

**LABORATORY CHARACTERIZATION OF AMINO ACIDS IN FROZEN ENCELADUS BRINES.** T. H. Vu<sup>1</sup>, M. L. Cable<sup>1</sup>, R. Hodyss<sup>1</sup>, and P. V. Johnson<sup>1</sup>, <sup>1</sup>Jet Propulsion Laboratory, California Institute of Technology, 4800 Oak Grove Dr, Pasadena, CA 91109, ([tuan.h.vu@jpl.nasa.gov](mailto:tuan.h.vu@jpl.nasa.gov))

**Introduction:** The distribution of organics on ocean worlds is a topic of immense interest in the ongoing search for habitable environments and evidence of life in the Solar System. The past two decades have seen a wealth of information returned from space missions revealing not only the presence but also the impressive diversity of organic materials on the icy satellites of outer planets (e.g. hydrocarbon lakes and tholins on Titan [1], aromatics and amino acid precursors in Enceladus' ice grains [2], aliphatic carbon on Ceres [3]). While not yet formally detected, organic matter has also been long speculated for Europa, with their search one of the primary objectives of upcoming missions to the Jupiter system. Despite the differences in their internal geophysics, these bodies share a common feature: a subsurface ocean or liquid reservoir that is/was highly enriched in salt minerals. Such combinations of organics, salts, and water/ice may present complex chemical environments that favor conditions suitable for the emergence of life. To date, however, the chemical behavior of organic species embedded in brines upon exposure onto ocean world surfaces has not yet been established.

The goal of this work is to fill that knowledge gap, by providing an experimental framework to understand the partition and distribution of small, astrobiologically relevant organics (e.g. amino acids) in putative ocean world brines (containing Na<sup>+</sup>, Cl<sup>-</sup>, and CO<sub>3</sub><sup>2-</sup>). We aim to address fundamental questions such as (i) how do organics and brines freeze together? (ii) is there an enrichment of organics at the salt/ice grain boundaries? and (iii) is there a tendency for certain organics to preferentially associate with particular salt minerals? Together, this information will reveal the full details of how organic matter is distributed within briny frozen matrices, in generating surface observables that could be detectable from flyby or in situ.

Understanding the relationship between organic matter and the associated salt mineralogy would help provide constraints into where biosignatures might be preserved and accumulate on ocean world surfaces. Additionally, it will enable meaningful connection to be made between the observable surface mineralogy and the composition of the underlying ocean, yielding important insights into their potential for habitability and the internal geochemistry of ocean worlds. Such information will be extremely useful to future missions targeting salt-rich icy bodies (e.g. Clipper, Enceladus Orbilander, Ceres lander).

**Experimental Method:** Organic-bearing solutions are made by dissolution of the amino acid and salt species (NaCl, Na<sub>2</sub>CO<sub>3</sub>) in deionized water at room temperature. Glycine and aspartic acid (Sigma Aldrich, 99%) is each prepared at 0.1 M, while the brine is comprised of [Na<sup>+</sup>] = 0.68 M, [Cl<sup>-</sup>] = 0.4 M, and [CO<sub>3</sub><sup>2-</sup>] = 0.14 M, with a resultant pH of ~10. These concentrations are chosen to ensure sufficient spectral signal while maintaining relevance to Enceladus [4]. In order to simulate Enceladus plume ice grains, small droplets (~ 5 μL) of the aqueous solutions are flash frozen to 85 K inside a liquid nitrogen-cooled Linkam LTS420 optical cryostage. The cooling rate of this quenching method is estimated to be ~40 K/s [5].

The frozen samples are then investigated using a high-resolution confocal dispersive Raman microscope (Horiba Jobin-Yvon LabRam HR) equipped with a 532 nm laser as the excitation source. Spectra are acquired with a spectral resolution of 1.5 cm<sup>-1</sup>, first at 85 K and then at 220 K. At the latter temperature, spectra are subsequently obtained point-by-point over a 20×20 μm area at 1 μm steps. From this, 2D compositional maps are constructed to reveal the spatial distribution of ice, salt, and amino acid by integrating the experimental spectra over the respective peaks of the constituents.

**Results:** The top spectrum in Figure 1 shows the glycine-bearing brine upon flash freezing at 85 K. Aside from the characteristic water ice peaks between 3100-3600 cm<sup>-1</sup>, the spectrum is relatively featureless, indicating vitrification of the salt hydrates (particularly that of NaCl). Similar behaviors have been previously observed in several organic-free brine systems [4-6].

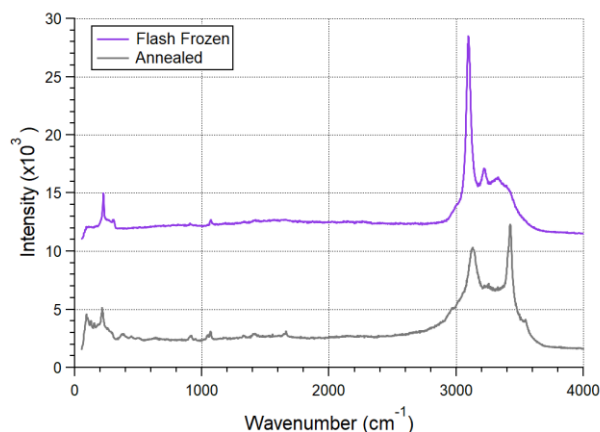


Figure 1. Raman spectrum of an analog Enceladus brine containing glycine upon flash freezing at 85 K (top) and after annealing at 220 K (bottom).

As vitrification significantly hinders detection, the sample needs to be annealed to a higher temperature to induce crystallization of the materials that are ‘hidden’ in the vitreous phase. The spectrum at 220 K (Fig 1, bottom trace) subsequently reveals the presence of natron ( $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ , carbonate peak at  $1068\text{ cm}^{-1}$ ), glycine (C-H stretch at  $2966\text{ cm}^{-1}$ ) and hydrohalite ( $\text{NaCl} \cdot 2\text{H}_2\text{O}$ , sharp peaks at  $3425$  and  $3545\text{ cm}^{-1}$ ).

These features are then used to construct a 2D qualitative map of the surface layer, following a 12 hr-long acquisition of 400 point spectra (Figure 2, top). The sample is found to segregate into a pure water ice region after annealing, while the glycine tends to be co-located with the salts in discrete units separate from the water ice. Preliminary experiments with aspartic acid also indicate a similar result (Figure 2, bottom).

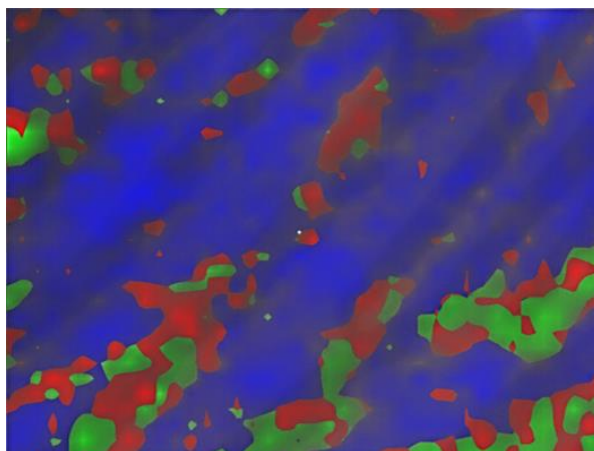
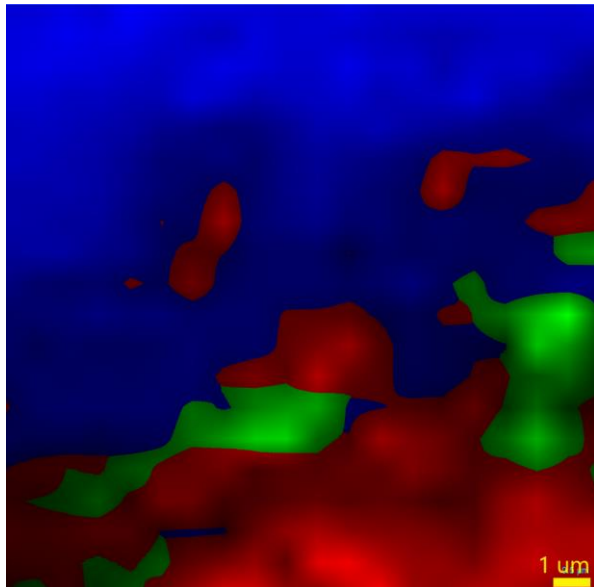


Figure 2. 2D Raman map of glycine (top) and aspartic acid (bottom) embedded in an analog Enceladus brine. In these maps, the amino acid is shown in green, while blue denotes water ice and red the salt hydrates.

**Conclusions:** These results indicate that glycine and aspartic acid coordinates preferentially with salt minerals rather than with water ice in frozen brine systems, despite their different functional side groups. Whether this trend extends to all amino acids or other types of organics (e.g. fatty acids, aromatics) requires further experimental work in this area. Nevertheless, these initial observations suggest that organic species might indeed be concentrated within salt-rich ice grains, which could have important implications for future sampling of plume materials and the search for organics on ocean worlds. However, the tendency for salt hydrates to vitrify upon flash freezing is an important factor that necessitates special consideration during sample processing.

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**References:** [1] Cable M.L. et al. (2012) *Chem Rev* 112, 1882 [2] Khawaja N. et al. (2019) *Mon Not R Astron Soc* 489, 5231 [3] De Sanctis M.C. et al. (2017) *Science* 355, 719 [4] Fox-Powell M.G. & Cousins C.R. (2021) *JGR Planets* 126, e2020JE006628 [5] Johnson P.V. & Vu, T.H. (2022) *PSJ* 3, 151 [6] Vu T.H. et al. (2020) *Icarus* 349, 113746