ORGANIC COMPOUNDS IN EARLY SOLAR SYSTEM AQUEOUS FLUIDS.

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Introduction: Two thermally-metamorphosed ordinary chondrite regolith breccias (Monahans 1998, hereafter simply "Monahans" (H5) and Zag (H3-6)) contain fluid inclusion-bearing halite (NaCl) crystals [1,2] dated to be ~4.5 billion years old [1,3,4]. Thus, compositional data on fluid inclusions in these halites will reveal unique information regarding the origin and activity of aqueous fluids in the early solar system, and especially their interactions with organic material. Our initial analyses of solid inclusions in Monahans halite has shown the presence of olivine, high- and low- Ca pyroxene, feldspars, magnetite, sulfides, phyllosilicates, zeolites, metal, phosphates and abundant organics [5,6]. We have reported a diverse assemblage of carbon, carbonates and organics in these residues [6], and low but significant amino acids concentrations in Monahans and Zag halite [7].

Techniques: Lamadrid et al. [8] recently succeeded in measuring compositions of solid daughter minerals and ice inside aqueous fluid inclusions using Time of Flight Secondary Ion Mass Spectrometry (TOF-SIMS) employing a freezing stage at the Texas Materials Institute of the University of Texas at Austin - we repeated this for our fluid inclusions. To reach the fluid inclusions located several microns below the sample surface, we performed TOF-SIMS depth profiling and attempted to determine the fluid composition of several Monahans halite fluid inclusions. We used a TOF-SIMS 5 instrument (ION-TOF GmbH) equipped with a pulsed Bi^+ analysis ion beam (30 keV ion energy) and a O_2^+ sputtering ion beam (1 kV ion energy). To access the inclusions in the halite crystals we sequentially sputtered areas of 500 x 500 μm^2 with the O_2 ion beam in steps of ~0.5 µm and analyzed the center of the sputtered area (200 x 200 μm^2) with the Bi ion beam. The analysis beam was set in either the high current (HC, ~1 µm lateral resolution, ~3.5 pA measured sample current, mass resolution m/dm >3000) or burst alignment (BA, ~200 nm lateral resolution, ~0.4 pA measured sample current, mass resolution ~100) modes, depending on whether the analysis required high mass resolution or high spatial resolution. Once the inclusion depth was reached, the location of interest was mapped in 100 x 100 μm^2 and 200 x 200 μm^2 areas in both positive and negative polarity and both HC and BA mode. This ensured that the inclusions were mapped with both high mass and lateral resolution. Samples were cooled to approximately -160º C to prevent immediate evaporation (sublimation) of the frozen aqueous fluids.

Results and Discussion: As we recently described in our preliminary report at LPSC [9] the best results were on a fluid inclusion measuring ~15 by 50 µm. The presence of water in the inclusion was confirmed by the detection two representative secondary ion species, $NaOH^-$ and H_2O^+, that map at the inclusion location. While the $NaOH^-$ fragment is mostly concentrated in the inclusion, the water content appears only slightly higher, a result of water being trapped throughout the halite (which we confirmed by FIBing a Zag halite crystal), which renders the H_2O^+ signal virtually uniform at any depth. One consequence of the high water content in the NaCl matrix is that the OH^- signal, a common marker for water, is simply saturated at the inclusion depth and thus does not show any enhancement at the inclusion location. A large number of organic species are identified: C^+, CH_3^+, $C_2H_3^+$ and $C_2H_2NO_2^+$, and C^-, C_2^-, CN^-, CNO^-, $CNCl^-$, $CHNCl^-$ and CNF^-/ CHO_2^-. The detection of larger C-bearing fragments confirms the presence of larger organic molecules in the inclusion, such as amino acids and possibly nitroethylene ($C_2H_3NO_2$). A possible parent molecule in the inclusion is C2H2NO2, which could be a fragment of nitroethylene (C2H3NO2). We also detect expected inorganic species such as K^+, Si^+, $K_3(OH)_2^+$, K_3O^+, H_2O^+, NaOH-, NO- and Si-, and trace amounts of Fe+.

Conclusions and future work: The fluid inclusion in Monahans halite contained a high concentration of organic species. Our next step will be to use artificial halite crystals spiked with a known carbon content to permit quantification of the total carbon in the astromaterial halites. TOF-SIMS can be used successfully for astromaterial fluid inclusion composition measurements, provided sufficiently large inclusions are available. Inclusions we have located in carbonates, oxides and sulfides will be measured.

References: [1] Zolensky et al. (1999) Science 285, 1377-1379; [2] Rubin et al. (2002) *MAPS* **37**, 125-142; [3] Whitby et al. (2000) Science 288, 1819-1821; [4] Bogard et al. (2001) *MAPS* **36**, 107-122; [5] Zolensky et al. (2013) *Abstracts, 76th Annual Meeting of the Meteoritical Society*; [6] Kebukawa et al. (2016) *47th Lunar and Planetary Science Conference*. Abstract; [7] Chan et al. (2018) *Science Advances* 4, eaao3521; [8] Lamadrid et al. (2017) *Nature Communications* **8**, 16107 doi: 10.1038/ncomms16107; [9] Bodnar et al., *50th LPSC Conference*, abstract.