FREEZING OF OCEANIC WATER ON EUROPA: THEORETICAL MODELING. M. Yu. Zolotov and E. L. Shock, Department of Earth and Planetary Sciences, Washington University, St. Louis, MO 63130-4899. E-mails: zolotov@zonvark.wustl.edu, shock@zonvark.wustl.edu.

Introduction: Spectroscopic evidence for endogenic hydrated salts [1] and sulfur compounds [2] on the surface on Jupiter's moon Europa, magnetic measurements obtained by the *Galileo* spacecraft [3], and surface morphology features [4] indirectly indicate the existence of an electrolyte water ocean beneath the satellite's icy crust. A broad association of non-icy salty material of a uniform composition with disrupted areas (e.g., linea and mottled terrain, chaos regions) on Europa's surface can be caused by freezing of oceanic water followed by sublimation/sputtering of ice [e.g., 1,5]. Freezing of oceanic water is unavoidable during upwelling of oceanic water in linear fractures of the icy crust, during appearance of water on the surface, and shortly after the formation of "ice holes" caused by meteoritic impacts or internal tectonic/heating events. Preliminary experimental [6] and theoretical thermodynamic models [7,8] for freezing of Europa's ocean gave some initial insights about chemical evolution of model solutions. Here we present results of additional thermodynamic calculations and discuss them in terms of composition and distribution of the non-icy material and oceanic chemistry.

Model: We modeled changes of aquatic chemistry and the equilibrium precipitation of ice and salts during freezing of Europa's oceanic water for an assumed composition (see below). Calculations of phase composition of the low-temperature aqueous system containing concentrated, strong electrolyte solutions were performed by the Gibbs free energy minimization method using the Pitzer model for activity coefficients of aqueous species and water activity [9]. Testing calculations for freezing of terrestrial sea water show good agreement with experimental data [10]. For Europa, the calculations were conducted for the H_2O(liquid, solid)-Na-K-Mg-Ca-S-Cl system. The nominal molar composition of the oceanic water (H_2O, 55.508; Na, 0.049; K, 1.96×10^{-3}; Mg, 0.0619; Ca, 0.02; SO_4, 0.096; Cl, 0.021) corresponds to our working model for the satellite's ocean [11]. The calculations were done at 10^5 Pa total pressure. Temperature was decreased gradually below 0°C until complete freezing was calculated.

Results: The calculation for Europa's water of the nominal composition shows that complete freezing occurs at -45°C. The amount of unfrozen solution decreases rapidly with decreasing temperature, as shown in Fig. 1a. Below ~ -10°C, the solution represents less than a few percent of the initial mass of water. In addition to ice, crystalline salts form during freezing. Temperatures of the first appearance of solid phases formed from freezing water are as follows: ice, -0.5°C; mirabilite (Na_2SO_4•$10H_2O$), -4.3°C; epsomite ($MgSO_4$•$7H_2O$), -12.0°C; bischofite ($MgCl_2$•$12H_2O$), -36.5°C. Once they first appear, all of these phases form until complete freezing occurs. Fig. 1b shows how the volume fraction of various salts changes with freezing. One can see that magnesium and sodium sulfates are the most abundant salts formed.

The formation of ice during freezing leads to increasing salinity of the unfrozen solution, which generates a brine shortly after the ice forms. This is illustrated in Fig. 1c, which shows the increase in ionic strength as temperature decreases. Molar concentrations of aqueous species undergo dramatic changes caused by the increase in total salinity and by the deposition of salts. The latter factor causes changes in relative concentrations among aqueous species during freezing, as shown in Figs. 1d and 1e. The deposition of salts decreases concentrations of salt-forming solutes and increases abundances of other components in the aqueous phase. This can be seen at temperatures below -36.5°C where $MgCl_2$•$12H_2O$ forms. Calcium and potassium do not form precipitated salts from our ocean composition and concentrations of Ca^{2+} and K^+ increase during freezing.

Discussion: The calculated predominance of magnesium and sodium sulfates formed from freezing Europa's water is in agreement with current spectroscopic models for the non-icy material in near infrared and ultraviolet wavebands [1,2], with leaching/freezing experiments of F. Fanale [6], and thoughts based on cosmochemical arguments [12,13].

Calculated changes in chemistry of freezing water suggest that the composition of salts and salty ices in colored, disrupted zones on Europa's surface are not identical to the composition of the ocean. In particular, the surface material in those areas should have higher K/Na and Ca/Mg ratios compared to the ocean. However, the composition of non-icy material can be used to retrieve the oceanic composition using inverse modeling.

Note that our calculations correspond to a slow freezing. Faster, non-equilibrium freezing, which could occur at the contact with the cold surface, should lead to a less profound differentiation compared to the equilibrium model. Nevertheless, the fractionation of freezing water seems to be unavoidable on the surface and when water ascends through fractures in the 1-15 km thick icy crust. The presence of colored non-icy material along linea is consistent with differentiation. When water appears on the surface, the profound heat consumption by surface material should drive the freezing front to move upward. It follows that the uppermost parts of freezing water flows and lakes will be enriched in aqueous species leading to a salty surface when freezing is complete.

Ices formed by rapid non-equilibrium freezing of impact-generated "ice holes" may more closely represent oceanic water. Remote or *in situ* sampling of fresh areas of this type would give more direct information about the oceanic water composition than would non-icy material in disrupted zones. However, a comparison of the salt composition in disrupted zones and in areas where oceanic water was frozen instantaneously would help to better constrain models of the freezing fractionation of the ocean.

Summary: Freezing oceanic water on Europa changes its composition leading to sequential but uneven enrichment in electrolytic solutes. Salts on the surface of linea and other disrupted zones should have higher K/Na and Ca/Mg ratios compared to oceanic water, and will only indirectly represent the composition of the ocean. In the future, the oceanic composition can be restored using inverse models based on the composition of salty ices and salt lag deposits.

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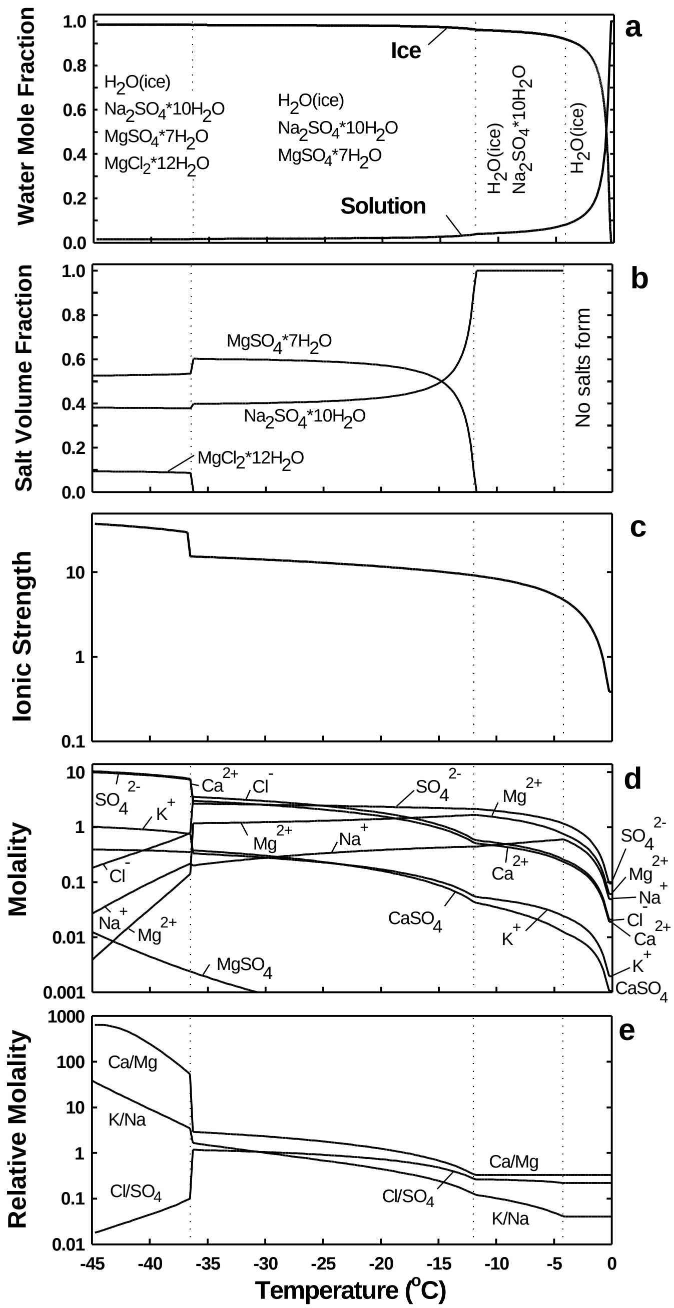

Fig. 1. Changes in chemistry and mineralogy during freezing of Europa's ocean water.