AQUEOUS AND SOLID-PHASE EQUATIONS OF STATE FOR THE H_2O-MGSO$_4$ SYSTEM: PREDICTION OF OCEAN AND ICE THICKNESSES FOR GANYMEDE AND OTHER ICY WORLDS.

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Introduction: The largest icy satellites in the solar system contain vast stores of liquid water, providing a key ingredient for habitability. Ganymede, Callisto, and Titan are weaker candidates for habitability than Europa, in part because of the assumption that high-pressure ice layers cover their seafloors and prevent significant water-rock interaction thought necessary for creating and sustaining life. Water-rock interactions may occur, however, if heating at the rock-ice interface is sufficient for melting. Highly saline fluids would be gravitationally stable, and might accumulate due to upward migration and refreezing of less concentrated liquids. We combine new thermodynamic data for aqueous $MgSO_4$—covering the range of pressure temperature relevant to Ganymede's ocean—with available phase-equilibrium data to calculate activity coefficients and predict water- ice freezing. The new equation of state is combined with thermal profiles in Ganymede to assess the influence of ocean salinity on the thickness of layers of ice I, V, and VI in Ganymede's interior. Ocean concentrations with salinities higher than 10 Wt% are found to have little high pressure ice—or none if heat flux is very high—and can exist in the presence of ice III. We discuss the likelihood for achieving such high salinities in Ganymede's ocean, the consequences for the moon's habitability, and prospects of future missions for testing these predictions.

Development of the Equation of State: We calculate the chemical potential of a $MgSO_4$ solution using the general law for the chemical potential of a non-ideal solution,

$$\mu^L_{H_2O}(P,T,X^L_{H_2O}) = \mu^L_{H_2O,pure} + RT\ln(\gamma^L_{H_2O}X^L_{H_2O}) \qquad (1)$$

To provide a fit to the phase behavior we use a formulation based on the Margules equations, in which the activity coefficient is expressed as

$$RT\ln\gamma = W(1-X^L_{H_2O})^2 \qquad (2)$$

The formulation for the Margules coefficient W adopted here depends on both temperature and pressure:

$$W = w_0\left(1+w_1\tanh(w_2P)\right)\left(1+\frac{w_3}{(T-T_o)^2}\right) \qquad (3)$$

with w_0=-1.8.106 J mol^{-1}, w_1=150, w_2=1.45.10^{-4} MPa^{-1}, w_3=-12 K^2 and T_o=246 K. The resulting coefficients reproduce available data, allowing us to construct a phase diagram for pure ice up to the pressure- and temperature-dependent eutectic composition.

Available experimental phase data for the pure water ice phase boundary in the presence of dissolved magnesium sulfate are employed as follows: Fortes and Choukroun [1], covering the liquidus with Ice Ih at atmospheric pressure; Hogenboom et al. [2], covering the liquidus with Ice V at P = 390 MPa. We also use information for the eutectic melting curve (temperature of the eutectic or lowest-melting-point composition) as a function of pressure. The majority of these data come from [2]. For $P > 390$ MPa, we adopt a polynomial fit between the experimental melting points of Nakamura and Ohtani [3] at pressures near 2 GPa and eutectic data at 390 MPa from Hogenboom et al. [1], with additional data from Grasset et al. [4] in the range from 0-600 MPa. The highest-pressure data of Nakamura and Ohtani [3] are viewed with skepticism because the experiments, as described, did not wait for thermodynamic equilibrium to be achieved, implying a large error that might be associated with supercooling. Further experimental work would be

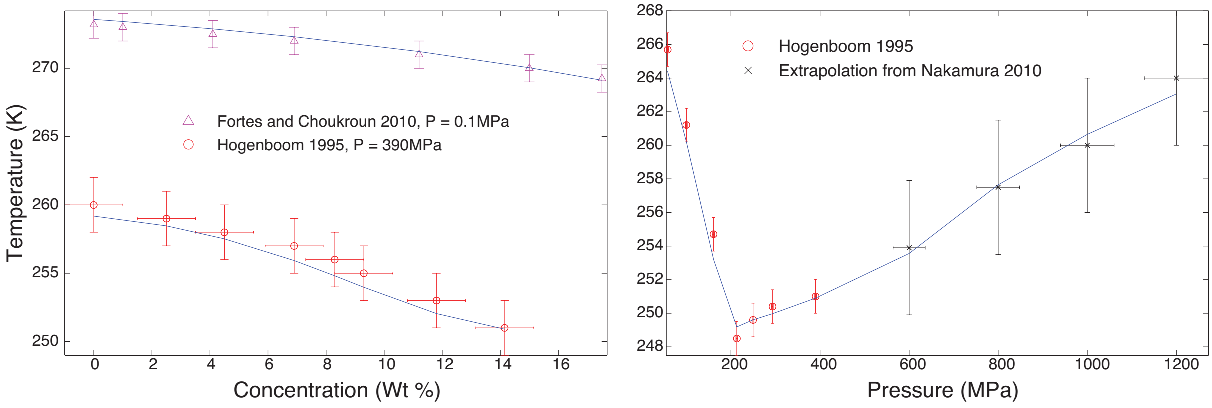

Figure 1. Predictions of phase equilibria for aqueous $MgSO_4$ (solid lines). Left: Equilibrium melting tempreatures for the MgSO4 system vs concentration at 0.1 MPa (upper) and 390 MPa (lower). Right: Eutectic temperature as a function of pressure.

helpful to clarify the eutectic melting curve between 600 MPa and 2 GPa. Fit results with assessed errors are summarized in Fig. 1.

Application to Ganymede To assess the effect of dissolved $MgSO_4$ on melting of water ices in Ganymede using our equations of state, we construct thermal models consistent with the expected range of internal heat fluxes from Ganymede's interior.

We consider a H_2O layer with P_{max} set to 1.2 GPa at the lowest depth and T_o=110 K, the average surface temperature of Ganymede. Thermal profiles are determined using an iterative method. At each step of depth, the new pressure, temperature, ice-liquid equilibrium state, and associated thermodynamic properties are calculated using the values found at the preceding step. The calculation for Ganymede's uppermost ice I layer is divided by 20 steps, and the remaining region below is divided into 50 steps, corresponding to errors of up to 5% and 4% in the estimate of layer thicknesses, respectively. For the purposes of calculating depths and buoyancies, gravity is assumed uniformly equal to 1.428 ms^{-2}.

The conductive temperature profile for the ice I upper layer assumes temperature-dependent conductivity of the form $k = D/T$, for which the temperature profile may be represented as a function of depth z as

$$T(z) = T_b^{z/z_b} T_o^{(1-z/z_b)} \tag{4}$$

with corresponding heat flux at the ice I-water interface (z_b and T_b),

$$q_b = D\frac{\ln T_b}{z_b} \tag{5}$$

We use D=632 W m^{-1} [5]; other thermodynamic properties for water ice are taken from Choukroun and Grasset [6]. Temperature values of {255, 260, 265, 270} K chosen for the lower boundary condition T_b correspond to the liquidus with ice I over the range of eutectic temperatures for the (aq)$MgSO_4$ system. For a 10 Wt% ocean, T_b=250 K produces a thin ocean layer with ice III underneath. Equilibrium heat flow values are in the range anticipated for radiogenic heating alone (≈20 mW m^{-2}) to the upper limit for tidal heating [≈120 mW m^{-2}; e.g., 7], except for the seemingly unphysical situation in which T_b=270 for concentrations exceeding 5 Wt%.

The liquid ocean is assumed to be unstratified for simplicity, with a convective adiabatic thermal profile, $dT/dP=\alpha T/\rho C_P$, based on fluid properties obtained by Vance and Brown [revision submitted]. Profiles were calculated to the base of Ganymede's H_2O-bearing layer for the purpose of evaluating buoyancy.

Results and Discussion Bounding conditions of the ice I melting temperature constrain the thickness of Ganymede's ice I upper layer to between 13 km and 150 km. $MgSO_4$ ocean concentrations of up to 5 Wt% would lead to oceans of thickness between 125 km and 500 km, depending on heat flux. Concentration closer to 10 Wt% would be sufficient to melt the high pressure ices, but would require high heat flux and maintaining a highly saline ocean after dilution with hundreds of km of melted ice. Concentrations higher than 10 Wt% are negatively buoyant at the ice VI-rock interface. The creation of highly saline fluids at the rock interface through accumulation of precipitates provides a potential means for sustaining water-rock interactions that can inject salt into Ganymede's ocean over long time scales, possibly leading to a highly saline and habitable ocean with very little or no high-pressure ice at its base.

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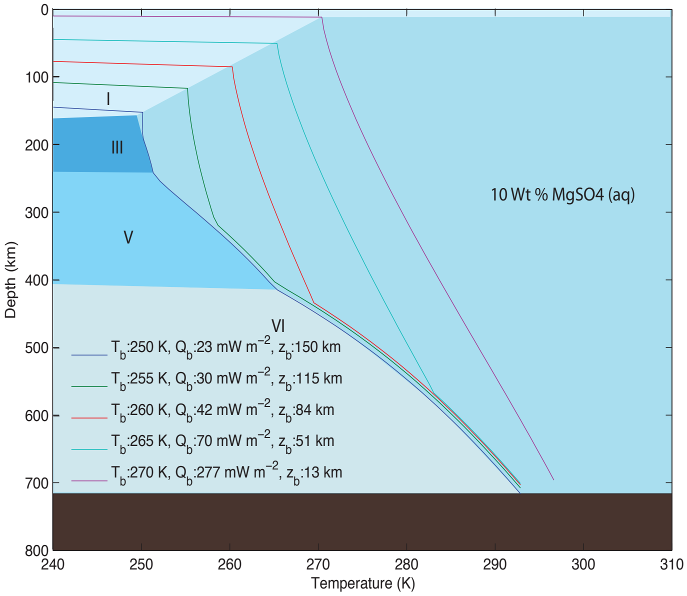

Figure 2. Thermal profiles for Ganymede's interior with a 10 Wt% $MgSO_4$ for bottom melting temperature T_b={250, 255, 260, 265, 270} K. Ice I layer thicknesses and heat flux values are provided for each. T_b=250 K shows the coexistence of a thin ocean with ice III, V, and VI. T_b=270 K eliminates high pressure ice altogether, but requires equilbrium heat flux a factor of two higher than predicted for current maximum heat dissipation [e.g. 7].