

Supplementary Materials for

Prebiotic chemicals—amino acid and phosphorus—in the coma of comet 67P/Churyumov-Gerasimenko

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Supplementary Materials

Fragmentation pattern

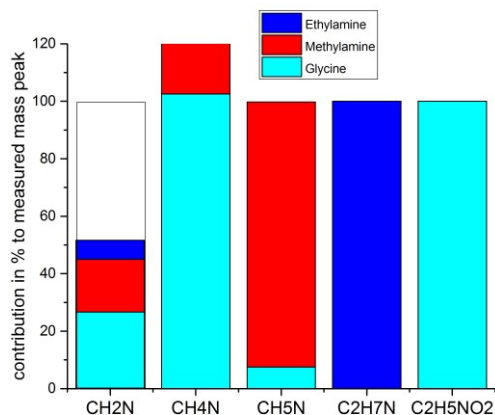


fig. S1. Contribution of the main fragments of glycine, methylamine, and ethylamine for a DFMS mass spectrum on Aug. 3, 2015.

Figure S1 shows the contribution to the main fragments from glycine, ethylamine and methylamine. Glycine has several isomers. The isomers nitroethane and ethyl nitrite don't yield any ionized parent on mass 75 dalton, while methylcarbamate and acetohydroxamic acid have their largest fragments on mass 44 dalton (CH₂NO) and 43 dalton (C₂H₃O) respectively. There is no CH₂NO in the spectrum of DFMS and the peak at mass 46 dalton, which belongs to the fragmentation pattern of methylcarbamate is missing as well. Therefore, we can exclude the presence of this molecule. The amount of C₂H₃O measured is compatible with a contribution to mass 75 dalton from acetohydroxamic acid. However, the peaks on mass 57 dalton and 59 dalton, present on the same level as the ionised parent in the NIST mass spectrum are completely missing and therefore we also exclude acetohydroxamic acid. Methylcarbamic acid could contribute to mass 75 (32). This molecule is unstable and yields methylamine and CO₂ upon sublimation. Both molecules can be found in our data. Methylcarbamic acid cannot be completely excluded, but from the non-detection of the fragment on mass 58 dalton (C₂H₄NO) we can give an upper limit of 10% for its contribution to the peak on mass 75 dalton. The non-detection on mass 58 dalton, however, is fully compatible with the fragmentation pattern for glycine. The largest fragment of glycine, ~20 times more abundant than the ionised parent, is found at mass 30 dalton (CH₄N). The measured fragmentation pattern clearly is compatible with glycine, although the peak measured for CH₄N is too small compared to the peak of the ionised parent molecule on mass 75 dalton. However, this difference can most likely be explained by the lower ionisation energy used in DFMS compared to NIST. That means glycine is less fragmented, which enhances the ratio of [C₂H₅NO₂] / [CH₄N]. CH₄N could in principle be a parent on its own. However, with the amount of glycine, methylamine and ethylamine measured we can explain the amount of CH₄N without requiring an additional parent. On mass 28 dalton, CH₂N cannot be explained by the species mentioned here. Some of the CH₂N is most probably due to methylhydrazine (CH₃N₂H₃) used by the spacecraft. Methylhydrazine does not fragment into any of the other masses.

Methylamine has a much simpler structure and therefore no isomers. Ethylamine has one isomer (dimethylamine) which produces mainly a fragment on mass 44 dalton (C_2H_6N) which is not found in the mass spectrum of DFMS.

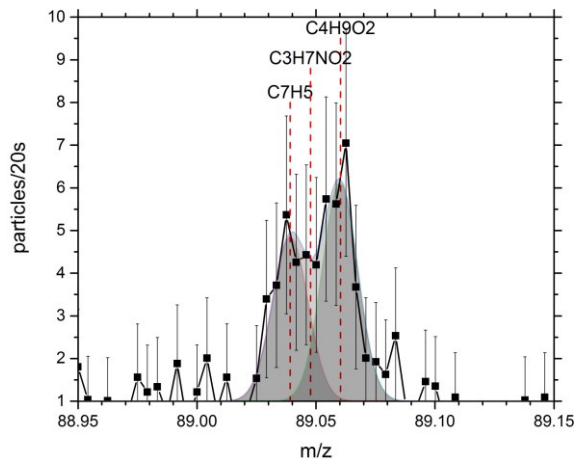


fig. S2. Mass spectra of mass 89 Da/e, taken adjacent to the mass spectra in Fig. 1. For the mass spectrum at 89 Da/e the two peaks for C_7H_5 and $C_3H_7NO_2$ have been fitted with the well calibrated Gaussian shape of the DFMS mass spectra.

Search for the amino acid alanine

The Stardust samples contained traces of the amino acid β -alanine. The amount was not high enough to verify its cometary origin by determination of the ^{13}C isotopic signature. The parent of alanine has a mass of 89.047 dalton. For the α -alanine the most abundant fragment would be on mass 44 dalton, 100 times more abundant than the parent. For the β -alanine the highest fragment is CH_4N as for glycine, but the ratio of the fragment relative to the parent is less than 20. There are two competing peaks at mass 89 Da/e, namely C_7H_5 and $C_4H_9O_2$ (see fig. S2). Fitting the data with two Gaussians with the well calibrated width known for DFMS peaks in this mass range, leaves no possibility for a third peak at the position of alanine, despite the large error bars due to low counting statistics. On mass 44 Da/e no traces of the α -alanine fragment C_2H_6N can be found. This leads to the statement that at that time we have no detection of one of the two forms of alanine. However, at the time of writing this paper the Rosetta mission is still ongoing. It is planned to end the mission by spiraling down to the nucleus surface. Future operations will allow a search for very rare species as densities will increase with $1/r^2$, r being the cometocentric distance. We have therefore deferred the search for additional amino acids to the time when we have collected all data.

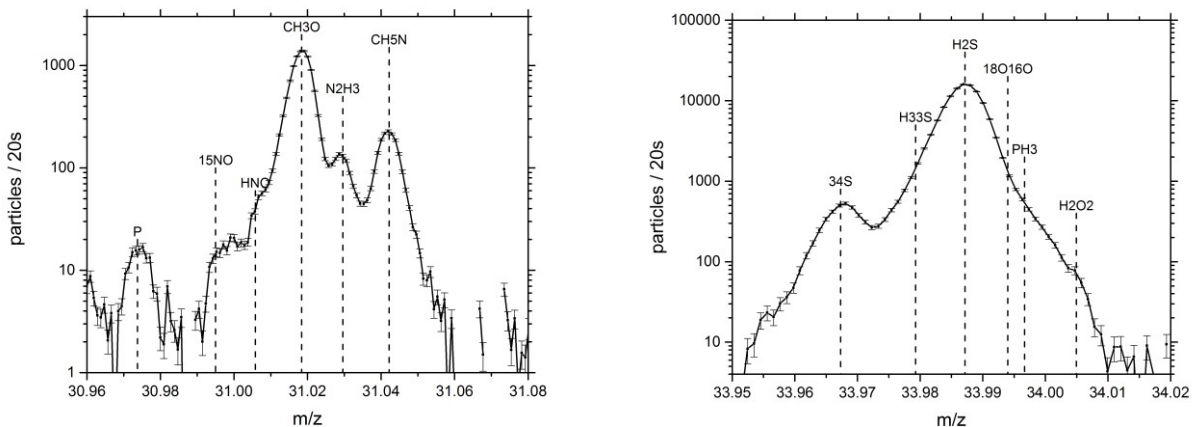


fig. S3. Mass spectra of masses 31 and 34 Da/e. Phosphorus is clearly seen on mass 31 dalton, whereas PH_3 is not evident, but could be hidden in the slope of the large H_2S peak together with $^{18}\text{O}^{16}\text{O}$. Error bars represent 1 sigma counting statistics.

Phosphorus

Figure S3 shows a spectrum of mass 31 dalton with a clear peak at the position of the ionized phosphorus. On mass 34 dalton it is not clear if PH_3 is present. This molecule, if it is present at all, is hidden by the large signal of H_2S . A fit to the data including all 5 species (^{34}S , H_2S , $^{18}\text{O}^{16}\text{O}$, PH_3 and H_2O_2) yields a slightly higher R-square value than without PH_3 taken into account, but the result is not conclusive. Unfortunately, there is no conclusive evidence for the fragments of PH_3 (PH_2 and PH) either because PH is located between the very large peaks of sulfur and O_2 and PH_2 on the slope of the large HS peak. The same is true for other possible parents of the phosphorus ion: HPC , PO or PN . It is therefore not clear which parent molecule produces the fragment seen in the DFMS spectra. Assuming that it is mainly PH_3 and taking the fragmentation pattern from the NIST database and the electron impact ionization cross section as 4 \AA^2 (33) one arrives at an abundance of PH_3 from the spectrum shown of $1.8 \cdot 10^{-3}$ relative to water. Assuming that 75 % of the volatile oxygen is in water, the remaining oxygen being in CO_2 , CO and O_2 this would give a P/O ratio of $1.4 \cdot 10^{-3}$ which is close to the solar value (25). However, there is considerable variation in this value; most of the time phosphorus is below the sensitivity limit of DFMS. The uncertainty of course is also very high, estimated to be at least a factor 2, as there exist no calibration data for PH_3 for DFMS and the ionization energy is different from the NIST database.