OXYGEN AND HYDROGEN ISOTOPIC COMPOSITION OF ZAG WATER MEASURED BY CAVITY RING-DOWN SPECTROSCOPY

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Introduction: Fluid inclusions in halite found in Zag (H3–6 regolith breccia) are one of the only samples of extraterrestrial liquid water available for laboratory study. The precise H and O isotopic composition of asteroidal water is important for determining the origin of water on the terrestrial planets. The isotopic compositions of individual fluid inclusions in Zag and Monahans were measured using SIMS with a cryogenic sample holder by [1]. In recent years, cavity ring-down spectroscopy (CRDS) has matured into a high-precision technique to measure O and H isotopes in small amounts ($\sim$1 μL) of liquid water [2]. Here we report CRDS H and O isotope measurements of water liberated by crushing a whole stone of Zag.

Samples and Methods: We built a device to crush whole stones (up to $\sim$5 cm in size) under vacuum. Solenoid coils, controlled with a timer, drive a steel piston into a steel chamber containing the sample. Liberated water vapor (and other volatiles) from the crushed rock leaves the chamber via a dust-guarded feed-through into stainless steel vacuum line connected to the input of a Picarro-L2120-i CRDS.

We crushed a $\sim 3\times2\times1$ cm whole stone of Zag with a near-complete fusion crust (chosen to minimize the loss of halite due to terrestrial weathering), as follows. After loading and pumping on the sample using the vacuum line until the pressure and apparent leak rate (as determined using a vacuum gauge) was below an acceptable level to minimize background contamination over the expected duration of the crushing experiment, water vapor, and possibly other volatile compounds, liberated from crushing, was cold trapped in a stainless steel U-trap built into the vacuum line. This U-trap allows us to concentrate small water samples to a small volume before being thawed and carried into the CRDS using Ultra-High-Purity nitrogen gas for isotopic analysis. We measured the O an H isotopic composition of released water vapor after five different $\sim$30 min crushing episodes (we heated the outside of the crushing chamber to 50–60° C with a heat gun after the second episode). We bracketed these samples with water standards (GISP) to monitor the response of the CRDS instrument over the duration of the experiment.

Results: The H and O isotopic composition of water released from Zag during five crushing episodes is shown in Figure 1. Each measurements contained 2–3×10^4 ppmv of water vapor under flow conditions as measured by the CRDS. We are currently calibrating the CRDS under similar conditions to determine the amount of water in each measurement.

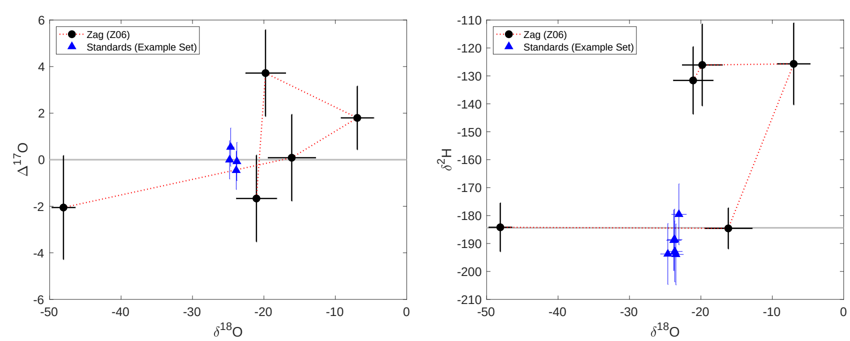

Figure 1: Left) Δ^{17}O vs. δ^{18}O for Zag (black circles) and a representative set of four standard analyses (blue triangles). Red dotted line shows the order of measurements from the five crushing episodes. Right) δ^2H vs. δ^{18}O for the same samples.

Discussion: The first two measurements showed contamination from adsorbed terrestrial water. The fourth measurement showed the largest Δ^{17}O anomaly: $3.7 \pm 1.9‰$ (2σ), and is likely the highest fidelity measurement of the isotopic composition of Zag water. The H composition of the fourth sample was measured to be δ^2H$=-126 \pm 15‰$ (δ^2H in samples 3–5 were consistent). However, fractionation of H isotopes during the measurement (δ^2H in samples 1–2) may be significant and will be investigated. Our measured Δ^{17}O is consistent with one Zag inclusion measured by [1] (3.5±10.0) but lower than three others (20.4, 25.4, 27.0).

Conclusions: Our CRDS measurements of water released from a crushed Zag stone yield higher precision H and O isotope ratios but lack the *in-situ* capability of SIMS measurements made by [1]. CRDS and SIMS can serve as complementary techniques to measure the isotopic composition of asteroidal liquid water in meteorite fluid inclusions.

References: [1] Yurimoto, H. et al. 2014. *Geochemical Journal* 48.6:549 [2] Salvo, C. et al. 2013. *Analytica chimica acta* 804:176.