

Direct Analysis of Early Solar System Aqueous Fluids by TOF-SIMS

M. ZOLENSKY¹, R. J. BODNAR², A. DOLOCAN³, H. LAMADRID⁴, Y. KEBUKAWA⁵, E. SENDULA², Q. H.-S. CHAN⁶, Z. RAHMAN⁷
¹ARES, NASA JSC, Houston TX 77058, USA, michael.e.zolensky@nasa.gov, ²Dept. of Geosciences, Virginia Tech, Blacksburg VA 24061 USA, ³Texas Materials Institute, Univ. of Texas, Austin, TX 78712 USA, ⁴Dept. Geol. Sciences, Univ. of Missouri Columbia, Columbia MO 75211, USA, ⁵Faculty of Engineering, Yokohama National Univ., Yokohama 240-8501, Japan, ⁶School of Life Sciences, University of London, Egham TW200EX, UK, ⁷Jacobs JETS, Houston, TX 77058 USA.

Introduction: We lack 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. Through previously-published O, H, Cr isotopic work we have established that the fluid-bearing halite originated in the outer solar system [8].

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. [9]), and dissolved species including organics. Halite is effective at very long-term preservation (at least 250 MY) of organic phases and structures [10,11]. 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 [12,13]. 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 [13], and low but significant amino acids concentrations in Monahans and Zag halite [14].

Techniques: Lamadrid et al. [15] recently succeeded in measuring compositions of solid daughter minerals and ice inside frozen aqueous fluid inclusions containing a mixture of mineral phases and ionic species 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 μm 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 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 $500 \times 500 \mu\text{m}^2$ with the 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 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 ~ 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 with various magnifications, ranging from $15 \times 15 \mu\text{m}^2$ to $100 \times 100 \mu\text{m}^2$ 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 2×10^{-6} mbar base pressure by leaking ultra-high purity Ar gas into the analysis chamber, otherwise at a base pressure of 1×10^{-9} mbar. Samples were cooled to approximately -160°C to prevent immediate evaporation (sublimation) of the frozen aqueous fluids.

Results and Discussion: The best results were obtained for fluid inclusion FIM1 measuring ~ 15 by $50 \mu\text{m}$, and FI1 measuring 4 by $7 \mu\text{m}$ (Fig. 1). Figs. 2 to 4 show TOF-SIMS secondary ion maps of various ions/molecules of interest in these inclusions in both positive and negative polarities. The presence of water in the inclusions was confirmed by the detection two representative secondary ion species, NaOH^- and H_2O^+ , that map at the inclusion locations. While the NaOH^- fragment is mostly concentrated in the inclusions, confirming the water reaction with the NaCl matrix, the water fragment appears only slightly higher relative to the surrounding areas. This is likely a result of water being trapped throughout the halite, 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 locations. A large number of organic species are identified in inclusion FIM1: C^+ , CH_3^+ , C_2H_3^+ and $\text{C}_2\text{H}_2\text{NO}_2^+$, and C^- , C_2^- , CN^- , CNO^- , CNCl^- , CHNCl^- and $\text{CNF}^-/\text{CHO}_2^-$. The detection of larger C-bearing fragments

confirms the presence of larger organic molecules in the inclusions, such as amino acids and nitroethylene ($C_2H_3NO_2$), a liquid that behaves like water thermally and is very soluble in water. Besides the carbonaceous species, we also detect inorganic species such as K^+ , Si^+ , $K_3(OH)_2^+$, K_3O^+ , H_2O^+ and trace amounts of Fe^+ , together with $NaOH^-$, NO^- and Si^- .

Halite fluid inclusion FI1 (Fig 4) contains H_2O , K, Na, Cl and $NaCl \cdot 2H_2O$ and C-N-O-H species originating from organic molecules. Mass overlap with $NaOH$ species prevented definitive identification of Ca in FI1.

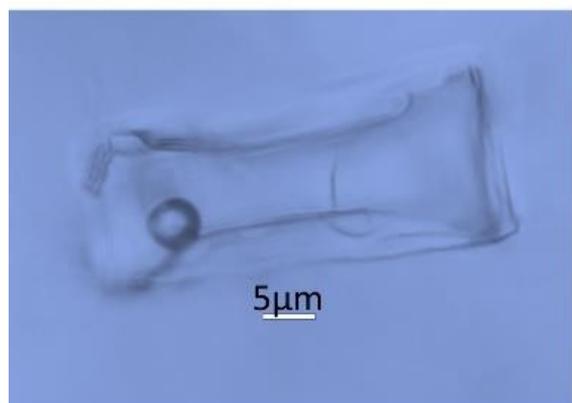


Figure 1: Transmitted light view of target aqueous fluid inclusion FIM1 in Monahans halite crystal, a “vacuum” bubble is at left.

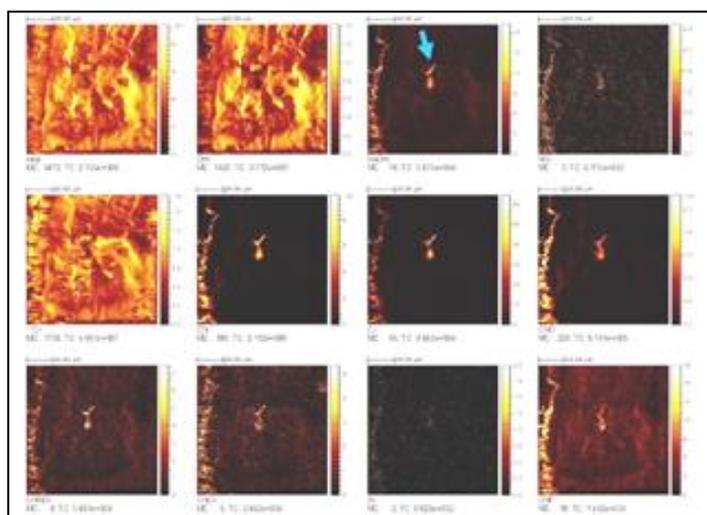


Figure 2: TOF-SIMS maps of several species of interest in the fluid inclusion FIM1 in negative polarity. The blue arrow indicates the inclusion location in one map.

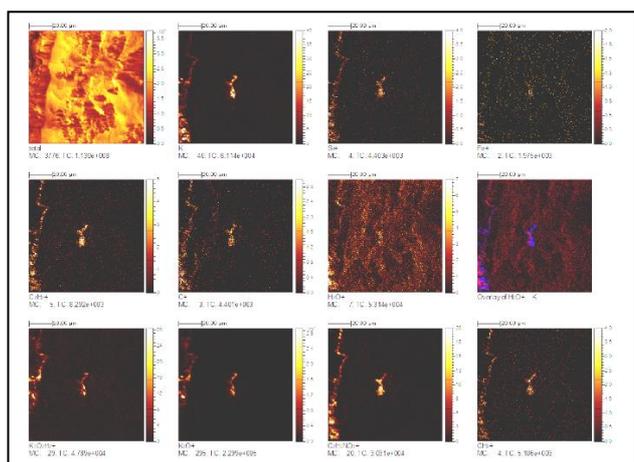


Figure 3: TOF-SIMS maps of several species of interest in fluid inclusion FIM1 in positive mode (same view as Figure 2). The inclusion is centered.

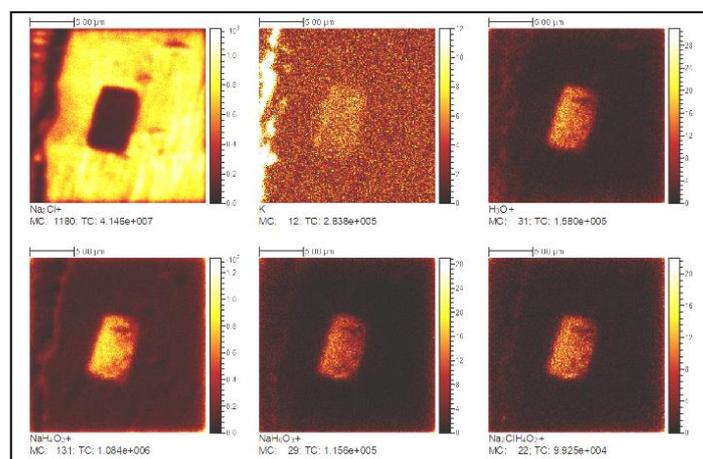


Figure 4: TOF-SIMS maps of several species of interest in fluid inclusion FI1.

Conclusions: TOF-SIMS can be used successfully for astromaterial fluid inclusion composition measurements, provided sufficiently large inclusions are available. The fluid inclusions in Monahans halite contain a high concentration of organic species. The individual fluid inclusions show considerable variations in inorganic and organic content, and we can now use them to track the evolution in the composition of organic-aqueous fluids in an early, outer solar system ocean world.

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] Kebukawa et al. (2019) *Nature Scientific Reports* 9, article 3169; [9] Yurimoto et al. (2014) *Geochemical Journal* 48, 1-12; [10] Satterfield et al. (2005) *Geology* 33, 265–268; [11] Schubert and Lowenstein (2005) In *Abstracts with Prog., GSA Ann. Meeting*, p 124; [12] Zolensky et al. (2013) *Abstracts, 76th Annual Meeting of the Meteoritical Society*; [13] Kebukawa et al. (2016) *47th Lunar and Planetary Science Conference*. Abstract; [14] Chan et al. (2018) *Science Advances* 4, ea03521; [15] Lamadrid et al. (2017) *Nature Communications* 8, 16107 doi: 10.1038/ncomms16107.