HYDROGEN ISOTOPIC FRACTIONATION AND THE ROLE OF DUST DURING SUBLIMATION FROM COMETARY ICE. D. S. Lauretta R. H. Brown, B. Schmidt, and J. Moores, Lunar and Planetary Laboratory, University of Arizona. Tucson, AZ 85721, USA. lauretta@lpl.arizona.edu

Introduction: The isotopic compositional variations in solar system materials are important indicators of the origin and evolution of the sun, the planets and the small bodies of the solar system. The deuterium-to-hydrogen ratio (D/H) is particularly important in this regard. Primordial deuterium was synthesized in the first few minutes of the Big Bang [1]. Since then nucleosynthesis in stellar interiors has converted a large fraction of the primordial D to $^3$He. D has the lowest binding energy per nucleon of all the stable isotopes and can only be formed in extreme environments. There is no way to produce significant amounts of D during the chemical evolution of the galaxy [2].

Cosmochemical and geochemical processes are capable of significantly fractionating D from H. At low temperatures sizeable differences in the zero-point energies of a deuterated molecule and its H-bearing counterpart lead to strong fractionation effects in kinetically controlled chemical reactions [3]. Thus, the D/H ratio could provide a detailed record of temperatures during processing of materials in the interstellar medium and the solar nebula.

Comets are remnant icy and rocky material from the earliest stages of solar system evolution. Long-period comets were likely icy planetesimals that originally formed in the outer solar system and were ejected into the Oort cloud by encounters with the gas giant planets. Short-period comets formed in the Kuiper Belt, outside the orbits of Uranus and Neptune [5]. Because of its potential for constraining the source material and formation mechanisms of comets, the D/H ratio in comet ice has been the subject of intense interest over the past two decades.

The recent apparition of two exceptionally bright comets provided the first opportunity for ground-based detections of cometary D. [6] announced the first positive detection of HDO in Comet C/1996 B2 (Hyakutake) and an upper limit of 0.01 for (D/H)$_{HCN}$. One year later [7] reported on the double-detection of HDO and DCN in Comet C/1995 O1 (Hale-Bopp). These results, combined with water measurements from available IR, UV, and radio measurements made with other instruments, provide constraints on the bulk D/H ratio in water vapor in the cometary coma.

Two independent mass spectrometers aboard the Giotto spacecraft recorded mass-resolved ion spectra of H$_3$O$^+$ with a dynamic range large enough to detect the rare isotopes at masses 20$^+$ and 21$^+$. From these data the (D/H)$_{H_2O}$ ratios for Comet 1P/Halley have been constrained. Measurements of D/H in the coma of these three Oort cloud comets show a D/H ratio that is roughly a factor of 2 higher than the value for standard mean ocean water (VSMOW), and an order of magnitude higher than the protosolar value [8]. These results place fundamental constraints on models large-scale mixing of the solar nebula [9] and the amount of cometary material accreted by the Earth [10].

Discussion: Though these measurements are ground-breaking and important, we urge caution in their interpretation. To obtain an accurate D/H ratio in water using telescopic techniques, one would ideally want to compare HDO with an optically thin line of the rare isotopic molecules H$_2$^{16}O or H$_2$^{17}O using the same instrument; however, all of the stronger transitions of these were inaccessible for the equipment used to detect HDO in both Hale-Bopp and Hyakutake. Hence, observations of HDO abundances in the coma of these comets had to be compared with production rates measured elsewhere at about the same time. For Hale-Bopp, follow-up measurements of HDO indicated that the absolute calibration of the receiver was not fully reliable at the time of the HDO experiment and the temperature scale had to be adjusted to account for this discrepancy [7].

We have noted some inconsistencies in the analysis of the Giotto data of the composition of the coma of Halley. The composition of the coma was determined using ion currents measured by the Neutral Mass Spectrometer in the 17.5 amu/e to 21.5 amu/e mass range. The $^{16}$O/$^{16}$O ratio in the coma was determined using the intensities recorded at masses 19$^+$ and 21$^+$ assuming that there was no contribution from F$^+$, HF$^+$, or H$_2$F$^+$ and that no Ne was present [11]. Using these assumptions the $^{18}$O/$^{16}$O ratio in the coma of comet Halley was determined to be 2130 +/- 180 ppm. While [11] claim that this value is “identical to the average terrestrial value”, it in fact deviates from the $^{16}$O/$^{16}$O of VSMOW by 82 ‰. This observation is important for calculating the D/H ratio in Halley’s coma.

Determination of the D/H ratio in the coma of comet Halley relies on several factors including the measured ion densities at masses 18$^+$, 20$^+$, and 21$^+$, the relative contribution of the H$_2$O$^+$ ion to mass 18$^+$, and the $^{16}$O/$^{16}$O and $^{17}$O/$^{16}$O ratios. When calculating the D/H ratio, [11] used terrestrial values for both $^{16}$O/$^{16}$O and $^{17}$O/$^{16}$O, despite having directly measured the $^{18}$O/$^{16}$O at various positions within the coma. We have recalculated the D/H ratio using the same technique as [11] with two exceptions. We used the individual values for $^{18}$O/$^{16}$O determined at each position in the
comas. Furthermore, we assumed that $^{17}$O/$^{16}$O is related to $^{18}$O/$^{16}$O via the equation, $\delta^{17}$O = 0.52 * $\delta^{18}$O, which is true if the isotopes are separated via a mass-dependent fractionation process. This treatment not only decreases the calculated D/H ratio (from 255 down to 212 ppm) but also reveals a gradient in the D/H ratio with distance from the nucleus. If this gradient is real, it raises the question: what processes are capable of fractionating the isotopes of H during this process?

Our entire knowledge about the chemical composition in cometary nuclei is tied to studies of the coma composition. In the past the question has been raised, whether, and how closely, observed D fractionations in the coma actually represent the conditions in the nucleus. In the absence of surface probes, it has generally been assumed that the D/H ratio measured spectroscopically in the comet coma is identical to that in the comet ice. [12] developed a simple model of sublimation from a cometary surface. Their results provide a strong indication that significant isotopic fractionation may occur during cometary sublimation in the inner solar system. If so, any inferred consequences for solar nebula models and the origin of terrestrial volatiles must be viewed with caution.

**Experimental Study:** In light of the importance in understanding the bulk D/H ratio in cometary ices and the questions raised as to the relationship between this value and the HDO/H$_2$O ratio in cometary coma, we performed an experimental study of ice sublimation under conditions relevant to the surface of a comet in the inner solar system. Our experimental results strongly suggest that the interpretations of measurements of the HDO/H$_2$O ratio in the coma are oversimplified. In addition, we have discovered some important, fundamental aspects of the mechanism of water ice sublimation in a vacuum.

We have observed a systematic increase in the D/H ratio of the vapor relative to the bulk composition for experiments using pure ice with small ice grain sizes. In these samples deuterated water molecules are able to diffuse relatively rapidly downward into the sample as the result of the many grain boundaries present. We have also performed experiments in which the D/H ratio of the vapor oscillates around the bulk composition. In these experiments, the ice was frozen slowly to produce large crystals and minimal grain boundaries. Finally, in experiments that contain a significant dust component, arguably the most realistic simulation of a comet surface, the D/H ratio in the vapor phase is depleted by as much as 70% relative to the bulk starting composition. Thus, depending on the experimental parameters, the vapor liberated from the icy surface can be enriched, depleted or equivalent in D/H relative to the bulk, starting composition. Therefore, we consider it highly unlikely that the D/H ratio observed as HDO/H$_2$O in cometary nuclei is representative of the bulk D/H ratio in the nuclei.

The second major result of our study is that we have discovered a previously unreported and fundamental characteristic about the sublimation behavior of ice into a vacuum. In particular, we have observed the development of significant outbursts of vapor from a system which occur quasi-periodically. These bursts are accompanied by a significant (~10 degree) drop in the surface temperature of the sample. The decrease in temperature is consistent with transfer of energy to compensate for the latent heat of sublimation. The most D-enriched vapors are liberated during these pressure bursts.

Based on re-analysis of the Halley data and our experimental results we conclude that the reported D/H ratios in cometary comae are not robust. This is due in part to the fact that HDO and H$_2$O are not measured simultaneously in ground-based observations. In addition, analyses of data from the NMS on Giotto are subject to questionable models and assumptions. Our experiments show that, depending on environmental conditions, vapor liberated from a sublimating cometary nucleus can be enriched, depleted or equivalent in D/H relative to bulk composition. Therefore, it is highly unlikely that the D/H ratio observed in a cometary coma is representative of the bulk D/H ratio in the nucleus. In every experiment performed, large pressure bursts were observed that correlate with a large decrease in the surface temperature of the sample. This phenomena is a fundamental characteristic of ice sublimation and is likely the cause of the massive outbursts observed from cometary nuclei.

**References:**