

**PRELIMINARY RESULTS OF SUBLIMATION FRACTIONATION IN DUSTY DISAGGREGATED SAMPLES.** J. E. Moores<sup>1</sup>, R. H. Brown<sup>1</sup>, D.S. Lauretta<sup>1</sup> and P.H. Smith<sup>1</sup> <sup>1</sup>Lunar and Planetary Laboratory, University of Arizona (1629 E University Blvd, Tucson AZ, 85721-0092 [jmoores@lpl.arizona.edu](mailto:jmoores@lpl.arizona.edu))

**Introduction:** Using a cryostat, the behavior of particulate rich ice as an analogue for the ice-rich polar regolith of Mars is investigated. In particular, we examine the isotopic enrichment of this ice in deuterium and its role as a sink for the heavier isotope. We have chosen an appropriate concentration and size (1.6 microns in radius) for these particles based on the assumption that martian ices could be emplaced by precipitation from the atmosphere under near-current conditions. A 25wt% mixture of this size of TiO<sub>2</sub> dust in a 5vol% deuterium D<sub>2</sub>O/H<sub>2</sub>O solution was used as a regolith simulant and was found to undergo significant deuterium fractionation.

Unlike previous crystalline samples [2], the fractionation did not end rapidly – typical of solid samples with limited molecule mobility within the bulk. Instead, the hydrogen content of the sublimed gas continued to increase with time possibly as a result of preferential movement of deuterium away from the surface towards the colder part of the sample. Using a petrographic microscope ice grain sizes were confirmed to be consistent with snows seen by Viking Lander 2 in 1979[1].

**Sublimation Fractionation:** Any physical process that depends on the atomic mass of a molecule is capable of separating and fractionating isotopes of different masses. One example of this is thermal escape at the top of a planetary atmosphere that preferentially removes the lighter isotopes from the planet. Fractionation is also known to occur in liquid systems, such as the enhancement of H<sub>2</sub>O, the lighter isotopic form of water, over D<sub>2</sub>O and HDO as observed in rainwater or snow compared to oceanic values on Earth. More recent work has also shown that this type of fractionation may be important in solid sublimation under certain conditions [2].

Unlike a liquid or a gas, we cannot assume that a solid is well mixed. Thus, it is much harder for molecules to move in the lattice and maintain the bulk isotopic concentrations of the sample at the surface where sublimation occurs. As a result, we would expect the surface to become enriched in the heavier isotope as the lighter isotope is preferentially removed by sublimation since the energy to remove it from the surface is lower. As the surface becomes enriched with the heavier isotope, the concentration of the heavier isotope in the sublimated gas increases

until it reaches the same concentration as that of the bulk sample. At this point, equilibrium has been reached and fractionation stops. Thus, to have effective fractionation, it is important to have a mechanism for removing the heavier isotope from the surface.



*Figure 1: 25wt% TiO<sub>2</sub> in water – the grains seem to flash in from the glassy state. Typical Grain Size ~ 10 to 20 microns.*

**Manufacturing Icy Regolith:** Various mixtures of dust with pure water having concentrations covering 0-50wt% of dust, a range consistent with the northern polar caps of mars [4] were prepared using insoluble TiO<sub>2</sub> dust grains (density = 4.23g/cc). These grains were of similar size to martian dust particles, as determined by the Imager for Mars Pathfinder [3]. Next, these ice-dust mixtures were flash frozen by pipetting into liquid nitrogen in order to prevent the dust from being excluded from the matrix and to bring the ice down below the crystalline-amorphous transition temperature. Using a petrographic microscope [Figure 1] we then verified the grain sizes as the frozen samples warmed up. From this analysis, we determined that the size of precipitation “frost” seen by Viking [1] was best simulated with about 25wt% dust which gave a constant ice grain size of <25microns.

Next, using this concentration of dust, a sample was prepared in which the ice had been salted with 5vol% (5.3mol%) D<sub>2</sub>O. These were set in the Lunar and Planetary Laboratory Cryostat and allowed to

sublimate. A gradient in temperature was achieved in the sample by cooling from below using a liquid helium cold finger set to 160 K and heated from above using a focused xenon lamp. Analysis of the initial sublimate gas indicated that the temperature at the top of the sample was 202.88 K, temperature sensors imbedded in the chamber did not detect a significant change over the course of the experiment. During sublimation, this gas was monitored by a 10 mTorr pressure gage and a mass spectrometer.

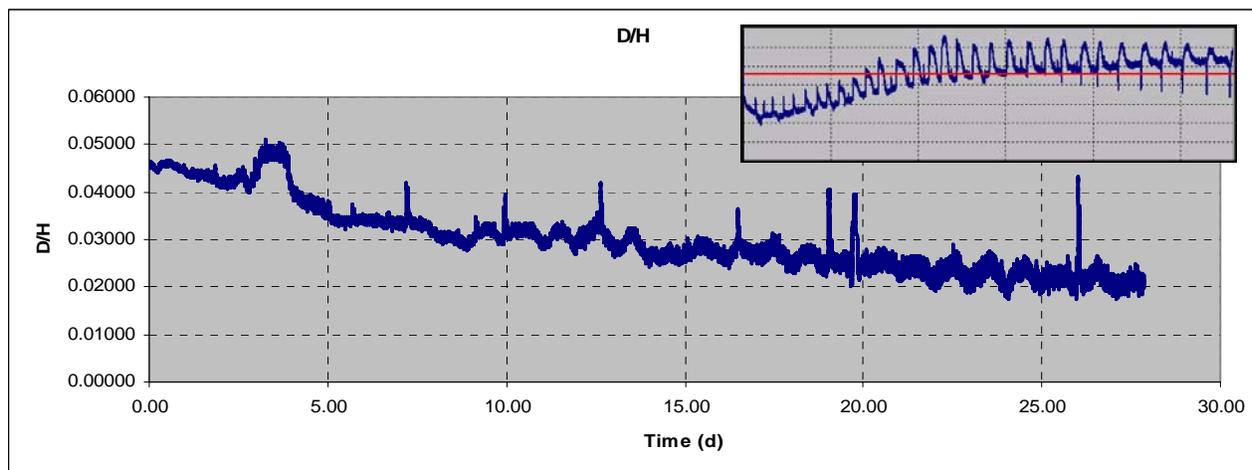
**Results:** At the time of this writing, the first dusty sample has been sublimating for approximately 28 days. The calculated D/H ratio of the sublimate gas over that time is provided in figure 2. It shows depletion of deuterium in the sublimate gas by approximately a factor of two over the D/H ratio of the bulk solid. This is a puzzling result and very different from what we observe in crystalline samples whose sublimate gas is typically slightly enriched in deuterium [2]. What is even more surprising about this depletion is the trend of decreasing D/H values in the sublimate gas over time. As can be seen from the inset in figure 2, this is the opposite of the typical trend.

A second important feature of this process is the sublimation spikes. These events are not discontinuities, but are smooth on a scale of hours and are accompanied by a substantial increase in the observed pressure and a corresponding decrease in the observed surface temperature (due to latent heat

of sublimation). These “sublimation cascades” are also typical of crystalline samples where they occur on regular timescales [2]. While the disaggregated, particulate rich sample shown here does show these events they seem to lack the periodicity of typical crystalline cascades.

**Conclusions:** At this point our research is only preliminary. Still, there are some interesting possibilities for the cause of the decrease of D/H in the sublimate gas with time; for instance, it could represent vapor transport within the sample and preferential adsorption of the heavier isotopes onto the abundant grain surfaces in the colder parts of the sample. This could result in a progressively depleted surface layer. Without more data we cannot draw a definite conclusion as to the mechanism responsible. However, it seems clear that the presence of dust in the matrix is affecting the isotopic fractionation of the host ice during sublimation. Thus sublimation on bodies with dusty ices may be more complicated than has been previously thought.

**References:** [1] Jet Propulsion Laboratory (1997) Planetary Photojournal Entry #PIA00571. [2] Weirich J.R., Brown R.H., Lauretta D.S. (2004) AAS:DPS XXXVI Abstract #33.01 [3] Tomasko, M et al (1990) *JGR* vol 104-E4 p. 8987-9008 [4] Clifford, et al (2000) *Icarus* vol.144 (2000) pp210-242.



**Figure 2:** Evolution of the Measured D/H Ratio with time. The initial D/H Ratio is 0.053 mol/mol. **Inset Frame:** A crystalline sample profile over the same period with the initial bulk concentration of the sample shown in red.