PREFERENTIAL FORMATION OF SODIUM SALTS FROM FROZEN SODIUM-AMMONIUM-CHLORIDE-CARBONATE BRINES: IMPLICATIONS FOR CERES' BRIGHT SPOTS.

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Introduction: Recent observations of the bright deposits on Ceres' surface by the Dawn spacecraft have revealed large quantities of natrite (Na_2CO_3) and smaller amounts of NH_4Cl or NH_4HCO_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 Na^+-NH_4^+-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.

Experiment	*Na^+*	*NH_4^+*	*Cl^-*	*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	-

Results: The concentration of solution 1 was chosen 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). Raman spectra show formation of hydrohalite, Na_2CO_3, NH_4HCO_3, and $NaHCO_3$ upon freezing. Thus, all possible sodium salts were observed to form in the frozen mixture when the [Na^+] and [NH_4^+] concentrations are equal, signifying a thermodynamic preference towards sodium salts.

Solution 2 was examined in order to determine whether sodium salts could form in a solution dominated by ammonium ions. The Raman spectrum of the frozen brine (Figure 1) showed that a significant amount of hydrohalite was formed, along with Na_2CO_3. Thus, despite a 6:1 deficit in concentration between Na^+ versus NH_4^+, the two major sodium salts (natrite and hydrohalite) still feature predominantly in the frozen solid.

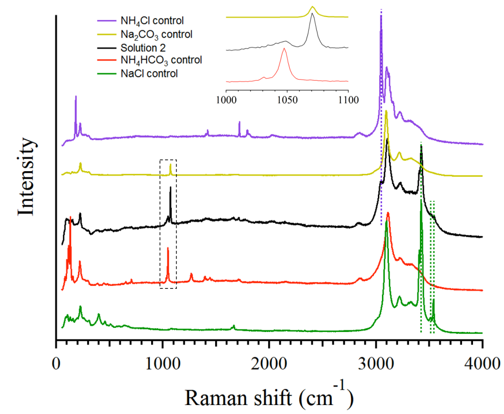

Figure 1. *Raman spectrum of frozen solution 2 (black) in comparison with control spectra of Na_2CO_3 (yellow), NH_4Cl (purple), NaCl (green), and NH_4HCO_3 (red) solutions. Inset shows an expansion of the boxed region.*

Solution 3 was examined in order to determine whether natrite could be formed in a chloride-rich environment. Large quantities of hydrohalite as well as NH_4Cl hydrates were observed along with Na_2CO_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, Na_2CO_3 has the lowest solubility at cryogenic temperatures, making it the most likely to precipitate upon freezing.

Conclusions: De Sanctis et al. (2016) have proposed that the salt compounds constituting Ceres' bright spots (Na_2CO_3, NH_4Cl or NH_4HCO_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 Na_2CO_3 and NH_4HCO_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 NH_4Cl 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.