

**FIRST DIRECT MEASUREMENTS OF COMPOSITIONS OF EARLY SOLAR SYSTEM AQUEOUS FLUIDS.** R.J. Bodnar<sup>1</sup>, A. Dolocan<sup>2</sup>, M.E. Zolensky<sup>3</sup>, H. Lamadrid<sup>4</sup>, Y. Kebukawa<sup>5</sup>, Q.H.-S. Chan<sup>6</sup>; <sup>1</sup>Dept. of Geosciences, Virginia Tech, Blacksburg VA 24061 USA; <sup>2</sup>Texas Materials Institute, Univ. of Texas, Austin, TX 78712 USA; <sup>3</sup>ARES, NASA JSC, Houston TX 77058, USA; <sup>4</sup>Dept. of Geological Sciences, Univ. of Missouri Columbia, Columbia MO 75211, USA; <sup>5</sup>Faculty of Engineering, Yokohama National Univ., Yokohama 240-8501, Japan; <sup>6</sup>Dept. of Physical Sciences, The Open Univ., Milton Keynes, MK7 6AA, UK.

**Introduction:** Despite its obvious importance, we are still lacking fundamental information related to the location and timing of the aqueous alteration in the early solar system, and the detailed nature of the aqueous fluid itself [1,2,3]. Two thermally-metamorphosed ordinary chondrite regolith breccias (Monahans 1998, hereafter simply “Monahans” (H5) and Zag (H3-6)) contain fluid inclusion-bearing halite (NaCl) crystals [4,5]. The halites were dated by K-Ar, Rb-Sr and I-Xe systematics to be ~4.5 billion years old [4,6,7] and thus the trapped aqueous fluids are at least as ancient. Heating/freezing studies of the aqueous fluid inclusions in Monahans halites [4] demonstrated that they were trapped at low temperature, and that the brines must contain species besides Na and Cl. Halite contains no structural oxygen, carbon or hydrogen, making it ideal for the measurement of the isotopic composition of oxygen and hydrogen in fluid inclusions (performed by Yurimoto et al. [8]), and dissolved species including organics. Halite is effective at very long-term preservation (at least 250 MY) of organic phases and structures [9,10]. Thus, compositional data on fluid inclusions in halite has the potential to reveal unique information regarding the origin and activity of aqueous fluids in the early solar system, and especially their interactions with organic material. This information will also constrain, and perhaps uniquely identify, the source of the briny water from which the halite precipitated. However, until now we have been unable to identify aqueous species contained in the inclusions.

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 [11,12]. Since the enclosing halite has not been appreciably heated, the organic inclusions may include primitive species not previously available for laboratory analysis. We have found a diverse assemblage of carbon, carbonates and organics in these residues [12], and low but significant amino acids concentrations in Monahans and Zag halite [13].

**Techniques:** Our attempts to measure fluid inclusion compositions by laser ablation-ICPMS were not successful – the inclusions were too small for this technique. However, Lamadrid et al. [14] 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 decided to repeat 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. The inclusions we chose were by necessity more than 5-10  $\mu\text{m}$  beneath the sample surface, because bringing them closer to the surface by polishing at room temperature caused decrepitation and loss of the contained fluid.

We used a TOF-SIMS 5 instrument (ION-TOF GmbH) equipped with a pulsed  $\text{Bi}^+$  analysis ion beam (30 keV ion energy) and a  $\text{O}_2^+$  sputtering ion beam (1 kV ion energy). To access the inclusions in the halite crystals we sequentially sputtered areas of  $500 \times 500 \mu\text{m}^2$  with the  $\text{O}_2$  ion beam in steps of  $\sim 0.5 \mu\text{m}$  and analyzed the center of the sputtered area ( $200 \times 200 \mu\text{m}^2$ ) with the  $\text{Bi}$  ion beam; that is, we performed depth profiling. The analysis beam was set in either the high current (HC,  $\sim 1 \mu\text{m}$  lateral resolution,  $\sim 3.5 \text{ pA}$  measured sample current, mass resolution  $m/dm > 3000$ ) or burst alignment (BA,  $\sim 200 \text{ nm}$  lateral resolution,  $\sim 0.4 \text{ pA}$  measured sample current, mass resolution  $\sim 100$ ) modes, depending on whether the analysis required high mass resolution or high spatial resolution. During depth profiling we set the analysis beam in the BA mode to clearly identify the tiny inclusions. Once the inclusion depth was reached, the location of interest was mapped in  $100 \times 100 \mu\text{m}^2$  and  $200 \times 200 \mu\text{m}^2$  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. Due to the highly insulating nature of the sample, a low energy (21 eV) electron beam was sprayed on the sample during the analysis. To further alleviate charging effects the analysis was performed at  $2 \times 10^{-6}$  mbar base pressure by leaking ultra-high purity Ar gas into the analysis chamber, otherwise at a base pressure of  $1 \times 10^{-9}$  mbar. Samples were cooled to approximately  $-160^\circ \text{C}$  to prevent immediate evaporation (sublimation) of the frozen aqueous fluids.

**Results and Discussion:** The best results were obtained for a fluid inclusion measuring  $\sim 15$  by  $50 \mu\text{m}$ , the largest one we examined (Fig 1). The presence of water in the inclusion was confirmed by the detection two representative secondary ion species,  $\text{NaOH}^-$  and  $\text{H}_2\text{O}^+$ , that map at the inclusion location. While the  $\text{NaOH}^-$  fragment is mostly concentrated in the inclusion, confirming the water reaction with the NaCl matrix, the water fragment appears only slightly higher. This is likely a result

of water being trapped throughout the halite, which renders the  $\text{H}_2\text{O}^+$  signal virtually uniform at any depth. One consequence of the high water content in the NaCl matrix is that the  $\text{OH}^-$  signal, a common marker for water, is simply saturated at the inclusion depth and thus does not show any enhancement at the inclusion location. Figs. 2 and 3 show TOF-SIMS secondary ion maps of various ions/molecules of interest in the largest inclusion in both positive and negative polarities. A large number of organic species are identified:  $\text{C}^+$ ,  $\text{CH}_3^+$ ,  $\text{C}_2\text{H}_3^+$  and  $\text{C}_2\text{H}_2\text{NO}_2^+$ , and  $\text{C}^-$ ,  $\text{C}_2^-$ ,  $\text{CN}^-$ ,  $\text{CNO}^-$ ,  $\text{CNCl}^-$ ,  $\text{CHNCl}^-$  and  $\text{CNF}^-/\text{CHO}_2^-$ . The detection of larger C fragments confirms the presence of larger organic molecules in the inclusion, such as amino acids and nitroethylene ( $\text{C}_2\text{H}_3\text{NO}_2$ ), a liquid that behaves like water thermally and is very soluble in water. Besides the carbonaceous species, we also detect inorganic species such as  $\text{K}^+$ ,  $\text{Si}^+$ ,  $\text{K}_3(\text{OH})_2^+$ ,  $\text{K}_3\text{O}^+$ ,  $\text{H}_2\text{O}^+$  and trace amounts of Fe+, together with NaOH-, NO- and Si-. It appears that one parent molecule in the inclusion is

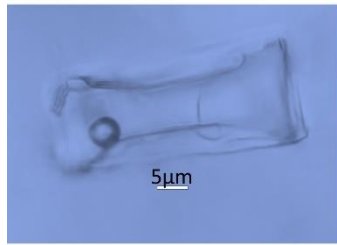


Figure 1: Transmitted light view of target aqueous fluid inclusion in Monahans halite crystal, a “vacuum” bubble is evident at left.

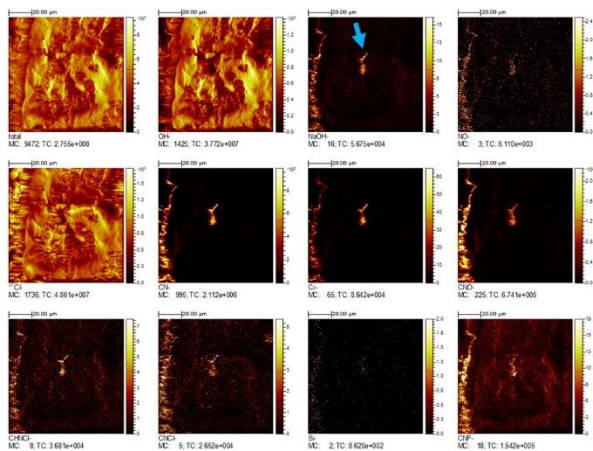


Figure 2: TOF-SIMS maps of several species of interest in the target fluid inclusion in negative polarity. The blue arrow indicates the inclusion location in one map.

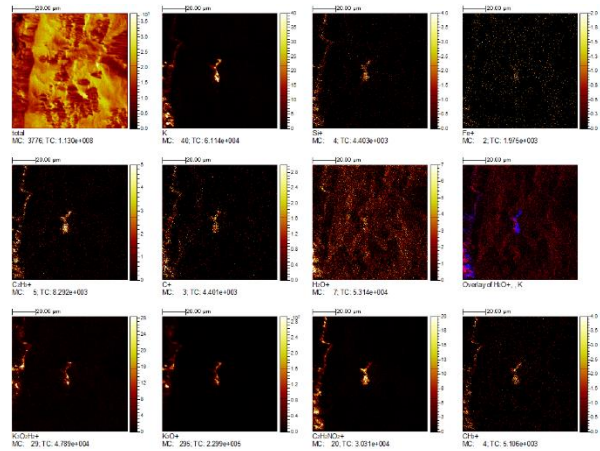


Figure 3: TOF-SIMS maps of several species of interest in target fluid inclusion in positive mode (same view area as Figure 2). The target inclusion is centered.

**Conclusions:** The fluid inclusion in Monahans halite contained a high concentration of organic species. TOF-SIMS can be used successfully for astromaterial fluid inclusion composition measurements, provided sufficiently large inclusions are available. Inclusions in carbonates, oxides and sulfides should be measured.

**References:** [1] Brearley (2006) In *Meteorites and the Early Solar System II*, Lauretta and McSween, Eds., U. of A. Press, 587-624; [2] Zolensky et al. (2008) In *Oxygen in the Solar System, MSA Reviews in Mineralogy and Geochemistry Volume 68*, (MacPherson et al., Eds.), Mineralogical Society of America, pp. 429-462; [3] Krot et al. (2006) In *Meteorites and the Early Solar System II*, Lauretta and McSween, Eds., U. of A. Press, 525-554; [4] Zolensky et al. (1999) *Science* 285, 1377-1379; [5] Rubin et al. (2002) *Meteoritics and Planetary Science* 37, 125-142; [6] Whitby et al. (2000) *Science* 288, 1819-1821; [7] Bogard et al. (2001) *Meteoritics & Planetary Science* 36, 107-122; [8] Yurimoto et al. (2014) *Geochemical Journal* 48, 1-12; [9] Satterfield et al. (2005) *Geology* 33, 265-268; [10] Schubert and Lowenstein (2005) In *Abstracts with Prog., GSA Ann. Meeting*, p 124; [11] Zolensky et al. (2013) *Abstracts, 76th Annual Meeting of the Meteoritical Society*; [12] Kebukawa et al. (2016) *47th Lunar and Planetary Science Conference*. Abstract; [13] Chan et al. (2018) *Science Advances* 4, eaao3521; [14] Lamadrid et al. (2017) *Nature Communications* 8, 16107 doi: 10.1038/ncomms16107.