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D/H in the refractory organics of comet 67P/Churyumov-Gerasimenko measured by *Rosetta*/COSIMA

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ABSTRACT

The D/H ratio is a clue to the origin and evolution of hydrogen-bearing chemical species in Solar system materials. D/H has been observed in the coma of many comets, but most such measurements have been for gaseous water. We present the first *in situ* measurements of the D/H ratios in the organic refractory component of cometary dust particles collected at very low impact speeds in the coma of comet 67P/Churyumov-Gerasimenko (hereafter 67P) by the COSIMA instrument onboard *Rosetta*. The values measured by COSIMA are spatial averages over an approximately $35 \times 50\ \mu m^2$ area. The average D/H ratio for the 25 measured particles is $(1.57 \pm 0.54) \times 10^{-3}$, about an order of magnitude higher than the Vienna Standard Mean Ocean Water (VSMOW), but more than an order of magnitude lower than the values measured in gas-phase organics in solar-like protostellar regions and hot cores. This relatively high averaged value suggests that refractory carbonaceous matter in comet 67P is less processed than the most primitive insoluble organic matter (IOM) in meteorites, which has a D/H ratio in the range of about 1 to 7×10^{-4}. The cometary particles measured *in situ* also have a higher H/C ratio than the IOM. We deduce that the measured D/H in cometary refractory organics is an inheritance from the presolar molecular cloud from which the Solar system formed. The high D/H ratios observed in the cometary particles challenges models in which high D/H ratios result solely from processes that operated in the protosolar disc.

Key words: comets: general – comets: individual: 67P – protoplanetary discs.

1 INTRODUCTION

Deuterium and hydrogen have the largest relative mass difference of all stable isotopic pairs. As a result of this mass difference and a very wide range of formation temperatures of hydrogen-bearing matter, the D/H ratios measured in extraterrestrial materials exhibit large variations. The D/H ratio in H_2 in the solar protoplanetary disc (SPD) was ($2.1 \pm 0.4 \times 10^{-5}$; Geiss & Gloeckler 1998), and this value is preserved in the atmospheres of Jupiter and Saturn, but the values observed in bodies such as the Earth, bulk chondritic meteorites, and water in comets are all roughly an order of magnitude higher (Altwegg et al. 2017). These enrichments in the D/H values of the Solar system material, relative to the protosolar value, have been attributed to the incorporation of very high D/H material synthesized in the interstellar medium at very low temperatures by ion-molecule and gas-grain reactions (Caselli & Ceccarelli 2012).

The D/H variations among individual Solar system materials has often been used as an indication of the regions in which they formed, with the specifics being necessarily model-dependent (Furuya et al. 2013; Yang et al. 2013; Albertsson, Semenov & Henning 2014). 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 (Bockelee-Morvan et al. 1998; Caselli & Ceccarelli 2012; Altwegg et al. 2015). However, there is considerable uncertainty in these constraints because water would not have been the only source of hydrogen when a comet was accreted by Earth (e.g. Alexander et al. 2012). Estimates of the bulk composition of comet 67P and comet 1P/Halley also suggest that it is composed of roughly equal masses of minerals, water ice and refractory organics, although the dust-to-ice ratio in comet 67P is still a matter for debate (Choukroun et al. 2020; Marschall et al. 2020). In this case, the refractory organics would have been almost as important a source of hydrogen as the water ice, yet to date nothing is known about the D/H ratio of the refractory organics. It has been argued that the refractory organics in comets 1P/Halley and 67P share some structural similarities with the insoluble organic material (IOM) in the most primitive chondritic meteorites (Alexander et al. 2007; Altwegg et al. 2015; Fray et al. 2016, 2017; Isnard et al. 2019), although the H/C ratio in 67P is higher than in IOMs extracted from

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these meteorites (Isnard et al. 2019). If similarly deuterium-rich refractory organics are present in comets with less deuterium-rich water than Halley and 67P, their potential contributions to Earth's volatile budget must have been lower than previously estimated. This debate must also consider the possibility that comets could all have a terrestrial-like D/H ratio in their water (Lis et al. 2019), although the results of Marty et al (2017) suggest that water from comets contributed less than 1 per cent of the terrestrial water. If the contribution from refractories is of the same order then the contribution of comets is not important for the D/H ratio of terrestrial water. To put constraints on the origin of the refractory organics in comets and increase our understanding of the bulk D/H ratios of comets, here we present the results of measurements of the D/H ratio in cometary dust collected within the coma of comet 67P using the COSIMA instrument. Because of a dearth of evidence for the presence of hydrated minerals and a likely absence of ices in COSIMA dust due to the temperature and pressure in the instrument, we consider that the D/H ratio measured is that of the refractory organic component of the dust.

1.1 Chondrites and cosmic dust

In the relatively unheated chondrites, hydrogen is present in organics and, in aqueously altered meteorites, in phyllosilicates that likely formed by aqueous alteration in the meteorite parent bodies. In general, at the time of accretion of their parent bodies the D/H ratios of water in chondrites appears to have been significantly lower than in the IOM. However, there are significant variations in water and IOM D/H ratios within individual chondrites, as well as within and between chondrite groups (e.g. Deloule et al. 1998; Busemann et al. 2006, Alexander et al. 2007; Bonal et al. 2013; Piani et al. 2015, 2018). There is considerable debate about the causes of these variations, with explanations including: modification of their compositions in the parent bodies, heterogeneous accretion and mixing of solar and interstellar ices, and formation/modification in the solar nebula under variable conditions. Due to its deuterium enrichment, the IOM in chondrites, or its precursors, has historically been considered to have formed in the interstellar medium (Robert & Epstein 1982; Kerridge 1983; Yang & Epstein 1983, 1984), but a model has been proposed (Remusat et al. 2006) in which the enrichment occurred in the SPD via ion-grain reactions with H_2D^+ (Aikawa et al. 2018).

Cosmic dust particles (Interplanetary Dust Particles – IDPs and micrometeorites MMs) are thought to have both asteroidal and cometary sources (e.g. Bradley 2014). The anhydrous chondritic porous (CP) IDPs and CP-MMs appear to have been essentially unmodified by thermal or aqueous processes in their parent bodies, although they have been heated during atmospheric entry, and are thought to have most likely come from comets (e.g. Bradley 2014; Noguchi et al. 2015). Ultracarbonaceous Antarctic Micrometeorites (UCAMMs) that are dominated by organic matter also have a very probable cometary origin (Duprat et al. 2010; Yabuta et al. 2017; Dartois et al. 2018). Deuterium enrichments are common in CP-IDPs/MMs and UCAMMs, and can be very large. For example, IDPs that are probably associated (due to their pristine nature and time of collection) with comet 26P/Grigg-Skjellerup and some UCAMMs show D/H ratios that range from a few times to 30 times the Vienna Standard Mean Ocean Water (VSMOW) value (Busemann et al. 2009; Duprat et al. 2010). The most extreme enrichment recorded in an IDP is roughly 50 times the terrestrial value (Messenger 2000). These high D/H ratios are always associated with solid organic matter (Wooden 2017) and can be highly variable on micrometre scales within dust particles. For comparison, chondritic IOM also contains several volume per cent of micron to submicron isotopic hotspots (Busemann et al. 2006), with the most deuterium-rich of these so-called hotspots reported to date having a D/H ratio that is about 40 times the VSMOW value (Busemann et al. 2007). Such small-scale variations in cometary dust particles will not be observable by COSIMA due to the $35 \times 50\ \mu m^2$ size of its beam spot.

1.2 Previous measurements in comets

Almost all measurements of D/H ratios in comets have been performed on molecules in the gaseous phase, mostly water vapour. If the evolution of cometary ices was not linked to that of the refractory material, as has been suggested (Meier & Owen 1999), then comparison between values measured in the gas phase and in the dust may not be especially fruitful. The value for comet C/1995 O1 (Hale-Bopp) measured in DCN/HCN of $(2.30 \pm 0.6) \times 10^{-3}$ (Meier et al. 1998; Crovisier et al. 2004) and the recent measurements in singly deuterated and doubly deuterated methanol from comet 67P are perhaps more relevant to the main focus of this paper because they are measured in organic molecules, albeit volatile ones, rather than in water or hydronium. Thus, they may be more directly comparable to the COSIMA results discussed in this paper, although both are present in cometary ices.

Measurements of returned particle from comet 81P/Wild 2 by the Stardust mission have produced the only non-gas phase measurements of D/H in comets. Bulk D/H ratios of 81P/Wild 2 samples range from $(1.18 \pm 0.20) \times 10^{-4}$ to $(4.14 \pm 1.06) \times 10^{-4}$ in fragments of five particles (McKeegan et al. 2006). 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 the highest measured in organic matter from cometary dust collected on Earth (CP-IDPs/MMs and UCAMMs) or bulk IOM from the primitive chondrites, or from HCN in comet Hale-Bopp. Because of the possibility of thermal alteration of Stardust samples during their high-speed ($\sim$6 km s^{-1}) capture in the aerogel, it could not be ascertained whether the relatively low D/H ratios that were measured were due to an intrinsic difference between CP-IDPs/MMMs, UCAMMs and chondritic IOM, on the one hand, and Wild 2 on the other.

2 INSTRUMENT AND MEASUREMENT TECHNIQUE

COSIMA was an instrument onboard the *Rosetta* orbiter. It captured cometary dust particles within the coma of comet 67P on metal targets. The particles could then be imaged by a microscope camera, and a fraction of them were analysed with COSIMA, a time-of-flight secondary ion mass spectrometer (TOF-SIMS). Since the incident velocities of the particles that COSIMA collected were low, on the order of a few m s^{-1} (Rotundi et al. 2015), they did not suffer the degree of thermal alteration experienced by particles collected by flyby missions (such as Stardust) where incident velocities experienced by particles are thousands of times higher. However, the relatively high temperature within the instrument of 10–15 °C (Hilchenbach et al. 2016) did lead to a depletion of any remaining ices in COSIMA-collected dust. In addition, COSIMA remained close (tens to hundreds of kilometres) to the nucleus of 67P for over 2 yr. A complete description of the COSIMA instrument can be found in Kissel et al. (2007).

The measurement technique used in this work is similar to that described in a number of COSIMA papers (Paquette et al. 2017,

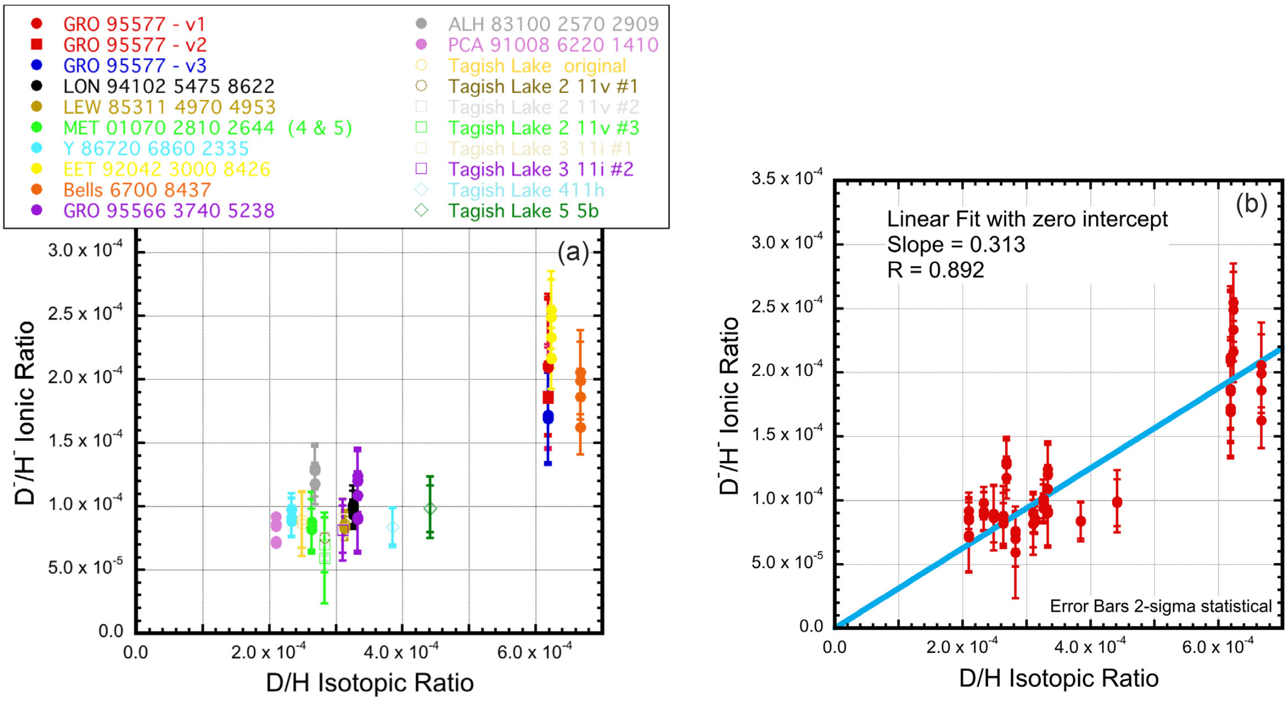

Figure 1. Panel (a) shows the D^-/H^- ionic ratio measured in the COSIMA reference model for samples of insoluble organic matter (IOM) from a selection of chondrites provided by the Carnegie Institution plotted versus the D/H isotopic ratio measured in the lab at Carnegie. The difference between the two measurements is due to the COSIMA instrument mass fractionation (IMF). Panel (b) shows the same data, fit with a line forced to pass through the origin. The inverse of the slope of the line gives the IMF for the D/H ratio in COSIMA: a factor of 3.19.

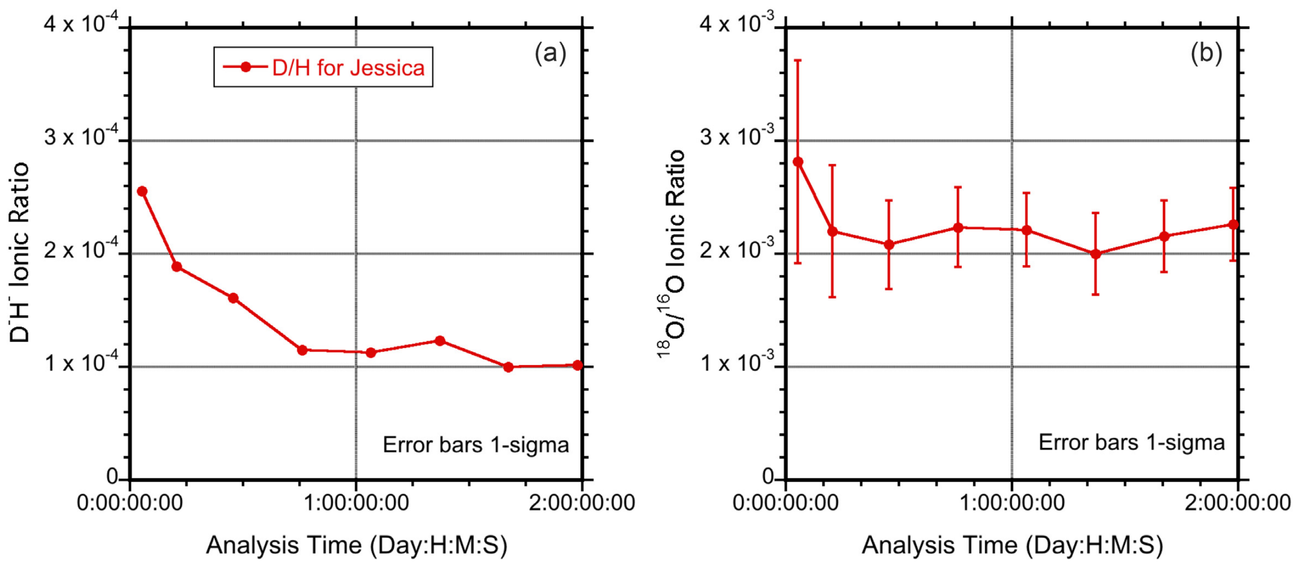

Figure 2. Ratios plotted versus analysis time during the long measurement of the particle Jessica. Panel (a) shows the D^-/H^- ratio, panel (b) shows the $^{18}O^-/^{16}O^-$ ratio. The ratios are not corrected for relative sensitivity factor (RSF) or IMF, thus they are ionic ratios rather than elemental or isotopic ratios. There is a significant change during the long measurement in the D^-/H^- ratio, but not in the oxygen isotopes.

2018). Negative secondary ion mass spectra generated by a primary In^+ beam were used, that is, spectra generated when COSIMA was collecting negative ions. The primary reason for this is that the H_2^- anion, a potential isobaric interference for D, is unstable, with a lifetime of ≤ 0.52 microseconds (Heber et al. 2006), much less than the approximately 12.5 μs flight time of D^-. Therefore, the signal at *m/z* 2 in negative mode is purely due to D, with no significant interferences. Another reason is that a long measurement taken on the particle Jessica Lummene.2 (COSIMA particles − actually corresponding sets of target coordinates − are given names for ease of reference) for other isotopic measurements (Paquette et al. 2017, 2018) provides plentiful data.

Since neither *m/z* 1 nor *m/z* 2 has any significant interferences, a simple sum over the appropriate mass interval and a background subtraction yields the total peak counts. Since COSIMA's beam spot on a target is about 50 × 35 μm^2, and because the particles on the

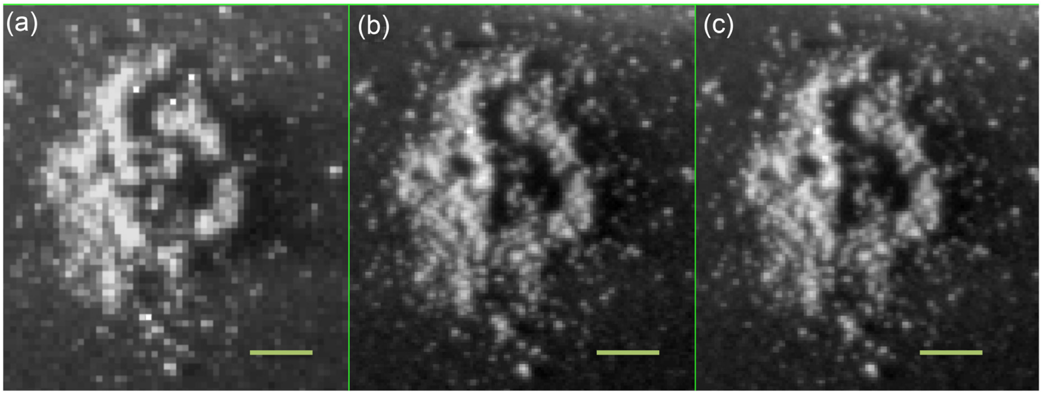

Figure 3. Three views of the dust particle Jessica Lummene.2, at three different times. The scale bar in the lower right of each plot is 140 microns in length. Panel (a) shows the particle just after collection on the gold target 2CF, on 2015 January 28. Panel (b) shows the particle on 2016 March 30, just prior to the long measurement that was done upon it, and panel (c) shows Jessica just after that long measurement, on 2016 April 4. There is little visible rearrangement between panels (a) and (b), and almost none between panels (b) and (c), despite the intervening long measurement.

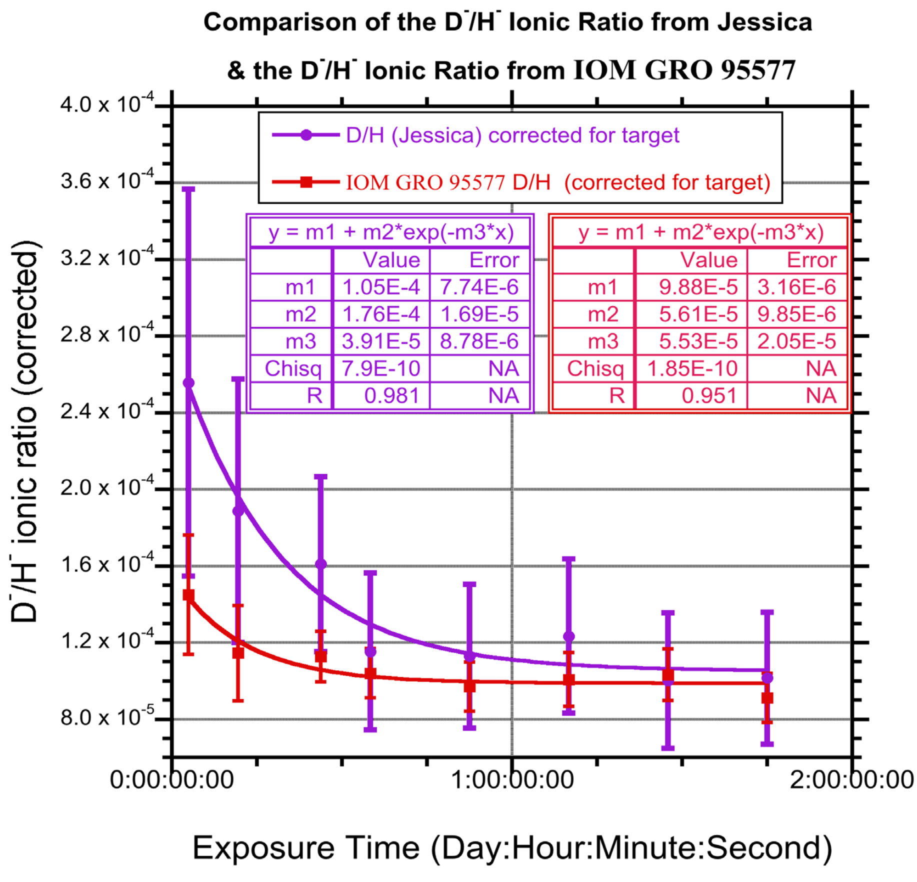

Figure 4. The violet line and circles are the D/H ratio measured on Jessica, with the normalized target contribution subtracted but without any IMF correction. All four locations are summed together to obtain better statistics. The red line and squares show the measurements on two samples of IOM GRO 95577. These samples were on target 574. There are more measurements for the D/H ratio here than in Fig. 2 because the first period of the long measurement has been split into two parts (before and after a cleaning, see the text). The IOM measurements are the result of a two long measurements on the IOM designed to emulate the long measurement on Jessica in both time and ion beam flux. The D/H ratio in the IOM shows a smaller decrease with time than that measured on Jessica which decreases by almost a factor of 2. We attribute this decrease to a change in the IMF rather than to measurement of a different location or layer of the dust particle.

COSIMA targets tend to be porous aggregates, all COSIMA spectra contain some contribution from the target substrate. This target contribution is removed by subtracting appropriately normalized target spectra, as described in a number of papers, e.g. (Paquette et al. 2018). The ratio of the corrected counts at masses 2 and 1 yields an ionic ratio: D^-/H^-. To get to the D/H in the sample, it is necessary to account for instrument mass fractionation due to the differing sensitivity of COSIMA to D and H, as described in the next section.

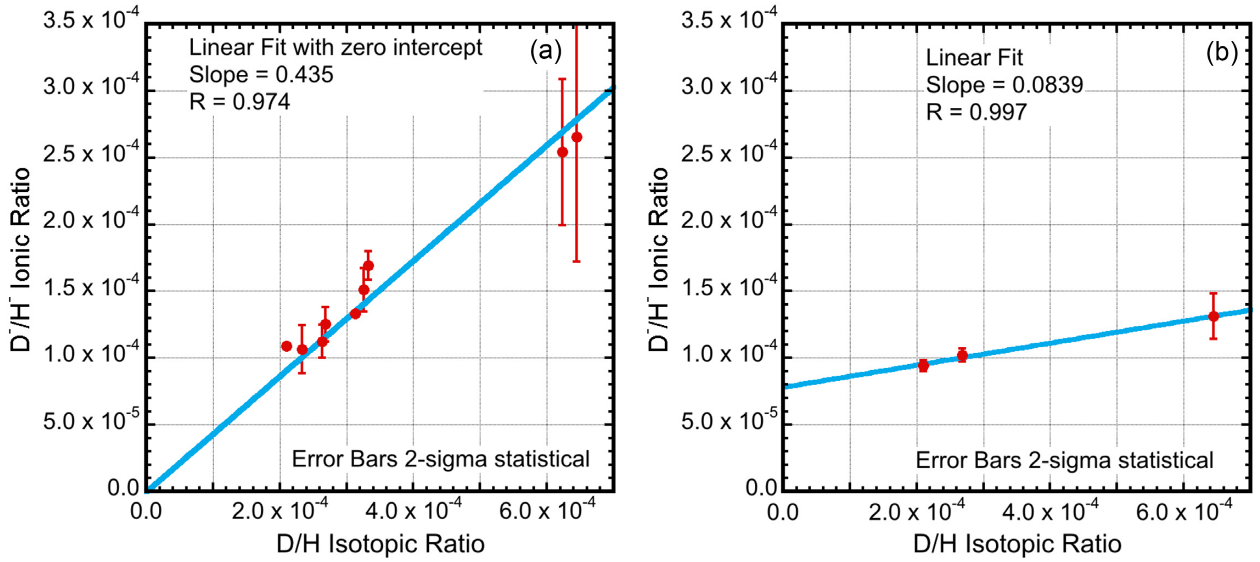

Figure 5. The results of measuring some of the IOM samples provided by Carnegie in another SIMS apparatus, a commercial IonToF 4 with a Bi^{3+} beam. Both panels show the D^-/H^- ionic ratios plotted versus the D/H isotopic ratio measured for the samples at Carnegie. Panel (a) shows the ionic ratio prior to sputtering (compare to Fig. 1b, above). The slope is 0.435, implying an IMF of 2.30, not dissimilar to the value derived for COSIMA of 3.19. Panel (b) shows the ionic ratio after sputtering. The slope of 0.0839 is much decreased, implying a greatly increased IMF of 11.9.

2.2 Instrument mass fractionation

The effect of instrument mass fractionation (hereafter IMF) varies from element to element. For sulphur isotopes, the effect was too small to be measured with COSIMA. For oxygen isotopes, the effect was a few per cent. Because D and H have the largest relative mass difference of any isotopes of any element, the effect of IMF is expected to be quite strong. This effect must be measured, using a suitable analogue for the cometary dust. The measurement was undertaken with the COSIMA reference model (RM) using samples of insoluble organic matter (IOM) from carbonaceous chondrites.

Because no evidence for hydrated minerals has been seen in the cometary dust particles analysed by COSIMA (Bardyn et al. 2017) and because water is unlikely to remain in dust particles collected by COSIMA grains (as discussed above), it is expected that the H measured with COSIMA will be coming primarily from the high molecular weight organic matter of the sort discussed in Fray et al. (2016). Meteorite IOM is also macromolecular, with a complex structure. There is a similarity in SIMS response between the two substances, although the H/C ratio in the cometary matter tends to be higher than that in IOM (Fray et al. 2016; Isnard et al. 2019). Such organic matter has been estimated to constitute 45 per cent of the cometary dust particles by weight (Bardyn et al. 2017). Because of this, IOM seems to be the best available choice as an analogue material to measure IMF. IOM samples provided by the Carnegie Institution of Washington were subjected to TOF-SIMS analyses in the COSIMA RM. The D^-/H^- ratios measured for the various samples in COSIMA are plotted versus the D/H isotopic ratio measured at Carnegie by elemental analysis (Alexander et al. 2010) in Fig. 1(a), while Fig. 1(b) shows the same data with a line that is forced to pass through the origin fitted to it. The inverse of the slope of that line gives the IMF for D/H in COSIMA – a factor of 3.19 ± 0.86. The uncertainty in this result – which is the dominant source of systematic error in the D/H isotopic ratio – is considered in the next section.

2.3 The particle Jessica Lummene.2

The particle Jessica is different from the other particles in that a very long measurement was done upon it – over 12 h at each location for four locations, when for other particles the typical measurement time was 5 min. Thus, Jessica presented an unusual challenge. As shown in Fig. 2(a), the D/H ratio for Jessica decreases over the course of the long measurement, and then nearly levels off. This could be explained as the exposure of fresh material with time, since SIMS has been known to remove pieces of dust particles, but there are several reasons to reject this hypothesis. Fig. 2(b) shows that the oxygen isotopic ratio does not exhibit this behaviour, remaining basically constant; the dramatic change in the hydrogen isotopic ratio is not present in the oxygen isotopic ratio. In addition, comparing panels (a) and (b) of Fig. 3 shows that there is only a little visible rearrangement in Jessica after a brief initial measurement. Comparing panels (b) and (c) shows virtually no rearrangement.

A long measurement, attempting to replicate the parameters of the long measurement on Jessica, was done on a sample of IOM. The result is shown along with the comparable Jessica measurement in Fig. 4. The large decrease in the D^-/H^- ionic ratio on Jessica is seen to a smaller degree in the IOM.

To understand this, we undertook an experiment. The D^-/H^- ionic ratio was measured for several samples of IOM. Analyses of the IOMs were performed in a ToF-SIMS IV instrument (ION-TOF GmbH, Germany) located at RISE Research Institute of Sweden in Borås in Sweden. Samples were analysed by rastering a 25 keV Bi^{3+} beam over a 100×100 to 150×150 μm^2 area for 2000–8000 s. The analyses were performed in negative mode at high-mass resolution (bunched mode: $m/\Delta m \geq 5000$ at m/z 30, $\Delta l \sim 5$ μm) with a pulsed current of 0.1 pA. As the samples were insulating, the sample surface was flooded with electrons for charge compensation. One to five areas were analysed on each IOM.

The sputtering was performed using the 25 keV Bi^{3+} beam with a direct current of ~2.5 nA on a 500×500 μm^2 area for 300 s, which meant an accumulated ion dose of $\sim 2 \times 10^{15}$. This is meant to be

Table 1. The 25 particles whose D/H isotopic ratios are measured in this work are described in this table. Given are the particle names, the target substrate upon which they were collected, the collection data, the first date that they were subjected to SIMS analysis, the particle typology as described in (51). Here, S: Shattered Cluster; R: Rubble Pile; G: Glued Cluster; C: Compact. Notations like R/S or R/G or G/S indicate particles with some similarities to more than one typology. The final column is the measured D/H isotopic ratio. The errors are 2σ statistical added in quadrature to a systematic error resulting from instrument mass fractionation.

Particle name	Target	Collection date	Date of first SIMS analysis	Particle morphology	D/H ratio $\times 10^3$
Jessica.Lummene.2	2CF	2015 January 26–27	2015 March 21	S	0.852 $\pm$ 0.17
Barmal.Orivesi.4	1CD	2015 July 31–August 1	2015 August 13	R[a]	2.08 $\pm$ 1.1
David.Toisvesi.2	2D1	2015 May 11–12	2015 May 20	S	1.07 $\pm$ 0.85
Günther.Jerisjarvi.1	1D2	2016 February 29–March 1	2015 April 14	R	1.56 $\pm$ 0.39
Jakub.Toisvesi.2	2D1	2015 May 11–12	2015 May 20	R/S	3.25 $\pm$ 1.3
Juliette.Hankavesi.1	1D2	2015 October 23–29	2016 June 16	R	1.66 $\pm$ 0.52
Sora.Ukonvesi.4	2D1	2015 May 17–18	2015 June 17	R	3.02 $\pm$ 1.4
Devoll.Orivesi.4	1CD	2015 July 31–August 1	2015 October 15	R[a]	1.27 $\pm$ 0.61
Alicia.Ala-Kitla	1CF	2014 December 16–20	2015 December 10	R	2.08 $\pm$ 0.22
Isbert.Lummene.4	1CF	2014 January 28–29	2015 December 16	R	1.30 $\pm$ 0.90
Andre.Jonkeri.1	1CF	2015 January 9–15	2015 December 16	G	1.39 $\pm$ 1.0
Hase.Kolima.3	1CF	2015 January 24	2015 December 16	R	0.579 $\pm$ 0.86
Justus.Lummene.4	1CF	2015 January 28–29	2015 June 24	G	0.941 $\pm$ 0.69
Rolf.Kolima.3	1CF	2015 January 24	2015 December 16	R/G	0.678 $\pm$ 0.58
Uli.Enonvesi	1CF	2014 December 20–27	2015 December 10	C	1.39 $\pm$ 1.1
Aarni.Rikkavesi	1D0	2014 October 18–24	2016 April 22	G/S	1.27 $\pm$ 0.46
Boris.Enovesi	1D0	2014 October 11–18	2014 September 6	R	1.86 $\pm$ 0.67
Sigrid.Vesijako	1D0	2014 November 14–21	2016 April 21	G	1.40 $\pm$ 0.35
Amelie.Kolima.2	1D2	2015 November 16–18	2015 November 25	R[b]	3.40 $\pm$ 1.8
Vihtori.Kolima.3	2CF	2015 January 24	2015 December 31	G	1.44 $\pm$ 0.71
Fred.Kolima.3	2CF	2015 January 24	2015 December 30	R/G	1.28 $\pm$ 0.34
Jean-Baptiste.Kolima.3	2CF	2015 January 24	2015 December 30	G/S	1.32 $\pm$ 0.35
Estelle.Nilakka	2D0	2014 September 25–October 3	2014 September 27	S	1.19 $\pm$ 0.35
Matt .Kolima.3	3CF	2015 January 24	2016 January 13	R	1.45 $\pm$ 0.54
Kerttu.Rikkavesi	3D0	2014 October 18–24	2014 September 6	C	1.09 $\pm$ 0.33

[a]Part of a huge shattered cluster that itself became a rubble pile;
[b]Central component could be C, if you trust albedo evolution related to central component, may be covered with other stuff.

comparable to the ion dose in the long measurements on Jessica. After the sputtering one to two areas on each IOM sample were analysed in the same way as described above.

This allowed the creation of Fig. 5(a), analogous to Fig. 1(b). The slope of the fit line in this plot is reasonably similar to that seen for COSIMA in Fig. 1(b), despite the different instrument.

The samples after sputtering show a decrease in the D^-/H^- ionic ratios as shown in Fig. 5(b). The fit line shown in Fig. 5(b) has a much smaller slope, indicating that the effect of the sputtering is a change in the IMF. Because of this behaviour, and the other reasons stated above, we attribute the decrease of the D^-/H^- ionic ratio in the long measurements on the Jessica particle and on the IOM sample to a change in IMF, not to the removal of material leading to the exposure of fresh surface.

The IMF determined from Fig. 1(b) is taken from short measurements (with a time-scale of about 5 min), and (apart from the long measurement on Jessica) so are all the measurements on the particles. Thus this IMF is used to determine the actual D/H ratio, with only the initial portion of the Jessica measurements being considered.

If we instead assumed that the asymptotic ionic ratio in the long measurements was the more correct number (both for Jessica and for the IOM sample), we would get from the constant term in the fit in Fig. 4 that the D^-/H^- ionic ratio for the IOM was 9.88×10^{-5}. Since the D/H isotopic ratio measured at Carnegie was 6.19×10^{-4}, this implies an IMF of 6.27, much higher than the 3.19 determined from Fig. 1(b). An increase is consistent with the change seen due to a large ion dose in commercial SIMS as shown in Fig. 5. If we corrected the asymptotic Jessica ionic ratio (from the fit in Fig. 4) of 1.05×10^{-4} with an IMF of 6.27, we get a D/H isotopic ratio of 6.58×10^{-4}, which is within 23 per cent of the value determined from short measurements of 8.52×10^{-4}.

No other long measurements (like the one done on Jessica) were practical in space, but an assumption that the time variation seen in the Jessica long measurement would hold for all such measurements allows us to consider the possible results. Since the initial value for the D^-/H^- ionic ratio for Jessica is 2.68 × the asymptotic value, it could be argued that the ionic ratios for other particles should actually be divided by 2.68 to get an asymptotic D^-/H^- ionic ratio. But they would then be subjected to an IMF of 6.27, which is 1.96 times larger than the IMF of 3.19 determined for short measurements. In that case the isotopic ratios for the other particles would be decreased by a factor of 1.96/2.68 = 0.73.

Considering that almost all measurements on both particles and IOM samples were of short duration, we use the results from the short measurements in this work. However, in view of the other considerations above a systematic error of 27 per cent is assumed.

3 RESULTS

The D/H ratios from 25 67P dust particles collected by COSIMA are shown in Table 1. They are also plotted in Fig. 6, and for comparison shown along with VSMOW (De Laeter et al. 2003), the ROSINA results in the water of comet 67P (Altwegg et al. 2015; Altwegg et al. 2017) and methanol (Drozdovskaya et al. 2021), the most anomalous chondritic IOM (Alexander et al. 2010), and the value measured in HCN for comet Hale-Bopp (Meier et al. 1998). The

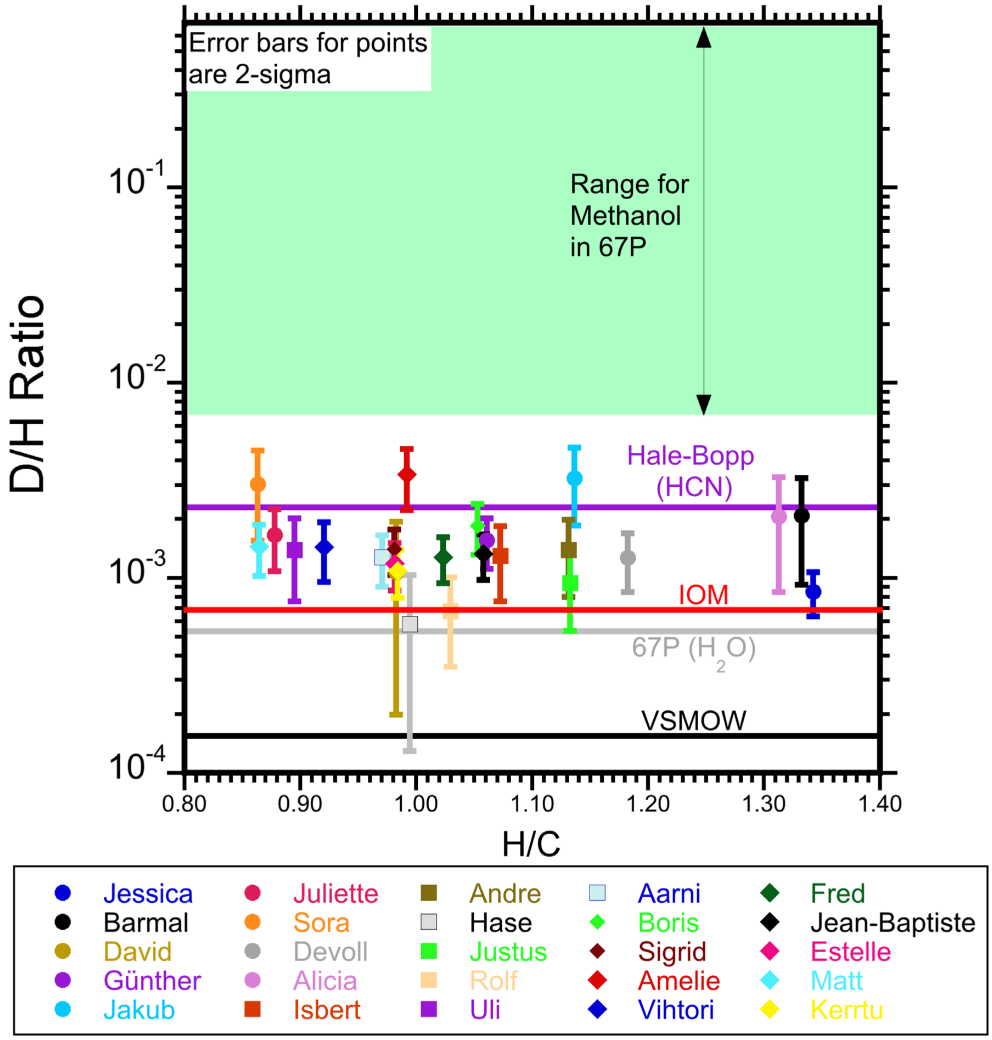

Figure 6. The D/H isotopic and H/C (at.) ratios measured on 25 dust particles by the COSIMA instrument (filled symbols) compared with the Vienna Standard Mean Ocean Water (VSMOW; black line) value (De Laeter et al. 2003), considered as representative of the terrestrial value, and with the D/H seen in water vapour by ROSINA (grey line; Altwegg et al. 2017) and methanol (green box; Drozdovskaya et al. 2021) for the same comet, and the most anomalous chondritic IOM (red line; Alexander et al. 2010) and in HCN from comet Hale-Bopp (purple line; Meier et al. 1998; Crovisier et al. 2004). The most primitive IOM has an H/C ≈ 0.8 (Alexander et al. 2010). The ROSINA value for water is already a factor of three higher than VSMOW, and the most anomalous chondritic IOM is higher still, but the COSIMA value is nine times VSMOW $(1.41 \pm 0.12) \times 10^{-3}$. This agrees within errors of D/H in HCN in comet C/1995 O1 (Hale-Bopp) which was also a measurement in one gaseous organic molecule. However, the D/H recently measured in singly and doubly deuterated methanol from comet 67P is higher than any value measured in the refractory organics.

water D/H value from ROSINA is three times VSMOW, but the D/H values measured by COSIMA in 67P particles are much higher, and are more comparable to the value measured in HCN. There is a suggestion that three particles (Sora, Jakub, and Amelie) have higher D/H values than the others, but because of the uncertainties such a claim cannot be made with confidence. If we instead consider that all 25 values are consistent with a single D/H ratio, the error weighted mean and the statistical uncertainty is $(1.57 \pm 0.54) \times 10^{-3}$, where the error quoted here is the 2σ standard error in the mean of the 25 values added in quadrature to the estimated systematic error.

4 DISCUSSION

In Fig. 7, the average D/H ratio for COSIMA particles is compared to that in the protosolar molecular cloud (hereafter PMC) and the interstellar medium (combined gas and dust; Ceccarelli et al. 2014), the Earth (McKeegan et al. 2006), the gas giant planets (Ceccarelli et al. 2014), the ice giant planets (Ceccarelli et al. 2014), the Saturnian moon Enceladus (Ceccarelli et al. 2014), the most primitive IOM from meteorites (Alexander et al. 2010), CP-IDPs (Aléon et al. 2001; Messenger et al. 2003), UCAMMs (Duprat et al. 2010; Dartois et al. 2013; Yabuta et al. 2017), and water from a large number of comets (Ceccarelli et al. 2014; Altwegg et al. 2017). The cometary measurements are broken into Oort cloud (OCCs) and Jupiter Family (JFCs) comets. It was once considered (Duncan & Levison 1997) that the OCCs formed among the giant planets (one reason for this was the observation that the D/H ratios of their water roughly match that of water from Enceladus), while the JFCs formed further out. The discovery that Hartley 2 and 45P (both JFCs) had low D/H ratios (close to VSMOW) contradicts this simple picture. While models have been proposed to explain the unexpected range of water D/H values in comets (Yang et al. 2013; Ali-Dib et al. 2015), the high value seen by ROSINA in 67P (another JFC) is a challenge for models like these to explain. It has been suggested that the similar

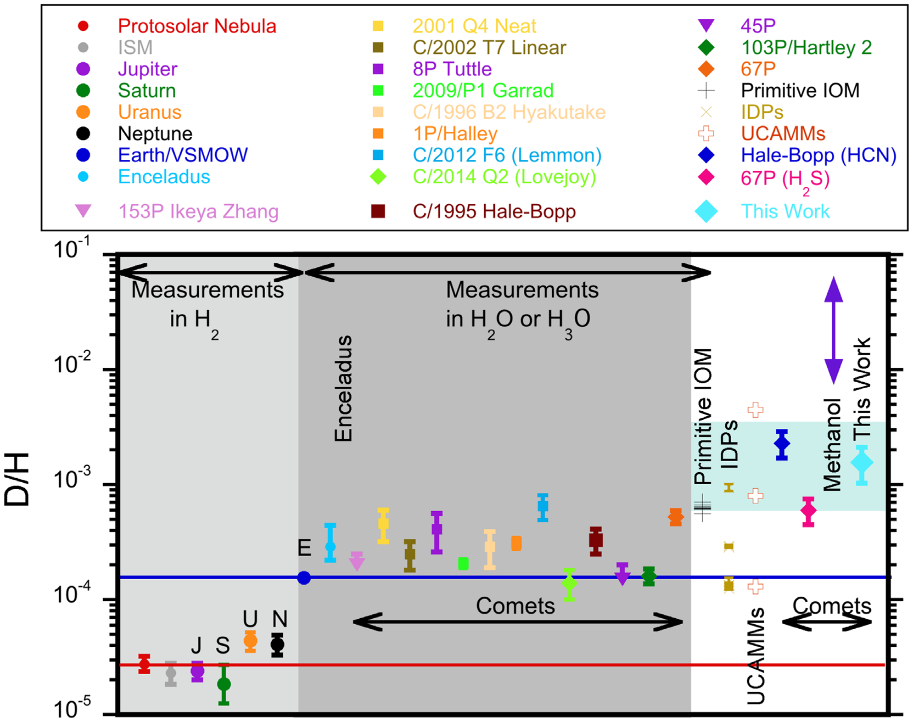

Figure 7. The D/H isotopic ratio measured in this work compared to that in the protosolar molecular cloud and the local interstellar medium (Ceccarelli et al. 2014) and in various objects in the Solar system, including the Earth (De Laeter et al. 2003), primitive IOM from meteorites (Alexander et al. 2012), bulk values for interplanetary dust particles (IDPs; Aléon et al. 2001; Messenger et al. 2003), ultracarbonaceous Antarctic micrometeorites (UCAMMs; Duprat et al. 2010), Jupiter and Saturn (Ceccarelli et al. 2014), Saturn's moon Enceladus (Ceccarelli et al. 2014), Uranus and Neptune (Ceccarelli et al. 2014), Oort-Cloud comets (Ceccarelli et al. 2014; Altwegg et al. 2017), and Jupiter-family comets (Ceccarelli et al. 2014; Altwegg et al. 2017; Drozdovskaya et al. 2021). Measurements in H_2 are grouped to left (light-grey-shaded area), measurements in water or hydronium are in the middle (dark-grey-shaded area), and measurements in organics and H_2S are grouped to the right. The light blue box shows the range of ratios measured in the dust particles. The D/H ratio of the gas giants agree with the protosolar value, and ice giants are but little higher. Inner Solar system objects like the Earth have a higher value, but comets show a range of values (as do IDPs which may be of cometary origin). The OCCs were once thought to have higher D/H than the JFCs, but more recent measurements have invalidated this picture. The high D/H value in the HCN from comet Hale-Bopp is similar to the results of this work, which were also measured in organics. The D/H in methanol from comet 67P is even higher, greater than the highest results seen in refractory organics. The D/H ratio measured in the most primitive IOM is significantly lower than that seen in cometary organics and comparable to the higher values measured in UCAMMs.

water D/H ranges imply a common parent population for the OCCs and JFCs (Hallis 2017). Scenarios involving planetary migration can scatter objects both outward and inward from a wide range of orbital radii, so present-day dynamical families do not necessarily have similar compositions (Ceccarelli et al. 2014). The proposition that all comets have a terrestrial-like D/H ratio of their water ice (Lis et al. 2019) would be compatible with a model of comet formation from a single reservoir close to Jupiter, that was scattered to different locations due the dynamical evolution of the giant planets in the early Solar system. However, the high D_2O/HDO ratio in comet 67P (Altwegg et al. 2017) is probably not compatible with such a scenario.

As stated above, the hydrogen isotopes measured by COSIMA most probably originate in the organic component of the dust, a high molecular weight carbonaceous material with a SIMS ion signature that shows a pattern in the peaks at masses 12–15 in positive mass spectra in which the C^+ ion peak is higher than the CH^+, $CH_2{}^+$, and $CH_3{}^+$ ion peaks. This pattern is not seen in most organic materials analysed in the COSIMA Reference Model, but it is seen in IOM samples (Fray et al. 2016). In addition, the N/C elemental ratio in COSIMA cometary dust particles is close to that of IOM (Fray et al. 2017), but it has a slightly higher H/C elemental ratio (Fray et al. 2016, Isnard et al. 2019). The carbonaceous component constitutes about half of the dust by mass in comet 67P (Bardyn et al. 2017).

The two other measurements of the D/H ratios in cometary organic molecules that have been reported are also shown in Fig. 7. The D/H ratio measured in HCN from Hale-Bopp, has a value that agrees (within errors) with the value from this work, but the value recently measured in singly and doubly deuterated methanol from 67P is much higher (Drozdovskaya et al. 2021). A comparison to CP-IDPs and to UCAMMs, which are probably cometary in origin, shows that the highest values agree within errors with the results of this work. The proposed cometary component identified in an IDP by Aléon et al. (2001) actually matches both the D/H and H/C values of the cometary dust measured by COSIMA rather well. The D/H value from this work agrees with the most D-rich IDPs and UCAMMs shown. Note that the D/H values in 'hot spots' are, however, not relevant for a comparison to COSIMA (which would average over such small spatial variations due its large beam spot). The D/H ratios in the most primitive IOM are significantly less than that measured by COSIMA. The high D/H ratio measured in H_2S by ROSINA is attributed to dust-grain chemistry in the PMC (*2*).

Fig. 8 shows the data measured in the 67P dust particles versus the H/C ratio, along with IOM (Alexander et al. 2010), IDP (Aléon et al. 2001), and UCAMM (Duprat et al. 2010) D/H ratios for comparison. Alexander et al. (2010) identify three trends in their data, one of which is shown by the solid curve in Fig. 8. The placement of the 67P dust particles suggests that it could be considered as part of this

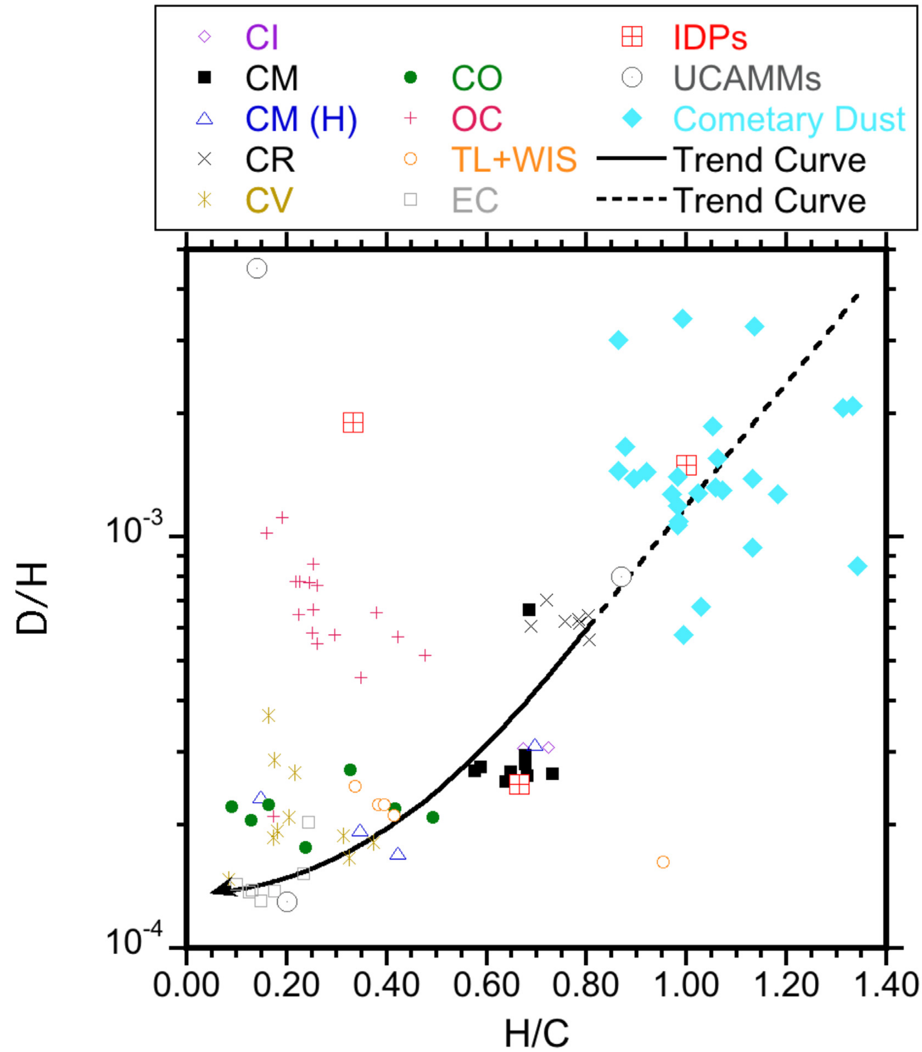

Figure 8. The D/H isotopic ratio measured in various samples of meteorite IOM extracted from chondrites (taken from Alexander et al. 2010; cf. fig. 1b of that paper) plotted along with the D/H ratio measured in IDP organic end members (Aléon et al. 2001), in UCAMM end members (Duprat et al. 2010), and in 25 cometary particles as a function of the H/C elemental ratio. The D/H measured in cometary particles likely comes from hydrogen contained in macromolecular organic matter (Fray et al. 2016) which constitutes about half the dust by mass (Bardyn et al. 2017) and may be somewhat comparable to meteorite IOM structurally, but which has a higher H/C ratio (Fray et al. 2017) and an even higher D/H ratio than even the most primitive IOM samples shown here. The solid curve schematically and simply indicates a trend described in (Alexander et al. 2010); the dotted line is an extension of that trend to include the cometary data. This suggests the possibility that the IOM may have started with D/H and H/C ratios that are similar to those of the cometary dust, with varying degrees of processing in the chondrite parent bodies then corresponding to movement along the curve towards lower D/H and H/C ratios. Note that two of the IDP end members and two of the UCAMM end members lie along the trend line also, suggesting that it applies to those sorts of extraterrestrial matter also.

trend (dotted curve). This suggests the possibility that the IOM may have started with D/H and H/C ratios that were similar to those of the cometary dust, with varying degrees of processing in the chondrite parent bodies (and possibly the PSD) then producing the movement along the curve toward lower D/H and H/C ratios.

Fig. 9 shows the D/H ratio for the 25 67P particles plotted versus the date of collection by COSIMA, the interval between collection and SIMS analysis, and the particle typology (Langevin et al. 2016). There is no evidence that the D/H ratio varies with the date of collection, which is equivalent to a lack of dependence on 67P's season or distance from the Sun. Since dust from different portions of the comet reached the instrument at different times during the mission, the simplest interpretation is that there is little, if any, variation of the dust D/H ratio over the cometary surface. Similarly, neither a long stay nor a short stay on a COSIMA target seems to have had any influence on the isotopic ratio. This is consistent with the thesis that the D/H ratio measured is that of the cometary dust, and not that of contaminants (which should be closer to VSMOW in any event). Finally, particle morphology might seem to be correlated with the D/H ratio, in that the 6 highest D/H particles of the 25 are all of the (R) rubble pile type as defined in Langevin et al. (2016). However, the wide variation in the D/H ratios in particles of the R type casts some doubt upon this idea; the mean D/H for type R particles is within 1.2 σ of the mean D/H of every other particle type. A lack of variation is understandable if the different particle types do not result mainly from a difference in composition, but rather are due to a difference in a particle's initial size and incident speed, as laboratory simulations suggest (Ellerbroek et al. 2017, 2019).

A comparison with extrasolar gas-phase organic molecules is shown in Fig. 10. The isotopic ratios plotted to the left are from

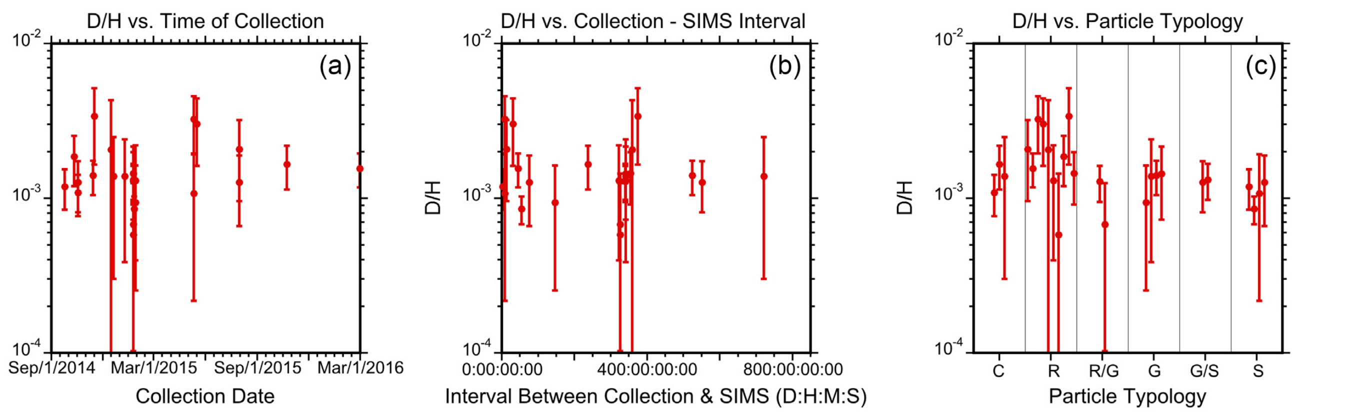

Figure 9. The D/H isotopic ratio measured in 25 cometary dust particles by COSIMA versus collection date of the particle (panel a), the interval between collection and secondary ion mass spectrometry (panel b), and particle typology (panel c). In panel (c), C means 'Compact', R means 'Rubble pile', G means 'Glued Cluster', and S means 'Shattered cluster' as described in (Langevin et al. 2016). R/G and G/S denote particles that are crossovers (Rubble pile/Glued cluster, and Glued cluster/Shattered cluster). No dependence on time of collection or the collection-SIMS interval is visible. While the highest D/H is seen in rubble piles, the mean value of D/H for type R particles agrees within errors with the other types.

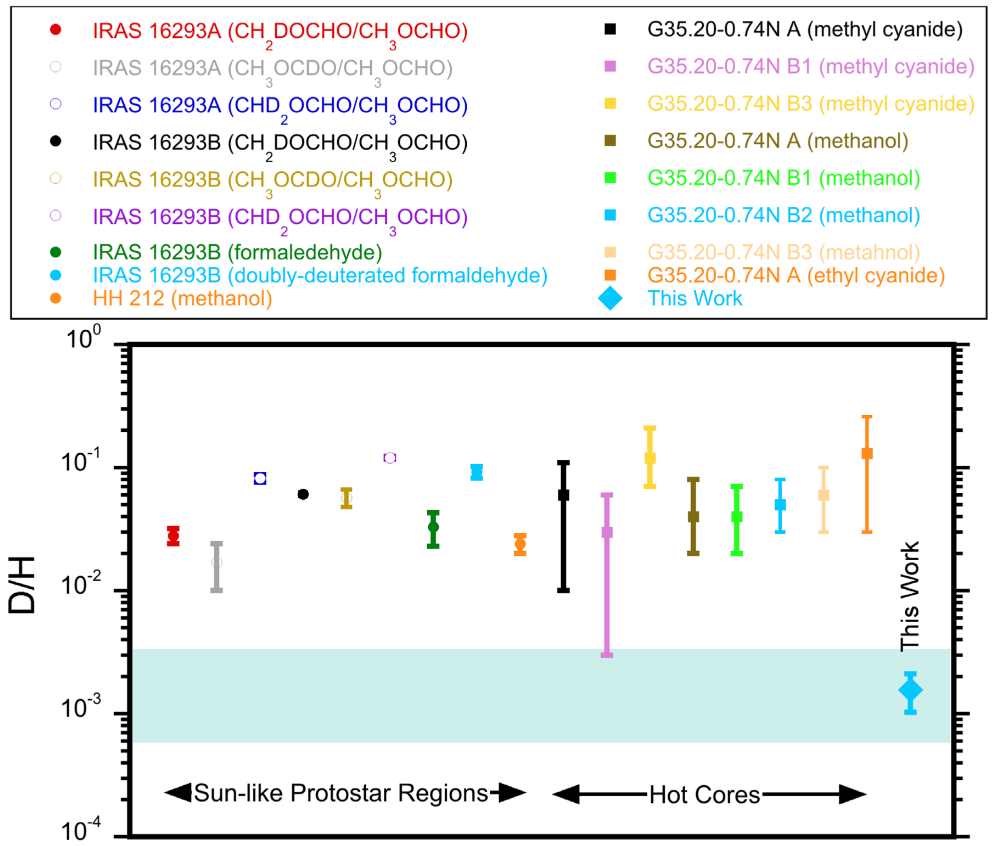

Figure 10. Comparison of the D/H isotopic ratio seen in solar-like protostar regions (circles; Bianchi et al. 2017; Manigand et al. 2019) and hot cores (squares; Allen et al. 2017) with the result of this work. The light blue box indicates the range of values measured in the 25 cometary dust particles. The D/H ratio observed in the cometary organics is significantly lower than that measured in both types of objects.

the regions around Sun-like protostars. The D/H ratios have been measured in three isotopologues of methyl formate, and singly and doubly deuterated formaldehyde in IRAS 16293A and IRAS 16293B (Manigand et al. 2019), and in methanol in HH 212 (Bianchi et al. 2017). Further to the right are isotopic ratios measured in organics in hot cores (relatively small, dense, and hot structures occurring in star-forming regions). The values for methyl cyanide, methanol, and ethyl cyanide correspond to four different regions (denoted A, B1, B2, and B3) in the hot core G35.20–0.74 N (Allen et al. 2017).

The values seen in these molecules in such regions are significantly higher than the isotopic ratio measured in the dust of comet 67P, but not all molecules in such regions have such high degrees of deuteration. The D/H ratios measured in 67P cometary dust by COSIMA are higher than those seen in primitive chondritic IOM, and in the range of the high values found in IDPs and UCAMMs. The chemical/structural similarities between the organic matter in the cometary dust and meteorite IOM and IDPs argue for a common origin for the materials, with various degrees of processing. The curve on Fig. 8 suggests the possible direction of processing, with the cometary organic matter being less processed (either in the PSD or in the chondrite parent bodies) than the most primitive IOM. Modelling work casts doubt upon the possibility of high levels of D enrichment – or even levels as high as VSMOW – being attainable in the discs around solar-like stars, due to the exclusion of Galactic Cosmic Rays by intense stellar winds and the higher densities, as compared to the PMC (Cleeves et al. 2016). The mechanisms commonly proposed for the formation of refractory organics in the solar nebula are direct formation from the gas or irradiation of icy mantles on grains in the outer nebula (Alexander et al. 2017). The first mechanism is supposed to occur at relatively high temperatures (Morgan et al. 1991; Kress & Tielens 2001; Nuth et al. 2008). This makes them poor candidates to explain the cometary dust by COSIMA due to its high D/H ratio. In the laboratory, ultraviolet irradiation of astrophysical ice analogues (containing simple molecules such as methanol) has produced a variety of organic molecules (Ciesla & Sandford 2012), although the resultant material, while refractory, is not similar to IOM (Nuevo et al. 2011) – and thus probably not to cometary organic dust either. Leaving that aside, the high D/H recently measured in gaseous methanol in 67P (Drozdovskaya et al. 2021) is much higher than the D/H ratio of the cometary dust, comparable to that seen in hot cores and Sun-like protostar regions. If cometary refractory organics formed from irradiated ices, it seems strange that the resulting dust has a much lower degree of deuteration than the ices themselves. Thus, we must consider the possibility that the refractory organics in 67P were inherited from the PMC. It has been argued that even if interstellar ice sublimated completely, temperatures in the outer PSD were not high enough to substantially alter the organics (Bertaux & Lallement 2017). The D/H ratio measured in cometary dust does not approach that seen in some gas phase interstellar molecules such as methanol or methyl formate, but the degree of deuteration depends of the molecule in question, with some organic molecules having much lower D/H ratios (Kalvāns et al. 2017). Another possibility is that highly deuterated infalling matter from the PMC is mixed with warmer material in the PSD, leading to a lower D/H ratio in the mixture. The exact formation mechanism of the macromolecular organics in the cometary dust is unknown, but if they are formed from a mixture of organic molecules in the PMC the D/H ratio observed in cometary dust is consistent with a direct inheritance from the PMC.

5 CONCLUSIONS

The D/H ratio measured in cometary dust is $(1.57 \pm 0.54) \times 10^{-3}$, about ten times that seen in VSMOW, and higher than in primitive IOM samples. The H/C ratio in the cometary dust is also somewhat higher than that seen in primitive IOM. The similar N/C ratios and SIMS response of the refractory organic matter and of the IOM samples extracted from chondrites suggest a strong chemical similarity and a common origin, but with the cometary organic matter being less processed. While the D/H ratio of the dust is an order of magnitude lower than that seen in the most deuterated molecules near Sun-like protostars or in hot molecular cores, most organic molecules in those regions have a much lower D/H ratio. If recent models are correct, and even terrestrial values of the D/H ratio are not attainable in the disc, then the highly deuterated cometary organic matter must be an inheritance from the cloud from which the Solar system formed. The high D/H ratio of the organic matter is another indication that comets – or at least comets like 67P were not major contributors to the Earth's store of hydrogen.

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DATA AVAILABILITY

The COSIMA mass spectra are available via the *Rosetta* archive at https://www.esa.int/Science_Exploration/Space_Science/Rosetta/(archive)/0.

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