CAVITY RINGDOWN SPECTROSCOPY FOR CHARACTERIZING THE COMPLETE ISOTOPIC COMPOSITION OF EXTRATERRESTRIAL WATER SAMPLES

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Introduction: 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]. Because of the requirement that the sample exist in a highly purified chemical state, IRMS requires purification and extraction techniques that tend to limit its portability, wide-spread use and ability to provide time-resolved isotopic information. This is particularly true for the stable isotopic analysis of H2O samples.

A promising (and field-portable) alternative to IRMS is tunable infrared laser-based Cavity Ringdown absorption spectroscopy (CRD). 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. Here we detail how we have incorporated one of these commercially available instruments to carry out a suite of laboratory experiments, including the extraction and analysis of small (~52 µmol) water samples.

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.

CRD Spectroscopy Measurements. The Picarro L2120-i was designed to operate in two modes. In the first mode, 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 as a carrier gas, into a cavity-ringdown cell where signals associated with the rovibrational lines of H2O isotopologues are recorded (See Figure 2). 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 the second mode, flow configuration, samples of water from the ambient air or attached vacuum system can be analyzed.

Figure 1. ICE apparatus for studies of the isotopic composition of water samples.

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

Solenoid-Driven Piston Vacuum Crushing of “rock” samples is achieved by placing whole stones (~2.5-5 cm sized) into a stainless steel crushing device that can be vacuum sealed. Crushing of samples under vacuum conditions allows us to liberate water that may be found in mineral inclusions (e.g. halite crystals). Cu tubing, aluminum foil packing and salted-ice water and a water pump are used to dissipate the significant heat generated by the solenoid-based drive mechanism (See Figure 3).
Ancient Water hosted in halite inclusions in the Zag Chondrite (H3-6): As previously reported, we have successfully extracted and isolated liquid water samples from the Zag chondrite (H3-6) [4].

*Sample Extraction* was done as follows. A whole, fusion-encrusted Zag stone (2-3 cm in size) was loaded into the 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 (~1 µL) was released to make an analytical determination of the water’s isotopic composition. The sample was then concentrated cryogenically (~77 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 4 shows the H$_2^{16}$O signal associated with a recent Zag water extraction experiment.

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.

**Uncertainties and Future Work:**
The uncertainties presented in Figures 4-6 are statistical and do not include systematic shifts introduced by the analysis method and incomplete water recovery due to interactions between the vacuum-line surfaces and water. To address this issue, we have developed a method of introducing water standards into the vacuum line using sealed glass vials that are crushed and processed identically to Zag. We will describe this technique and the vacuum line corrections derived from these experiments at LPSC.

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