IN-SITU WATER VAPOR PROBE FOR A ROBOT ARM-MOUNTED, COMPACT WATER VAPOR ANALYZER: PRELIMINARY RESULTS. [1]Richard A. Socki, [2]Paul B. Niles, [1]Mike Cabiran, [3]Chris Rossi and [2]Tao Sun, [1]ESCG and [2]NASA Johnson Space Center, Houston, TX 77058, [3]Massachusetts Institute of Technology, Cambridge, MA 02139. *richard.a.socki@nasa.gov*

Introduction: This work describes the ongoing development of an instrument package for the in-situ detection and isotopic analysis of water (from ice, icy soils, and hydrated minerals) on future lunar, asteroid, or martian exploration missions. Lessons learned from the Mars Phoenix mission demonstrated that manipulating, sampling, or analyzing icy material is highly complex. This instrument is intended to be mounted on a robotic arm and be brought to the sample (similar to the APXS and Mossbauer instruments on the Mars Exploration Rovers), rather than necessitating expensive and complicated sample handling to bring the sample to the instrument. The analyzer will be capable of in-situ analysis of water-bearing materials on a millimeter scale providing high precision measurements of water abundance and isotopic composition. The high precision isotopic analysis will include D/H, $^{17}O/^{16}O$, and $^{18}O/^{16}O$. Water is central to NASA's strategic goals for exploration of the solar system and high precision isotopic analysis, especially of ^{17}O, provides a key tool in answering fundamental scientific questions about its origin and history. In addition, these measurements can serve as an important component of ISRU operations helping to identify, characterize, understand, and predict the occurrence of volatile deposits. Additionally, this instrument could be utilized in both manned and unmanned missions to a wide range of high priority NASA mission targets including Mars, the Moon, and Near Earth Objects. It also can serve as a key component of an ISRU instrument package - providing in-situ prospecting.

Our prototype design currently utilizes an "off-the-shelf" instrument (*Los Gatos Research, model DTL-100 Water Vapor Isotope Analyzer* [1-4]) that measures both abundance (ppm) and isotopic ($\delta^{18}O$, δD) composition by tunable diode laser infrared spectroscopy. This analyzer is coupled to a prototype of a sampling "end effector" that can collect and vaporize water-bearing materials. Preliminary tests of the instrument have consisted of analyzed ice samples for O and H isotopic composition. $\delta^{18}O$ and δD (V-SMOW) variations were approximately ±2‰ and ±4‰, respectively at a 95% confidence level. The long-term goal of this work is to provide a "proof of concept" working prototype where this measurement concept can be fully tested in the laboratory and in the field. We report here initial results from our testing of this instrument prototype where we are examining the effects of gas flow rate, isotope exchange, and different sampling methods for understanding how to acquire high precision isotopes measurements.

Instrument Design: A diagram and photo of our in-situ water vapor probe instrument, designed for sampling ice, is shown in figure 1. This device measures ~ 25" high and 14" in diameter and consists of three (24 VDC) gear motors for drilling, raising and lowering the drill stem, and capturing the ice sample. The entire system is contained within a vacuum bell jar and is attached to a vacuum pump and N_2 purge as a means of maintaining ambient pressure. The drill tip is tungsten carbide with a fishtail point. The base of the instrument consists of a ice sample "pool" ~500cc volume made of aluminum that allows for water samples to be frozen by means of circulating chilled (-20 to -50°C) ethanol on

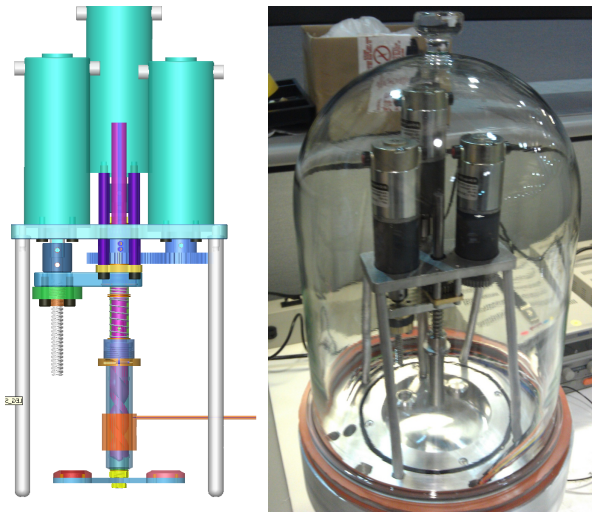

Figure 1. Diagram and photo of our in-situ water vapor probe instrument. This devise measures ~25" high and 14" in diameter. Ice is made in the base

the outside of the base. Samples are withdrawn from the base by drilling, capturing and heating the ice. Once heated, water vapor from the ice sample is sent to the analyzer by means of an Ultra High Purity (UHP) N_2 carrier gas. Isotope ratios are measured by the analyzer using variations of laser absorption spectroscopy, a strategy that exploits the different vibrational modes in water isotope molecules by passing a laser though the gas and measuring the absorption at relevant wavelengths. Water vapor derived from the sampler is diverted by either pumping through the analyzer by means diaphragm pump or by flowing the water vapor to the analyzer by using a carrier gas.

In order to test the sampling configuration, initial isotope analyses were conducted using an experimental set-up intended to test some of the measurement concepts that might evolve from this type of sampling

instrument. In this setup an open ended conical object (funnel) was placed in contact with an icy surface, and carrier gas (N_2) was directed inside the funnel in order to carry water vapor into the WVIA. The WVIA has one inlet port with a 1⁄4" Teflon tube and an outlet port that leads to a low vacuum diaphragm pump. The sample was contained in a custom glass flask approximately 800 mL in volume. An estimated 120 mL of water of known composition was contained within the flask. A UHP N_2 supply was connected toward the bottom of the glass chamber, so as to direct the flow toward the WVIA intake, thus water vapor samples were assumed to be water derived solely from sublimation of the ice.

Two methods were used to remove air and laboratory ambient moisture from water vapor before sampling experiments were conducted. One method was to flow UHP nitrogen through the system and into the WVIA for 5 minutes. The second method was to repeatedly pump down the system and backfill with UHP nitrogen. The rational was that as a percentage of pressure is withdrawn from the sample chamber, that same percentage of water vapor is also withdrawn since it is assumed to be a well mixed gas. By reaching the minimum 300 Torr pressure within the analyzer in five consecutive runs at minimum flow rate, the quantity of water vapor remaining should be less than 1% of the original. Note that equilibrium rate calculations at laboratory conditions indicate that it takes about 5 minutes to reach 1% of the equilibrium quantity of water vapor. Thus, there is not a significant amount of water vapor re-entering the chamber during the 15 minutes this process takes.

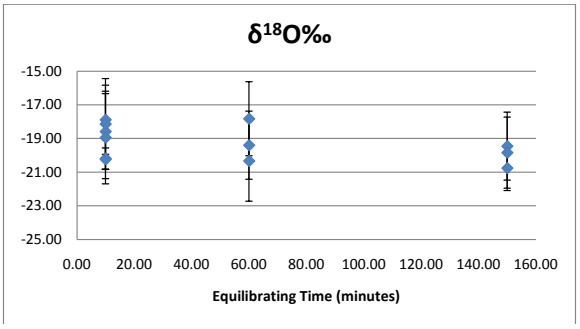

Figure 2. Averaged oxygen isotope ($\delta^{18}O_{(V\text{-}SMOW)}$) compositions as a function of variable equilibrating times. No significant isotope variation was seen.

Two different sampling experiments were performed. The first experiment varied the time given to let the ice equilibrate between sampling runs, with times varying from 10 minutes to 2.5 hours. Data analysis resulted in no apparent significant variation in isotope compositions between runs. Data were processed by averaging measurements during the sampling time, and using double the standard deviation as a 95% confidence interval error. This was done for all experiments. Figure 2 shows averaged data for the variable equilibrating time experiment.

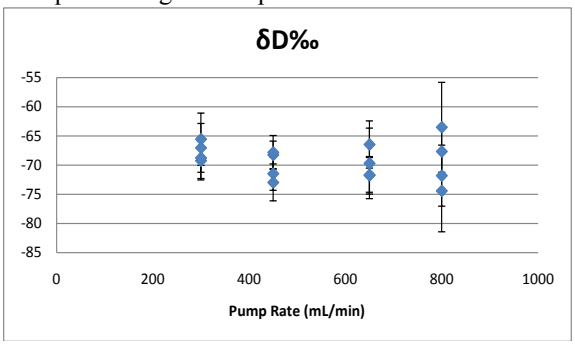

Figure 3. Averaged hydrogen isotope ($\delta D_{(V\text{-}SMOW)}$) compositions as a function of variable pump rates. No significant isotope variation was seen.

Another separate experiment investigated the effect of sample pump rate on ice measurements over the available range of the WVIA pump. Once again, no significant variation in final measurement was observed. However, as expected, the response time needed to reach the measurement varied. The response time seems to be approximately proportional to the pump rate, with higher pump rates resulting in faster response times. Figure 3 demonstrates the lack of significant variation seen in averaged hydrogen isotope data with respect to pump rate. Overall, the averaging used in data analysis showed that over a 90 second sampling period at a measurement rate of .5 Hz, $\delta^{18}O$ and δD variations were approximately ±2‰ and ±4‰, respectively at a 95% confidence level.

Summary: The water vapor isotope analyzer technology shown and tested here is theoretically capable of providing crucial measurements on extraterrestrial surfaces. Our design alleviates sample-handling problems encountered in other planetary missions by bringing the instrument to the sample, rather then the sample to the instrument. Preliminary tests of the instrument have consisted of analyzed ice samples for O and H isotopic composition. Our data show that our measurement concept can allow for the successful analysis of water isotopes in vapor that are reproducible within ~+/-2‰ and 4‰ (V-SMOW) for oxygen ($\delta^{18}O$) and hydrogen (δD) isotopes, respectively. Further work will include drilling and analyzing ice and icy-soils using the sampling prototype integrated with the WVIA. Also, variation in ambient pressures and ice temperatures will allow us to simulate different planetary conditions where ice is believed to exist.

References: [1] Sturm, P. and Knohl, A. Atmos. Meas. Tech., 3, 67-77, 2010. [2] Dong, F., Baer, D., *EGU General Assembly*, May 3 - 7, 2010. [3] Rothman, L.S. et al., J. Quant. Spectrosc. Radiat. Transfer 82 (2003). [4] Baer, D., et al., Appl. Phys. B-Lasers, 75, 261–265, 2002.