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To cite this version:

Kathrin Altwegg, Hans Balsiger, Jean-Jacques Berthelier, André Bieler, Ursina Calmonte, et al.. D2O and HDS in the coma of 67P/Churyumov–Gerasimenko. Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences, Royal Society, The, 2017, 375 (n° 2097), 10.1098/rsta.2016.0253 . insu-01530459

PHILOSOPHICAL
TRANSACTIONS A

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Research

Cite this article: Altwegg K *et al.* 2017 D_2O and HDS in the coma of 67P/Churyumov–Gerasimenko. *Phil. Trans. R. Soc. A* **375**: 20160253.
http://dx.doi.org/10.1098/rsta.2016.0253

Accepted: 12 January 2017

One contribution of 14 to a discussion meeting issue 'Cometary science after Rosetta'.

Subject Areas:
astrophysics, solar system, space exploration

Keywords:
67P/Churyumov–Gerasimenko, comets, deuterium, Rosetta

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D_2O and HDS in the coma of 67P/Churyumov–Gerasimenko

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The European Rosetta mission has been following comet 67P/Churyumov–Gerasimenko for 2 years, studying the nucleus and coma in great detail. For most of these 2 years the Rosetta Orbiter Sensor for Ion and Neutral Analysis (ROSINA) has analysed the volatile part of the coma. With its high mass resolution and sensitivity it was able to not only detect deuterated water HDO, but also doubly deuterated water, D_2O and deuterated hydrogen sulfide HDS. The ratios for $[HDO]/[H_2O]$, $[D_2O]/[HDO]$ and $[HDS]/[H_2S]$ derived from our measurements are $(1.05 \pm 0.14) \times 10^{-3}$, $(1.80 \pm 0.9) \times 10^{-2}$ and $(1.2 \pm 0.3) \times 10^{-3}$, respectively. These results yield a very high ratio of 17 for $[D_2O]/[HDO]$ relative to $[HDO]/[H_2O]$. Statistically one would expect just 1/4. Such a high value can be explained by cometary water coming unprocessed from the presolar cloud, where water is formed on grains, leading to high deuterium fractionation. The high $[HDS]/[H_2S]$

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ratio is compatible with upper limits determined in low-mass star-forming regions and also points to a direct correlation of cometary H_2S with presolar grain surface chemistry.

This article is part of the themed issue 'Cometary science after Rosetta'.

1. Introduction

Rosetta has followed comet 67P/Churyumov–Gerasimenko since August 2014. On board this spacecraft the Rosetta Orbiter Sensor for Ion and Neutral Analysis (ROSINA) is almost constantly analysing the gases in the coma of the comet. Already early in the mission it was able to measure the D/H in cometary water, a value which is important for understanding the origin of the comet, the formation temperature of water, and finally the formation of the solar system. In the following we use the D/H ratio as well as the ratio of [HDO]/[H_2O] whereby [HDO]/[H_2O] is twice the D/H ratio, as statistically two hydrogens can be replaced by deuterium. This value is also considered to be important for the origin of terrestrial water as some solar system formation models explain terrestrial water by impacts of comets in the early history of the Earth. Some D/H values measured for comets, star-forming regions and hot cores can be found in table 1 and references therein. D/H was found to be approximately 3×10^{-4} for most Oort cloud comets (OC), whereas for Jupiter family comets (JFCs) there were two measurements prior to the value measured by ROSINA which were close to terrestrial. The D/H in water of 67P was found to be very high (5.3×10^{-4}), higher than those measured in all comets before. This was quite puzzling as solar system formation models assumed two distinct formation zones for the two comet families; close to the giant planets for Oort cloud comets [22,23] and further out, outside Neptune's orbit for JFCs [24]. Recently, two more D/H values for comets were reported, one close to terrestrial $(1.4 \pm 0.4) \times 10^{-4}$ in comet C/2014 Q2 (Lovejoy), the other one again a very high value of $(6.5 \pm 1.6) \times 10^{-4}$ in comet C/2012 F6 (Lemmon) (see table 1). Both comets are Oort cloud comets. This shows that D/H in cometary water is very variable, for Oort cloud comets as well as for Jupiter Family comets, spanning the range from terrestrial D/H of 1.5×10^{-4} to 6.5×10^{-4} and overlapping for the two families. It was assumed that D/H reflects the distance from the Sun where comets formed, increasing with solar distance. After it became clear that some JFCs, for example Hartley 2, have terrestrial D/H ratios another model was invoked [25] which explained the lower D/H ratio for objects formed at larger distances from the Sun. From the large variation in D/H in cometary water and the overlap for D/H of the two families of comets it has now to be concluded that most probably the formation regions of the two families of comets overlap [26], that 67P (JFC) was formed relatively far from the Sun as was comet Lovejoy (OC), whereas comet Hartley 2 (JFC) and comet Lemmon(OC) were formed much closer to the Sun. D/H in water is therefore not typical for a comet family, but probably still reflects the region of comet formation.

The increase of the D/H ratio in water is a two-step process: first by enhancing the atomic D/H ratio by ion–molecule reactions in the gas phase and second by dust grain chemistry. Recent models have suggested that ion–molecule reactions in the solar nebula are inefficient [27]. High D/H values in water have been found recently in low-mass star-forming regions (see table 1) with values of [HDO]/[H_2O] of a few per mille. These values are generally higher than in comets, although for 67P the difference is not large, and are most probably due to grain surface chemistry. Brown & Millar [28,29] and Charnley *et al*. [30] have shown that grain surface reactions can enhance the deuterium fractionation considerably. It has also been shown for hot cores that it takes more than 10^4 years after sublimation of these icy dust layers to lower the deuterium value again. The values are, however, quite diverse which is explained by dust layering and the corresponding time when they were formed on dust, the later in time the more fractionated [10]. A recently published paper by Furuya *et al*. [31] clearly shows that high D/H values in water from prestellar clouds can persist even if the water ice is reprocessed in the stellar disc depending on the distance from the central star and on the amount of turbulent mixing. D/H is therefore not a very clear indication of whether the water ice is inherited from the presolar cloud

Table 1. HDO/H_2O, D_2O/HDO and HDS/H_2S ratios for comets, low-mass protostar discs, hot cores and outer regions of protostars.

object	$[HDO/H_2O]$ $(=2 \times [D/H])$	$[D_2O/HDO]$	$[D_2O/HDO]/[HDO/H_2O]$	HDS/H_2S	ref.
comets					
67P/Churyumov–Gerasimenko	1.06×10^{-3}				[1]
	1.04×10^{-4}	1.8×10^{-2}	17	1.2×10^{-3}	this work
1P/Halley	6.16×10^{-4}				[2]
	3.06×10^{-4}				[3]
C/2014 Q2 Lovejoy	2.8×10^{-4}				[4]
C/2012 F6 Lemmon	1.3×10^{-3}				[4]
C/1996 B2 (Hyakutake)	5.8×10^{-4}				[5]
C/1995 O1 (Hale-Bopp)	6.6×10^{-4}				[6]
8P/Tuttle	8.18×10^{-4}				[7]
103P/Hartley 2	3.22×10^{-4}				[8]
C/2009 P1 (Garradd)	4.12×10^{-4}				[9]
solar-type protostar regions					
NGC1333 IRAS2A	$0.3\text{–}8 \times 10^{-2}$				[10]
NGC1333 IRAS4A	$0.2\text{–}3 \times 10^{-2}$				[10]
NGC1333 IRAS2A	1.7×10^{-3}	1.2×10^{-2}	7		[11]
IRAS16293	5×10^{-2}	11×10^{-2}	2.2	0.1	[12–14]
NGC 1333-IRAS4B	$< 6 \times 10^{-4}$				[15]
IRAS 16293–2422	$(9.2 \pm 2.6) \times 10^{-4}$				[16]
NGC 1333-IRAS 2A	$(7.4 \pm 2.1) \times 10^{-4}$				[17]
IRAS 4A-NW	$(19.1 \pm 5.4) \times 10^{-4}$				[17]
IRAS 4B	$(5.9 \pm 1.7) \times 10^{-4}$				[17]
hot cores					
Orion KL	3×10^{-3}	1.6×10^{-3}	0.5		[18]
G34.2 + 0.2	1.2×10^{-3}				[19]
W51d	0.8×10^{-3}				[19]
W51e1/e2	0.9×10^{-3}				[19]
Sgr B2(N)	1.6×10^{-3}				[19]
G10.47 + 0.03				1.4×10^{-3}	[20]
G31.41 + 0.31				4.9×10^{-3}	[20]
G34.26 + 0.15				2.0×10^{-3}	[20]
cold envelopes					
NGC1333 IRAS2A	7×10^{-2}				[21]

or if it is reprocessed in the star-forming disc. The same authors show, however, that the ratio of $[D_2O]/[HDO]$ over $[HDO]/[H_2O]$ is a better indication for the history of the water ice. Whereas in prestellar clouds this ratio is generally $\gg 1$, reprocessed water ice in stellar nebula has a ratio less than 1.

Therefore, more indications about the history of water in comets come from the $[D_2O]/[HDO]$ ratio. The first detection of D_2O in a solar-type protostar region has yielded $[D_2O]/[HDO] \sim 1.2 \times 10^{-2}$ and $[HDO]/[H_2O] \sim 1.7 \times 10^{-3}$ (table 1) which means $[D_2O]/[HDO] \sim 7 \times [HDO]/[H_2O]$. From a statistical point of view one would expect a $[D_2O]/[HDO]$ ratio of $0.25 \times [HDO]/[H_2O]$. The deviation is explained by a mixture of water coming from thermal desorption from grain mantles which gives a high D_2O abundance and by water formation at high temperatures in the gas phase which lowers the $[HDO]/[H_2O]$ ratio. We report here the first detection of D_2O in a comet.

Also H_2S is a very interesting molecule. It is most probably formed on dust grains in the presolar cloud as gas phase chemistry is very inefficient to form H_2S (see [32] and references therein). From the detection of S_3 and S_4 in comet 67P, Calmonte *et al.* [33] concluded that dust grain chemistry has most probably played a major role in formation of H_2S for 67P. As dust grain chemistry tends to fractionate deuterated species, we expect a rather high D/H in H_2S if cometary H_2S represents the presolar cloud material.

A very high ratio of $[HDS]/[H_2S] = 0.1$ has been measured in the cold star-forming core IRAS 16293 (table 1). This low-mass star-forming region, although being a low-mass star-forming region resembles more a high-mass star-forming region based on its composition. This is explained by its age. Hatchell *et al.* [20] found upper limits for several hot cores of $1–2 \times 10^{-3}$ (table 1). They discuss these limits in the framework of either formation of H_2S in hot, post-shock gas or formation of H_2S in hot core ices at a temperature of 60–80 K. In the first case the ratio of D/H in H_2S should be close to the cosmic D/H ratio (approx. 10^{-5}). In this paper we report the first measurement of $[HDS]/[H_2S]$ in a comet, which is $(1.8 \pm 0.9) \times 10^{-3}$. This is clearly far higher than the cosmic abundance and therefore points to grain surface chemistry for H_2S. This is very well in agreement with the findings by [32].

2. Measurements

The previously published D/H value in water measured for 67P [1] was determined early in the mission outside of 3.0 AU, that is outside of the water snow line. Although several studies were done about possible fractionation effects in the nucleus or in the coma (e.g. [34,35]) and most studies concluded that these effects have to be minor, it is nevertheless interesting to follow the evolution of the D/H ratio during the orbit of 67P around the Sun. In this paper we concentrate on two periods for the analysis of D/H in water, one in December 2015, when Rosetta was again within about 100 km from the comet after having been much farther away most of the time around perihelion due to interference of its star trackers with cometary dust. At that time 67P was at 2 AU, still well within the water snow line. The Southern Hemisphere was in summer, contrary to the first period analysed in Altwegg *et al.* [1]. The Southern Hemisphere has a short but very intense summer, losing several metres of its surface [36]. It is therefore believed to be more pristine than the northern hemisphere as the seasonal heat wave penetrates more slowly than the surface erosion. The second period chosen is March 2016, during equinox at 2.6 AU near the water snow line when the subsolar point was at the equator and water started to die off. At that time the spacecraft was within 20 km of the comet. This led to relatively high local densities at the position of the spacecraft and ROSINA, making the analysis of [HDO] and [D2O] feasible. For D/H in $[H_2S]$ we used data from May 2016. At that time water production was already quite low and concentrated around the subsolar latitude of 10° north. However, the more volatile species CO, CO_2, and most of the Sulphur-bearing species had still a high production mostly from the Southern Hemisphere. The S/C was within 10 km from the nucleus centre. This allowed separating very nicely the HDS peak from interfering peaks of the less volatile species.

The sensor used was the ROSINA Double Focusing Mass Spectrometer (DFMS). It was run in high resolution mode with an electron emission current of 200 µA used for electron impact ionization. Integration time per mass was 20 s. The instrument is described in [37]. Details on data analysis including discussion on sources of the measurement uncertainties can be found in [38] and in [34]. From calibration measurements we know that mass peaks are fitted best using

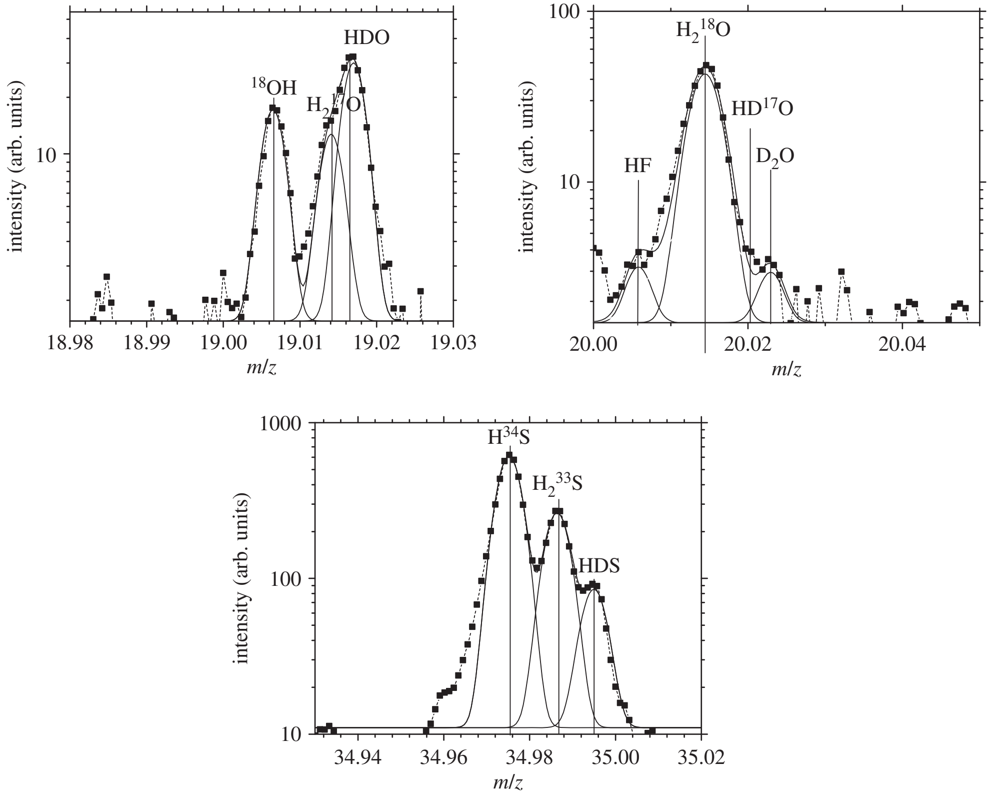

Figure 1. Samples of DFMS data for masses 19 Da, 20 Da and 35 Da with the corresponding peak fits.

a double Gaussian distribution where the second Gaussian has a peak height of approximately 0.1 of the first one and a width approximately three times broader than the narrow Gaussian [38]. All peaks belonging to the same integer mass share the same width of the primary and secondary Gaussian distributions, respectively. This means, if there are multiple peaks, then, with known masses, there is one common width and peak height per Gaussian for each mass to be fitted. This makes the curve fits normally unique. Figure 1 shows three examples of DFMS data and the corresponding fits for masses 19 Da, 20 Da, and 35 Da. For mass 19 Da and 35 Da the resulting error is given mostly by the fit uncertainty, which is approximately 25%, whereas for 20 Da, due to low count rates for D_2O, the uncertainty is a combination of statistical error and fit uncertainty (approx. 45%).

The selected spectra are representative of whole comet rotations sampling all longitudes (see table 2 for details on sub-spacecraft longitude and latitude for the individual measurements). DFMS with its wide field of view of 20° samples at any time gas from all facets of the comet which are oriented towards the spacecraft as long as the spacecraft is at distances more than 5 km. As has been shown by Bieler *et al.* [39], outgassing is mostly illumination driven and shadowed areas contribute less than 10% of the outgassing. The signal is modulated due to the shape of 67P by sub-spacecraft longitude and -latitude due to different illumination conditions. However, no spatial information from where exactly the gas originates can be derived. Due to low count rates especially for D_2O not all latitudes could be sampled in the same way, especially not latitudes experiencing winter, where illumination conditions are less favourable. It cannot be completely excluded that there is some inhomogeneity in D/H over the nucleus.

Figure 2 shows the results for the analysed spectra for D/H in H_2O and HDS and $[D_2O]/[HDO]$. A list of all measurements with their time stamp and the corresponding sub-spacecraft longitudes and latitudes is given in table 2. The lines represent the mean values and the

Table 2. List of analysed spectra.

	date	time (UTC)	sub-S/C longitude	sub-S/C latitude	D/H in water
1	03/12/2015	07:33	105.8	64.7	5.74×10^{-4}
2	03/12/2015	08:52	64.3	64.6	5.77×10^{-4}
3	03/12/2015	10:17	25.2	64.4	4.42×10^{-4}
4	03/12/2015	12:46	−44.8	64.0	4.89×10^{-4}
5	15/03/2016	04:33	−4.1	−18.4	5.70×10^{-4}
6	15/03/2016	05:16	−25.7	−20.9	5.13×10^{-4}
7	15/03/2016	19:11	−88.2	−70.7	4.02×10^{-4}
8	15/03/2016	20:47	−136.3	−76.3	5.40×10^{-4}
9	15/03/2016	21:30	−157.5	−78.7	5.74×10^{-4}
10	16/03/2016	07:13	92.3	−70.4	7.00×10^{-4}
11	16/03/2016	07:57	70.4	−68.2	5.68×10^{-4}
12	19/03/2016	11:36	152.7	−9.6	4.88×10^{-4}
13	20/03/2016	06:51	−58.6	−87.5	5.11×10^{-4}
14	21/03/2016	02:57	−122.8	−12.9	4.90×10^{-4}
15	21/03/2016	03:49	−148.7	−9.5	5.02×10^{-4}
16	21/03/2016	04:32	−170.3	−6.7	6.18×10^{-4}
17	21/03/2016	05:15	168.2	−3.9	4.48×10^{-4}
18	21/03/2016	09:56	28.6	14.3	5.39×10^{-4}

	date	time (UTC)	sub-S/C longitude	sub-S/C latitude	D_2O/HDO
1	03/12/2015	12:46	−44.8	64.0	0.012
2	03/12/2015	15:14	−113.4	63.3	0.00496
3	06/03/2016	06:52	67.8	54.5	0.0384
4	15/03/2016	04:33	−4.1	−18.4	0.01237
5	15/03/2016	05:16	−25.7	−20.9	0.03316
6	15/03/2016	19:11	−88.2	−70.7	0.04105
7	15/03/2016	20:03	−114.5	−73.7	0.04645
8	15/03/2016	20:47	−136.3	−76.3	0.02523
9	15/03/2016	21:30	−157.5	−78.7	0.012
10	16/03/2016	06:07	125.4	−73.7	0.01246
11	16/03/2016	07:13	92.3	−70.4	0.01403
12	16/03/2016	07:57	70.4	−68.2	0.00581
13	16/03/2016	08:41	48.6	−66.1	0.02729
14	16/03/2016	10:54	−17.7	−59.7	0.01875
15	20/03/2016	06:51	−58.6	−87.5	0.0209
16	20/03/2016	11:46	−26.6	−73.3	0.01023
17	20/03/2016	13:08	−70.0	−67.5	0.02116

(*Continued*.)

Table 2. (*Continued*.)

	date	time (UTC)	sub-S/C longitude	sub-S/C latitude	D/H in H_2S
1	23/05/2016	04:35	−124.9	15.6	0.00101
2	26/05/2016	09:21	164.5	79.8	0.00128
3	26/05/2016	11:21	62.8	65.9	0.00102
4	27/05/2016	11:04	−119.5	−35.7	8.42×10^{-4}
5	27/05/2016	13:13	172.5	−16.4	8.60×10^{-4}
6	27/05/2016	14:07	144.3	−8.3	8.38×10^{-4}
7	27/05/2016	16:16	77.2	11.1	0.00137
8	27/05/2016	18:15	14.8	28.9	0.00156
9	27/05/2016	20:14	−49.1	46.5	0.00136
10	27/05/2016	22:14	−117.9	63.8	0.00132
11	28/05/2016	01:38	36.4	79.1	9.75×10^{-4}
12	28/05/2016	03:47	−65.9	63.2	8.29×10^{-4}
13	28/05/2016	07:36	167.1	29.9	7.96×10^{-4}
14	28/05/2016	09:01	122.4	17.3	9.35×10^{-4}
15	28/05/2016	09:52	95.7	9.7	1.11×10^{-3}
16	28/05/2016	09:53	95.2	9.5	9.98×10^{-4}
17	28/05/2016	10:14	84.3	6.4	1.15×10^{-3}
18	28/05/2016	10:35	73.3	3.3	0.00113
19	28/05/2016	10:56	62.4	0.1	0.0012
20	28/05/2016	11:17	51.5	−3.0	0.00117
21	28/05/2016	11:59	29.6	−9.3	0.00125
22	28/05/2016	12:20	18.6	−12.5	0.00113
23	28/05/2016	13:13	−9.1	−20.4	1.02×10^{-3}
24	28/05/2016	18:08	−177.7	−65.5	0.00115

grey areas the standard deviation. D/H in H_2O has a value of $(5.25 \pm 0.7) \times 10^{-4}$, very close to the value published in [1] of $(5.3 \pm 0.7) \times 10^{-4}$. This value confirms therefore the first published value and shows that indeed fractionation during sublimation or in the nucleus of 67P seems to play a very minor role. $[D_2O]/[HDO]$ is $(1.8 \pm 0.9) \times 10^{-2}$ which is a factor 17 higher than $[HDO]/[H_2O]$. D/H in HDS is $(1.2 \pm 0.3) \times 10^{-3}$, thus higher by more than a factor 2 than in water.

3. Discussion

The $[D_2O]/[HDO]$ ratio of 1.8% is compatible within 1 sigma with the values measured by [11] in a solar-type protostar region. They reported a $[D_2O]/[HDO]$ ratio of approximately 1.2% and $[HDO]/[H_2O] \sim 1.7 \times 10^{-3}$ which means $[D_2O]/[HDO] \sim 7 \times [HDO]/[H_2O]$. Our $[D_2O]/[HDO]$ ratio is a factor 17 higher than $[HDO]/[H_2O]$, mostly due to a lower $[HDO]/[H_2O]$ ratio. Generally, $[HDO]/[H_2O]$ ratios in low-mass star-forming regions are found to be slightly higher than in 67P, whereas in hot cores values are very comparable. According to the modelling done by Furuya *et al*. [31] this means that water ice in 67P is mostly inherited from the presolar stage without much reprocessing. The variations among comets could then be explained by how

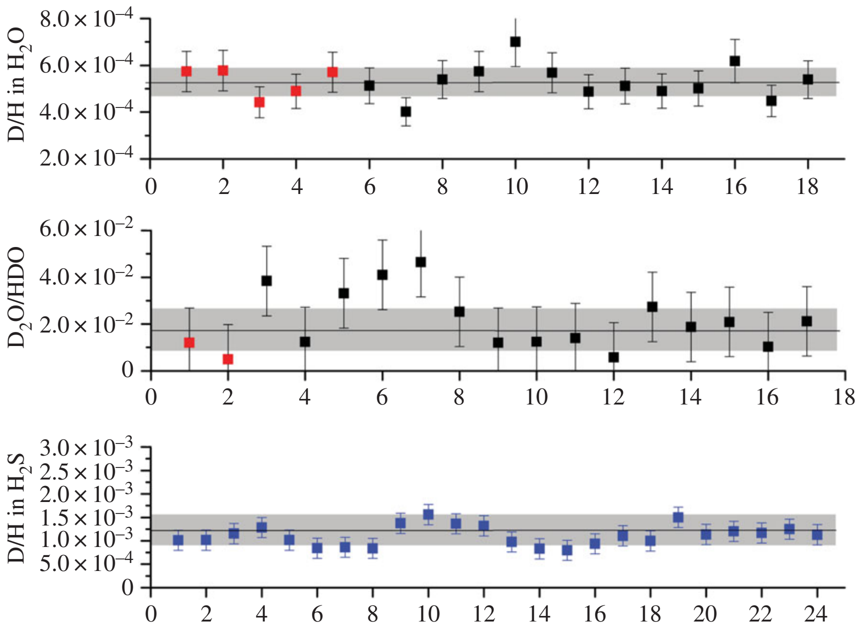

Figure 2. From top to bottom: D/H in [H_2O], [D_2O]/[HDO], D/H in [H_2S] measured in the coma of 67P during December 2015 (red)/March 2016 (black) and May 2016 (blue), respectively. For time stamp and geometrical information see table 2.

much reprocessing at the location of formation of the specific comet took place. The very high [D_2O]/[HDO] ratio in 67P probably represents water, which has sublimated from grains that have been highly fractionated with respect to the heavier isotope.

The high D/H in H_2S is very consistent with the upper limits determined in hot cores (table 1). According to these authors the D/H in H_2S is either due to hot, post-shock gas or formation of H_2S in hot core ices at a temperature of 60–80 K. In the first case the ratio of D/H in H_2S should be close to the cosmic interstellar D/H ratio of approximately 10^{-5}. Our value is clearly much higher. We therefore conclude that H_2S in comets is the product of dust grain chemistry processes in the presolar cloud. This is consistent with the detection of S_3 and S_4 in comet 67P [29] from which the authors concluded that dust grain chemistry has most probably played a major role in the formation of H_2S for 67P.

From the high deuterium values in water and hydrogen sulfide and the very high [D_2O]/[HDO] we conclude that comet 67P contains material (water and hydrogen sulfide) from the presolar disc, which was formed on dust grains and which was not significantly processed before accretion by the comet.

Data accessibility. All ROSINA data have been released to the Planetary Science Archive of ESA (www.cosmos.esa.int/web/psa/psa-interfaces) and to the Planetary Data System archive of NASA (https://pds.nasa.gov/). All data needed to evaluate the conclusions in the paper are present in the paper. Additional data related to this paper may be requested from the authors.

Authors' contributions. K.A. analysed the flight data and wrote the paper. H.B., J.J.B., J.D.K., B.F., S.A.F., T.I.G. provided the hard- and software for the instrument. A.B., U.C., S.G., L.L.R., M.R., T.S. and C.-Y.T. did the operation of the instrument as well as the necessary calibration in the lab. All co-authors helped with the interpretation of the data, critically read the paper and approved it.

Competing interests. We declare we have no competing interests.

Funding. Work at University of Bern was funded by the State of Bern, the Swiss National Science Foundation, and the ESA PRODEX (PROgramme de Développement d'Expériencesscientifiques) program. Work at Southwest Research Institute was supported by subcontract #1496541 from the Jet Propulsion Laboratory (JPL). Work at the Royal Belgian Institute for Space Aeronomy (BIRA-IASB) was supported by the Belgian

Science Policy Office via PRODEX/ROSINA PRODEX Experiment Arrangement 90020. This work was supported by CNES (Centre National d'Etudes Spatiales). Work at the University of Michigan was funded by NASA under contract JPL-1266313.

Acknowledgements. ROSINA would not give such outstanding results without the work of the many engineers, technicians, and scientists involved in the mission, in the Rosetta spacecraft, and in the ROSINA instrument team over the last 20 years, whose contributions are gratefully acknowledged. Rosetta is a European Space Agency (ESA) mission with contributions from its member states and NASA. We acknowledge herewith the work of the whole ESA Rosetta team.

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