



Analysis of Direct Samples of Early Solar System Aqueous Fluids

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Over the past three decades we have become increasingly aware of the fundamental importance of water, and aqueous alteration, on primitive solar-system bodies. Some carbonaceous and ordinary chondrites have been altered by interactions with liquid water within the first 10 million years after formation of their parent asteroids. Millimeter to centimeter-sized aggregates of purple halite containing aqueous fluid inclusions were found in the matrix of two freshly-fallen brecciated H chondrite falls, Monahans (1998, hereafter simply “Monahans”) (H5) and Zag (H3-6) (Zolensky et al., 1999; Whitby et al., 2000; Bogard et al., 2001) In order to understand origin and evolution of the aqueous fluids inside these inclusions we much measure the actual fluid composition, and also learn the O and H isotopic composition of the water. It has taken a decade for laboratory analytical techniques to catch up to these particular nanomole-sized aqueous samples. We have recently been successful in (1) measuring the isotopic composition of H and O in the water in a few fluid inclusions from the Zag and Monahans halite, (2) mineralogical characterization of the solid mineral phases associated with the aqueous fluids within the halite, and (3) the first minor element analyses of the fluid itself.

A Cameca ims-1270 equipped with a cryo-sample-stage of Hokkaido University was specially prepared for the O and H isotopic measurements. The cryo-sample-stage (Techno. I. S. Corp.) was cooled down to c.a. -190°C using liquid nitrogen at which the aqueous fluid in inclusions was frozen. We excavated the salt crystal surfaces to expose the frozen fluids using a 15 keV Cs^{+} beam and measured negative secondary ions. The secondary ions from deep craters of $\sim 10\ \mu\text{m}$ in depth emitted stably but the intensities changed gradually during measurement cycles because of shifting states of charge compensation, resulting in rather poor reproducibility of multiple measurements of standard fluid inclusions of $\pm 90\%$ (2σ) for δD , and $\pm 29\%$ (2σ) for $\delta^{18}\text{O}$. On the other hand, the reproducibility of $\Delta^{17}\text{O}$ is $\pm 8\%$ (2σ) because the observed variations of isotope ratios follow a mass dependent fractionation law. Variations of δD of the aqueous fluids range over $\delta 330(90; 2\sigma)$ to $+1200(90)\%$ for Monahans and $\delta 300(96)\%$ to $+90(98)\%$ for Zag. $\Delta^{17}\text{O}$ of aqueous fluids range over $\delta 16(22)\%$ to $+18(10)\%$ for Monahans and $+3(10)\%$ to $+27(11)\%$ for Zag. These variations are larger than the reproducibility of standard analyses and suggest that isotope equilibria were under way in the fluids before trapping into halite. The mean values of δD and $\Delta^{17}\text{O}$ are $+290\%$ and $+9\%$, respectively. The mean values and the variations of these fluids are different from the representative values of ordinary chondrites, verifying our working hypothesis that the fluid inclusion-bearing halites were not indigenous to the H chondrite parent-asteroid but rather represent exogenous material delivered onto the asteroid from a separate cryovolcanically-active body. This initial isotopic work has demonstrated the feasibility of the measurements, but also revealed sample processing and analytical shortcomings that are now being addressed.

Examination of solid mineral inclusions within Monahans and Zag halite grains by confocal Raman spectroscopy at the Carnegie Geophysical Laboratory has revealed them to be metal, magnetite, forsteritic olivine ($\text{Fo}\approx 98$), macromolecular carbon (MMC), pyroxenes, feldspar with Raman spectral affinity to anorthoclase and, probably, fine-grained lepidocrocite ($\text{FeO}(\text{OH})$). In addition, one inclusion features aliphatic material with Raman spectral features consistent with a mixture of short-chain aliphatic compounds.

We have initiated analyses of the bulk composition of the fluids within the inclusions in Zag and Monahans halites at Virginia Tech by LA ICPMS using an Agilent 7500ce quadrupole ICPMS and a Lambda Physik GeoLas 193 nm excimer laser ablation system. Preliminary results reveal that the inclusion aqueous fluids contain highly charged cations of Ca, Mg and Fe.



The minerals and compounds discovered thus far within Monahans/Zag halites are indicative of an originating body at least partly composed of unequilibrated anhydrous materials (high Fo olivine, pyroxenes, feldspars, possibly the metal) which were subjected to aqueous alteration (the halite parent brine) and containing a light organic component (the short-chain aliphatic compounds). This material was ejected from the originating body with little or no disruption, as evidenced with the presence of fluid inclusions. An actively geysering body similar to modern Enceladus (Postberg et al., 2011) may be a reasonable analogue in this respect. Also, the originating body should have been within close proximity to the H chondrite parent in order to generate the number of halite grains seen in Monahans and Zag. Other candidates for Monahans/Zag halite parent bodie(s) may include a young Ceres with its possible liquid ocean, or Main Belt comets.

References

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