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ABSTRACT

Here, we report the detection of phosphorus and fluorine in solid particles collected from the inner coma of comet 67P/Churyumov–Gerasimenko measured with the COmetary Secondary Ion Mass Analyser (COSIMA) instrument on-board the *Rosetta* spacecraft, only a few kilometers away from the comet nucleus. We have detected phosphorus-containing minerals from the presented COSIMA mass spectra, and can rule out e.g. apatite minerals as the source of phosphorus. This result completes the detection of life-necessary CHNOPS-elements in solid cometary matter, indicating cometary delivery as a potential source of these elements to the young Earth. Fluorine was also detected with CF^+ secondary ions originating from the cometary dust.

Key words: comets: general – comets: individual: 67P/Churyumov–Gerasimenko.

1 INTRODUCTION

Comets are remnants from the Solar protoplanetary disc (Willacy et al. 2015). Being formed beyond the ice-line orbiting the Sun, on average, at distances further than the asteroid belt, and experiencing less processing, they are thought to represent the most pristine matter of the Solar system.

The first detection of phosphorus in a comet came over 30 yr ago from the report by Kissel & Krueger (1987) with a line at $m/z = 31$ in the PUMA mass spectrometer. This was from the summed spectra from cometary dust collected during flyby of Comet 1P/Halley by the Vega 1 mission in 1986. The interpretation was that no molecule could have survived the impact during dust capture at a velocity of >70 km s^{-1}, and thus this line could only be attributed to atomic phosphorus (Kissel, private communication). It is unknown in what kind of parent mineral this phosphorus was contained.

The second detection of phosphorus has been reported in dust particles collected by the NASA Stardust spacecraft during the flyby of comet 81P/Wild in 2004, and returned to Earth in 2006 (Flynn et al. 2006; Joswiak et al. 2012). It was further analysed by Rotundi et al. (2014), where phosphorus was detected in a single cometary particle and associated with the presence of calcium. They concluded that phosphorus was most likely contained within an apatite particle (Rotundi et al. 2014). However, studies of the nanoscale mineralogy of Wild 2 also suggested phosphide minerals as phosphorus carriers (Joswiak et al. 2012).

Another detection of phosphorus and fluorine came from the ROSINA DFMS instrument on board *Rosetta* (Altwegg et al. 2016; Dhooghe et al. 2017; Rivilla et al. 2020). In these cases, they detected elemental phosphorus, PO and CF in the gas phase of 67P/Churyumov–Gerasimenko (67P/C-G).

We report here the detection phosphorus and fluorine in mass spectra measured from solid dust particles of 67P/C-G. Previous studies have already reported detection of C, H, N, and O in the dust particles of comet 67P/C-G (Fray et al. 2016, 2017; Bardyn et al. 2017; Paquette et al. 2018; Isnard et al. 2019). It is also estimated that the organic component of the dust particles is made of high molecular weight material (Fray et al. 2016) that represents about 45 per cent in mass of the dust particles (Bardyn et al. 2017). S has been well detected showing a strong signal in the mass spectra (Bardyn et al. 2017; Paquette et al. 2017)

In the process of forming life, water soluble reactive phosphorus compounds were required to convert nucleotide precursors by phosphorylation to active nucleotides.

Reduced phosphorus minerals, such as schreibersite $(Fe,Ni)_3P$ (Pasek, Gull & Herschy 2017), could have been available on early Earth both from meteoritic, and very hot volcanic sources (Britvin et al. 2015; Pasek 2017; Turner et al. 2018). However, unlike the other elements required for life (CHNOS), gaseous forms of phosphorus were unlikely to have been present as a major species in the early Earth atmosphere, and thus was required to be in solid and soluble form (Pasek et al. 2017; Pasek 2019).

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2 METHODS

The COmetary Secondary Ion Mass Analyser (COSIMA), designed in the late 1990s and launched on-board *Rosetta* in 2004, is a Time-of-Flight Secondary Ion Mass Spectrometer (TOF-SIMS) with a mass resolution of about $m/\Delta m = 1400$ at $m/z = 100$ on board the *Rosetta* spacecraft, which accompanied the comet 67P/Churyumov–Gerasimenko from 2014 August to 2016 September (Glassmeier et al. 2007; Kissel et al. 2007; Hilchenbach et al. 2016). During this time period COSIMA collected particles that originate from 67P/C-G (Langevin et al. 2016; Merouane et al. 2017), at low impact velocity ($<10\,\mathrm{km\,s^{-1}}$) (Rotundi et al. 2015) on silver and gold substrates. The grand total number of dust particle fragments collected by COSIMA is more than 35 000 from an estimated 1200–1600 original particles (Merouane et al. 2017), which were fractured upon impact or in the subsequent collisions inside the instrument.

A beam of primary $^{115}\mathrm{In^+}$ ions accelerated to 8 keV impacts the sample and releases secondary ions from the top surface of the particle or substrate (Kissel et al. 2007). The m/z of these secondary ions is measured by the time of flight spectrometer. The temperature inside the COSIMA instrument is about 283 K (Bardyn et al. 2017). We suppose that the interior of the instrument is in equilibrium with outside gas pressure of about 5×10^{-11} mbar, as measured by the instrument COPS (Hoang et al. 2017), the pressure changes due to heliocentric distance, latitude, and location, but is correct to an order of magnitude. This is practically a vacuum, so the volatiles on the surface of the particles are lost between collection and measurement. The particles were stored between a few days and up to a year and a half before measurement, giving ample time for volatiles to escape. The instrument has two modes, positive and negative, sensitive to positive and negative ions, respectively.

Mass spectra were obtained from particles collected on 21 substrates, but due to limited time and resources, only about 250 particles have been analysed by TOF-SIMS. Most of the particles were given a name, to ease discussion about specific particles, and very small particles were numbered.

The instrument has a known contaminant, polydimethylsiloxane (PDMS), with significant peaks at $m/z = 73.05$, in positive mode and $m/z = 74.99$ is negative mode. These correspond to the ion fragments: $\mathrm{Si(CH_3)_3^+}$ and $\mathrm{CH_3SiO_2^-}$, respectively.

For the fitting process of spectra we have used a Levenberg–Marquardt fit, fitting up to four peaks at each integer mass (Stenzel et al. 2017). The method does not have a fixed peak list, but attempts to search for the combination, which best fits the overall shape.

3 THE DETECTION OF PHOSPHORUS AND FLUORINE IN PARTICLES COLLECTED BY COSIMA

For the purpose of this study, a set of summed spectra from 24 selected particles were analysed, comparing them to a sample of a nearby background set. A background set is a reference location on a substrate close to a particle, where there is no visible cometary matter. Summing spectra allows elements with lower yields to be detected. For example, $\mathrm{P^+}$ is particularly challenging for TOF-SIMS, as it yields signals over an order of magnitude lower than $\mathrm{Fe^+}$ (Stephan 2001).

The main focus in this study was to find various ionic species of phosphorus present in TOF-SIMS spectra. We look for $\mathrm{PO_X^-}$ in negative spectra, ionic P in negative and positive spectra and any other phosphorus associated compounds.

$\mathrm{PH_3^+}$ (phosphine) and $\mathrm{PH_4^+}$ (hydrogenated phosphine) were absent from any analysed individual and summed positive spectra, which was expected due to their volatile nature. This is the same result as obtained by the ROSINA instrument in the gas phase, where $\mathrm{PH_3^+}$ was not reliably detected (Altwegg et al. 2016). They also did not find any indication of a parent mineral for phosphorus, but attribute it to be from a PO molecule (Rivilla et al. 2020).

We noticed that phosphorus (P), mono-isotopic at $m/z = 30.97$, is detected when we sum a large amount of spectra. However, the signal is too weak when viewed spectrum by spectrum. To aid detection we summed the positive spectra acquired from a given particle. Out of the tested 24 particle sets, we found a significant contribution of phosphorus in comparison to a local background in four particles: Uli, Vihtori, Günter, and Fred (see supplementary materials for more details). Fred and Uli (shown in Fig. 1), as well as Vihtori and Günter (see supplementary material), show clear cometary signals for $\mathrm{CF^+}$ ($m/z = 30.9984$) as well as $\mathrm{P^+}$. This marks the first detection of both $\mathrm{CF^+}$ and $\mathrm{P^+}$ in solid cometary dust. The detection of $\mathrm{CF^+}$ originating from the dust particles complements the previous detection of $\mathrm{F^+}$ presented in Dhooghe et al. (2017). We searched for the signal of $\mathrm{PO^{2-}}$ and $\mathrm{PO^{3-}}$ in the cometary particles, but as the background spectra present a quite high signal of $\mathrm{PO^{2-}}$ and $\mathrm{PO^{3-}}$, there was no clear contribution of the cometary particles to these ions to be found.

4 COMPARISON TO REFERENCE SAMPLES

Using our reference COSIMA instrument at Max Planck Institute für Sonnensystemforschung (MPS), G"ottingen, Germany, we measured and analysed two reference samples, fluoroapatite and schreibersite. Both of these belong to families known to be found in meteorites (Hazen 2013). The first reference sample, fluoroapatite, $\mathrm{Ca_5(PO_4)_3F}$ contains oxidized phosphorus. Apatite was chosen for its terrestrial availability and its presence in meteorites. It was commercially purchased and sourced from Cerro de Mercado, Durango, Mexico. The apatite shows a clear signature of $\mathrm{Ca^+}$, $\mathrm{P^\pm}$, $\mathrm{PO_2^-}$, and $\mathrm{PO_3^-}$. We do not see calcium in significant amounts in these cometary dust samples, so the phosphorus likely cannot be explained by apatite-like minerals. See Table 1 for a comparison of the cometary particles' yield of calcium and iron in comparison to the reference samples. For all the particles on which P has been detected, the $\mathrm{Ca^+/P^+}$ ionic ratio is much smaller than on apatite (Table 1). Thus, we can rule out the apatite as the source of phosphorus.

Another reference sample was from the Fe–Ni–P phosphide group, schreibersite $\mathrm{(Fe,Ni)_3P}$ with reduced phosphorus. The schreibersite sample, of unknown (meteoritic, terrestrial, or otherwise) origin, was obtained from the Mineral Sciences at Smithsonian Museum of Natural History. It shows a clear signature of P and Fe. Our cometary samples show these, with a lower Fe to P ratio (Table 1), which cannot confirm that the source of phosphorus is schreibersite. This is expected, if the phosphorus containing area is smaller than the beam size of the COSIMA primary beam ($35 \times 50\ \mu\mathrm{m}^2$).

Our conclusion is that here, the measured phosphorus is not from apatite. The ion ratios for schreibersite also do not fit our findings. Phosphorus must come from another source, such as elemental phosphorus, or some other non-calcium containing mineral, although, as previously mentioned, it is probably not a phosphate because we could not find a clear cometary contribution of $\mathrm{PO^{2-}}$ and $\mathrm{PO^{3-}}$. Also, this means that the source of the fluorine is not from a fluorapatite.
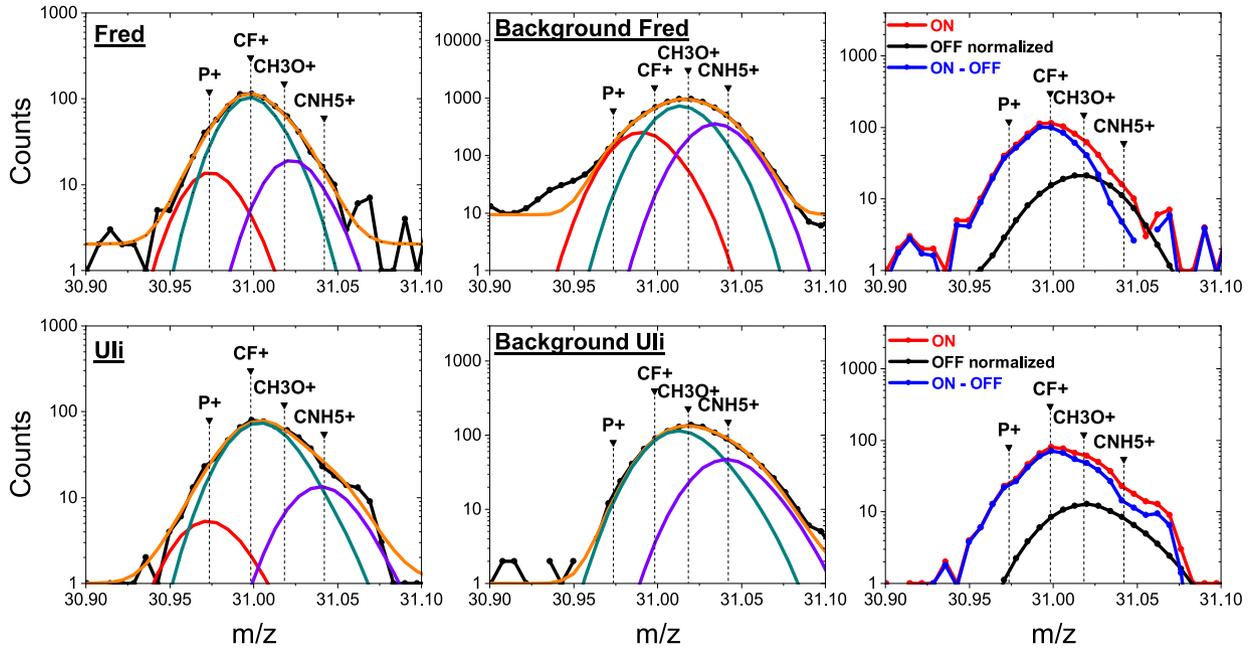
Figure 1. Summed positive spectra (black line) for particle Fred (top left, 17 spectra) and Uli (bottom left, 10 spectra), and their comparative background sets (black line in the middle column, 5 and 2 spectra, respectively). The plots show the individual fits (red, cyan, and purple) of multiple ions and the overall fit (orange line).The positions of the m/z of P^+, CF^+, CH_3O^+, and CNH_5^+ are shown in all panels to guide the eye. The right column shows the subtraction between the spectra on the particles and the normalized respective background spectra, where red shows the sum of the selected spectra taken on the particle and black shows the sum of the selected spectra taken on the target (next to the particle and at the same date), which has been normalized to the intensity of the PDMS fragment at $m/z = 73.05$. The spectra taken on the particles present a shift towards the left compared to the spectra acquired on the target (contamination). Thus at $m/z = 31$, the cometary contribution is located on the left side of the peak (the cometary contribution should have a negative mass defect at $m/z = 31$) which is an argument in favour of a contribution of the cometary particles to the signal attributed to P^+ and CF^+. The red and cyan individual fits (left column) are attributed to P^+ and CF^+, respectively. The errors on the position of these fits are less than one TOF channel which is of the same order than the difference between the positions of these fits and the exact mass of P^+ and CF^+.

Table 1. Ionic ratios of $^{40}Ca^+/P^+$ and $^{56}Fe^+/P^+$. In all the cases, both of the ratios are much lower on the cometary particles than on the reference samples of apatite and schreibersite, which allows to rule out, at a significant level, the presence of Apatite, and possibly schreibersite in the cometary particles. Thus, the main carrier of phosphorus remains unknown. The errors are calculated from the Poisson error for the fitted lines, and are equivalent to 1σ errors.

Substrate and particle name	$^{40}Ca^+/P^+$	$^{56}Fe^+/P^+$
1CF/Uli	8.57 ± 1.93	38.17 ± 7.46
2CF/Vihtori	1.20 ± 0.15	7.75 ± 0.70
2CF/Fred	2.95 ± 0.53	20.24 ± 2.83
1D2/Günter	0.74 ± 0.09	6.17 ± 0.49
Apatite	1332.5 ± 218.1	N/A
Schreibersite	N/A	428.4 ± 15.0

5 DISCUSSION

One of the challenges in understanding the origin of life processes, is the lack of soluble phosphorus containing molecules in the terrestrial environments (Yamagata et al. 1991).

It has been experimentally shown that soluble P, HCN, and H_2S can serve as suitable feed stock for the prebiotic synthesis of nucleotides, amino acids, and phosphoglycerine backbones (Patel et al. 2015; Stairs et al. 2017).

These reactions could be driven most efficiently by highly reduced phosphorus, e.g. different mineral phosphides, such as those belonging to the iron-nickel-phosphide group, known to occur mostly in meteoritic materials (Pasek & Lauretta 2005; Bryant & Kee 2006; Gull et al. 2015; Herschy et al. 2018) or possibly elemental phosphorus. The phosphite anion (PO_3^{3-} or, given the conditions, HPO_3^{2-}) is a soluble and highly reactive molecule, and is readily formed e.g. by the hydrolysis of schreibersite (Gull et al. 2015).

So far, the different organic materials and feed-stocks regarding the origin of life have been suggested to be derived either from meteoritic or geochemical origins (Bada 2013; Kurosawa et al. 2013; Patel et al. 2015; Britvin et al. 2015, and references therein). However, the detection of all the life promoting compounds, i.e. various CH compounds (Fray et al. 2016; Isnard et al. 2019), N (Fray et al. 2017), O (Paquette et al. 2018), S (Paquette et al. 2017), and here, the solid forms of P, in comet 67P/C-G, means that we have detected, in solid form, many ingredients regarded as important in current theories about origin of life. It is conceivable that early cometary impacts on to the planet surface have been less energetic, as compared to the impacts of the heavy stony meteorites (Morbidelli & Rickman 2015), thus preserving the prebiotic molecules in a more intact condition. Clark (1988) and Clark & Kolb (2018) suggested primeval procreative comet ponds as the possible environment for the origin of life, while Chatterjee (2016) suggested that hydrothermal impact craters in icy environments could create another suitable cradle for life. In both cases phosphorus could be delivered by comets.

The results here indicate that elements for life can originate from solid cometary matter. It is possible to seed the required elements with solid cometary matter, that is rich in volatiles. Although, more importantly, the compounds must be reactive and soluble, no matter how they are delivered. The solubility of the detected cometary phos-

phorus from 67P/C-G is not clear, but we can conclude that it cannot be Apatite, which is a common mineral source of phosphorus in meteorites. Additionally, other phosphate minerals are unlikely, because we could not find a clear cometary contribution of PO^{2-} and PO^{3-}.

The presence of all the CHNOPS-elements gives a strong premise for a future cometary sample-return mission to a comet. This could confirm the presence of all compounds and their possible mineral sources and the possible solubility of the matter. This would also allow for a comprehensive analysis of the relative amounts of these CHNOPS-elements.

DATA AVAILABILITY

The data underlying this article are available in the Planetary Science Archive of ESA https://www.cosmos.esa.int/web/psa/psa-introduction, and in the Planetary Data System archive of NASA https://pds.nasa.gov/.

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SUPPORTING INFORMATION

Supplementary data are available at *MNRAS* online.

Table S1. Summary of particle information, including collection substrate, collection time and particle type as well as the amount of spectra summed for the particle.
Table S2. Summary of particles analysed by not found to have phosphorus, including collection substrate, collection time and particle type as well as the amount of spectra summed for the particle.
Figure S1. As Fig. 1 for particles Vihtori and Günter.
Figure S2. Positive spectra for the reference materials measured on Earth on the reference COSIMA instrument, showing the presence of phosphorus as well as the main positive peak present in the substance.
Figure S3. As Fig. 1 showing the abundance of Ca and Fe on the particle Uli.

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