



Preferential formation of sodium salts from frozen sodium-ammonium-chloride-carbonate brines – Implications for Ceres' bright spots

Tuan H. Vu^{a,b,*}, Robert Hodyss^{a,b}, Paul V. Johnson^{a,b}, Mathieu Choukroun^{a,b}

^a Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California 91109, USA

^b NASA Astrobiology Institute, USA

ARTICLE INFO

Keywords:

Raman
Composition
Ceres

ABSTRACT

Observations of bright deposits in Ceres' Occator crater have revealed large quantities of natrite (Na_2CO_3) and smaller amounts of NH_4Cl or NH_4HCO_3 . These materials have been suggested to originate from the crystallization of brines that reached the surface from below. Here we report a systematic study of the chemistry of frozen brines containing sodium, ammonium, chloride, and carbonate ions via micro-Raman spectroscopy. Natrite and hydrohalite ($\text{NaCl}\cdot 2\text{H}_2\text{O}$) are found to form preferentially, even in ammonium-dominated solutions. Additionally, NH_4Cl could only form when NH_4^+ or Cl^- (or both) are present in excess in the brine solutions. The detection of NH_4Cl on Ceres' surface may thus imply an early subsurface reservoir rich in ammonium and/or chloride, placing an important constraint on modeling of the liquid composition.

1. Introduction

Ceres, the largest body in the main asteroid belt, has been a subject of astrobiological interests over the past decade (Castillo-Rogez and Lunine, 2012). The only dwarf planet located in the asteroid belt, Ceres is an ice-rich rocky body as indicated by its low density (2.162g/cm^3) (Park et al., 2016) and the detection of ammoniated phyllosilicates on its surface (De Sanctis et al., 2015). The Dawn spacecraft, which went into orbit around Ceres in March 2015, continues to revolutionize our understanding of this fascinating object. Prior to Dawn, limitations of density and shape determinations from ground and space-based telescopes resulted in competing models for the interior structure of Ceres that ranged from homogenous (Zolotov, 2009) to fully differentiated (McCord and Sotin, 2005; Castillo-Rogez and McCord, 2010). In the latter scenario, water ice in Ceres would have melted as a result of radioactive nuclide heating, forming a liquid mantle beneath a frozen ice crust. Lacking an additional heat source such as tidal heating, the water layer would have frozen from the crust inward as radioactive heating declined, leaving the possibility of liquid water persisting until the present. Recently, gravity and shape measurements from Dawn indicate that Ceres is in fact partially differentiated with a rocky core surrounded by a shell composed of volatiles mixed with denser materials such as silicates and salts (Park et al., 2016). This is supported by digital terrain models derived from the Dawn Framing Camera images that are inconsistent with an ice-rich subsurface, but suggest that rocks, salts and/or clathrate hydrates comprise 60–70% of the

shallow subsurface (Bland et al., 2016). However, if a partially differentiated Ceres formed as an ice-rich body, it is expected that a pure ice shell should have been present (McCord and Sotin, 2005). This has led to the hypothesis that Ceres formed in the outer Solar System and lost its ice shell after migrating to its present location in the main belt (Castillo-Rogez et al., 2016). This would then imply that the surface we see today is the top of the frozen ocean (base of the ice shell). In this scenario, Ceres can be viewed as a former member of the Solar System's family of Ocean Worlds, whose ocean has frozen over. Given the astrobiological potential that this implies, coupled with the accessibility of the frozen ocean and its relatively close proximity within the main asteroid belt, the interest in further Ceres exploration is expected to grow.

Observations by Dawn have also revealed that Ceres has a dark, cratered surface spotted with areas of higher albedo. The most prominent of these are the bright spots in the Occator crater, which were first resolved by Dawn just prior to orbital insertion. While ammonium-bearing minerals have been previously identified as a major component of the low-albedo surface of Ceres and Occator's dark floor (King et al., 1992; De Sanctis et al., 2015), recent high spatial and spectral resolution near-infrared observations of the bright spots found them to contain large quantities of sodium carbonate, together with a smaller amount of ammonium salts such as NH_4HCO_3 or NH_4Cl (De Sanctis et al., 2016). In addition to the spectral data, De Sanctis et al. (2016) noted a correlation of the bright areas with fracture systems, which may have formed due to impacts. It was proposed that brines

* Corresponding author.

E-mail address: Tuan.H.Vu@jpl.nasa.gov (T.H. Vu).

Table 1

Composition of aqueous solutions used in this study. Ionic concentrations are expressed in molar (moles per liter of H₂O).

Experiment	[Na ⁺]	[NH ₄ ⁺]	[Cl ⁻]	[CO ₃ ²⁻]	[HCO ₃ ⁻]	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	—	—
NH ₄ Cl control	—	7.2	7.2	—	—	—
Na ₂ CO ₃ control	0.6	—	—	0.3	—	—
NaCl control	6.2	—	6.2	—	—	—
(NH ₄) ₂ CO ₃ control	—	0.6	—	0.3	—	—
NH ₄ HCO ₃ control	—	0.6	—	—	0.6	—
NaHCO ₃ control	0.6	—	—	—	0.6	—

containing entrained altered solids rose to surface through these fractures where they froze, resulting in precipitation of salts and carbonates. Additionally, Neveu and Desch (2015) have hypothesized that the bright spots result from active effusion of solute-bearing liquid (possibly with fines of aqueously altered material) from a subsurface reservoir that is pressurized as it freezes.

In this paper, 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, as well as the conditions under which they formed.

2. Materials and methods

A series of experiments (summarized in Table 1) was conducted to determine the types of salt that would precipitate out during the freezing of fluids containing Na⁺, NH₄⁺, Cl⁻ and CO₃²⁻ ions. In experiments 1 and 2, mixed solutions of Na₂CO₃ (Fisher, ACS Certified) and NH₄Cl (Fisher, ACS certified) were prepared at room temperature at the stated concentrations. In order to achieve a higher [Na⁺] concentration of 3.1 M for experiment 3 (where M denotes molar, or moles per liter of H₂O), an aqueous mixture of NaCl (Mallinckrodt, ACS grade) and (NH₄)₂CO₃ was used instead. As (NH₄)₂CO₃ dissociates spontaneously into NH₃ and NH₄HCO₃ under standard pressure and temperature condition, commercial (NH₄)₂CO₃ samples that have been opened and exposed to the atmosphere are likely “contaminated” with unspecified amounts of NH₄HCO₃. Thus, in order to ensure accurate quantification of the carbonate concentration in our solutions, the following procedure was adopted. Commercial (NH₄)₂CO₃ powder (Alfa Aesar, ACS grade) was exposed to a dry atmosphere (via an NaOH drying tube) for over 2 days at room temperature and evacuated for ~30 min at a base pressure of 10⁻⁴ Torr. This was done to completely remove gaseous NH₃ as well as any residual water vapor. The resulting sample was then tested with a pH paper until no trace NH₃ was detected in the headspace, confirming that it only contained NH₄HCO₃. This pure NH₄HCO₃ powder was subsequently dissolved in NH₄OH in appropriate stoichiometric proportions to achieve the desired (NH₄)₂CO₃ concentration. An additional control solution was prepared by dissolving the dried NH₄HCO₃ powder in water. For each of the aqueous mixtures, a 10-μL aliquot was used for experiment. All

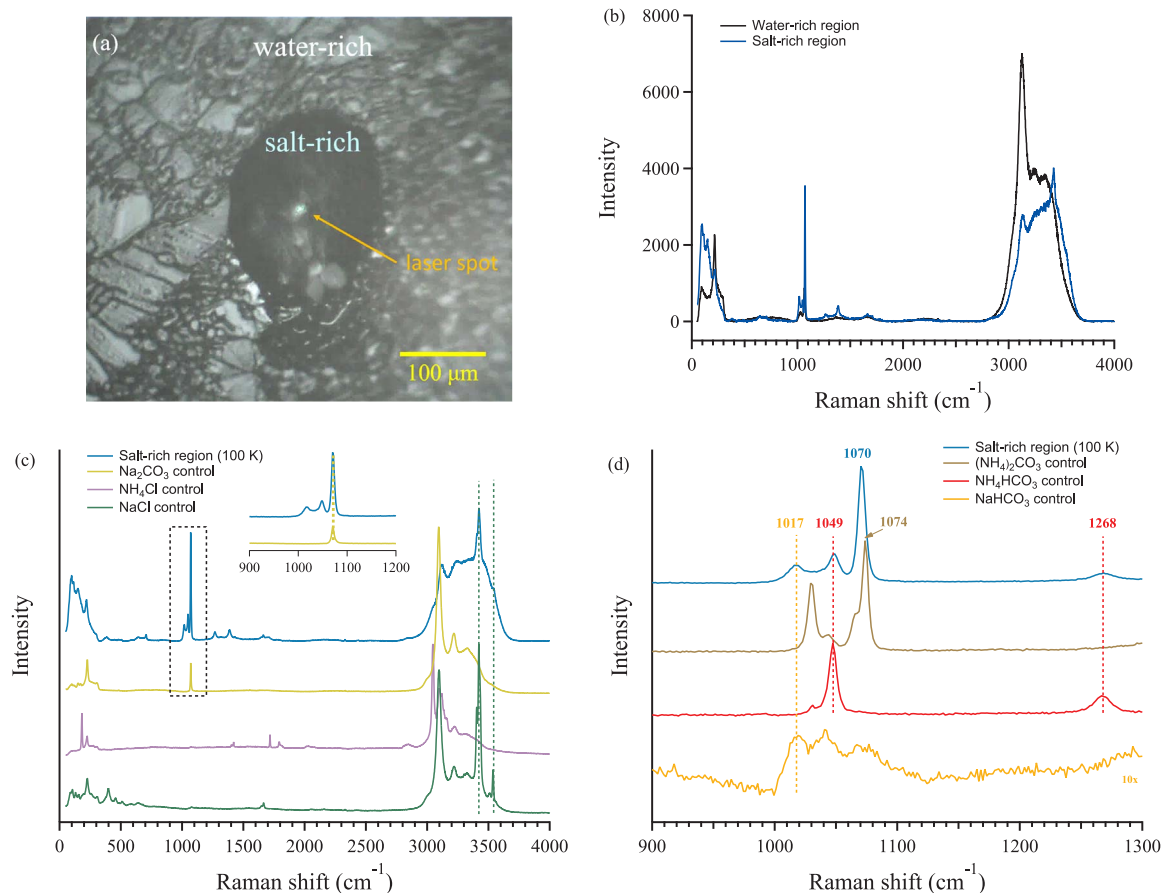


Fig. 1. (a) Microscope image of a frozen brine solution containing 0.6 M [Na⁺], 0.6 M [NH₄⁺], 0.6 M [Cl⁻], and 0.3 M [CO₃²⁻] at 165 K showing a salt-rich pocket and a surrounding water-rich region. The corresponding Raman spectrum of each region is shown in (b). (c) Spectrum of the salt-rich region taken at 100 K (blue) is compared to control spectra of Na₂CO₃ (yellow), NH₄Cl (purple) and NaCl (green) solutions at the same temperature. Inset shows an expansion of the carbonate stretch region (dashed box) between 900 and 1200 cm⁻¹. (d) Expansion of the carbonate stretch region from the salt-rich region in comparison with (NH₄)₂CO₃ (brown), NH₄HCO₃ (red) and NaHCO₃ (orange) control spectra at 100 K. Ionic concentrations of all samples are given in Table 1. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Download English Version:

<https://daneshyari.com/en/article/5488032>

Download Persian Version:

<https://daneshyari.com/article/5488032>

[Daneshyari.com](https://daneshyari.com)