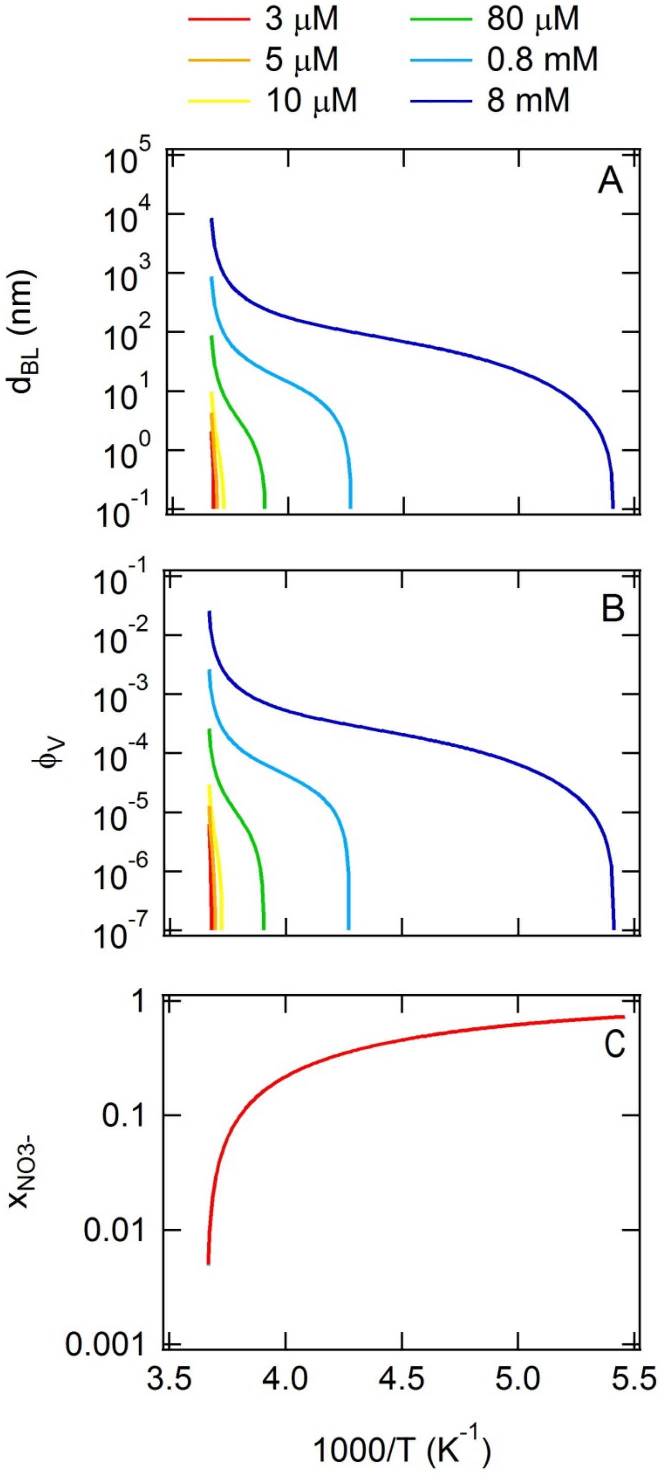

Figure S2: Model prediction for the scenario where solute partitioning is allowed based on gas-brine and gas-ice equilibrium for A) brine volume fraction, B) brine thickness calculated assuming spherical ice crystals, 1 mm in radius and C) nitrate mole fraction in the brine at different nitrate concentrations in the melt and a range of temperatures assuming ideal behavior.

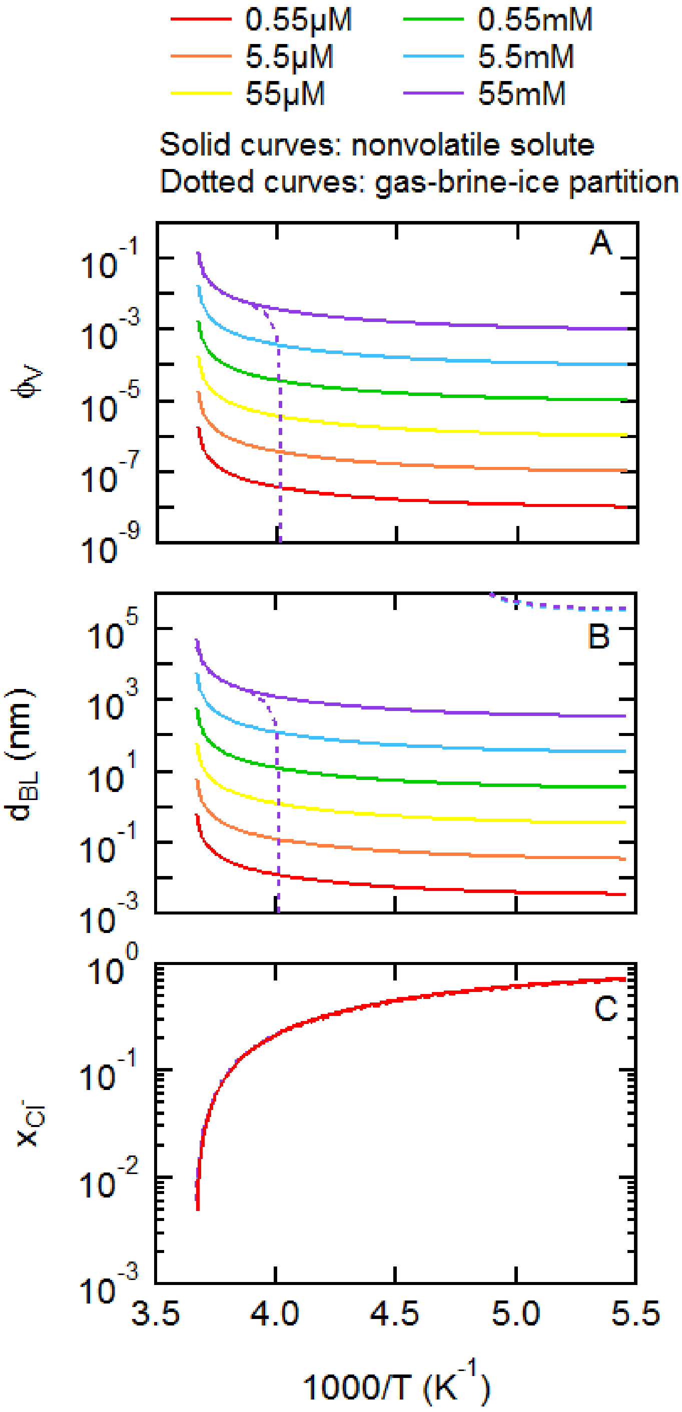

Figure S3: Model prediction of A) brine volume fraction, B) brine thickness calculated assuming spherical ice crystals, 1 mm in radius and C) chloride mole fraction in the brine at different chloride concentrations in the melt and at a range of temperatures assuming ideal behavior. The solid lines represent the non-volatile solute scenario. The dotted lines represent a partitioning scenario based on gas-brine and gas-ice equilibrium.