

**CHEMISTRY OF FROZEN SODIUM-MAGNESIUM-SULFATE-CHLORIDE BRINES: IMPLICATIONS FOR SURFACE EXPRESSION OF EUROPA'S OCEAN COMPOSITION.** T. H. Vu<sup>1</sup>, R. Hodyss<sup>1,2</sup>, P. V. Johnson<sup>1,2</sup>, M. Choukroun<sup>1,2</sup>, <sup>1</sup>Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA, USA, <sup>2</sup>NASA Astrobiology Institute.

**Introduction:** The composition of Europa's sub-surface ocean is a critical determinant of its habitability. However, our current understanding of the ocean composition is limited to its expression on the surface. We have begun to experimentally investigate the composition of mixed sodium–magnesium–sulfate–chloride solutions when frozen to 100 K, simulating conditions that likely occur as ocean fluids are emplaced onto Europa's surface.

Our goal is to systematically examine how chemical composition of Europa's surface reflects subsurface ocean chemistry and composition, and thus enable constraints to be placed on ocean composition through the observation of surface materials.

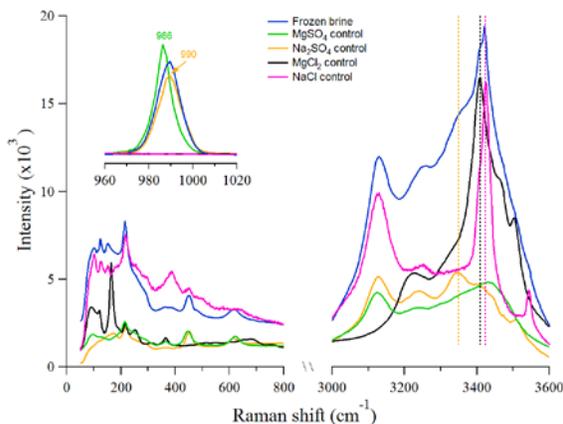
**Experimental:** Frozen  $\text{Na}^+$ - $\text{Mg}^{2+}$ - $\text{Cl}^-$ - $\text{SO}_4^{2-}$  brines were investigated using a confocal dispersive Raman spectrometer (Horiba Jobin-Yvon LabRam HR) with a cryogenic optical stage (Linkam LTS 350). Ten microliter droplets of solution were placed inside the cryostage on a glass microscope slide, and cooled to the temperature of interest. In some cases, samples were annealed at a higher temperature before recooling.

Raman spectra were acquired at  $\sim 1 \text{ cm}^{-1}$  resolution (532 nm excitation, 10 s, 2 accumulations, 600 grooves/mm grating). Optical images of the samples were also acquired. Table 1 gives the concentrations of the ionic solutions used in this work.

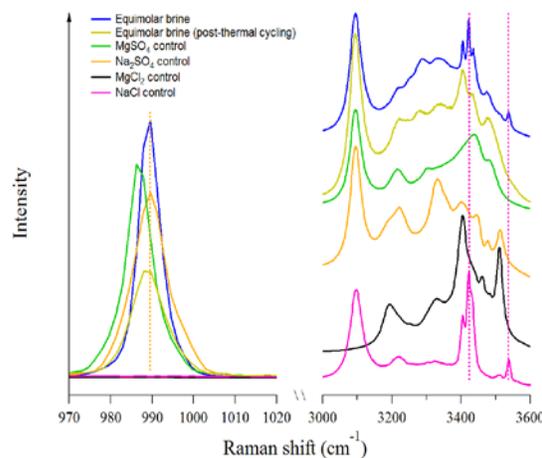
Expt.	$\text{Na}^+$	$\text{Cl}^-$	$\text{Mg}^{2+}$	$\text{SO}_4^{2-}$	$\text{H}^+$	$\text{Na}^+:\text{Mg}^{2+}$
sat.	3.07	3.07	1.44	1.44		2.13 : 1
eq. M	1	1	1	1		1 : 1
ox-salt	1.6	0.3	2.6	3.5	0.5	0.55 : 1

**Table 1.** Concentrations in molar (M) for various ions in the experimental mixtures. Sat.: a 1:1 volume mixture of saturated NaCl and  $\text{MgSO}_4$ . Eq. M: an equimolar mixture of  $\text{Na}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$ . Ox-salt: the “oxidized-salty” composition from [1].

**Results:** Figure 1 shows the results of experiments examining the freezing behavior of a solution composed of a 1:1 volume mixture of saturated solutions of NaCl and  $\text{MgSO}_4$ . The molar concentrations of the ions in this solution are given in Table 1 (sat. experiment). The onset of freezing, indicated by the appearance of crystals, occurred at 211 K. Figure 1 compares the spectrum of the sat. solution with the spectra of control solutions composed of saturated solutions of  $\text{MgSO}_4$ ,  $\text{Na}_2\text{SO}_4$ , NaCl, and  $\text{MgCl}_2$ . We identify the peak at  $990 \text{ cm}^{-1}$  as the  $\nu_1$  symmetric stretching mode of the sulfate



**Figure 1:** Comparison of the Raman spectrum of a frozen brine mixture containing 3.07 M  $[\text{Na}^+]$ , 3.07 M  $[\text{Cl}^-]$ , 1.44 M  $[\text{Mg}^{2+}]$  and 1.44 M  $[\text{SO}_4^{2-}]$  (blue) to that of frozen  $\text{MgSO}_4$  (green),  $\text{Na}_2\text{SO}_4$  (orange),  $\text{MgCl}_2$  (black), and NaCl (magenta) control solutions at 211 K. Inset shows magnification of the sulfate stretch, illustrating the presence of  $\text{Na}_2\text{SO}_4$  in the frozen brine.

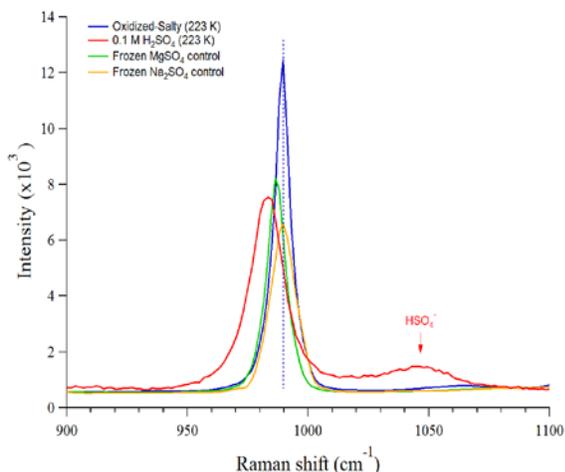


**Figure 2:** Raman spectrum of a frozen mixture containing 1 M each of  $\text{Na}^+$ ,  $\text{Cl}^-$ ,  $\text{Mg}^{2+}$ , and  $\text{SO}_4^{2-}$  at 100 K before (blue) and after (yellow) temperature cycling to 263 K. Control spectra of frozen  $\text{MgSO}_4$  (green),  $\text{Na}_2\text{SO}_4$  (orange),  $\text{MgCl}_2$  (black), and NaCl (magenta) solutions, also at 100 K, are included for comparison. Spectra are vertically offset for clarity.

anion. This position is diagnostic for the formation of mirabilite,  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$  [2]. Other features of interest include the sharp peaks around  $100\text{--}200 \text{ cm}^{-1}$  and especially at  $\sim 3420 \text{ cm}^{-1}$ . These likely indicate pres-

ence of both  $\text{MgCl}_2$  (black dotted line) and  $\text{NaCl}$  (magenta dotted line). The feature at  $3420\text{ cm}^{-1}$  is indicative of hydrohalite ( $\text{NaCl}\cdot 2\text{H}_2\text{O}$ ) [3].  $\text{MgCl}_2$  is likely also hydrated.

The sat. solution discussed above contains an excess of  $\text{Na}^+$ , perhaps biasing the results towards the formation of mirabilite. To test this possibility, we performed an experiment with 1 M each of  $\text{Na}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  frozen to 100 K. In this solution, stoichiometry of the salts would yield an excess of  $\text{Mg}^{2+}$  and  $\text{SO}_4^{2-}$  in the solution. The results are shown in Figure 2. Again, the frequency of the  $\nu_1$  sulfate stretch at  $990\text{ cm}^{-1}$  indicates the formation of mirabilite. Peaks at  $3420$  and  $3536\text{ cm}^{-1}$  (magenta dotted lines) point to the formation of hydrohalite. The sample was subsequently warmed to its melting temperature (263 K), allowing the sample to equilibrate before refreezing it at 100 K. After thermal cycling, virtually all of the remaining hydrohalite had melted and did not recrystallize upon subsequent cooling, suggesting that this species is not to be expected at thermodynamic equilibrium.



**Figure 3:** Raman spectrum of a frozen oxidized-salty mixture (blue), whose composition is detailed in Table 1. Spectra of frozen  $\text{MgSO}_4$  (green),  $\text{Na}_2\text{SO}_4$  (orange), and  $0.1\text{ M H}_2\text{SO}_4$  (red) solutions are included for comparison. The broad feature at  $\sim 1050\text{ cm}^{-1}$  in the latter is due to the presence of bisulfate anions.

Figure 3 shows the results of an experiment using the “oxidized-salty” composition defined in Table 1. This solution more closely mimics the possible composition of the European ocean. The same behavior is observed with this solution as with the sat. solution and the equimolar solution. This solution was highly acidic ( $\text{pH} \sim 1$ ), so a  $0.1\text{ M H}_2\text{SO}_4$  solution was frozen to 233 K for comparison. The  $\nu_1$  sulfate stretch peak is again found at  $990\text{ cm}^{-1}$ , indicating the formation of mirabilite.

**Conclusions:** Our results indicate that solutions containing  $\text{Na}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$  form  $\text{Na}_2\text{SO}_4$  and  $\text{MgCl}_2$  preferentially on freezing. As such, epsomite ( $\text{MgSO}_4\cdot 7\text{H}_2\text{O}$ ) cannot form directly upon freezing of an Na-rich ocean unless the  $\text{SO}_4^{2-}$  concentration is more than half that of  $\text{Na}^+$ .

If  $\text{NaCl}$  is present on the surface, as suggested by Hand & Carlson (2015) [4], then either the ocean is very rich in  $\text{Na}^+/\text{Cl}^-$  and poor in  $\text{Mg}^{2+}/\text{SO}_4^{2-}$ , or  $\text{Na}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Cl}^-$ , and  $\text{SO}_4^{2-}$  concentrations are comparable, and freezing rate is rapid.

This work and its implications are further discussed in a publication in press at the time this abstract was written [5]. Future work will examine the effects of vacuum and radiolytic processing.

#### References:

- [1] Marion, G. M., et al. (2005) *GeCoA*, 69, 259.
- [2] Hamilton, A., and Menzies, R. I. (2010) *JRSp*, 41, 1014.
- [3] Samson, I. M., and Walker, R. T. (2000) *Can. Mineral.*, 38, 35.
- [4] Hand, K. P., and Carlson, R. W. (2015) *GeoRL*, 42, 3174.
- [5] Vu, T.H., et al. (2016) *ApJLett.*, in press.