

SUBLIMATION FRACTIONATION IN DUSTY DISAGGREGATED SAMPLES

J. E. Moores*, R. H. Brown, D.S. Lauretta and P.H. Smith (jmoores@lpl.arizona.edu)

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 TiO₂ dust in a 5vol% deuterium D₂O/H₂O 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. Fractionation is known to occur in liquid systems, such as the enhancement of H₂O, the lighter isotopic form of water, over D₂O 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 sublimating 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.

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 TiO₂ dust grains. 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. 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%) D₂O. During sublimation, the sublimate gas was monitored by a 10 mTorr pressure gage and a mass spectrometer.

Results: The first dusty sample showed a distinct depletion of deuterium in the sublimate gas by approximately a factor of two over the D/H ratio of the

bulk solid during sublimation. Furthermore, the sublimate gas of this sample was seen to become isotopically lighter with time. 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] and the theory which predicts increasing deuterium concentration with time.

In order to determine whether this was an outlying case, the experiment was repeated with similar results. Next in an attempt to determine whether porosity or grain size was more important we prepared dustless samples by the same procedure. The sublimate gas from these samples did not exhibit any fractionation.

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.

Implications for Phoenix: In 2008 the phoenix lander will dig into the northern polar layered deposits of Mars. These are expected to be a mixture of water ice along with substantial regolith and dusty components. In this work, we have observed very different sublimation characteristics for pure water ice and dusty samples. Thus, fully characterizing the sublimation properties of these dusty ices may yield a method which can be used to differentiate between different emplacement methods for martian ices.

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.