THE D/H RATIO IN COMETARY DUST MEASURED BY ROSETTA/COSIMA. J. A. Paquette[1], N. Fray[2], H. Cottin[2], C. Engrand[3], A. Bardyn[4], O. J. Stenzel[1], S. Merouane[1], M. Hilchenbach[2], C.M.O'D. Alexander[4], and Y. Langevin[5], [1]Max-Planck-Institut für Sonnensystemforschung, Justus-von-Liebig-Weg 3, 37077 Göttingen, Germany, [2]LISA, UMR CNRS 7583, Université Paris Est Créteil et Université Paris Diderot, Institut Pierre Simon Laplace, 94000 Créteil, France, [3]CSNSM, CNRS/IN2P3-Univ. Paris Sud (UMR8609), Bat. 104, 91405 Orsay, France, [4]Department of Terrestrial Magnetism, Carnegie Institution of Washington, 5241 Broad Branch Rd. NW, Washington DC, 20015, USA, [5]Institut d'Astrophysique Spatiale, CNRS / Univ. Paris-Sud 11, Orsay, France.

Introduction: Deuterium and hydrogen have the largest relative mass difference of all stable isotopic pairs. Thus the D/H ratio measured in extraterrestrial materials exhibits large variations. The D/H ratio in protosolar disc hydrogen was $(2.2 \pm 0.4) \times 10^{-5}$ [1], and this value is preserved in the atmospheres of Jupiter and Saturn, but the values observed in bodies such as the Earth, chondritic meteorites, and comets are up to 2 orders of magnitude higher (e.g. [2] and references therein). The enrichment of the D/H values of solar system material relative to the protosolar value has been attributed to the incorporation of materials that acquired very high D/H ratios by ion-molecule reactions at very low temperatures, either in the interstellar medium or in the cold regions of the protoplanetary disk [3]. The variation among individual solar system materials has often been used as a tracer or indication of the region in which the particular material formed, with the specifics being necessarily model-dependent. In addition, the D/H ratios measured in cometary water have been used to constrain the amount of water that could have been delivered to the Earth by comets (e.g., [4, 2]). In this work, we will present D/H measurments on the solid high molecular weight organic component of dust particles from comet 67P and analyzed by the COSIMA TOF-SIMS instrument onboard Rosetta.

Chondrites, IDPs, and UCAMMs: In chondritic meteorites hydrogen is present in organics and in phyllosilicates, and shows a distribution of values that peaks close to the Vienna Standard Mean Ocean Water (VSMOW) ratio of value of 1.5576×10^{-4}, with CR Chondrites showing the highest values [3]. Reference [3] also reports that in solar system objects the deuterium enrichment in water seems to be coupled to that in organic matter. Thus, if the D/H observed in water is high, the enrichment in organic matter will be higher still. There is no consensus about whether chondritic Insoluble organic matter (IOM) is interstellar or solar in origin (e.g. [5]). A comparison to organic matter will be of particular relevance later, as material having some resemblance to the IOM has been seen in COSIMA dust particles [6].

In Interplanetary Dust Particles (IDPs) deuterium enriched hotspots are common in the organic matter, the most xtreme of which is 50 times VSMOW [7]. This is of particular interest because the IDPs are believed to be essentially unaltered by thermal or aqueous processes, and a class of IDPs are associated with comets. For example, IDPs that are associated (due to their pristine nature and time of collection) with comet 26P/Grigg-Skjellerup show D/H ratios in hotspots that range from a few times to 30 times the VSMOW value [8]. Some of these variations occur on micrometer scales and such small-scale variations in cometary dust particles will not be observable by COSIMA due to its 35 x 50 micron beam size.

A study of 4 IDPs found a D enhancement in three different organic components, one of which was similar to the IOM from carbonaceous chondrites [9]. It has been claimed that large D/H ratios in chondritic porous IDPs are associated abundant hydrocarbons, and refractory organic matter of probable cometary origin [10].

In UCAMMs, the bulk D/H of the organic matter is D-rich [11, 12], and it can reach up to 30 times VSMOW in small areas, as is observed for CP-IDPs and primitive chondrites. The large amount of organic matter in UCAMMs and this D enrichment suggest that they could also have a cometary origin.

Previous Measurements in Comets: Almost all measurements of D/H in comets have been in the volatiles. If the evolution of cometary ices was not linked to that of the refractory material as suggested in reference [13], then comparison between values measured in the gas phase and the dust may not be especially fruitful. Nonetheless, the results of such measurements are briefly summarized in the following paragraphs.

The D/H ratio was measured in hydronium ions at large distances from the nucleus of comet 1P/Halley [14]. The first results had a large uncertainty, giving a value ranging from 6.0×10^{-5} to 4.8×10^{-4}, but later refinements produced values for the D/H ratio of $3.08^{+0.38}_{-0.53} \times 10^{-4}$ [15] and $(3.16 \pm 0.34) \times 10^{-4}$ [16]. Both are higher than the VSMOW ratio by close to a factor of 2, a significant difference.

The factor of two difference observed at Halley is similar to the value of $(2.9 \pm 1.0) \times 10^{-4}$ that was measured for comet C/1996 B2 (Hyakutake) using submilimeter astronomy [4]. The isotopic ratio was computed from the ratio of the production rates of HDO to H_2O. The same technique was used on comet C/2009 P1 (Garrad) to get a D/H value of $(2.06 \pm 0.22) \times 10^{-4}$ [17]. Both these values are above the VSMOW value and broadly similar to what was measured for Halley. The James Clerk Maxwell telescope was used to measure HDO and H_2O production in comet C/1995 O1 (Hale-Bopp), thus deriving a D/H ratio of (3.3 ± 0.8) x 10^{-4} [18], another value similar to the Halley numbers. Measurement of the OD/OH ratio in comet C/2002 T7 resulted in a D/H value of (2.5 ± 0.7) x 10^{-4} [19], once again above VSMOW and not dissimilar to the ratios measured in the Halley data. A value of (1.4 ± 0.4) × 10^{-4} was found in C/2014 Q2 (Lovejoy)[20] but another technique gave D/H of (3.02 ± 0.87) × 10^{-4} for the same comet [21]. Finally, a D/H ratio of (2.3 ± 0.6) x 10^{-3} was measured in cometary HCN from C/1995 O1 (Hale-Bopp) [22].

A D/H value for comet 67P/Churyumov-Gerasimenko of (5.3 ± 0.7) x 10^{-4} was derived from HDO/H_2O measurements using the ROSINA-DFMS mass spectrometer on Rosetta [2]. This is three times the VSMOW value, and somewhat higher than previous cometary measurements in the volatiles.

The samples brought back by the Stardust mission from Comet 81P/Wild 2 are the only ones that provided D/H measurements in solid phases for samples with cometary origins. D/H ratios in Wild 2 organic matter are as high as 3 times that of VSMOW in fragments of five particles [23]. All of these particles are associated with carbon, although only one of them is composed mainly of carbonaceous material. The highest D/H values measured are not as large as those measured in organic matter from IDPs, UCAMMs, or IOM from carbonaceous chondrites or from HCN in comet Hale-Bopp. The possibility of alteration of Stardust samples due to high-speed impacts with the aerogel leads to an inability to ascertain whether the relatively low D/H ratios are due to an intrinsic difference between IDPs, UCAMMs, and chondrites on the one hand and Stardust samples on the other [23].

COSIMA: COSIMA was an instrument aboard the Rosetta orbiter designed to capture, image, and measure the composition of cometary dust particles using Time of Flight Secondary Ion Mass Spectrometry (ToF-SIMS) [24, 25]. Because of Rosetta's months-long proximity to comet 67P/CG, cometary dust particles were collected within the coma, and with velocities orders of magnitude lower than in previous cometary flyby missions.

Measuring the D/H Ratio With COSIMA: Hydrogen seen in COSIMA mass spectra comes from the cometary dust, but also from the instrument (i.e., contamination). Separation of the cometary contribution from contamination is one hurdle that must be overcome to measure D/H in the cometary dust. The other is instrument mass fractionation (IMF). This effect is caused by differences in instrument sensitivity to the two isotopes. Since it has been shown that dust particles from 67P/C-G contain macromolecular carbonaceous material that shows mass spectral similarities to IOM, and since this organic material is the main source of cometary hydrogen originating from the dust, measurements of samples of IOM were performed with the COSIMA Reference Model on the ground to gauge the strength of IMF for hydrogen measured in space.

The measurements on cometary dust particles were performed on 7 different dust particles. These particles are shown in Figure 1. We will present the D/H ratio measured for each of these particles.

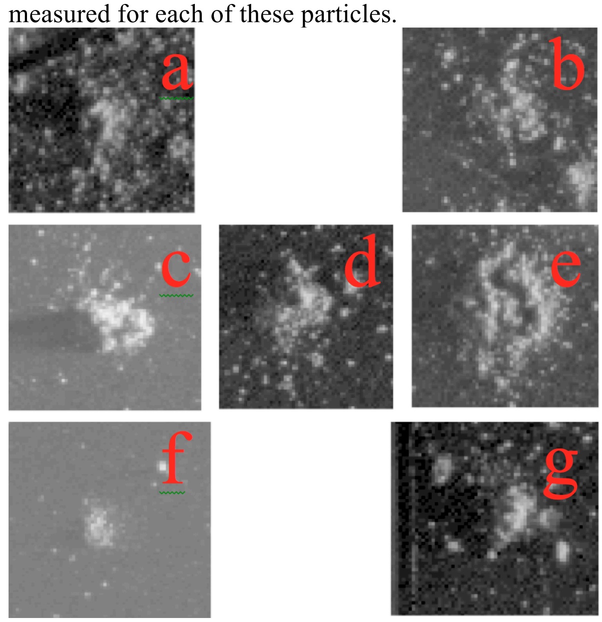

Figure 1: The D/H ratio was measured on seven particles: Barmal (a), David (b), Günther (c), Jakub (d), Jessica (e), Juliette (f), and Sora (g).

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