

**EXPERIMENTAL RESULTS ON ISOTOPIC FRACTIONATION OF DUSTY DEUTERATED WATER ICE DURING SUBLIMATION** J.E. Moores<sup>1</sup>, P.H. Smith<sup>1</sup>, R.H. Brown<sup>1</sup>, D.S. Lauretta<sup>1</sup>, W.V. Boynton<sup>1</sup> and M.J. Drake<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)

**Introduction:** The isotopic fractionation of water ice during sublimation on planetary bodies has been considered a simple temperature-driven process in which colder ices tended to fractionate more heavily than warmer ones due to the differences in lattice binding energy between H<sub>2</sub>O and HDO [1,2,3]. Typically, in planetary analyses, either just this equilibrium value was used [4] or was first combined with the concept of a static lattice in which no fractionation occurs due to a buildup of the more refractory isotope on the surface until the ice sublimates at the bulk ratio [5]. As a result, explanations for large variations in the observed D/H ratios between different Solar System bodies, such as the 5.5-fold enrichment of the heavy isotope seen in the Martian atmosphere [6] compared to VSMOW or the 15-fold enrichments in comets compared to protosolar values [7,8] have largely ignored the potential long term isotopic effects of sublimation processes.

Recent laboratory experiments, have shown that the sublimation of water ice is not a simple and steady process, and that D/H ratios in the vapor can be time variable, mimicking at a much lower level, Rayleigh fractionation seen in the evaporation of liquids [9,10,11]. Previous work also indicates that realistic samples containing mixtures of ices [12] or contaminating dusts [13] can severely impact the sublimation rate and isotopic character of the escaping gas. As such, a study was undertaken to examine the effect of dust on the isotopic fractionation of water ice.

**Experimental Setup:** Two different apparatuses were employed for experiments. First, a medium-sized (150mL) closed cycle cooler-driven cryostat described previously [9,10,11,13] was employed to examine the effect of mixed water ice and dust over a range of dust sizes, compositions, contamination ratios and temperatures (Basal 60-165K, surface 190-230K). Secondly, a new, larger apparatus (2500mL) intended to operate at higher temperatures under a 6.1 mBar atmosphere of CO<sub>2</sub> and cooled by a liquid nitrogen heat exchanger was constructed to study the effects of regolith overburdens at different grain sizes and temperatures. The smaller apparatus was intended to simulate a cometary environment and the larger a Martian polar environment.

In each case, samples were heated from the top using a Quartz Tungsten Halogen (QTH) lamp and a temperature gradient in the sample was established.

Sublimation gases (and CO<sub>2</sub> for the larger apparatus) were drawn off by a turbomolecular pump and sampled by a quadrupole mass spectrometer to obtain isotopic ratios. In order to ensure sufficient signal to noise and eliminate the effects of oxygen isotopes, the samples were isotopically enriched with 5% by volume D<sub>2</sub>O (5.3 mol%).

A total of seven different materials were used as dust; 1.5- $\mu$ m particles of TiO<sub>2</sub>, 1.5- $\mu$ m particles of SiO<sub>2</sub>, cutting dust from the Fukang pallasite with grain sizes ranging from 10  $\mu$ m to 50  $\mu$ m and JSC Mars-1 regolith simulants palagonite? in four different grain sizes: in raw form with a distribution of different grain sizes, sieved 105-150  $\mu$ m, sieved 500-1000  $\mu$ m and water-settled 1- $\mu$ m particles. These samples are incorporated as overburden layers ranging from 3 mm to 20 mm in thickness or directly combined with liquid water and flash frozen with mixtures ranging from 1 wt% to 27 wt% dust.

**Results:** Of the two data sets the most striking are the results for mixed dust and water ice at low temperatures. In several cases, samples were observed to progress from the initial D/H concentration of 5.3 mol% to no detectable deuterium in the sublimate gas within a few weeks. An example of this type of trend is shown on the next page for a 9 wt% mixture of 1- $\mu$ m palagonite particles. This behavior of fractionation increasing with time was exhibited for all very fine grained dusty samples at all temperatures and is markedly different from results seen with pure water ice in which the fractionation of the heavy isotope is seen to decrease with time [9,10]. The only sample for which a decrease was not observed used 500  $\mu$ m – 100  $\mu$ m palagonite, suggesting that the amount of available surface area may be more important than the mass of particulate incorporated in the water ice.

Fractionations were also observed in the second data set for dust overburden. Again, the water ice that was present was enriched at 5.3 mol% HDO and was verified as unfractionated prior to the addition of overburden by sublimating a small fraction. Once this regolith was added, the sublimate gas escaping the surface was initially quite fractionated and remained more fractionated than could be thermally explained for the duration of the experiment. In fact, most samples appeared to be approaching steady state at the end of their runs at D/H ratios lower than expected.

Finally, when this system was diurnally cycled using the lamp while maintaining the same basal temperature, the isotopic nature of the sublimate gas was also seen to cycle between different distinct values. This case is shown in figure 2 and demonstrates that within the long term evolution of the samples, a sudden step change in temperature can still cause a step change in the observed isotopic character of the gas.

**Conclusions:** Dust, whether mixed in with water ice or as dry overburden can have a significant isotopic effect. The largest effect is observed for mixtures containing large quantities of fine dust for which deuterium disappears almost entirely from the gas within a few weeks. The presence of overburden is also seen to cause a less extreme but still significant fractionation in the sublimed gas. This fractionation was seen to change in response to a changing

thermal environment, in this case, diurnal cycling. If these fractionations persist for long periods they would be able to lead to significant changes in the isotopic character of the remaining water ice and the observed D/H ratio.

**References:** [1] Merlivat and Nief (1967) *Tellus* **19** 122-127 [2] Daansgard (1964) *Tellus* **16** 436-468 [3] Van Hook (1972) *J. of Phys Chem.* **76** 3040-3043 [4] Yung (1988) *Icarus* **76** 146-159 [5] Carr (1996) *Water on Mars* [6] Krasnopolsky (1997) *JGR* **102** 6525-6534 [7] Meier (1999) *Space Sci. Rev.* **90** 33-43 [8] Geiss (2003) *Space Sci. Rev.* **106** 3-18 [9] Laurretta (2005) *Workshop on Dust in Planetary Systems* #4067. [10] Weirich (2004) *Bull. Amer. Astron. Soc.* **36**, 1143. [11] Brown (2008) in preparation [12] Mastrapa (2007) AGUFM n°P13G-03 [13] Moores (2005) LPSC XXXVI n°1973

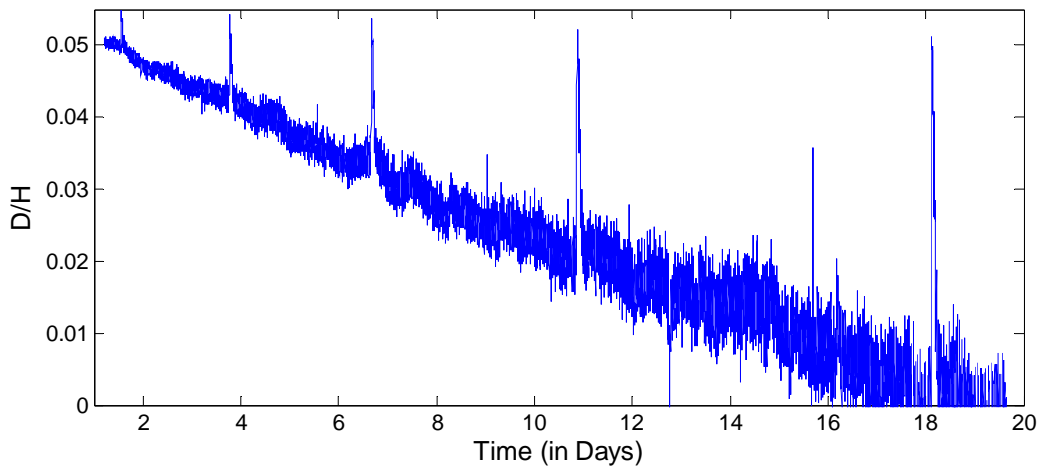


Figure 1 – Decrease in D/H ratio over 20 days in a 9wt% dust in 5.3mol% water ice mixture with 1-10 $\mu$ m palagonite dust. Rapid fractionation of the gas (shown) indicates a concentration of the heavier isotope in the solid sample. Spikes in D/H are sublimation cascades, as described in references 9, 10 and 11.

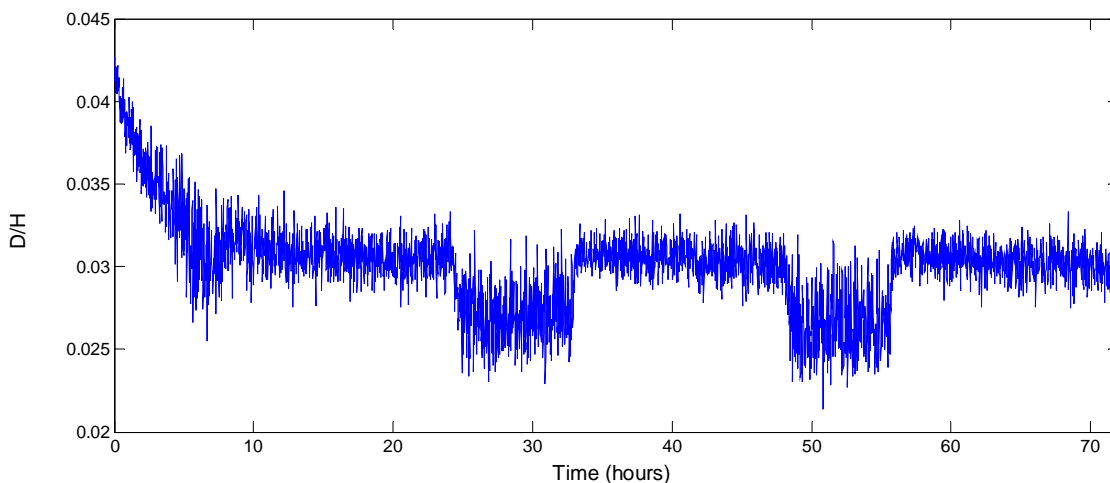


Figure 2 – D/H during diurnal cycling (lamp ~ 250W/m<sup>2</sup>-thermal as seen in the sample) of a 5.3mol% ice sample overlain by 5mm of JSC Mars-1 at a constant basal temperature of 213K. Higher fractionations are observed with the lamp turned off. Equilibrium D/H ratio at this temperature is ~0.04.