

Chemical highlights from the Rosetta mission

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Abstract. The overall goal of the ESA *Rosetta* mission was to help decipher the origin and evolution of our solar system. Looking at the chemical composition of comet 67P/Churyumov-Gerasimenko is one way of doing this. The amount of very volatile species found and the insight into their isotopic abundances show that at least some presolar ice has survived the formation of the solar system. It shows that the solar nebula was not homogenized in the region where comets formed. The D/H ratio in water furthermore indicates that Jupiter family comets and Oort cloud comets probably formed in the same regions and their difference is then purely due to their different dynamical history. The organics found in 67P are very diverse, with abundant CH- and CHO- bearing species. Sulphur bearing species like S₃ and S₄ and others show evidence of dust grain chemistry in molecular clouds.

Keywords. astrochemistry, comets: individual (67P/C-G), planetary systems: protoplanetary disks

1. Introduction

After a 10 year long cruise phase the European Rosetta mission finally reached its goal, comet 67P/Churyumov-Gerasimenko in August 2014. On board was a large payload consisting of 10 instruments on the Rosetta spacecraft and 8 instruments on the lander Philae (Glassmeier *et al.*, 2007). The scientific goal of Rosetta, and that is why the mission was called Rosetta, was to decipher the origin of our solar system, the Earth and finally the emergence of life from a tiny piece of well-preserved material from the time of solar system formation, namely a comet. If we want to follow the formation of the solar system, we have to look back to the interstellar medium. This interstellar medium is cold and very tenuous, but it already contains some characteristics which are the starting point of the composition of the solar system. The material is provided by the remnants of stars. Depending on what stars contributed we find isotopic differences which especially in dust can survive all the following stages. Once the interstellar medium forms a molecular cloud, more chemistry sets in. Depending on densities and temperature there is gas phase chemistry, but probably a lot of dust grain chemistry. The question now is how much of this material will be reprocessed during solar system formation and how much will survive the different stages from the molecular cloud through the star forming region and the early stages of our solar system until it is embedded in comets. Looking at isotopic ratios but also at molecules and their formation pathways help us to trace back this early solar system material to its origin. Comparing isotopic abundances with what we find in the Sun, in planets and especially on Earth gives us boundary conditions on how the solar system evolved and finally how life could emerge on Earth. In this review we will summarize the most important findings up to date on isotopic and molecular composition of comet 67P and draw some conclusions on what this means for the formation and evolution of the solar system.

2. Method

In order to be able to look at the chemical composition of the volatile material of comet 67P/Churyumov-Gerasimenko, Rosetta carried several mass spectrometers as well as optical spectrometers with different wavelength. Here we review some of the most important findings concerning cometary chemistry. Most of the measurements on cometary chemistry were done with the Rosetta Orbiter Sensor for Ion and Neutral Analysis (ROSINA) (Balsiger *et al.*, 2007). This instrument suite consists of two mass spectrometers, namely the Double Focusing Mass Spectrometer (DFMS) and the Reflectron Time of Flight spectrometer (RTOF). While DFMS has a very good mass resolution of 9000 (FWHM) at $m/z = 28$ and a high sensitivity with a dynamic range of 10^{10} , RTOF was measuring much faster giving the context to the DFMS measurements. Also part of ROSINA is the COmet Pressure Sensor (COPS), consisting of two ion gauges for the total density and the ram pressure from which gas dynamics could be deduced. All three sensors were measuring during most of the mission time which lasted from August 2014, when Rosetta was within 100 km of the comet to end of September 2016, when Rosetta softly crash-landed on the comet. By now by far not all data have been analysed and more results are to be expected. Details on the data analysis can be found in Le Roy *et al.* (2015) and Calmonte *et al.* (2016).

The trajectory of Rosetta around the comet was very variable. Early in the mission, as long as the comet was well outside 2 au from the Sun, Rosetta orbited the comet mostly in the terminator plane between 10 and 30 km from the comet. In spring 2015 two flybys with lower phase angles were done, whereby the second led to a safe mode of the spacecraft. This forced the spacecraft to move further from the comet. During the summer months of 2015 with perihelion on August 13, Rosetta spent most of the time several hundred kilometers from the comet. Only in 2016 lower altitudes could be flown again. In May 2016, the spacecraft spent an extended period between 10 and 7 km from the comet center. In August 2016 it finally went into elliptical orbits, gradually lowering the pericenter down to 4 km above surface. High dust impact forced it to stay above the 4 kilometers till September 30, when it softly crash-landed on the comet which was the end of the mission.

During all of these periods ROSINA was measuring the volatile part of the coma, dealing with large variations in coma density, but also composition. A full mass spectrum with DFMS between $m/z = 13$ to 100 amu/e lasts about 40 to 50 minutes. A comet rotation was between 12.2h when the spacecraft arrived at the comet and 12h when the mission ended. Every 6h the spacecraft performed a reaction wheel off-loading by burning some hydrazine, which forced the mass spectrometers to stop working for about an hour. Every few days there was a spacecraft maneuver lasting 6h during which time ROSINA was off. This means ROSINA-DFMS got on average 10 mass spectra per comet rotation, or 1.9 million single integer mass spectra over the mission, RTOF ~ 200000 full mass scale spectra and COPS ~ 20000 density measurements per month. By now, we are far from analysing all of them.

To get a quantitative assessment, species need to have been calibrated beforehand in the lab due to the individual fragmentation patterns which are especially in the case of DFMS different from e.g. the NIST database because DFMS uses a lower electron impact energy of 45 eV compared to 70 eV that is normally used in mass spectrometry. ROSINA measures local densities at the position of the spacecraft. These densities are affected by many parameters: heliocentric and cometocentric distances, sub-spacecraft latitudes and longitudes, seasons on the comet. To calculate production rates needs therefore a detailed shape model of the comet and a coma model. To derive bulk abundances is even more

Table 1. Measured minor isotopes in the coma of 67P

Isotope	Molecule	Isotopic ratio rel. to main isotope	Reference
D	H ₂ O	$(5.3 \pm 0.7) \times 10^{-4}$	Altwegg <i>et al.</i> , 2014
	HDO	$(1.80 \pm 0.9) \times 10^{-2}$	Altwegg <i>et al.</i> , 2017
	H ₂ S	$(1.2 \pm 0.3) \times 10^{-3}$	Altwegg <i>et al.</i> , 2017
¹³ C	CO	0.0116 ± 0.0012	Rubin <i>et al.</i> , 2017
	CO ₂	0.0119 ± 0.0006	Hässig <i>et al.</i> , 2017
¹⁸ O	H ₂ O	$(1.8 \pm 0.2) \times 10^{-3}$	Altwegg <i>et al.</i> , 2014
	CO ₂	$(2.03 \pm 0.03) \times 10^{-3}$	Hässig <i>et al.</i> , 2017
²⁹ Si	N/A	0.0434 ± 0.0050	Rubin <i>et al.</i> , 2017
³⁰ Si	N/A	0.0263 ± 0.0038	Rubin <i>et al.</i> , 2017
³³ S	H ₂ S	$(6.64 \pm 0.2) \times 10^{-3}$	Calmonte <i>et al.</i> (2017)
	CS ₂	$(6.5 \pm 0.3) \times 10^{-3}$	Calmonte <i>et al.</i> (2017)
	OCS	$(6.06 \pm 0.45) \times 10^{-3}$	Calmonte <i>et al.</i> , 2017
³⁴ S	H ₂ S	$(4.3 \pm 0.2) \times 10^{-2}$	Calmonte <i>et al.</i> (2017)
	CS ₂	$(4.06 \pm 0.1) \times 10^{-2}$	Calmonte <i>et al.</i> (2017)
	OCS	$(4.2 \pm 0.15) \times 10^{-2}$	Calmonte <i>et al.</i> (2017)
³⁸ Ar	N/A	0.185 ± 0.04	Balsiger <i>et al.</i> , 2015
¹²⁸ Xe	N/A	0.076 ± 0.021	Marty <i>et al.</i> , 2017
¹²⁹ Xe	N/A	1.398 ± 0.122	Marty <i>et al.</i> , 2017
¹³⁰ Xe	N/A	0.184 ± 0.032	Marty <i>et al.</i> , 2017
¹³¹ Xe	N/A	0.864 ± 0.09	Marty <i>et al.</i> , 2017
¹³⁴ Xe	N/A	0.238 ± 0.049	Marty <i>et al.</i> , 2017
¹³⁶ Xe	N/A	0.166 ± 0.04	Marty <i>et al.</i> , 2017

difficult as species do not show the same desorption pattern with heliocentric distances (Gasc *et al.*, 2017). For relative isotopic abundances the problem is much simpler if the species are measured very close in time. For molecular abundances, species with similar volatilities often follow each other in sublimation, but not always. Details are given in the publications cited.

3. Isotopic ratios

Isotopic ratios play an important role when assessing on how much processing was done to the cometary material in the solar nebula and if / how much of the material is primordial coming unchanged from prestellar stages. A summary of all isotopic ratios measured so far in the volatile material of 67P is given in Table 1.

Deuterated water species Already early in the mission, when Rosetta was within 30km from the comet, D/H in cometary water could be determined (Altwegg *et al.*, 2014). Comet 67P shows an enrichment of more than a factor 3 relative to terrestrial water. The measured D/H is $(5.3 \pm 0.7) \times 10^{-4}$. However, there remained some doubts if this ratio was somehow fractionated relative to the bulk, mainly because early in the mission the comet temperature was still very low, but the water ice measured from the northern, summer hemisphere was probably transported from the south during the previous perihelion passage. The measurements were therefore repeated later in the mission in December 2015 and March 2016, but the results were very similar (Altwegg *et al.*, 2017). At the same time also D₂O could be measured which gave a high relative value compared to HDO of 1.8%. There are several conclusions which can be drawn from these results.

Furuya *et al.* (2016) looked at the ratio $D2/D1 = [D_2O/HDO] / [HDO/H_2O]$ and found that this ratio for reprocessed ice in the solar nebula would be close to the statistical value of 1/4. While HDO/H₂O ratios can remain largely unchanged even if water ice sublimates, reacts and then recondenses in the protosolar nebula, the D2/D1 ratio would not keep its primordial value. Measurements in molecular clouds give a D2/D1 ratio on the order of 10/1. D2/D1 is therefore indicative on how much water was reprocessed

in the protosolar nebula. The value found in 67P ($D_2/D_1 = 17$, Altwegg *et al.*, 2017) clearly demonstrates that prestellar ice survived solar system formation until it was incorporated in comets. Comparing the D/H in 67P with other cometary values shows that the range of values of Oort cloud comets and Jupiter family comets span a range between almost terrestrial (Hartogh *et al.*, 2011) values up to 6×10^{-4} (e.g. Table 2 in Paganini *et al.*, 2017). This overlap demonstrates that Oort cloud comets and Jupiter family comets most probably formed in a wide range of heliocentric distances, but in regions which overlapped. The fate of the comet to either become an Oort cloud comet or to be pushed out into the Kuiper belt is therefore just due to its dynamical history and encounters with giant planets. The high D/H value in 67P brings the mean value of measurements in comets up to now to about twice the terrestrial value. Although the statistical sample is by now just about 10 comets this fact most probably excludes a mainly cometary origin of the terrestrial surface and atmospheric water reservoirs.

Deuterated H_2S ROSINA was able to measure the D/H in H_2S in the cometary coma. The value of $(1.2 \pm 0.3) \times 10^{-3}$ (Altwegg *et al.*, 2017) is again high. H_2S is most probably formed by dust grain chemistry in the presolar cloud because gas phase chemistry is very inefficient to form H_2S (Woods *et al.*, 2015). Calmonte *et al.* (2016) reported the presence of S_3 and S_4 in the coma of 67P which demonstrate that dust grain chemistry played a major role for the sulphur bearing species as these species cannot be formed in the gas phase at all. Dust grain chemistry can fractionate deuterated species as discussed in Hatchell *et al.* (1999). A high D/H ratio in H_2S is therefore fully compatible with a prestellar origin of H_2S .

Sulfur isotopes Sulfur bearing species are quite abundant in the coma of 67P. For some of them it was possible to derive the $^{33}S/^{32}S$ and the $^{34}S/^{32}S$ ratios, namely HS, CS_2 and OCS (Calmonte *et al.*, 2017). While $^{34}S/^{32}S$ is slightly depleted in most molecules considered, $^{33}S/^{32}S$ is much more depleted. The effect is neither due to mass fractionation nor to fractionation due to photoionisation.

Silicon Silicon is non-volatile and could most of the time therefore not be measured by ROSINA. However, early in the mission, solar wind could still hit the nucleus, especially on the winter hemisphere where outgassing was low (Wurz *et al.*, 2015). On the summer hemisphere, the solar wind was already attenuated by collisions with cometary gases. Silicon was then sputtered by the solar wind mostly from the winter hemisphere as neutral Si and could be detected by ROSINA. Three isotopes of silicon could clearly be identified: ^{28}Si , ^{29}Si and ^{30}Si (Rubin *et al.*, 2017). Comet 67P is slightly depleted in the heavy isotopes of silicon compared to the light ones. This is in line with isotopic anomalies found in presolar grains.

Carbon isotopes in CO and CO_2 Due to overlapping peaks at mass 29 amu, the $^{13}C/^{12}C$ ratio in CO has a large error bar. Within this error bar the isotopic ratio is compatible with solar (Rubin *et al.*, 2017). For CO_2 , the overlap with other species is much smaller. The precision of the measurements did allow to deduce a $^{12}C/^{13}C$ ratio of 84 ± 3 , which is within 1 sigma just outside of the normally considered value of 89 for the solar system (Hässig *et al.*, 2017).

Argon and Xenon isotopes Already early in the mission, in September 2014, two isotopes of argon, namely ^{36}Ar and ^{38}Ar were detected in the coma of 67P. The $^{38}Ar/^{36}Ar$ ratio derived from these measurements have quite a large uncertainty. Within this uncertainty, they seem to be solar. This is completely different for xenon. Only very late in the mission, when the spacecraft could approach the comet to within 7 km from its center, was also xenon detected. Seven out of the nine isotopes were found. The different isotopic abundances, normalized to ^{132}Xe and to solar abundance look quite unusual

compared to what is known from the solar system. The cometary xenon is under abundant in ^{134}Xe and ^{136}Xe , but overabundant in ^{129}Xe (Marty *et al.*, 2017). While the depletion of the heavy ones can be explained by different nucleosynthetic processes, for ^{129}Xe there is most probably a contribution of the radioactive decay of ^{129}I responsible for the enhancement. This xenon signature resembles very much the U-xenon, postulated a long time ago by Pepin (2000), but never found.

Here are again several conclusions which can be drawn from the xenon isotopic ratios: 67P was formed somewhere where the composition of the solar nebula was not / not yet homogenized. The non-solar xenon isotopic ratios, combined with non-solar silicon and non-solar sulphur isotopes point to a protosolar nebula which still had some of its primordial heterogeneity due to contributions of different stars to the cloud like supernovae or AGBs.

The xenon isotopic ratios of the Earth atmosphere are neither solar nor chondritic. There is a mass dependent fractionation where heavier isotopes are less depleted than light ones. This fractionation was explained by loss from the Earth atmosphere. Corrected for this fractionation it turns out that ^{134}Xe and ^{136}Xe are heavily depleted in the Earth atmosphere. ^{129}Xe is enhanced and this was explained by contribution from ^{129}I from the Earth mantle. This for a long time served as a clock for the formation time of the Earth. If we now assume that 22% of the Earth atmospheric xenon was contributed by cometary impacts, we can easily explain the relative isotopic ratios of the atmospheric xenon, the depletion of the heavy isotopes as well as the enhancement of ^{129}Xe (Marty *et al.*, 2017). This also gives us a quantitative number for how much of the terrestrial water was contributed by comets. This value is low, a first estimate is below 1%, which is then fully compatible with the D/H difference in comets and the Earth water. What is more important is probably the contribution by comets of organics to the Earth which can be constrained by the xenon isotopes.

4. Molecular composition

The diversity of different species found by ROSINA was unexpected. Not only did ROSINA detect all the molecules found previously by in situ or remote sensing measurements in other comets (Le Roy *et al.*, 2015). ROSINA more than doubled the number of parent species known to exist in comets before Rosetta. Not all of the molecules were seen all the time in the cometary coma: some are highly volatile, but rare, like the noble gases and could only be found when the spacecraft was close to the nucleus. Others were associated to the dusty coma and were seen mainly during the perihelion passage in summer 2015. Because of the high numbers of unexpected species and therefore a lack of lab calibration data from the DFMS flight spare instruments, for many of the species, we still don't have quantitative abundances. In addition, the coma composition has been found to be highly heterogeneous and is a strong function of latitude and heliocentric distance (Hässig *et al.*, 2015) which makes a comparison e.g. to water not always very meaningful. To derive bulk abundances from coma measurements needs a good understanding of the kind of ice and the desorption patterns of the individual species and this work is still in progress. Here, we therefore do not give bulk abundances. For species, where there are numbers, which are mainly the sulfur species, we refer to the appropriate papers. Here we divide the molecules somewhat arbitrarily into highly volatiles where sublimation temperatures of the pure ices are well below CO_2 , volatiles mostly with sublimation temperatures between CO_2 and water, which are present most of the time and semi-volatiles, which have higher sublimation temperatures than water, which

Table 2. Identified parent-species in the coma of 67P

Mass	Molecule	Classification	Reference
16	CH ₄	highly volatile	Le Roy <i>et al.</i> (2015)
17	NH ₃	volatile	Le Roy <i>et al.</i> (2015)
18	H ₂ O	volatile	Le Roy <i>et al.</i> (2015)
20	HF	volatile	Dhooghe <i>et al.</i> , 2017
26	C ₂ N ₂	volatile	Le Roy <i>et al.</i> (2015)
27	HCN	volatile	Le Roy <i>et al.</i> (2015)
28	CO	highly volatile	Le Roy <i>et al.</i> (2015)
	N ₂	highly volatile	Rubin <i>et al.</i> , 2015
30	C ₂ H ₆	volatile	Le Roy <i>et al.</i> (2015)
31	P	parent unknown	Altwegg <i>et al.</i> , 2016
	CH ₃ NH ₂	volatile	Altwegg <i>et al.</i> , 2016
32	CH ₃ OH	volatile	Le Roy <i>et al.</i> (2015)
	O ₂	highly volatile	Bieler <i>et al.</i> , 2015
	S	volatile	Calmonte <i>et al.</i> (2016)
34	H ₂ S	volatile	Calmonte <i>et al.</i> (2016)
	H ₂ O ₂	highly volatile	Bieler <i>et al.</i> , 2015
36	Ar	highly volatile	Balsiger <i>et al.</i> , 2015
	HCl	volatile	Dhooghe <i>et al.</i> , 2017
41	C ₂ H ₃ N	volatile	Le Roy <i>et al.</i> (2015)
44	CO ₂	volatile	Le Roy <i>et al.</i> (2015)
	C ₃ H ₈	volatile	
	C ₂ H ₄ O	volatile	Le Roy <i>et al.</i> (2015)
45	C ₂ H ₅ NH ₂	volatile	Altwegg <i>et al.</i> , 2016
46	C ₂ H ₅ OH	volatile	
	CH ₂ S	volatile	Calmonte <i>et al.</i> (2016)
	CH ₂ O ₂	volatile	Le Roy <i>et al.</i> (2015)
48	SO	volatile	Calmonte <i>et al.</i> (2016)
	CH ₄ S	volatile	Calmonte <i>et al.</i> (2016)
50	CH ₃ Cl	volatile	Fayolle <i>et al.</i> , 2017
52	C ₂ N ₂	volatile	
58	C ₄ H ₁₀	volatile	
60	C ₃ H ₇ OH	volatile	
	OCS	volatile	Calmonte <i>et al.</i> (2016)
62	C ₂ H ₆ S	volatile	Calmonte <i>et al.</i> (2016)
	C ₂ H ₆ O ₂	volatile	
64	S ₂	highly volatile	Calmonte <i>et al.</i> (2016)
	SO ₂	volatile	Calmonte <i>et al.</i> (2016)
72	C ₅ H ₁₂	volatile	
74	C ₄ H ₉ OH	semi-volatile	
75	C ₂ H ₅ NO ₂	semi-volatile	Altwegg <i>et al.</i> , 2016
76	CS ₂	volatile	Le Roy <i>et al.</i> (2015)
	C ₃ H ₈ O ₂	semi-volatile	
78	C ₆ H ₆	volatile	
81	HBr	volatile	Dhooghe <i>et al.</i> , 2017
84	Kr	highly volatile	
87	C ₄ H ₉ NO	semi-volatile	
92	C ₇ H ₈	volatile	
96	S ₃	volatile	Calmonte <i>et al.</i> (2016)
86	C ₆ H ₁₄	volatile	
88	C ₅ H ₁₁ OH	semi-volatile	
100	C ₇ H ₁₆	volatile	
106	C ₈ H ₁₀	semi-volatile	
122	C ₇ H ₆ O ₂	semi-volatile	
128	C ₁₀ H ₈	semi-volatile	
	S ₄	volatile	Calmonte <i>et al.</i> (2016)
132	Xe	highly volatile	Marty <i>et al.</i> , 2017

are present only in the dusty coma. A list of so far identified species is given in Table 2 together with their classification.

4.1. Highly volatiles

CO and CH₄ have been known to exist in cometary comae in rather large abundances, especially CO. These molecules were also detected in 67P, although rather depleted compared to Oort cloud comets (see Le Roy *et al.*, 2015). In addition to these well known molecules ROSINA has detected N₂, O₂, S₂, and noble gases Ar, Kr and Xe. The most

surprising finding was probably O₂ (Bieler *et al.*, 2015). The O₂/H₂O ratio remained quite stable for the whole mission duration between 1-10%, O₂ following water outgassing remarkably well. O₂ is very scarce in the Universe. Up to now it was observed only in very few locations. Taquet *et al.*, 2016 explained the observed O₂ in comet 67P by grain surface chemistry in a moderately warm cloud whereas Mousis *et al.* (2016) found the O₂ abundance to be compatible with photolysis / radiolysis of water ice in presolar grains. Both scenarios are plausible. For the chemistry in molecular clouds the strong correlation between water and O₂ is not obvious, for the radiolysis scenario byproducts of this process are underabundant. While also H₂O₂ and HO₂ were found, the abundances are too low to be compatible with radiolysis. No O₃ was found. Other explanations like the one proposed by Yao and Giapis (2017) based on Eley-Rideal processes or by Dulieu *et al.* (2017) based on dismutation of H₂O₂ fail to reproduce the observed O₂ abundance without being in strong contradiction to the measured amounts of H₂O⁺ or H₂O₂, respectively, by orders of magnitudes.

N₂ relative to CO was found by Rubin *et al.* (2015) to be $(5.70 \pm 0.66) \times 10^{-3}$. This points to a low formation temperature of the cometary ice of 25-30K.

S₂ was found already very early in the mission (Calmonte *et al.*, 2016). This makes the explanation (A'Hearn *et al.*, 1983), that S₂ is the product of coma chemistry unlikely because at that time the coma was very tenuous not allowing much chemistry to take place. S₂ has a very short lifetime in the gas phase under UV irradiation. The presence of S₂ in the coma of 67P is therefore an indication that the cometary ice at least partially survived the formation of the solar system as ice, because otherwise S₂ would have disappeared before incorporation into comets.

For the first time in a comet the three noble gases Ar, Kr, and Xe were detected. A quantitative analysis of their abundances is under way.

4.2. Volatiles and semi-volatiles

While the bulk of the volatile material of 67P is water with a relatively high abundance of CO₂, the number of carbon bearing species is very high. An analysis of the species detected early at around 3 au in the mission is given by Le Roy *et al.* (2015). The authors compared relative abundances on the northern (summer) hemisphere and on the winter hemisphere. It can be well seen, that abundance ratios vary quite a lot and that it is difficult to derive from these measurements bulk abundances. Later in the mission, after the equinox in May 2015, the heterogeneity in the coma was much less pronounced as by that time all species were predominantly outgassing from the south. However, the coma got dustier with a lot of outbursts in between July and September (Vincent *et al.*, 2016), which again made the coma much more variable. During this time, however, all species given in Table 2 could be measured except the noble gases, where densities were too low due to the large distance of the spacecraft from the comet.

One of the highlights in this period was the detection of the amino acid glycine together with its precursor molecule methylamine (Altwegg *et al.*, 2016). At the same time a clear signal of phosphorous was detected. However, it could not be determined which parent species is responsible because PH₃, PO, PN and CP all could not be resolved from neighboring peaks. Together with the isotopic measurements of xenon it should now become feasible to assess how much organic material was inserted into the Earth atmosphere and oceans and how likely it is that such impacts actually triggered the emergence of life.

Apart from the highly volatile S₂ more refractory sulphur species like S₃ and S₄ were also detected. These species are probably due to dust grain chemistry in molecular clouds and make the scenario by Woods *et al.* (2015), that much of the H₂S was destroyed on

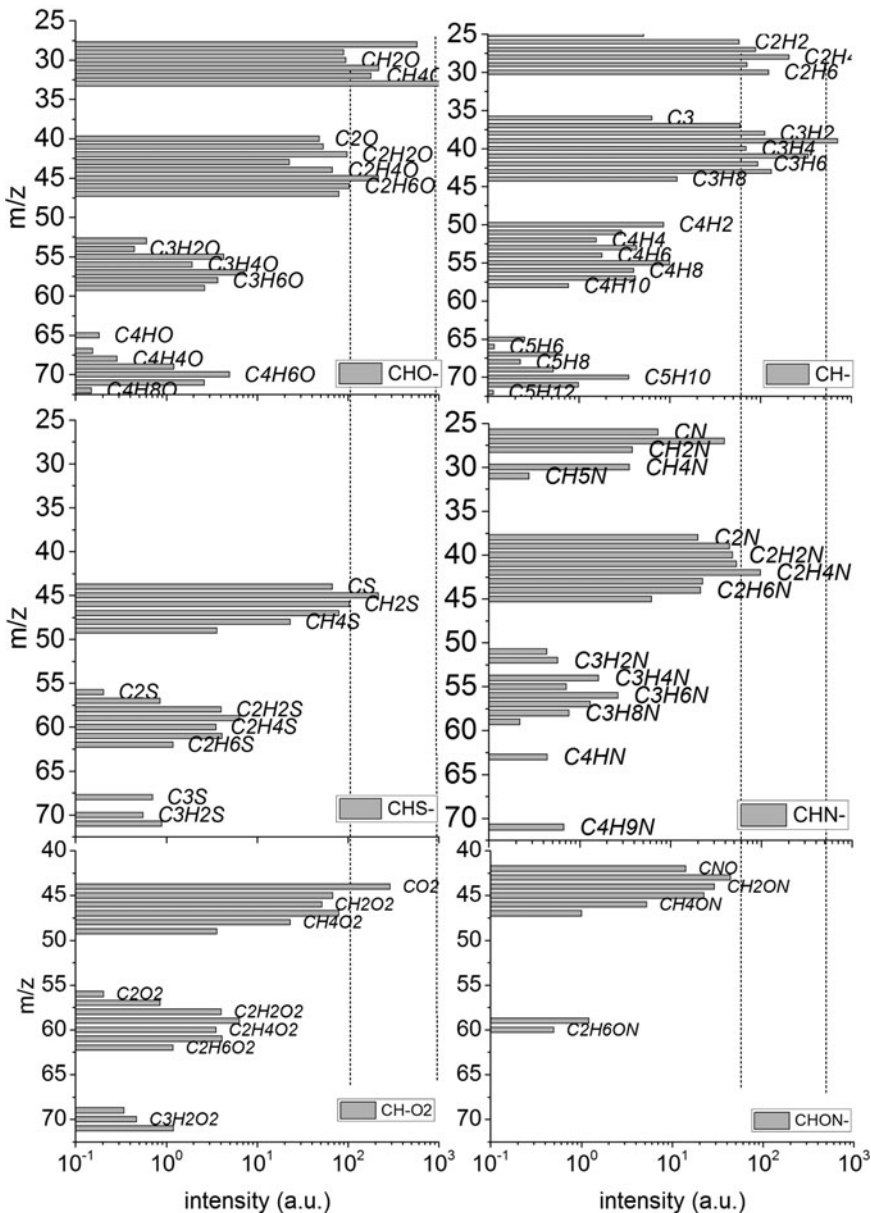


Figure 1. Fragments found in the mass spectra of DFMS during a dust impact on Sept. 5, 2016. For details see Altwegg *et al.* (2017a)

grains due to radiolysis and converted into more refractory sulphur, very likely. This would then also explain why sulphur is underabundant in molecular clouds relative to cosmic as these refractory species cannot be observed by remote sensing.

A direct hit by dust on September 5, 2016, when the spacecraft was 2 kilometers above the surface produced an enormous wealth of fragments in DFMS. Figure 1 shows the carbon bearing fragments detected in DFMS during this impact (Altwegg *et al.*, 2017a). DFMS got solid material into its ionization box which was at 1°C, allowing a relatively slow sublimation of the semi-volatile material. These fragments are due

partly to the fragmentation inside of the electron impact ionization source of the instrument, partly to non-saturated molecules. Only a thorough calibration campaign in the lab, which gives exact fragmentation patterns, can therefore give quantitative results. ROSINA found many aliphatic hydrocarbons from methane to heptane. However, it also detected aromatic compounds with benzene, naphthalene, toluene and benzoic acid. Abundances generally decrease with higher number of C's. Apart from CH- bearing molecules CHO- bearing species are quite abundant. Even CHO₂- bearing fragments are rather abundant. Organo-sulphur species are surprisingly high, whereas nitrogen bearing species are depleted. Apart from organics, there are also of course inorganics, especially sulphur bearing species like SO₂, H₂O or NH₃. By far not all of the detected peaks can be explained by fragmentation of saturated molecules inside the instrument. There are clearly non-saturated species contributing to the fragments seen. The number of parent species is therefore very likely to increase in the future.

The data analysis from ROSINA/*Rosetta* is likely to go on for a few years to come and more, but especially more quantitative results can be expected. But it is also clear already now, that the amount of results from the *Rosetta* mission is unique. These results will indeed help to decipher the origin of our solar system, the evolution of the Earth and finally the emergence of life.

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