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1 Measurement of molecular oxygen in the coma of 67P/Churyumov-Gerasimenko 2

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31

32

33 **Abstract**

34 **The composition of the neutral gas coma of a comet is dominated by H₂O, CO and CO₂, typically**
35 **comprising as much as 95% of the total gas density¹. In addition to these common species, the**
36 **cometary coma has been measured to contain a rich array of additional molecules including noble**
37 **gases, sulfuric compounds and complex hydrocarbons. Molecular oxygen (O₂), despite its detection on**
38 **other icy bodies, such as the moons of Jupiter and Saturn^{2,3}, had however remained undetected in the**
39 **cometary volatile inventory. Here we report the direct in situ measurement of molecular oxygen in the**
40 **cometary coma of 67P/Churyumov-Gerasimenko with a local abundance ranging from 1% to 10%**
41 **relative to H₂O and a mean value of 3.7 ± 1.5 %. Our observations indicate that the O₂/H₂O ratio is**
42 **isotropic in the coma and does not systematically change over a period of several months. This**
43 **suggests that O₂ was incorporated into the cometary nucleus primordially during the comet's**
44 **formation. Current Solar System formation models do not predict conditions that would allow this to**
45 **occur, suggesting that our detection may play a significant role in advancing our understanding of**
46 **comet formation and the prevailing conditions and processes in the early stages of our Solar System.**

47

48 Measurements of the coma of 67P/Churyumov-Gerasimenko (hereafter 67P) were made between
49 September 2014 and March 2015 with the ROSINA-DFMS mass spectrometer⁴ onboard the Rosetta
50 spacecraft. For this study we analyzed 2808 mass spectra taken in this time period. Due to the high
51 resolving power and sensitivity of ROSINA-DFMS it is possible to unambiguously differentiate between
52 the three main species present in the narrow mass range centered on 32 Da/e; molecular oxygen (O₂),
53 sulfur (S) and methanol (CH₃OH), something which has not been achieved by previous in situ or remote
54 measurements at comets. Fig. 1 shows several measurements centered at the O₂ peak. The green and
55 orange lines show data taken before the close encounter with 67P. Only minor signatures from the
56 tenuous neutral gas atmosphere of the Rosetta spacecraft can be identified and even after long thruster
57 firing maneuvers, which use N₂O₄ as an oxidizer, the contamination of the O₂ signal remains small (green
58 line in Fig. 1). Measurements while orbiting 67P, shown as the light blue, dark blue and purple line in Fig.
59 1, show a clear increase of the O₂ signal, indicating the presence of cometary O₂. These three
60 measurements were taken at decreasing distances (r) from the comet nucleus and follow the predicted
61 $1/r^2$ signal dependence that is expected for a conserved cometary species, further gaining confidence in
62 our detection.

63 As previously reported, the local number densities^{5,6} in the coma vary spatially and temporally^{5,6}, for
64 different compounds. The bottom panel of Fig. 2 shows an O₂ and H₂O measurement sequence taken
65 between the 5th and the 7th of November 2014 and the peaks and valleys occur with the rotation
66 frequency of 12.4 hours of 67P⁷. During this time range the radial distance from the comet is nearly
67 constant at roughly 30 km, the phase angle decreases from 115 to 102 degrees, the latitude linearly (in
68 time) increases from -22 to 22 degrees and all longitudes are covered multiple times (due to the short

69 rotation of 67P). Uncertainties of the individual measurements for both species are on the order of 30%
70 and are indicated by the shaded areas in Fig. 2. We observe a strong correlation between the absolute
71 abundances of H₂O and O₂, not only for the time span shown in Fig. 2, but for the entire dataset. This
72 strong correlation, with a Pearson correlation coefficient of 0.91, indicates that H₂O and O₂ are of similar
73 origin on the nucleus and their release mechanisms are linked. Despite the overall strong correlation the
74 O₂ ratio decreases for high H₂O abundances as can be seen in the top panel of Fig. 2. Because of the
75 radial dependence of the number density there is however not an absolute value above which this
76 saturation effect is observed. This effect is the main cause for the variability in the measured O₂ ratios as
77 shown in the time series in Fig 3.

78
79 A plausible mechanism for the strong O₂/H₂O correlation is the possibility to produce O₂ by radiolysis or
80 photolysis of water ice. Here we follow the nomenclature that photolysis refers to UV photons that break
81 bonds, whereas radiolysis refers to more energetic photons or fast electrons and ions depositing energy
82 into the ice and ionizing molecules. Creation of sputtered O₂ by radiolysis was demonstrated by Hart et
83 al.⁸ and is observed for the icy moons of Jupiter; Europa, Ganymede and Callisto⁹⁻¹¹, as well as for the
84 moons of Saturn; Dione and Rhea³. At comets, radiolysis does happen on different time scales: during
85 billions of years while they are residing in the Kuiper belt, over the period of several years once they
86 enter the inner Solar System and on very short time scales. In the first case, the skin depth for producing
87 O₂ is in the range of a meter, while in the latter it is only a few micrometers. Once a comet begins its
88 residence in the inner Solar System, it loses several meters of its surface material during each orbit
89 around the Sun, therefore we can safely assume that all radiolysis products created in the Kuiper Belt
90 phase are gone from 67P. Furthermore, radiolysis and photolysis by solar wind and UV radiation in the
91 inner Solar System only affect the top few micrometers of the cometary surface. Due to 67P's continuous
92 mass loss through outgassing, we estimate the surface loss to be in the range of several cm for the time
93 from August 2014 to March 2015. If recent production were the source of the measured O₂, our data
94 would show a continuous decrease of the O₂ ratio over the examined time period. Apart from the
95 variations related to the H₂O abundance, Fig. 3 shows that we do not observe a systematic change in the
96 O₂ ratio over several months. On line creation of the measured O₂ by radiolysis or photolysis at 67P
97 seems overall unlikely and would lead to anisotropic O₂ ratios. Given that radiolysis and photolysis, on
98 any of the discussed time scales, do not seem plausible production mechanisms for O₂, our preferred
99 explanation is the incorporation of primordial O₂ into the cometary nucleus.

100
101 Time dependent models of surface grain chemistry in molecular clouds predict an abundance of a few
102 percent of O₂ relative to H₂O on icy grains at time scales of >10⁶ years¹². Thereby O₂ is formed together
103 with H₂O by grain surface reactions, which would explain their correlation and be in line with the very low
104 abundances of HO₂ and H₂O₂ that we measured in the coma of 67P (see Fig. 4). A further consequence
105 would be that these icy grains have been incorporated into the comet mostly unaltered, a fact very much
106 under debate, but which has recently been proposed again by Cleaves et al.¹³ and would also be in
107 accordance with the measured D/H ratio in 67P¹⁴.

108 Constraints on the O₂ abundance are of great benefit for future theoretical studies and modeling efforts
109 as the current understanding of the grain-gas interaction is still evolving. In contrast, laboratory
110 experiments of photolysis or particle bombardment of H₂O ice find significantly higher abundances of
111 H₂O₂ than we measured¹⁵.

112 Interestingly, there has not been a direct detection of O₂ in interstellar ices, but upper limits for the
113 O₂/H₂O ratios of <0.1 have been published based on analysis of solid ¹³CO lines^{16, 17} on icy grains. These

114 limits then lead to a O_2/CO_2 ratio of approximately 0.75. Both of these ratios, albeit relatively
115 uncertain, agree with our findings and previous observations of 67P². So far, this non-detection has
116 preferably been explained by the high volatility and chemical reactivity of O_2 . This potential O_2 abundance
117 on icy grains on the order of a few percent relative to H_2O would have significant implications on our
118 current understanding of ices in interstellar molecular clouds and their importance for the formation of
119 comets. The global distribution of elemental O in the interstellar medium is probably not affected by our
120 findings, as O_2 on ice grains with an abundance of a few percent relative to H_2O accounts only for a small
121 fraction of the total O inventory.

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123
124 An alternative explanation for the O_2 is the incorporation of gaseous O_2 into water ice. Models of
125 protoplanetary disks do show that O_2 can be abundant in the comet forming zone. A rapid cooling
126 scenario from >100 K to less than 30 K is then needed to form water ice with trapped O_2 . However,
127 despite great efforts by remote sensing campaigns, O_2 has only been detected in two regions in the
128 interstellar medium so far¹⁸⁻²⁰. This lack of O_2 is not understood but as a consequence, molecular
129 oxygen is generally considered to be present only at very low abundances. However, the abundance
130 ratios of HO_2/O_2 and H_2O_2/O_2 determined by DFMS for the coma of 67P are very close to those observed
131 in the rho Oph A interstellar core, one of the two regions where O_2 was actually detected in the ISM. We
132 find ratios of $HO_2/O_2 = (1.9 \pm 0.3) \times 10^{-3}$ and $H_2O_2/O_2 = (0.6 \pm 0.07) \times 10^{-3}$, which are similar to $HO_2/O_2 \sim$
133 $H_2O_2/O_2 \sim 0.6 \times 10^{-3}$ as reported for rho Oph A^{21,22}. To what extent these gas-phase abundance ratios
134 reflect those in the ice is however still unclear.

135
136 The unique case of rho Oph A has been interpreted by having experienced slightly higher temperatures
137 of around 20-30 K over its lifetime, compared to ~10 K for most other interstellar clouds^{22,23}. Applied to
138 our own Solar System this might indicate it was formed from an unusual warm molecular cloud,
139 challenging our current understanding of the chemistry occurring during these early stages. Admittedly,
140 the observed ratios are in contrast to simulations of interstellar ice chemistry, which predict H_2O_2 and O_3
141 ice to be more abundant than O_2 ice by one to two orders of magnitude²⁴. We found no evidence for the
142 presence of ozone (O_3) (see Fig. 4) for which we give an upper limit of 1×10^{-6} relative to water.

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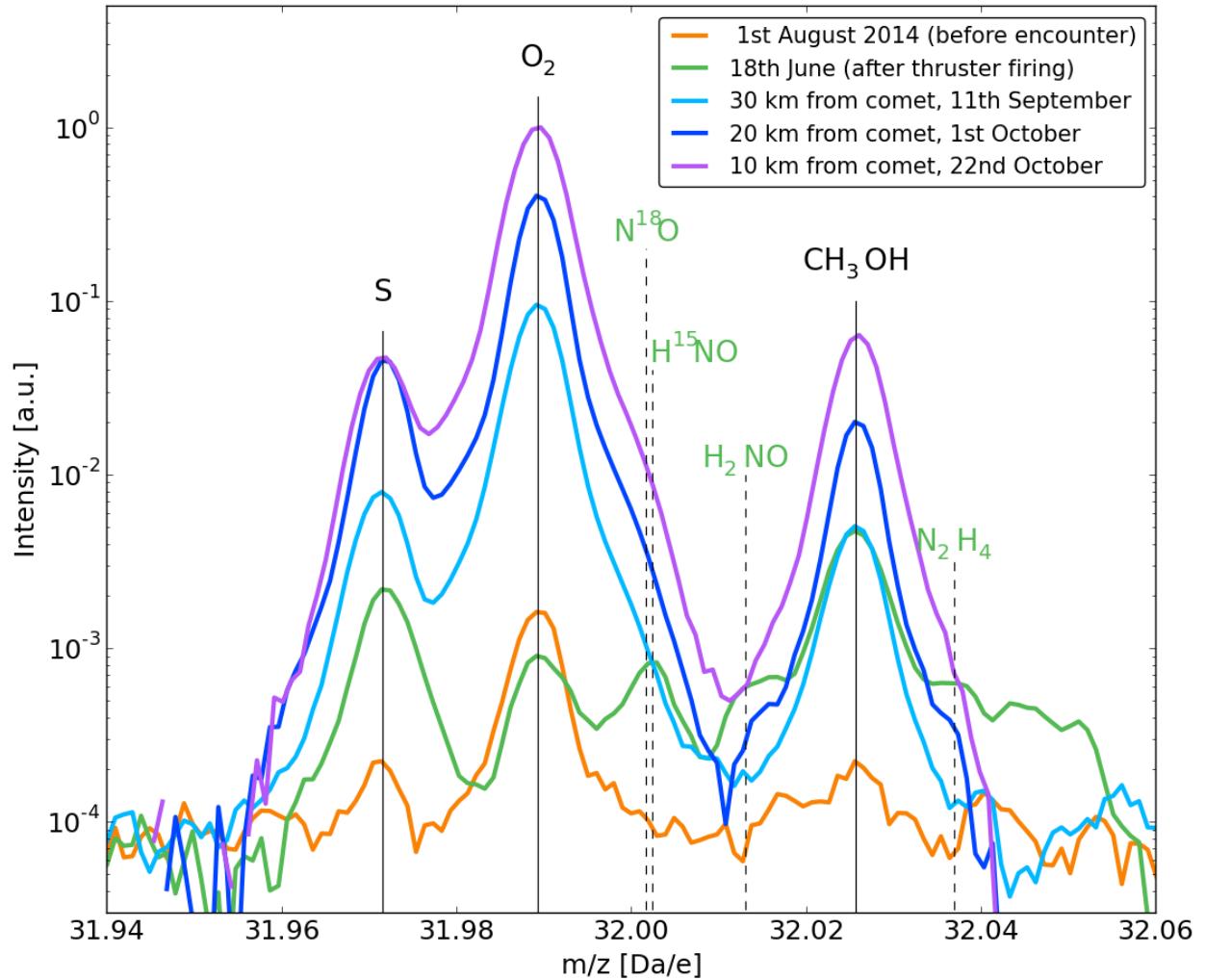
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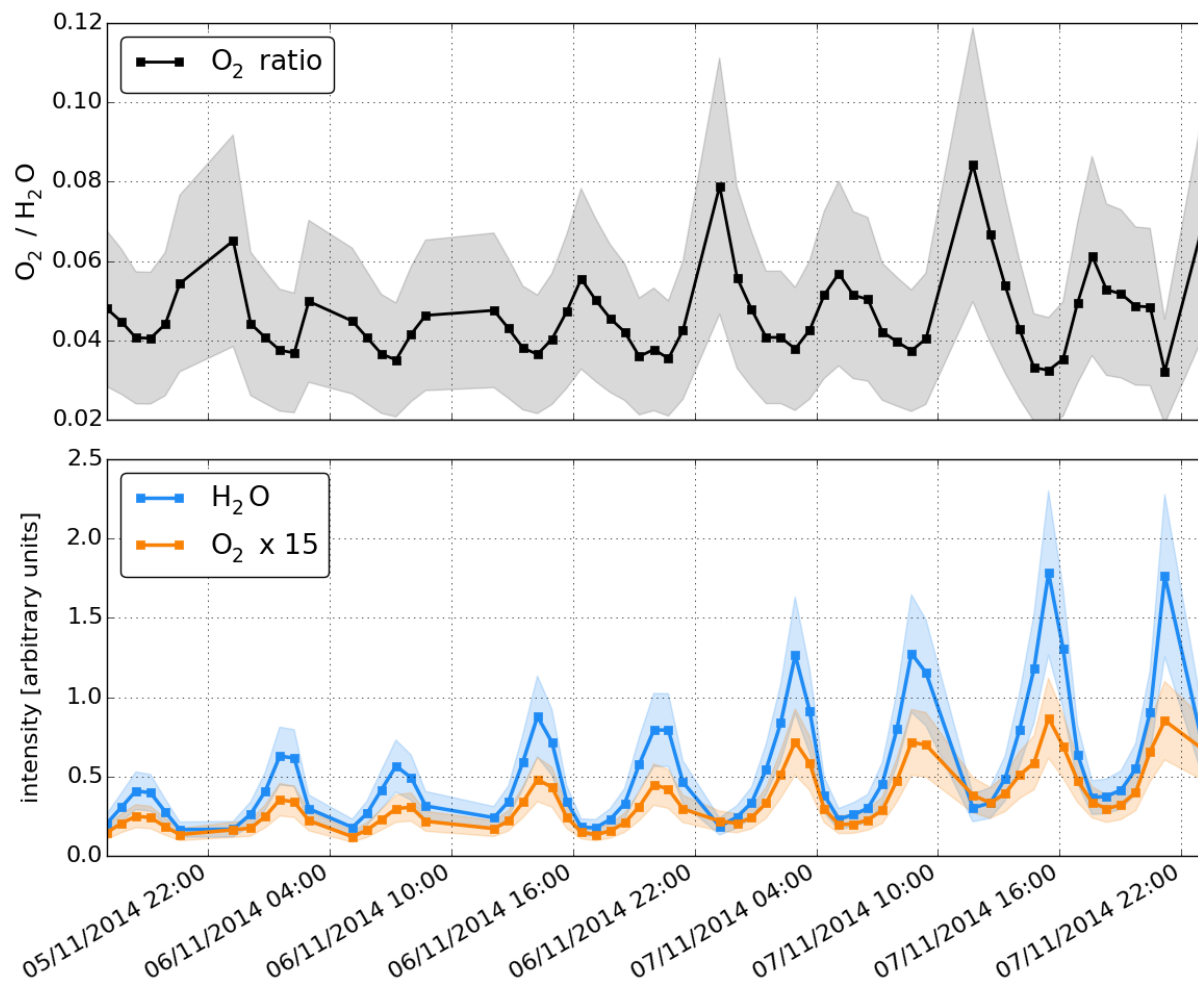
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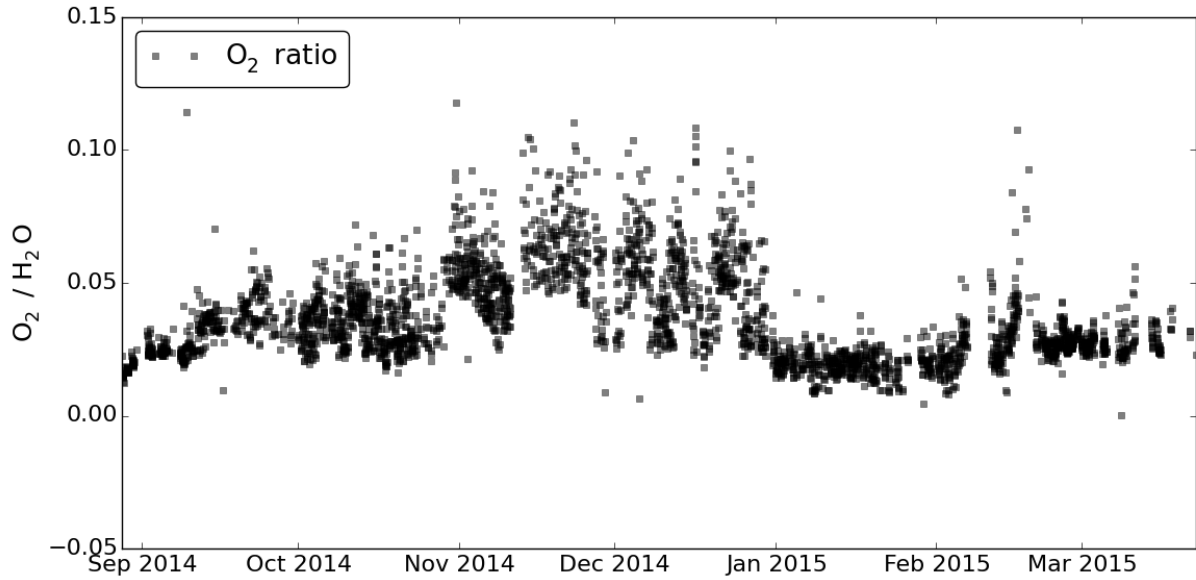


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 243 **Figure 1:** Normalized DFMS mass spectrum at 32 Da/e. The black labels indicate the three major species
 244 found in the coma of 67P at 32 Da/e. The green labels and graph identify contamination peaks from
 245 thruster firings, the contribution to the O₂ peak is very low. The light blue, dark blue and purple lines
 246 represent measurements taken at different distances from the comet nucleus.

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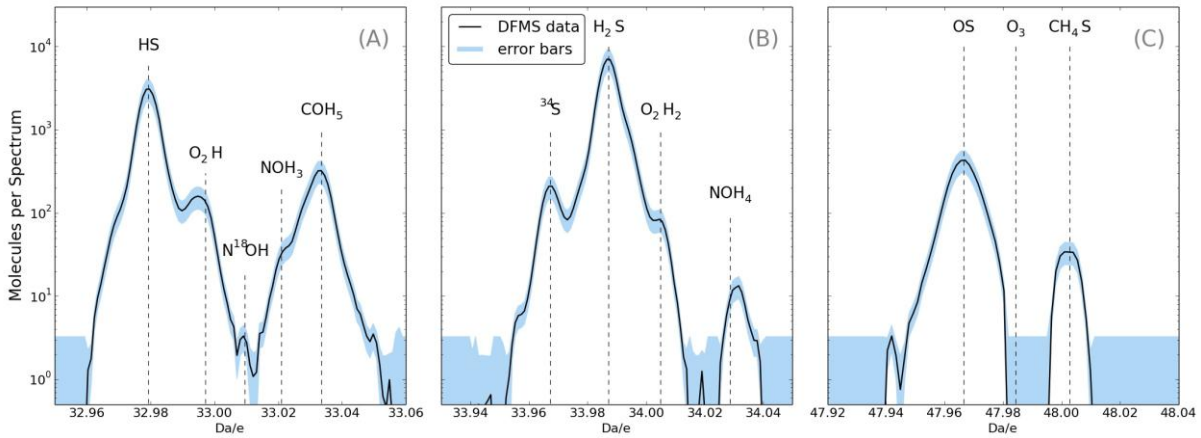


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 258 **Figure 2:** Correlation between O_2 ratio and the H_2O abundance for 5th to 7th of November 2014. Shaded
 259 areas indicate 1 sigma error limits. The O_2 signal in the bottom panel is multiplied by a factor of 15
 260 for visual clarity. The O_2 ratio systematically drops for high H_2O abundances.
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 270 **Figure 3:** O_2 ratio over time. There seems to be no systematic increase or decrease of the O_2 ratio, as the variances can be
 271 explained by Figure 2.
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 279 **Figure 4:** DFMS spectra for some of the common products of radiolysis of water ice; O_2 , O_2H , O_2H_2 and
 280 O_3 . This data was recorded on October 20th at around 01:00 UTC. With the exception of O_3 (see panel C),
 281 all the previously mentioned species are measured and can clearly be identified in the mass spectra of
 282 DFMS. Shaded areas mark 1 sigma error boundaries.

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303 **Methods**

304 **Spacecraft outgassing background**

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307 To clearly identify the measured O₂ as cometary in origin, all non-cometary sources of O₂ must be
308 considered and excluded. The Rosetta spacecraft produces a neutral gas cloud of its own, mainly due to
309 diffusion of volatiles out of spacecraft material and desorption of re-deposited volatiles from the
310 spacecraft. For example, by changing the spacecraft attitude, different components are illuminated by
311 the Sun, which then warm up and release gas. The orange line in Fig. 1 shows the low level signals from
312 this spacecraft contamination for O₂, S, and CH₃OH, referred to as “background”, in measurements taken
313 several days before the encounter with 67P. It is not possible to distinguish this background signal from
314 any potential cometary signature with DFMS, but it has been well characterized prior to the arrival at
315 67P and is usually orders of magnitude lower than the measured O₂ signals⁶. To keep the background
316 influence as low as possible, we only considered mass spectra where both the O₂ and H₂O abundances
317 are at least 10 times larger than the corresponding spacecraft contamination. Another potential source
318 of O₂ is the oxidizer, N₂O₄, used by the Rosetta spacecraft during thruster firings. Measurements taken
319 shortly after a large thruster firing maneuver from June 2014 (still before arrival at the comet) show
320 minor contaminations around 32 Da/e, but not directly affecting the O₂ peak (see green curve in Fig. 1).
321 Although contamination from thruster firings is small, DFMS measurements are usually performed hours
322 after thruster firings, in order to minimize influence thereof. Finally we can exclude the production of O₂
323 inside the instrument through a careful review of all oxygen-bearing molecules up to 150 Da/e, which
324 could potentially fragment into O₂ in the DFMS electron impact ion source. Many minor species contain
325 O₂ but these are too low in abundance to account for the large amount of O₂ detected. The remaining
326 possibility is CO₂, which is very abundant in the coma of 67P². However, due to its chemical structure it
327 only fragments into CO and O, not O₂^[7]. Finally, we exclude the production of O₂ from H₂O in the
328 instrument. For 81 mass spectra taken from May to the end of June 2014 we determine an O₂
329 abundance of (0.18 ± 0.07) % relative to H₂O, which is a factor of 20 lower than the cometary values.

330

331 **Correlation with H₂O**

332 The measured O₂ signal shows a very strong dependence on radial distance (r) from the comet. It
333 increases by roughly one order of magnitude when the radial distance from the comet decreases from 30
334 km to 10 km. This is in agreement with a predicted 1/r² dependence of the number density profile of a
335 non-reactive species. Examining the data further, we observe a strong correlation between H₂O and

336 O₂(see Fig. 2, Pearson correlation coefficient R = 0.91) for data from September 2014 to March 2015.
337 This correlation indicates that O₂ and H₂O are both of a similar cometary origin. In contrast, there is no
338 correlation between O₂ and H₂O for measurements taken before the arrival at the comet (R = -0.01).The
339 observed temporal variations in the O₂/H₂O ratio are largely due to a non-linear correlation between H₂O
340 and O₂ for high water densities. The O₂ ratio drops with increasing H₂O abundance as is indicated in Fig.
341 2. A possible explanation for this is a modification of the ice-dust matrix close to the surface, e.g.
342 sintering or re-deposition of ice grains as surface frost which then is depleted in O₂.The correlation
343 similarly supports the ruling out of CO₂ as a source of the O₂ because Hässig et al.² and Rubin et al.⁸ show
344 a lack of correlation between the abundance of H₂O and other species like CO, CO₂ and N₂.

345

346 Radiolysis

347 The production of O₂ from water ice by radiolysis is the result of several reactions, where initially H, O,
348 and OH are produced, followed by subsequent rearrangement to form H₂, HO₂ and H₂O₂ and ultimately
349 O₂^[10, 11]. These radiolysis products can either be trapped¹² inside voids in the water ice that are also
350 created by radiolysis, or can be scattered or desorbed directly from the surface

351

352 Sputtering

353 O₂ production through surface sputtering: Wurz et al.²¹ show that sputtering of refractory materials from the
354 cometary surface due to the solar wind is occurring now at 67P. This work demonstrates a clear difference
355 between the southern and northern latitudes in the measured abundances of the sputtered species. This
356 apparent spatial difference is explained via the asymmetry of the neutral coma, with higher number densities
357 in the northern hemisphere that is preferentially exposed to the Sun for the time span under study. The solar
358 wind, which is responsible for the sputtering, is therefore attenuated more efficiently by these denser parts of
359 the coma and thus has limited or no access to the surface. We find that the O₂/H₂O ratio is independent of
360 latitude and relatively constant over a period of 7 months. Furthermore, the major part of the top surface of
361 67P accessible by the solar wind does not contain any water ice²². This suggests that sputtering cannot be the
362 main source of the detected molecular oxygen. Moreover, the sputter yields by solar wind ions are orders of
363 magnitude too low to explain the observed amount of O₂.

364

365 Recent radiolysis

366 O₂ production after the comet formed: Zheng et al.²⁵ argue that Kuiper belt objects, such as 67P, subject to
367 radiolysis, reach an equilibrium abundance of O₂ and H₂O in the surface ice layer after some 10⁵ years, leading
368 to a relative abundance of O₂/H₂O of about 0.6%.Once these objects enter the inner Solar System they lose
369 (due to their activity and depending on their perihelion distance) material from the surface in the range of
370 several meters per orbit around the Sun. Therefore, as most products built up during the stay in the Kuiper
371 belt reside in the outer few meters, these should be released quickly on the first solar passages. A study by
372 Maquet²⁶ shows that 67P's perihelion distance was within the orbit of Jupiter for the last 250 years, possibly
373 even for more than 5000 years. Since a close encounter with Jupiter in 1959, the perihelion distance of 67P
374 has been about 1.3 AU with an orbital period of 6.4 years. Accumulated over the last perihelion passages we
375 can assume that 67P has lost hundreds of meters from its surface. Although Galactic Cosmic Rays with
376 energies well above 1 GeV can penetrate down to depths of hundreds of meters, the amount of O₂ that can
377 be produced by GCR-induced radiolysis appears to be at least several orders of magnitude too small if one
378 assumes that the present-day high-energy GCR flux represents the average flux over the history of the Solar
379 System. There are also uncertainties on the cross-sections, the relative proportion of high-Z cosmic rays, and
380 the role of porosity and defects in the cometary ice^{21, 27}. Overall, it appears unlikely that most of the O₂ in 67P
381 is of evolutionary origin.