

**BRINE POCKETS IN THE ICY SHELL ON EUROPA: DISTRIBUTION, CHEMISTRY, AND HABITABILITY.** M. Yu. Zolotov<sup>1</sup>, E. L. Shock<sup>1,2</sup>, A. C. Barr<sup>3</sup>, and R. T. Pappalardo<sup>3</sup>. <sup>1</sup>Department of Geological Sciences, <sup>2</sup>Department of Chemistry and Biochemistry, Arizona State University, Tempe, AZ 85287. <sup>3</sup>Laboratory for Atmospheric and Space Physics, University of Colorado, Boulder, CO 80309. E-mail: zolotov@asu.edu.

**Introduction:** On Earth, sea ice is rich in brine, salt, and gas inclusions that form through capturing of seawater during ice formation [1, 2]. Cooling of the ice over time leads to sequential freezing of captured seawater, precipitation of salts, exsolution of gases, and formation of brine channels and pockets. Distribution and composition of brines in sea ice depend on the rate of ice formation, vertical temperature gradient, and the age of the ice. With aging, the abundance of brine pockets decreases through downward migration. Despite low temperatures and elevated salinities, brines in sea ice provide a habitat for photosynthetic and chemosynthetic organisms [1-3].

On Europa, brine pockets and channels could exist in the icy shell that may be from a few km to a few tens of km thick [4,5] and is probably underlain by a water ocean [4,6]. If the icy shell is relatively thick, convection could develop, affecting the temperature pattern in the ice [7-9]. To predict the distribution and chemistry of brine pockets in the icy shell we have combined numerical models of the temperature distribution within a convecting shell [8,9], a model for oceanic chemistry [10], and a model for freezing of European oceanic water [10]. Possible effects of brine and gas inclusions on ice rheology and tectonics are discussed.

**Modeling:** Brine composition is modeled in the framework of temperature distributions within a convective icy shell 20 km thick. The temperature field is calculated using the numerical finite element model Citcom [11] with a Newtonian rheology for ice I and neglecting the effects of tidal heating inside the shell. We use a Rayleigh number of  $3.3 \times 10^6$ , which is calculated using a melting point viscosity at the base of the icy shell of  $5 \times 10^{13}$  Pa s, appropriate to the temperature at the base of an icy shell of 272.85 K. The surface of the shell is held at a constant temperature of 100 K, consistent with Galileo data [12] and earlier models [13], and the oceanic temperature is derived from our chemical model [10]. We neglect the effect of pressure on the temperature of freezing, which is only  $\sim 2^\circ$  at the depth of 20 km at  $\sim 24$  MPa. Note that results will change as a more accurate representation of the rheology of ice (i.e., non-Newtonian) is implemented in the convection model.

The calculated distribution of temperature is used to evaluate chemical composition of brine pockets with the FREZCHEM 5.2 program (written by Giles Marion), which uses the Pitzer model for activities of

solutes and water activity [e.g., 14]. At each temperature and bulk composition of the Mg-Na-Ca-K-SO<sub>4</sub>-Cl-H<sub>2</sub>O system, concentrations and activities of ions and water were calculated together with amounts of brines, precipitated salts, and ice. Slow convection rates obtained in the physical modeling (see next section) make the equilibrium chemical model highly applicable.

**Results:** Modeling with the Citcom code shows that the icy shell is slowly ( $\sim 10^{-9}$  m s<sup>-1</sup>) convecting with the exception of the upper 3-7 km where  $T < 215$  K and a "stagnant lid" is formed. Below this "lid", the shell is mixed in  $\sim 10^5$  years, and the swiftly convecting interior is mixed in  $\sim 10^3$  years. In central parts of convecting cells, temperature variations are small and  $T > \sim 260$  K, as shown in Fig. 1. The eutectic temperature of 237 K for the chosen chemical system (see [10]) is shown by the red isothermal curve. In upwelling parts of convective cells, that eutectic temperature represents conditions of complete freezing. In downwellings, it is the temperature at which brines form. The smallest depth of brine existence at 5.8 km corresponds to upwelling. Salinities of brine pockets are in the range of 200-240 g/kg H<sub>2</sub>O in the central parts of convective cells (Fig. 2). Typically, the pockets contain only 5-0.5 % of the initially captured water (Fig. 3). Concentrations of ions increase as temperature decreases, as can be seen for Cl<sup>-</sup> in Fig. 4. However, the composition of brines is different from that of the oceanic water owing to precipitation or dissolution of salts. For example, brines in the upper part of convective cells have an elevated Cl/SO<sub>4</sub><sup>2-</sup> ratio (Fig. 5). Major salts precipitated from brines are hydrated sulfates of Ca, Na, and Mg, and chlorides of Na and K.

**Discussion:** *Gas inclusions.* Expelling of distilled gases from growing ice crystals and lowering water activity in brines with decreasing temperature can lead to resolution of gases (e.g., CO<sub>2</sub>) that were dissolved in oceanic water. In addition, precipitation of carbonates, which should occur close to the ocean-ice interface, can result in formation of CO<sub>2</sub>, which condenses closer to the surface where brines are completely frozen. Presence of gas inclusions decreases ice density and facilitates its buoyancy.

*Formation and redistribution of brine pockets.* The distribution and amount of brine pockets in the icy shell should be affected by water capturing mechanisms and downward migration of brine. Slow ice convection and correspondingly sluggish formation of ice

at the base of the shell do not favor capturing of oceanic water. Even if captured in local high-velocity upwellings, water pockets can move down into the ocean, as observed in terrestrial sea ice. The temperature gradient and density differences between ice and captured water could be the major factors influencing downward migration. Disruptions of the icy shell through cracking followed by upwelling and freezing of oceanic water (i.e., diking) [15] could be a more effective mechanism of water capturing, at least near the base of the icy shell. Later, convection should disrupt the frozen dikes leading to redistribution of brine, gas, and salt inclusions in lower parts of the shell.

Tidal heating, if it occurs in the ice shell, could be localized in parts of the shell that are weaker due to higher content of brine and gas inclusions. However, the size and geometry of the weak zone, migration of brine pockets from surrounding ice in the temperature gradient and corresponding changes in ice density and in heat release must be taken into account. A coupled compositional-tidal-convective model is needed to best explore the links between the tidal forcing and the observed surface features.

Over time, large ice crystals might grow in the icy shell [16] causing brine, salt, and gas inclusions to be concentrated at grain boundaries. In the downwellings, melting should occur at the grain boundaries where impurities are concentrated. Redistribution of inclusions to the boundaries of large crystals may affect the rheology of the shell and make non-Newtonian flows of ice more likely, especially in downwellings.

*Habitability of brine pockets.* Neither low temperature nor high salinity forbids habitability of brine pockets. However, in contrast to Earth's sea ice, photosynthetic life probably does not exist on Europa. It has been proposed that organisms on Europa could produce methane and acetate from dissolved CO<sub>2</sub> and H<sub>2</sub>, and/or reduce sulfate by H<sub>2</sub> and organic compounds to get energy for metabolism [17,18]. To survive in brine pockets, captured oceanic organisms would have to adapt to low temperatures and high salinities. Limited sources of chemical energy and nutrients during a 10<sup>5</sup> year journey in convective cells also make survivability difficult. Radiolytically-produced oxidants would be harmful rather than useful for captured oceanic organisms that have developed in relatively reduced conditions. If they were to survive in brine pockets, organisms would likely be in a dormant state, except perhaps in the lowest parts of the shell.

**Summary:** Convection in a thick icy shell creates large zones with temperatures above ~240 K in which highly concentrated brines could exist. Brines can be present in the lower and middle parts of the ice shell, depending on the location in the convective pattern. Although the ocean would be a more habitable place

than the ice shell, brine pockets could provide the only habitable niches close to Europa's surface.

**Acknowledgements:** This work is supported by NASA Exobiology grants NAG5-7696 & NCC2-1340.

**References:** [1] Thomas D. N. and Dieckmann G. S. (Eds.) (2003) *Sea Ice*, Blackwell. [2] Horner R. A. (Ed.) (1985) *Sea Ice Biota*, CRC Press. [3] Thomas D. N. and Dieckmann G. S. (2002) *Science*, 295, 641-644. [4] Pappalardo R. T. et al. (1999) *JGR*, 104, 24015-24055. [5] Greenberg R. et al. (1998) *Icarus*, 135, 64-78. [6] Kivelson M. G. et al. (2000) *Science*, 289, 1340-1342. [7] McKinnon W. B. (1999) *GRL*, 26, 951-954. [8] Barr A. C. (2002) *LPS XXXIII*, Abstract 1545. [9] Barr A. C. and Pappalardo R. T. (2003) *LPS XXXVI*, Abstract 1477. [10] Zolotov M. Yu. and Shock E. L. (2001) *JGR*, 106, 32815-32828. [11] Zhong S. M. et al. (1998) *JGR*, 103, 15255-15268. [12] Spencer J. R. et al. (1999) *Science*, 284, 1514-1516. [13] Ojakangas G. W. and Stevenson D. J. (1989) *Icarus*, 81, 220-241. [14] Marion G. M. and Farren R. E. (1999) *GCA*, 63, 1305-1318. [15] Crawford G. D. and Stevenson D. J. (1988) *Icarus*, 73, 66-79. [16] Schmidt K. G. and Dahl-Jensen D. (2002) *LPS XXXIII*, Abstract 1469. [17] McCollom T. M. (1999) *JGR*, 104, 30729-30742. [18] Zolotov M. Yu. and Shock E. L. (2004) *JGR*, submitted.

