

Cavity Ringdown Spectroscopy for the Complete Isotopic Characterization of Lunar Surface Volatiles. Gerardo Dominguez¹, Jeffrey Gillis-Davis², Lauren Tafla¹, Ryan Ogliore², ¹Physics Department, California State University, San Marcos, CA USA (gdominguez@csusm.edu), ² Physics Department, Washington University in St. Louis, St. Louis, MO USA (rogliore@wustl.edu)

Introduction: Isotopic compositional measurements of lunar ice would provide insight into the origin and potentially the age of the reservoir. Multiple exogenic and endogenic sources have been proposed as the source of lunar volatiles (e.g., comets, interplanetary dust particles, meteorites, production on the surface via solar wind, and volcanic outgassing). An instrument that can measure isotopes in-situ lies in the critical path for determining the delivery and trapping process for lunar volatiles: e.g., source(s), transport to the polar regions, and ultimate storage. Hence, we are beginning to develop a flight-ready instrument, which will include extraction and analysis, for the purpose of measuring H, O and C isotopes of polar volatiles. Here we focus on our initial results with hydrogen and oxygen isotopes.

Historically, the method of choice for determining the stable isotopic composition of samples has been Isotope Ratio Mass Spectrometry (IRMS) utilizing the null method developed in the 1940s [1]. IRMS, however, requires purification and extraction techniques that tend to limit its portability, wide-spread use and ability to provide time-resolved isotopic information, particularly in the field. This is particularly true for the stable isotopic analysis of H₂O and CO₂ samples.

A promising (and field-portable) alternative to IRMS is tunable infrared laser-based Cavity Ringdown (CRD) absorption spectroscopy. The isotopic resolution of this technique may compete and, in some cases, surpass that of traditional IRMS systems, offering “per meg” resolutions and allowing for the continuous measurement of atmospheric gases such as CO₂ and H₂O with ~1 Hz time resolution. To demonstrate CRD data robustness, we report results from a suite of laboratory experiments, which includes the extraction and analysis of small (~52 μmol) water samples, carried out by commercially available off-the-shelf instrument.

ICE Apparatus: The Astrophysical Isotopic Characterization Experimental apparatus at California State University, San Marcos (CSUSM) was developed with the goal of measuring the isotopic composition of water samples synthesized or altered in astrophysical conditions [2]. Briefly, it consists of a 12-inch diameter UHV chamber that is pumped by a magnetically levitated turbo pump and is attached to a stainless steel vacuum line equipped with various gas-introduction ports, including a septum for injecting small liquid water samples and standards. Two U-shaped sections serve as cold-traps that can be used to concentrate or isolate water samples. Finally, the vacuum line is connected to a

Picarro L2120-i that has been customized for measurements of δ¹⁷O in addition to the advertised δ¹⁸O and δD measurements (See Figure 1). Ultra-high purity N₂ is used as a carrier gas for making isotopic determinations of H₂O samples.

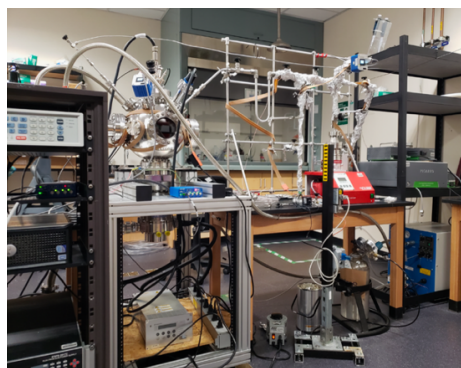


Figure 1. ICE apparatus for studies of the isotopic composition of water samples. Picarro CRD shown on far-right.

CRD Spectroscopy Measurements. The Picarro L2120-i was designed to operate in two modes. In the first, 1 μL samples of liquid H₂O (including saltwater) are injected, through a septum, into a thermally controlled (T=70 C) vaporization unit and then carried, using N₂, into a cavity-ringdown cell where signals associated with the rovibrational lines of H₂O isotopologues are recorded. The magnitude of these signals correlate with the abundances of specific isotopologues of water and the use of standards of known composition are used to calibrate the instrument. In flow configuration, samples of water from the ambient air or attached vacuum system can be analyzed (See Figure 2)

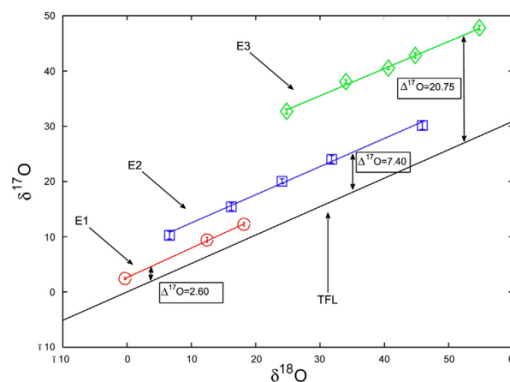


Figure 2. Multi-oxygen isotopic measurements of evaporated water samples using Cavity Ringdown Spectrometry (Picarro L2120-i) in injection mode. Figure taken from [3].

Example Results

Ancient Water in Halite Filled Inclusions from Zag Meteorite: As previously reported, we have successfully extracted and isolated liquid water samples of from the Zag meteorite using a solenoid driven vacuum sample crusher [4]. Future sample extracts will include frozen permafrost-analog regolith samples.

Sample Extraction was done as follows. One or more Zag stones were loaded into crushing device and vacuum sealed. The vacuum line and crushing device volume were pumped down overnight to minimize the analytical contribution of terrestrial water. Crushing was carried out until enough water vapor ($\sim 1 \mu\text{L}$) was released to make an analytical determination of the water's isotopic composition. The sample was then concentrated cryogenically ($\sim 77 \text{ K}$) in a U-trap close to the entrance of the CRD. Finally, the water sample was thawed and UHP N_2 was used to carry the sample into the CRD cell for isotopic measurements. Figure 3 shows the H_2^{16}O signal associated with a recent Zag water extraction experiment that yielded five different samples.

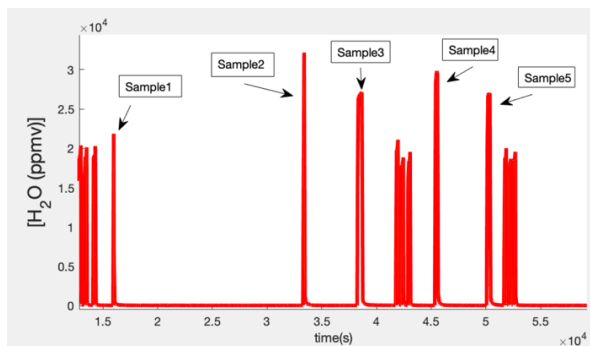


Figure 3. H_2^{16}O signal associated with water extracted from Zag meteorite [2].

The complete isotopic composition of water pulses presented in Figure 4 were done using concentration weighted time averaging reported in [2, 4]. The preliminary results of these isotopic analyses are replicated in Figures 5 and 6.

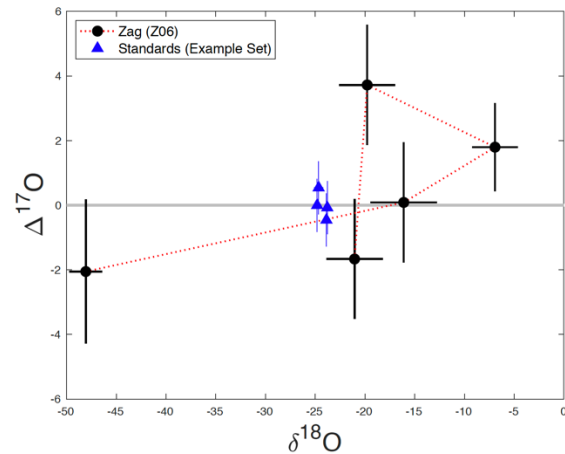


Figure 4. Preliminary multi-oxygen isotopic composition of water found in Zag using CRD [4]

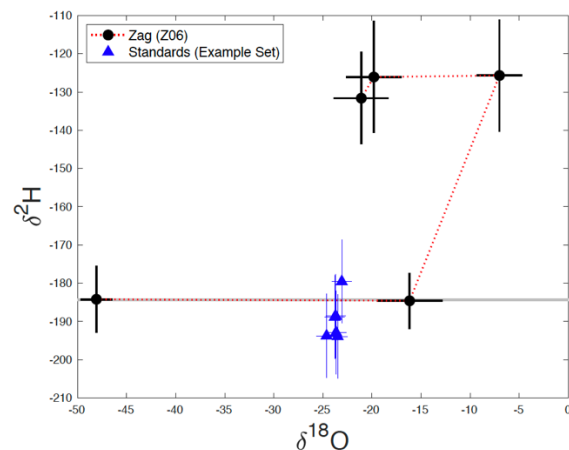


Figure 5. Preliminary D/H measurements of H_2O extracted from Zag using CRD [4]

Uncertainties and Future Work: The uncertainties presented in Figures 4-5 are statistical and do not yet include any systematic shifts introduced by the analysis method. To address this issue, we are currently conducting controlled experiments to determine the systematic shift induced by the incomplete sample recovery and analysis of H_2O using the ICE apparatus vacuum line and rock crushing device. Future work will include tests with CO_2 isotopic standards and optimization of the vacuum-line conditions to minimize any systematic shifts in the isotopic composition of these standards.

Acknowledgments: GD acknowledges support from NASA-Cosmochemistry and NSF Astronomy and Astrophysics programs. GD, JGD, and RO acknowledge support from NASA's SSERVI program.

References: [1] A.O. Nier (1947) *Rev. Sci. Instrum.* 18, 398. [2] Dominguez et al., *in prep* [3] Salvo et al. (2013) *Anal. Chim. Acta*, 804, 176-179 [4] R. Ogliore et al., (2019) *MetSoc*, 6442.