

**PREFERENTIAL FORMATION OF SODIUM SALTS FROM FROZEN SODIUM-AMMONIUM-CHLORIDE-CARBONATE BRINES: IMPLICATIONS FOR CERES' BRIGHT SPOTS.** T. H. Vu<sup>1,2</sup>, R. Ho-dyss<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.

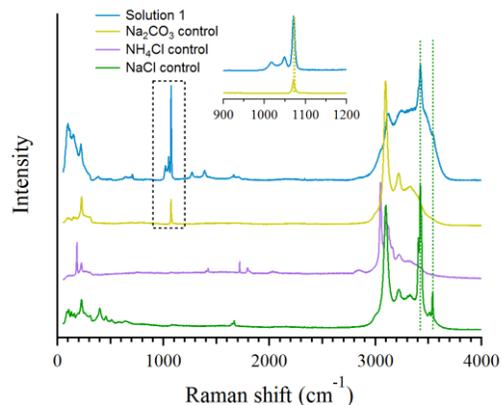
**Introduction:** Recent observations of the bright deposits on Ceres' surface by the Dawn spacecraft have revealed large quantities of natrite ( $\text{Na}_2\text{CO}_3$ ) and smaller amounts of  $\text{NH}_4\text{Cl}$  or  $\text{NH}_4\text{HCO}_3$  [1]. These materials have been suggested to originate from the crystallization of brines that reached the surface from below. In this work, we explore the chemistry of frozen brine mixtures containing sodium, ammonium, chloride, and carbonate ions, the likely constituents of Ceres' subsurface liquid reservoir. Characterizing what minerals would form as brines comprised of these ions freeze will enable constraints to be placed on the compositions of the fluids responsible for the material compositions found at the bright spots on Ceres.

**Experimental:** Frozen  $\text{Na}^+\text{-NH}_4^+\text{-Cl-CO}_3^{2-}$  brines were investigated with a confocal dispersive Raman spectrometer (Horiba Jobin-Yvon LabRam HR) using a cryogenic optical stage (Linkam LTS 350). Ten microliter droplets of solution were placed inside the cryostage on a glass microscope slide, and cooled at 30 K/min to their freezing temperatures. The molar concentrations of the ionic solutions being investigated are listed below. Optical images of the samples were obtained concurrently with the Raman spectra. All samples were excited with a 532 nm laser source, and spectra were collected at  $1\text{ cm}^{-1}$  resolution.

Experiment	$\text{Na}^+$	$\text{NH}_4^+$	$\text{Cl}^-$	$\text{CO}_3^{2-}$	pH
Solution 1	0.6	0.6	0.6	0.3	9.68
Solution 2	0.6	3.6	3.6	0.3	9.26
Solution 3	3.1	0.6	3.1	0.3	-

UV irradiation experiments were also carried out with a flash-frozen saturated sodium chloride solution. The sample was ground under liquid nitrogen and transferred into a vacuum cryostat (Oxford Instruments MicrostatN2) maintained at 100 K. After a base pressure of  $10^{-4}$  torr was established, the temperature was raised to 165 K in order to simulate Ceres' average surface conditions. UV irradiation was applied for 5 hours using a krypton resonance lamp operated at an 100 W. The Kr lamp emits primarily at 116.5 nm and 123.6 nm; however, only the latter wavelength would reach the sample given the sharp cutoff of the  $\text{MgF}_2$  window on the cryostage.

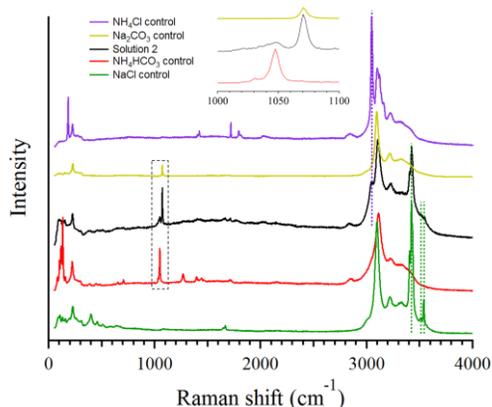
**Results:** Figure 1 shows the spectrum of a solution containing 0.6 M each of  $[\text{Na}^+]$ ,  $[\text{NH}_4^+]$ ,  $[\text{Cl}^-]$  and 0.3 M  $[\text{CO}_3^{2-}]$  (solution 1) upon freezing. This choice of



**Figure 1.** Raman spectrum of frozen solution 1 (blue) in comparison with control spectra of  $\text{Na}_2\text{CO}_3$  (yellow),  $\text{NH}_4\text{Cl}$  (purple), and  $\text{NaCl}$  (green) solutions. Inset shows an expansion of the boxed region.

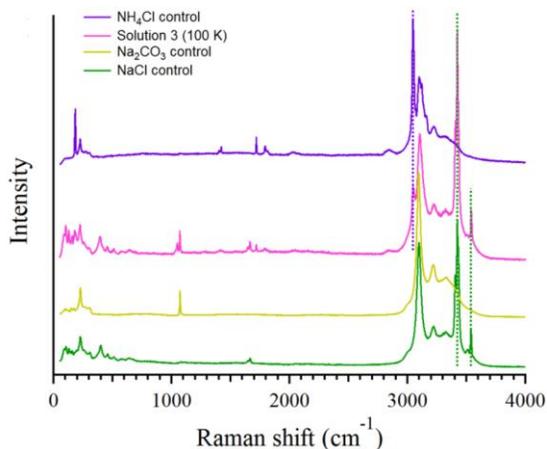
concentration was to ensure that the formation of any carbonate salts would be a result of purely ionic interactions rather than a bias in the cation concentrations. The onset of freezing occurred at 165 K (close to the average temperature of the surface of Ceres). Comparison of the spectrum of the frozen mixture (blue trace) with the controls indicates that the sharp resonance at  $3425\text{ cm}^{-1}$  and the weaker feature at  $3537\text{ cm}^{-1}$  correspond to those of hydrohalite [2], as seen in the control  $\text{NaCl}$  solution (green dashes). Meanwhile, the carbonate stretch region (inset) clearly shows the presence of  $\text{Na}_2\text{CO}_3$  (yellow dash), together with  $\text{NH}_4\text{HCO}_3$  ( $1049\text{ cm}^{-1}$ ) and  $\text{NaHCO}_3$  ( $1017\text{ cm}^{-1}$ ) [3]. Thus, all possible sodium salts were observed to form in the frozen mixture when the  $[\text{Na}^+]$  and  $[\text{NH}_4^+]$  concentrations are equal, signifying a thermodynamic preference towards sodium salts.

Experiment 2 examined whether sodium salts could form in a solution dominated by ammonium ions. Such environment was achieved by preparing a 1:1 mixture of saturated  $\text{NH}_4\text{Cl}$  and saturated  $\text{Na}_2\text{CO}_3$  solutions, which yielded an  $[\text{NH}_4^+]/[\text{Na}^+]$  ratio of 6:1 (solution 2). The Raman spectrum of the frozen brine is shown in Figure 2 (black trace). Again, it is evident that a significant quantity of hydrohalite was formed, as seen via its characteristic sharp peaks at  $3403$ ,  $3423$ , and  $3537\text{ cm}^{-1}$  (green dashes). Similar to solution 1, a distinct peak at  $1070\text{ cm}^{-1}$  indicative of  $\text{Na}_2\text{CO}_3$  was also observed. Thus, despite a 6:1 deficit in concentration between  $\text{Na}^+$  versus  $\text{NH}_4^+$ , the two major sodium salts (natrite and hydrohalite) still feature predominantly in the frozen solid.



**Figure 2.** Raman spectrum of frozen solution 2 (black) in comparison with control spectra of  $\text{Na}_2\text{CO}_3$  (yellow),  $\text{NH}_4\text{Cl}$  (purple),  $\text{NaCl}$  (green), and  $\text{NH}_4\text{HCO}_3$  (red) solutions. Inset shows an expansion of the boxed region.

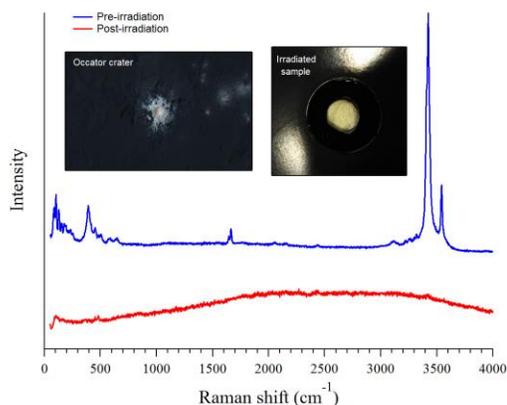
Figure 3 shows the results of freezing a brine solution containing a  $\sim 10:1$  molar ratio of  $[\text{Cl}^-]/[\text{CO}_3^{2-}]$  (solution 3). This was done in order to determine whether natrite could be formed in a chloride-rich environment. The excess of  $\text{Cl}^-$  in this solution resulted in large quantities of hydrohalite (green dashes) as well as  $\text{NH}_4\text{Cl}$  hydrates (purple dash). The carbonate stretch region continues to display a clear, distinctive peak at  $1070\text{ cm}^{-1}$ , again affirming the presence of  $\text{Na}_2\text{CO}_3$ . This is rather remarkable, considering the overwhelming proportion of chloride relative to carbonate in the solution. It is likely that, out of all the salts considered in this study,  $\text{Na}_2\text{CO}_3$  has the lowest solubility at cryogenic temperatures, making it the most likely to precipitate upon freezing.



**Figure 3.** Raman spectrum of frozen solution 3 (magenta) in comparison with control spectra of  $\text{Na}_2\text{CO}_3$  (yellow),  $\text{NH}_4\text{Cl}$  (purple), and  $\text{NaCl}$  (green) solutions.

All of the above experiments have demonstrated that hydrohalite would form alongside natrite during freezing of the brine mixtures. However, hydrohalite has yet to be detected on the surface of Ceres. A possi-

ble explanation is that the high surface temperature combined with the vacuum condition and/or UV irradiation can dehydrate hydrohalite and turn it into halite ( $\text{NaCl}$ ), which is featureless in the spectral range observed by Dawn. We conducted a UV irradiation study of a saturated  $\text{NaCl}$  solution and found that a large portion of the originally white hydrohalite sample was turned into a faint brown-yellow color after 5 h of irradiation under vacuum (Figure 4). This is similar to the color centers observed by Hand and Carlson (2015) using electron irradiation [4]. Such process might be occurring on the surface of Ceres, as hinted by a subtle yellow-brown coloration amidst the Occator crater (left inset). Thus,  $\text{NaCl}$  could be an important component of Ceres' surface that is worthy of further investigation.



**Figure 4.** Raman spectra of frozen saturated  $\text{NaCl}$  at  $163\text{ K}$  before (blue) and after (red) irradiation with a Kr lamp for 5 h. Inset shows a photograph of the sample post irradiation in comparison with an enhanced colored view of the Occator crater on Ceres. Image credit NASA/JPL-Caltech/UCLA/MPS/DLR/IDA/PSI/LPI.

**Conclusions:** De Sanctis et al. (2016) have proposed that the salt compounds constituting Ceres' bright spots ( $\text{Na}_2\text{CO}_3$ ,  $\text{NH}_4\text{Cl}$  or  $\text{NH}_4\text{HCO}_3$ ) were likely solid residues from the crystallization of brines that reached the surface from the interior ocean. Our results support the outcome of this scenario, as  $\text{Na}_2\text{CO}_3$  and  $\text{NH}_4\text{HCO}_3$  were preferentially formed in all of our brine mixtures upon freezing despite the wide range of ionic proportions and concentrations. In addition, the detection of  $\text{NH}_4\text{Cl}$  on Ceres' surface could imply that the ocean is rich in ammonium and/or chloride.

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**References:** [1] De Sanctis, M. C. et al. (2016) *Nature*, 536, 54. [2] Samson, I. M. and Walker, R. T. (2000) *Can. Mineral.* 38, 35. [3] Martinez, I. et al. (2004) *Chem. Geo.* 207, 47. [4] Hand, K. P. and Carlson, R. W. (2015) *GRL*, 42, 3174.