LETTER

Abundant molecular oxygen in the coma of comet 67P/Churyumov–Gerasimenko

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The composition of the neutral gas comas of most comets is dominated by H_2O, CO and CO_2, typically comprising as much as 95 per cent of the total gas density[1]. In addition, cometary comas have been found to contain a rich array of other molecules, including sulfuric compounds and complex hydrocarbons. Molecular oxygen (O_2), however, despite its detection on other icy bodies such as the moons of Jupiter and Saturn[2,3], has remained undetected in cometary comas. Here we report _in situ_ measurement of O_2 in the coma of comet 67P/Churyumov–Gerasimenko, with local abundances ranging from one per cent to ten per cent relative to H_2O and with a mean value of 3.80 ± 0.85 per cent. Our observations indicate that the O_2/H_2O ratio is isotropic in the coma and does not change systematically with heliocentric distance. This suggests that primordial O_2 was incorporated into the nucleus during the comet's formation, which is unexpected given the low upper limits from remote sensing observations[4]. Current Solar System formation models do not predict conditions that would allow this to occur.

Measurements of the coma of 67P/Churyumov–Gerasimenko (hereafter 67P) were made between September 2014 and March 2015 with the ROSINA-DFMS mass spectrometer[5] on board the Rosetta spacecraft. For the present study, we analysed 3,193 mass spectra taken in this time period. Because of the high mass resolving power and sensitivity of ROSINA-DFMS, it was possible to differentiate unambiguously between the three main species present in the narrow mass range centred at mass-to-charge (m/z) ratio 32 Da/e, namely, molecular oxygen (O_2), atomic sulfur (S) and methanol (CH_3OH); such differentiation has not been achieved by previous _in situ_ or remote sensing measurements at comets. Figure 1 shows several DFMS measurements centred at the O_2 peak. The green and orange lines show data taken before the close encounter with 67P. Only minor signatures from the tenuous neutral gas atmosphere of the Rosetta spacecraft can be identified, and even after long thruster firing manoeuvres, which use N_2O_4 as an oxidizer, the contamination of the O_2 signal remains small (see the green line in Fig. 1). Measurements taken while orbiting 67P, shown as the light blue, dark blue and purple lines in Fig. 1, show a clear increase of the O_2 signal, indicative of cometary O_2. These three measurements were taken at decreasing distances (r) from the comet nucleus, and follow the predicted $1/r^2$ signal dependence that is expected for conserved cometary species, giving further confidence in our detection.

As previously reported, the local number densities in the coma vary spatially and temporally[6,7] for different compounds. Figure 2 shows

correlation plots of H_2O with O_2, CO and N_2. Red symbols represent data from 17 to 23 October 2014, for which previously published data on N_2 are available. During this time the spacecraft was in closed orbits at 10 km from the nucleus centre. Black symbols are data from 1 September 2014 to 31 March 2015. For both periods, O_2 clearly shows the strongest correlation with H_2O. While CO shows a high correlation with H_2O from 17 to 23 October 2014, the correlation for the whole data set is fairly low. N_2 shows the weakest correlation with H_2O of all three species. The strong correlation between H_2O and O_2, with a Pearson correlation coefficient of 0.88 (and even 0.97 for the October data), indicates that they are of similar origin in the nucleus and that their release mechanisms are linked, in contrast to CO and
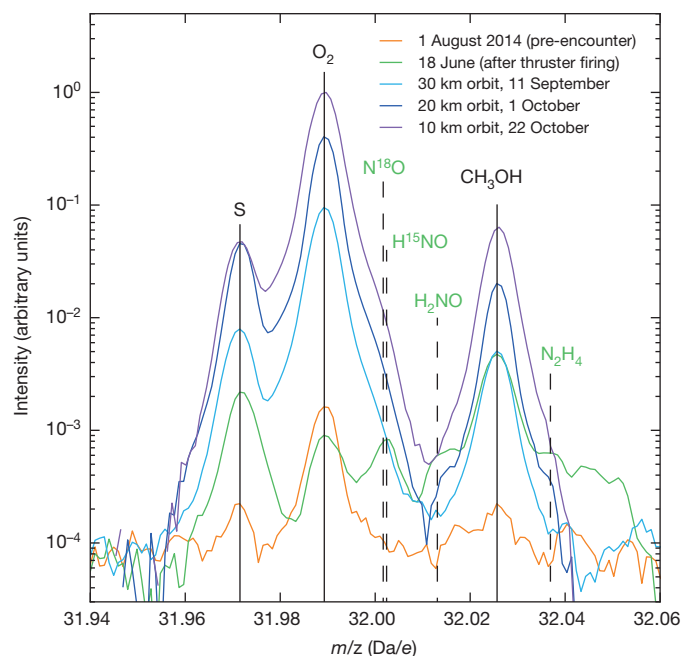
Figure 1 | DFMS mass spectra around 32 Da/e normalized to the spectrum with the largest signal. The black labels indicate the three major species found in the coma of 67P at 32 Da/e. The green labels and green line identify contamination peaks from thruster firings, showing that their contributions to the O_2 peak are very low. The light blue, dark blue and purple lines represent measurements taken at different distances from the comet nucleus.

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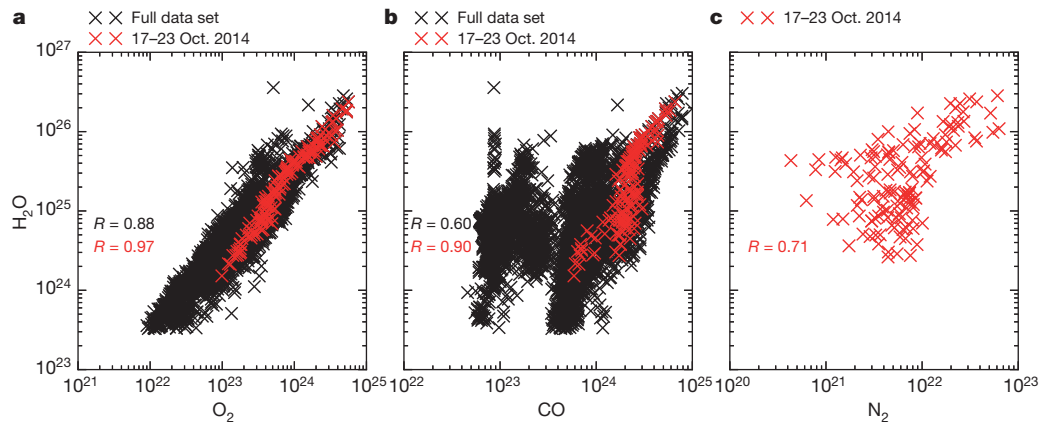
Figure 2 | Correlation between H_2O and O_2, CO and N_2. a, H_2O and O_2; **b**, H_2O and CO; **c**, H_2O and N_2. All three panels share a common y axis. Numbers on x and y axes are proportional to number density but in arbitrary units. Red crosses mark a subset of data for which N_2 data are also available. Panel **a** shows the strong correlation between H_2O and O_2, which is observed for all data. In contrast, the correlation of CO with H_2O (**b**) varies over time, which leads to a low overall correlation between those two species. N_2 has the lowest correlation with H_2O of the compared species for the October data (**c**).

N_2 which have a similar volatility but do not show a strong correlation with H_2O (see Fig. 2 for correlation coefficient values). The O_2/H_2O ratio decreases for high H_2O abundances, which might be caused by surface water ice produced by a cyclic sublimation–condensation process[8], although the total amount of surface ice is limited[9].

A plausible mechanism for the strong O_2/H_2O correlation would be the production of O_2 by radiolysis or photolysis of water ice. Here we follow the convention that photolysis refers to ultraviolet photons breaking bonds, whereas radiolysis refers to more energetic photons or fast electrons and ions depositing energy into the ice and ionizing molecules. Creation of sputtered O_2 by radiolysis has been demonstrated in laboratory experiments[10] and is observed for the icy moons of Jupiter—Europa, Ganymede and Callisto[11–13]—as well as for the rings of Saturn[3]. Comets are subject to radiolysis over various timescales: (a) over billions of years, while they reside in the Kuiper belt; (b) over the period of a few years once they enter the inner Solar System; and (c) on very short timescales, as for the present radiolysis. In the Kuiper belt, the skin depth for producing O_2 is in the range of metres, although the produced O_2 may diffuse deeper into the porous nucleus. Once a comet begins its residence in the inner Solar System, it loses its surface material to a depth of several metres during each orbit around the Sun, therefore we can safely assume that no O_2 from radiolysis in the Kuiper belt phase remains in 67P at the percentage level. Radiolysis and photolysis by solar wind and ultraviolet radiation in the inner Solar System only affect the top few micrometres of the cometary surface. Taking account of 67P's continuous mass loss through outgassing, we estimate the actively outgassing surface areas to be lost to a depth of several centimetres over the time from August 2014 to March 2015. If recent production by radiolysis or photolysis (only affecting the top few micrometres) were the source of the measured O_2, our data would show a continuous decrease of the O_2/H_2O ratio over the examined time period as the active surface continues to be shed over that time. Apart from the variations related to H_2O abundance, Fig. 3 shows that we do not observe a systematic change in the O_2/H_2O ratio over several months. Instantaneous creation of the measured O_2 by radiolysis or photolysis seems, overall, unlikely, and would lead to variable O_2 ratios due to different illumination conditions. Given that radiolysis and photolysis, on any of the discussed timescales, do not seem to be plausible production mechanisms, the preferred explanation of our observations is the incorporation of primordial O_2 into the cometary nucleus.

Despite great efforts by remote sensing campaigns, information on primordial O_2 is still limited. Solid O_2 has not yet been detected in interstellar ices, and upper limits for the O_2/H_2O ice ratios of <0.5 and for O_2/CO ratios of <1 are in agreement with our findings, but such high upper limits do not provide useful constraints[14,15]. Gaseous O_2 has only been detected in two interstellar clouds so far[4,16,17], and is generally known to have surprisingly low abundances[4]. Reports of very low upper limits for O_2 in a protostellar envelope suggest the material infalling to the accretion disk is very poor in molecular oxygen[18]. This has been ascribed
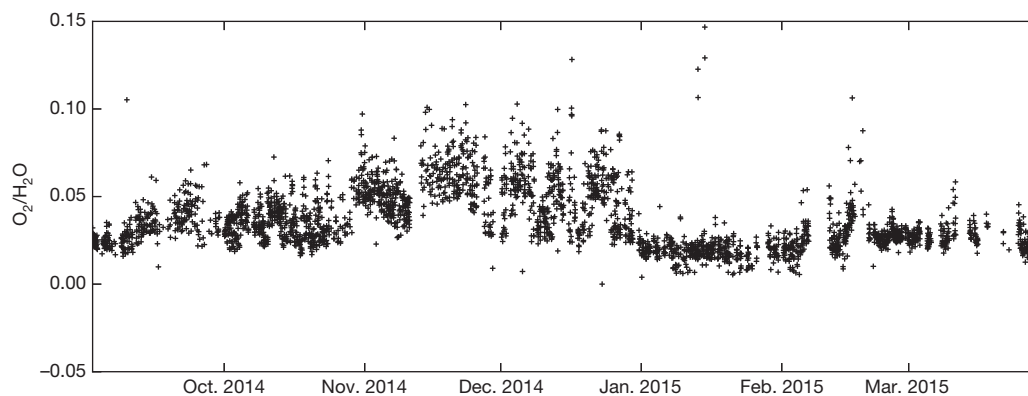
Figure 3 | O_2/H_2O ratio over several months. There seems to be no systematic increase or decrease of the O_2/H_2O ratio. The variances happen on very short timescales and can be explained by the decrease of the O_2 ratio for high H_2O abundances. It is not fully understood if the higher variability of the O_2 ratio from October to the end of December 2014 can be attributed to orbital changes of the spacecraft or to physical changes of the cometary nucleus.
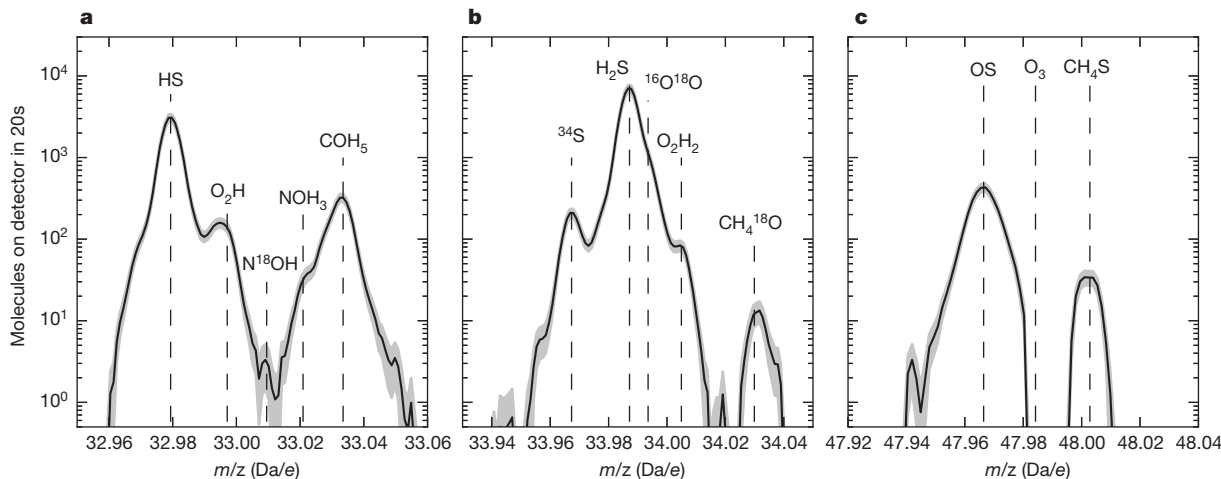
Figure 4 | DFMS spectra for some of the common products of radiolysis of water ice. a–c, Products are O_2H (seen in **a**), $^{16}O^{18}O$ and O_2H_2 (seen in **b**) and O_3 (not seen in **c**). These data were recorded on 20 October 2014 at around 01:00 UTC. With the exception of O_3 (**c**), all the previously mentioned species are measured and can clearly be identified in the mass spectra of DFMS. The grey area consists of the statistical error $N/\sqrt{N}$ and a 10% uncertainty from the individual pixel gains on the detector (here N is the number of molecules on the detector).

to the high volatility and reactivity of O_2, in particular the rapid transformation of O and O_2 to H_2O ice on cold grains[19].

However, in one of the two interstellar clouds where O_2 has been detected (the ρ Ophiuchi dense core), the chemically related species HO_2 and H_2O_2 have been measured[20,21] with gaseous abundance ratios of $HO_2/O_2 \approx H_2O_2/O_2 \approx 0.6 \times 10^{-3}$. Interestingly, the abundance ratios determined by DFMS for the coma of 67P are very close to these interstellar values: $HO_2/O_2 = (1.9 \pm 0.3) \times 10^{-3}$ and $H_2O_2/O_2 = (0.6 \pm 0.07) \times 10^{-3}$ (see Fig. 4). If these gas-phase abundance ratios reflect those in the cometary ice, this would support the existence of primordial O_2. The ρ Ophiuchi A core has been suggested to have experienced slightly higher temperatures of around 20–30 K over its lifetime (which is also typical of estimates for the comet-forming conditions in the outer early solar nebula), compared to ~10 K for most other dense interstellar clouds[21,22]. If higher temperatures are indeed needed to produce significant amounts of O_2, this would indicate that our Solar System was formed from an unusually warm molecular cloud, consistent with the low abundance of N_2 in 67P (ref. 23).

One aspect of the present results that remains unexplained is the high value (a few per cent) of the O_2/H_2O ratio in 67P. Models of gas-grain chemistry in molecular clouds predict O_2/H_2O ratios at least an order of magnitude lower[19]. They also over-predict ozone (O_3): we found no evidence for the presence of ozone (see Fig. 4), with an upper limit of 1×10^{-6} relative to water.

An alternative explanation for the presence of O_2 is the incorporation of gaseous O_2 into water ice in the protosolar nebula, and chemical models of protoplanetary disks do in fact show high abundances of gaseous O_2 in the comet forming zone[24]. Rapid cooling from >100 K to less than 30 K would then be needed to form amorphous water ice with trapped O_2 on dust grains. This could happen when young disks experience increased heating due to accretion bursts onto the star, followed by a rapid drop in temperature as soon as the burst is over. These O_2 rich grains then need to be accreted into larger bodies before further chemical modification occurs.

Finally, we discuss radiolysis of icy grains before accretion. When produced by radiolysis in water ice, O_2 can remain trapped in voids, while hydrogen can diffuse out[10]. This prevents the hydrogenation of O_2, which is otherwise a dominant reaction for the destruction of molecular oxygen, and could lead to increased and stable levels of O_2 in the solid ice[25]. Incorporation of such icy grains into the comet nucleus would explain the observed strong correlation with H_2O, in contrast to N_2 which is trapped from the gas phase and shows a lower correlation with water. However, O_3 (resulting from O_2 radiolysis) has been

reported to be trapped in Ganymede's surface[25], and at such a concentration would just be detectable by DFMS for O_2 levels at a few per cent of H_2O, but no O_3 could be detected. A further consequence would be that these icy grains have been incorporated into the comet mostly unaltered, a process that is much debated, but which has recently been proposed again[26] and that would also be in accordance with the measured high D/H ratio in 67P (ref. 27).

We note that our findings do not significantly affect our understanding of the global distribution of elemental O in the interstellar medium, as O_2 in ice with an abundance of a few per cent relative to H_2O accounts only for a small fraction of the total oxygen inventory.

Online Content Methods, along with any additional Extended Data display items and Source Data, are available in the online version of the paper; references unique to these sections appear only in the online paper.

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METHODS

Data reduction. The integration time for all evaluated spectra is 20 s. A single mass spectrum consists of the signals of 512 individual pixels, which are arranged along the dispersive axis of the mass spectrometer. We take the gain degradation of each individual pixel over time into account by determining its gain with a calibration sequence dedicated to this task every few weeks.

For every recorded mass spectrum, a third-degree polynomial is fitted to the baseline of the mass spectrum and subsequently subtracted from the signal. To avoid contamination in the baseline fit from the measured peaks, the centre of the mass spectrum (with the peaks) is ignored for those fitting purposes. Peaks are fitted with a Gaussian-shape curve. This introduces a systematic underestimation of the absolute magnitude of the signal, as at the 1% level and below the peaks are broader than Gaussian, but cancels out for the reported ratios of O_2/H_2O as both species are underestimated similarly. In a post-processing procedure, outliers are removed. An outlier occurs if one of the following criteria is met: (a) the signal amplitude changes by more than two orders of magnitudes between two measurements; (b) the centre of the fitted peak is not within a given window around the predicted position; (c) the width of the fitted peak curve is wider than a set limit.

For the CO measurements, the fraction contributed to the signal by CO fragments from CO_2 is subtracted. As DFMS measures one mass line at a time in high resolution mode, there are no simultaneous measurements of two species that are separated by more than 1 Da/e. To calculate ratios, the two measurements have to occur within 20 min; if no pair of measurements can be found within 20 min, the data point is ignored. In our error analysis we include uncertainties for the individual gain levels of the detector, the species branching ratios and their relative sensitivities as systematic errors. Individual pixel gains are treated as statistical error, as the peak position on the detector is not constant. A careful analysis confirmed that the O_2/H_2O ratio is independent of the peak centre positions.

Sample size. No statistical methods were used to predetermine sample size.

Spacecraft outgassing background. To clearly identify the measured O_2 as cometary in origin, all non-cometary sources of O_2 must be considered and excluded. The Rosetta spacecraft produces a neutral gas cloud of its own, mainly due to diffusion of volatiles out of spacecraft material and desorption of re-deposited volatiles from the spacecraft. For example, by changing the spacecraft attitude, different spacecraft elements are illuminated by the Sun, which then warm up and release condensed gas. The orange line in Fig. 1 shows the low-level signals from this spacecraft contamination for O_2, S and CH_3OH, referred to as "background". Those measurements were taken several days before the encounter with 67P. It is not possible to distinguish this background signal from any potential cometary signature with DFMS, but it has been well characterized before the arrival at 67P and is usually orders of magnitude lower than the measured O_2 signals[28]. To keep the background influence as low as possible, we only considered mass spectra where both the O_2 and H_2O abundances are at least 5 times larger than the corresponding spacecraft contamination. Another potential source of O_2 is the oxidizer, N_2O_4, used by the Rosetta spacecraft during thruster firings. Measurements taken shortly after a large thruster firing manoeuvre from June 2014 (still before arrival at the comet) show minor contaminations around 32 Da/e, but not directly affecting the O_2 peak (see green curve in Fig. 1). Although contamination from thruster firings is small, DFMS measurements are usually performed hours after thruster firings, in order to minimize influence thereof. Finally we can exclude the production of O_2 inside the instrument through a careful review of all oxygen-bearing molecules up to 150 Da/e, which could potentially fragment into O_2 in the DFMS electron impact ion source. Many minor species contain O_2 but these are too low in abundance to account for the large amount of O_2 detected. The remaining possibility is CO_2, which is very abundant in the coma of 67P (ref. 6). However, owing to its molecular structure it only fragments into CO and O, not into O_2 (ref. 29). Finally we exclude the production of O_2 from H_2O in the instrument. For 81 mass spectra taken from May to the end of June 2014 (before the encounter with 67P) we determine an O_2 abundance of $(0.18 \pm 0.07)\%$ relative to H_2O, which is a factor of 20 lower than the cometary values.

Coma chemistry. The production of O_2 from atomic oxygen in the neutral gas coma of 67P is possible through the reaction

$$O + OH \rightarrow O_2 + H$$
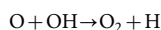
Owing to the tenuous nature of the coma, only very few collisions are expected within the first 100 km above the nucleus surface[30]. With increasing activity and therefore denser coma one would expect a higher O_2/H_2O ratio as both reactants (atomic oxygen and OH) are related to H_2O as well as the collision frequency. This is clearly not observed. Production of a significant amount of O_2 from coma chemistry hence seems unfeasible.

Correlation with H_2O. The measured O_2 signal shows a very strong dependence on radial distance (r) from the comet. It increases by roughly one order of magnitude when the radial distance from the comet decreases from 30 km to 10 km. This is in agreement with a predicted $1/r^2$ dependence of the number density profile of a non-reactive species. Examining the data further, we observe a strong correlation between H_2O and O_2 (see Fig. 2, Pearson correlation coefficient $R = 0.88$) for data from September 2014 to March 2015. This correlation indicates that O_2 and H_2O are both of a similar cometary origin. In contrast, there is no correlation between O_2 and H_2O for measurements taken before the arrival at the comet ($R = -0.01$). The observed temporal variations in the O_2/H_2O ratio are largely due to a nonlinear correlation between H_2O and O_2 for high water densities, where the O_2 ratio drops with increasing H_2O abundance. The correlation similarly supports the ruling out of CO_2 as a source of the O_2, as previous studies[6,23] and Fig. 2 show a lack of correlation between the abundance of H_2O and other species like CO, CO_2 and N_2.

Radiolysis. The production of O_2 from water ice by radiolysis is the result of several reactions, where initially H, O and OH are produced, followed by subsequent rearrangement to form H_2, HO_2 and H_2O_2 and ultimately O_2 (ref. 2). In a systematic study of the irradiation of pure cubic crystalline water ice at 10 K, it was estimated that comets in the Oort cloud would reach an equilibrium concentration of about 0.6% of H_2O_2 after $\sim 10^5$ years, and that the concentration of O_2 would be significantly lower[31]. As stated by the authors, the relative proportion of O_2 and H_2O_2 in actual astrophysical ices can be different as the presence of H_2O_2 ices may enhance the production of O_2 and vice versa.

Cosmic rays consist of energetic particles (mostly H^+) that can penetrate inside the cometary nucleus. Their penetration depth depends on their energy. The more energetic a cosmic ray, the deeper it deposits its energy into the cometary nucleus. Only the most energetic components, the Galactic cosmic rays (GCRs), can penetrate deeply into the cometary body. Today, the GCR flux peaks at energies around a few hundreds of MeV. At energies higher than ~ 1 GeV, the GCR flux drops exponentially, the flux at 10 GeV being approximately 100 times lower than the flux at 1 GeV. GCRs with energies near the GCR maximum of flux typically deposit their energy in the nucleus at depths of the order of metres to tens of metres[32]. There is some uncertainty on the evolution of the cosmic ray flux over the history of the Solar System related to the occurrence of supernovae which can drastically increase the cosmic ray flux at high energies (up to $\sim$PeV) during relatively short time periods (of the order of 10^5 years) or to the orbital motion of the Sun and of the Galaxy. There are also uncertainties on the cross-sections, the relative proportion of high-Z cosmic rays, and the role of porosity and defects in the cometary ice[33].

During 67P's stay in the Kuiper belt (~ 4.5 billion years) GCRs may have produced a significant amount of O_2. This O_2 is produced where the GCR energy is deposited, that is, in the first tens of metres below the comet surface. Once cometary objects enter the inner Solar System they lose (owing to their activity and depending on their perihelion distance) material from the surface in the range of several metres per orbit around the Sun. Therefore, as most products built up during the stay in the Kuiper belt reside in the outer few metres, O_2 produced by radiolysis should be released quickly on the first solar passages. 67P's perihelion distance has been within the orbit of Jupiter for the past 250 years, possibly even for more than 5,000 years, and since a close encounter with Jupiter in 1959, the perihelion distance of 67P has been about 1.3 AU with an orbital period of 6.4 years (ref. 34). Accumulated over the last perihelion passages we can assume that 67P has lost hundreds of metres from its surface.

However, O_2 molecules may have diffused into the comet and penetrated into deeper regions of the cometary nucleus. According to the estimated erosion of the comet, this requires significant diffusion of the O_2 molecules. Such efficient diffusion would dilute the produced O_2, resulting in a lower O_2/H_2O ratio hardly compatible with the elevated amount of O_2 observed by DFMS.

Recent radiolysis. The flux of the low energy component such as solar energetic particles (SEP) is several orders of magnitude higher than the flux of GCRs. The SEP flux peaks at energies around a few tens of MeV and only penetrates the first centimetres of the comet[32]. Considering the comet erosion rate, the production of O_2 by low energy cosmic rays would have to be very fast to account for the observed amount of O_2, requiring unrealistically high O_2 production rates. Consequently, it appears unlikely that most of the O_2 in 67P has been built up over the past few years.

O_2 production through surface sputtering. It has been shown that sputtering of refractory materials from the cometary surface due to the solar wind is occurring at 67P (ref. 35) and a clear difference between the southern and northern latitudes in the measured abundances of the sputtered species was demonstrated. This apparent spatial difference is explained via the asymmetry of the neutral coma, with higher number densities in the northern hemisphere that is preferentially exposed to the Sun for the time span under study. The solar wind, which is responsible for

the sputtering, is therefore attenuated more efficiently by these denser parts of the coma and thus has limited or no access to the surface. We find that the O_2/H_2O ratio is independent of latitude and relatively constant over a period of 7 months. Furthermore, the major part of the top surface of 67P accessible by the solar wind does not contain any water ice[9]. This suggests that sputtering cannot be the main source of the detected molecular oxygen. Moreover, the sputter yields by solar wind ions are orders of magnitude too low to explain the observed amount of O_2.

Code availability. The data reduction software was written in the Julia and Python programming languages and is available upon request from A.B.

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