Organic Components Hosted in Water-Bearing Salt Crystals Suggest an Origin from a Water-Rich Parent Body

Two meteorites that separately crashed to Earth in 1998 – Zag and Monahans (1998) – were found to contain 4.5-billion-year-old halite crystals that are hosts to brine inclusions. Associated with these trapped brines are ^{15}N-enriched organic compounds exhibiting wide chemical variations, representing organic precursors, intermediates and reaction products that include life's precursor molecules such as amino acids. The organic content of the halite deviates from the matrix of the meteorites, thus the meteorites contain organics synthesized on two distinct parent bodies. The asteroidal parent body where the halite precipitated, potentially asteroid 1 Ceres, shows evidence for a complex combination of biologically and prebiologically relevant molecules.

Samples of early solar system fluids are contained in 4.5-billion-year-old halite crystals hosted in two ordinary chondrite regolith breccias – Monahans (1998) and Zag [Fig. 1(A)]. These ancient, millimeter-sized halite crystals contain exogenous brine inclusions that record primitive aqueous processes on early planetesimals, and shed light on the nature, location and timing of the aqueous alteration event on a primitive asteroid.

The host lithologies of the Zag and Monahans meteorites are H3-6 which indicate significant thermal metamorphism up to 700°C. However, the continued presence of fluid inclusions in the meteorites indicates that the halite was formed and maintained at low temperatures (<50°C) [1]. In addition, the mineral components hosted within the halite crystals are comparable to the reported mineralogy of the Ceres regolith, which is similar to that of the CM/CI chondrites [2]. The similarities between the orbits of Ceres and asteroid 6-Hebe, a proposed parent body of H chondrites, permit the exchange of material today and possibly in the past [3]. We tested this hypothesis by studying in detail the organic compositions of the meteorites and their halite inclusions.

A Zag halite crystal was analyzed with two-step laser desorption/laser ionization mass spectrometry (L^{2}MS), which was optimized to detect aromatic/conjugated organic molecules at the μm-scale and the subattomole level (1 amol = 10^{-18} mol) [4]. The mass spectrum showed signatures of simple, low-mass polyaromatic hydrocarbons (PAHs) such as naphthalene, acenaphthene and fluorene, and their alkylated derivatives indicated by sequences of peaks of methylene (CH_2) groups [Fig. 1(B)].

We then investigated the crystalline ordering of the insoluble organic matter in a selected Monahans halite residue with high-resolution confocal Raman spectroscopy imaging, using a Witec α-scanning near-field optical microscope (SNOM). Macromolecular carbon contained in the halite showed variability indicating a complex formation and alteration history [Fig. 1(C)]. Several analytical points lying along a line trending between crystalline graphite and the typical chondritic carbon suggest partial amorphization of crystalline graphite, probably by shock [5].

Subsequent to Raman imaging, we subsampled a halite residue by the focused ion beam (FIB) technique [Fig. 2(A)] and analyzed it with scanning transmission X-ray microscopy (STXM) utilizing X-ray absorption near-edge structure (XANES) spectroscopy. In good agreement with the L^{2}MS and Raman results, the halite residue exhibited a highly diverse organic composition, which is comparable to that of organic matter in typical primitive chondrites (CM/CI/CR). The absence of a 1s-σ* exciton peak (at 291.7 eV) of a graphene structure [6] suggests that the organic matter did not experience temperatures higher than ~200°C [Fig. 2(B)].

We took C, N, H and O isotopic images of the halite residue with the JAMSTEC NanoSIMS 50L ion microprobe [Fig. 2(D)–(F)]. The C-rich area of the residue is depleted in ^{13}C (–37.6‰) and moderately enriched in ^{15}N (+164.5‰). Although the C and N isotopic compositions are consistent with that of the insoluble organics in unweathered CRs [7], the δD value (+42.5‰) is significantly lower than that of the CRs (~3,000‰ [7]). As the water on C-type parent bodies is typically D-poor [8], this δD value suggests that the OM was synthesized in and/or processed by the D-poor water on Ceres during a prolonged aqueous event.

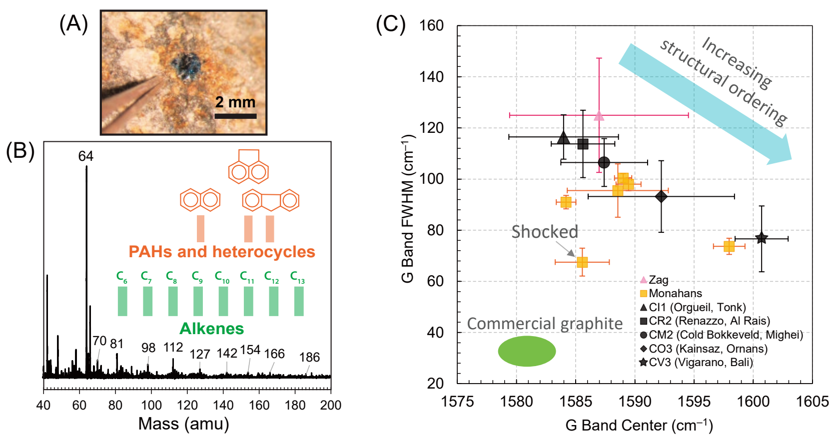

Figure 1: (A) A blue halite crystal of the Zag meteorite. (B) L^{2}MS spectrum of a Zag halite. (C) Raman G band spectral parameters (full width at half maximum and band center location) of Zag matrix, Monahans halite residues, and carbonaceous chondrite-hosted insoluble organics.

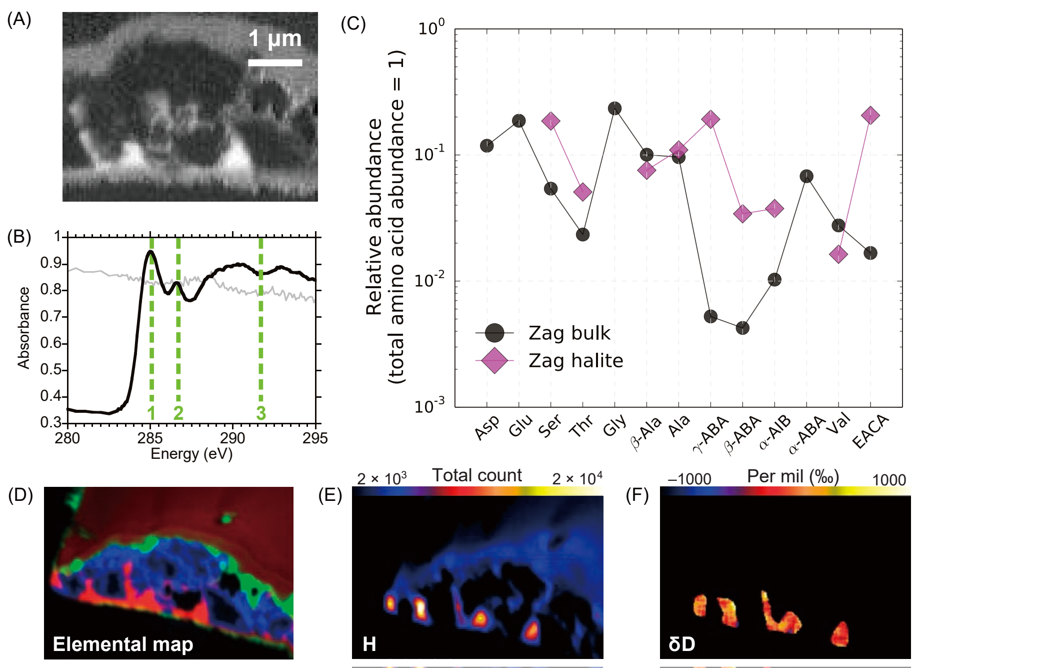

Figure 2: (A) STXM-XANES C map of the halite residue. (B) C-XANES spectrum of organic (thick line) and matrix area. 1 = aromatic C, 2 = ketone, 3 = graphene. (C) Relative amino acid abundances of the 6M HCl acid-hydrolyzed amino acid extract of the Zag bulk and halite. (D) NanoSIMS elemental image. Red, C; green, N; blue, O. (E) H map. (F) Isotope image of δD.

It has been shown by laboratory experiments that macromolecular carbon as well as amino acids can be synthesized under hydrous conditions at temperatures as low as 90°C [9], and we envision that similar organic synthetic processes could have occurred on Ceres that synthesized amino acids. Therefore, we opened a pristinely-preserved Zag meteorite stone and analyzed the newly revealed halite crystals for their amino acid contents using the ultra-performance liquid chromatography fluorescence detection and quadrupole time of flight hybrid mass spectrometry (UPLC-FD/QToF-MS) technique. While the Zag matrix was γ-ABA and EACA-deficient, the halite was shown to exhibit an opposite trend and to be enriched in γ-ABA and EACA [Fig. 2(C)]. The striking difference in the amino acid contents between the halite and matrix indicates their separate synthetic origins.

Our comprehensive analysis of the soluble and insoluble organic compounds found in the brine-containing halite crystals suggests material mixing between two asteroidal bodies. The halite represents an ideal sample to study prebiotic and possibly biotic processes on cryovolcanically-active bodies such as Enceladus and Europa.

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