

## Organic Matter in Extraterrestrial Water-Bearing Salt Crystals

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**Introduction:** Direct samples of early Solar System fluids are present in two thermally-metamorphosed ordinary chondrite regolith breccias (Monahans (1998) [H5] and Zag [H3-6]), which were found to contain brine-bearing halite (NaCl) crystals that have been added to the regolith of an S-type asteroid following asteroidal metamorphism [1, 2]. The brine-bearing halite grains were proposed to be formed on an icy C-type asteroids (possibly Ceres), and transferred to an S-type asteroid via cryovolcanic event(s) [3]. A unique aspect of these halites is that they contain abundant organic rich solid inclusions hosted within the halites alongside the water inclusions.

**Methods:** We analyzed in detail the compositions of the organic solids and the amino acid content of the halite crystals with two-step laser desorption/laser ionization mass spectrometry (L<sup>2</sup>MS), Raman spectroscopy, X-ray absorption near edge structure (XANES), nanoscale secondary ion mass spectrometry (NanoSIMS), and ultra-performance liquid chromatography fluorescence detection and quadrupole time of flight hybrid mass spectrometry (UPLC-FD/QToF-MS).

**Results and Discussion:** The L<sup>2</sup>MS results show signatures of low-mass polyaromatic hydrocarbons (PAHs) indicated by sequences of peaks separated by 14 atomic mass units (amu) due to successive addition of methylene (CH<sub>2</sub>) groups to the PAH skeletons [4]. Raman spectra of the  $\mu\text{m}$ -sized solid inclusions of the halites indicate the presence of abundant and highly variable organic matter that include a mixture of short-chain aliphatic compounds and macromolecular carbon. C-XANES analysis identified C-rich areas with peaks at 285.0 eV (aromatic C=C) and 286.6 eV (vinyl-keto C=O). However, there is no 1s- $\sigma^*$  exciton peak (291.7 eV) that is indicative of the development of graphene structure [5], which suggests the organics were synthesized cold. NanoSIMS analyses show C-rich and N-rich areas that exhibit similar isotopic values with that of the IOM in the unweathered CR chondrites and less metamorphosed meteorites [6], and are moderately enriched in <sup>15</sup>N ( $\delta^{15}\text{N} = 106.1\text{--}164.5\%$ ). The total amino acid distribution and abundance of the Zag matrix ( $\sim 1,940$  parts per billion [ppb]) is comparable to other ordinary chondrites (60–3,330 ppb) [7, 8]. While the Zag matrix is  $\gamma$ -ABA and EACA-deficient, the halite is shown to exhibit an opposite trend and is almost depleted in amino acids. The striking difference in the amino acid contents between the halite and matrix indicates their separate synthetic origins.

**Conclusion:** Abundant, primitive, and highly-diverse <sup>15</sup>N-rich organic compounds were detected in brine-water bearing halite crystals that were synthesized on a cryovolcanically-active asteroid. Our study suggests that the asteroidal parent body where the halite precipitated, potentially Ceres, is a host to abundance large variety organic precursors. Insoluble organic matter and amino acids can be synthesized from similar organic precursors under hydrous conditions [9]. We envision that similar organic synthetic processes could have occurred on Ceres that synthesized organic solids as well as biologically relevant molecules.

**References:** [1] Rubin A.E. *et al.* (2002) *MAPS*, 37, 125-141. [2] Zolensky M.E. *et al.* (1999) *Science*, 285, 1377-1379. [3] Fries M. *et al.* (2013) 76th MetSoc, 5266. [4] Clemett S.J. *et al.* (1993) *Science*, 262, 721-725. [5] Cody G.D. *et al.* (2008) *EPSL*, 272, 446-455. [6] Alexander C.M.O.D. *et al.* (2007) *GCA*, 71, 4380-4403. [7] Martins Z. *et al.* (2007) *MAPS*, 42, 1581-1595. [8] Chan H.S. *et al.* (2012) *MAPS*, 47, 1502-1516. [9] Kebukawa Y. *et al.* (2017) *Science Advances*, 3.