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Origin of Molecular Oxygen in Comets: Current Knowledge and Perspectives

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Abstract The Rosetta Orbiter Spectrometer for Ion and Neutral Analysis (ROSINA) instrument onboard the Rosetta spacecraft has measured molecular oxygen (O_2) in the coma of comet 67P/Churyumov-Gerasimenko (67P/C-G) in surprisingly high abundances. These measurements mark the first unequivocal detection of O_2 in a cometary environment. The large relative abundance of O_2 in 67P/C-G despite its high reactivity and low interstellar abundance poses a puzzle for its origin in comet 67P/C-G, and potentially other comets. Since its detection, there have been a number of hypotheses put forward to explain the production and origin of O_2 in the comet. These hypotheses cover a wide range of possibilities from various in situ production mechanisms to protosolar nebula and primordial origins. Here, we review the O_2 formation mechanisms from the literature, and provide a comprehensive summary of the current state of knowledge of the sources and origin of cometary O_2.

Keywords Molecular oxygen · Comets · Radiolysis · Ice · Astrobiology

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Ices in the Solar System
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1 Introduction

While atomic oxygen is the third most abundant element in the Universe, its molecular form, O_2, has been particularly elusive to observers in various astrophysical environments. O_2 is expected to be present in the interstellar medium (ISM) in both its solid (ice) and gas phases. However, O_2 is a highly chemically reactive molecule with no electric dipole moment, which makes it hard to detect. Indeed, solid O_2 is yet to be detected in interstellar grains or in protoplanetary disks, and gas-phase O_2 has only been observed in two interstellar clouds with very low concentrations relative to H_2 (Orion: $O_2/H_2 \approx 0.3\text{–}7.3 \times 10^{-6}$, and ρ Oph A: $O_2/H_2 \approx 5 \times 10^{-8}$; see e.g. Goldsmith et al. 2011; Chen et al. 2014; Larsson et al. 2007; Liseau et al. 2012). In the Solar System, O_2 has been detected on the icy moons of Jupiter and Saturn, where it is produced via photolysis and radiolysis followed by sputtering (e.g. Hall et al. 1995; Johnson 1996; Johnson and Quickenden 1997; Johnson and Jesser 1997; Cruikshank et al. 1998; Johnson et al. 2006; Bahr et al. 2001; Teolis et al. 2010), and from energetic particles accelerated in their magnetospheres (e.g. Spencer et al. 1995; Noll et al. 1997; Sieger et al. 1998). O_2 is also present in trace amounts in the atmosphere of Mars, and results from the complex photochemistry taking place in these environments (Barker 1972). Meanwhile, O_2 is the second most abundant atmospheric component at about 21% by volume in Earth's atmosphere, but it is the only known planetary environment in which O_2 is biologically produced.

Before the *Rosetta mission*, comets in general seemed to be oxygen poor, which was expected based on the generally low levels of O_2 observed in interstellar and protoplanetary environments, and its high reactivity. However, with the unprecedented capabilities of the European Space Agency's *Rosetta* mission came unprecedented discoveries. One of *Rosetta*'s most perplexing findings was the persistent detection of O_2 in the coma of comet 67P/Churyumov-Gerasimenko (hereafter: 67P/C-G) in surprisingly high abundances. These measurements were made by the Double Focusing Mass Spectrometer of the Rosetta Orbiter Spectrometer for Ion and Neutral Analysis (ROSINA/DFMS; Balsiger et al. 2007), and marked the first ever unequivocal detection of O_2 in a cometary environment. ROSINA/DFMS measured an O_2 concentration of 1–10% relative to water in the coma of 67P/C-G, with a mean value of $3.80 \pm 0.85\%$ (Bieler et al. 2015). The presence of O_2 in the coma of 67P/C-G was later independently confirmed by the Alice imaging spectrograph onboard *Rosetta*, with a somewhat larger mean relative column abundance of 25% (Keeney et al. 2017a). In addition, the recent reevaluation of the Neutral Mass Spectrometer (NMS) measurements from the *Giotto* flyby yielded data consistent with O_2 in the coma of comet 1P/Halley, with concentrations similar to those detected in the coma of 67P/C-G (Rubin et al. 2015b). Thus, the presence of cometary O_2 may not be unique to 67P/C-G, but rather it may be a common attribute of the otherwise dynamically different Jupiter-family (e.g. 67P/C-G) and Oort Cloud (e.g. 1P/Halley) comets.

The first ROSINA/DFMS measurements of O_2 in the coma of 67P/C-G were made over a six-month period between September 2014 and March 2015 at 10–30 km from the nucleus (Bieler et al. 2015). The measured local O_2 abundance relative to H_2O was persistently high over this period with a mean value of $3.80 \pm 0.85\%$, making O_2 the fourth most abundant species in the coma after H_2O, CO_2, and CO. Over this six-month time interval, O_2 was found to strongly correlate with H_2O, which led to the conclusion that the origin and/or release mechanism of O_2 and H_2O are linked. In addition, the analysis of Bieler et al. (2015) suggested that the O_2/H_2O ratio in the coma of 67P/C-G remained fairly constant, with a scatter of less than about 10%. Fougere et al. (2016) showed that the strong correlation with H_2O extended through February, 2016. Their modeling results also provided an O_2/H_2O production rate of 1–2%. While ROSINA/DFMS did not detect O_3 (ozone), it did measure the chemically related species H_2O_2 (hydrogen peroxide) and HO_2 (hydroperoxyl) with relative abundances of $H_2O_2/O_2 \approx HO_2/O_2 \approx 6 \times 10^{-4}$ (Bieler et al. 2015).

The remarkably high concentration of gaseous cometary O_2 contrasts with the remarkably low O_2 concentrations across the Universe. Because comets are leftover planetesimals whose accretion and growth took place in the protosolar nebula (PSN), they contain some of the best-preserved materials from before and during planet formation. Cometary nuclei likely agglomerated either from minimally-altered icy grains formed in the ISM, or from more processed grains directly condensed in the PSN. Hence, comets are often thought of as "cosmic freezers". Whether O_2 is present in all or a multitude of comets, in just a few, or in 67P/C-G only, the production mechanism and origin of cometary O_2 would provide crucial information about the formation of our Solar System, and for interstellar-, disk-chemistry, and astrochemical models. Since its first detection in 67P/C-G, several hypotheses have emerged for the production and origin of cometary O_2. These hypotheses cover a wide range of possibilities from *in situ* production mechanisms to various primordial or protosolar nebula origins. The proposed formation mechanisms of cometary O_2 existing in the current literature are shown in Fig. 1.

One possibility for the presence of molecular oxygen in the coma of 67P/C-G is that it was present before comet formation. In that case, the nucleus would have been agglomerated from O_2-rich icy grains formed in the ISM that did not undergo further chemical modification before and after being incorporated into the nucleus (primordial origin). If cometary O_2 is primordial, then the comet would have agglomerated in the coldest regions of the disk, where chemical reactions may be slow enough to preserve O_2 in cometary nuclei. Possible production mechanisms for primordial O_2 in interstellar ices include the radiolysis of H_2O ice by galactic cosmic rays (GCRs) in a low-density environment, such as a molecular cloud (Mousis et al. 2016b). Radiolysis of icy grains requires very large GCR fluxes, but the irradiation itself would stabilize the O_2 formed by the development of cavities in the H_2O ice matrix, where the O_2 molecules get trapped. Alternatively, oxygen atom recombination on the surfaces of interstellar grains in warm ($\sim$ 20–30 K) and dense ($\geq 10^5$ cm^{-3}) dark clouds could produce O_2 in the observed abundances (Taquet et al. 2016). The latter scenario requires warmer and denser conditions than typically found in dense clouds, but is in good agreement with the physical conditions in ρ Oph A, as noted in Taquet et al. (2016). Both of these primordial scenarios require an intimate relationship between O_2 and H_2O; thus explaining the strong observed correlation between O_2 and H_2O. These observations must be taken in conjunction with other measurements pertaining to the origins of cometary H_2O. For instance, the elevated D/H ratio observed at 67P/C-G pre-inbound equinox (Altwegg et al. 2015) would be another constraint on the (primordial) formation scenario of 67P/C-G's ice.

Gaseous O_2 could have also been formed and incorporated into icy grains in the PSN before being agglomerated into the nucleus. Luminosity outbursts (Taquet et al. 2016) or accretion bursts (Bieler et al. 2015) could have increased the temperature to exceed 100 K, aiding the formation of gas-phase O_2. Subsequent rapid cooling would then be needed to trap the O_2 in amorphous icy grains. In this case though, CO and N_2 (and other volatiles) should also be trapped in amorphous ice and correlate with H_2O, which was not the case for observations over a six-month period by Bieler et al. (2015). O_2 also readily traps in clathrates, but in that case it would be expected to strongly correlate with CO and even CO_2 instead of H_2O (Mousis et al. 2016b). In addition, O_2 may form crystalline ice in the PSN, but that would make the N_2 and Ar depletion problematic in 67P/C-G compared to the protosolar values (Mousis et al. 2016b). However, O_2 embedded in interstellar icy grains may remain stable even during a phase transition upon heating in the disk. While CO, Ar,

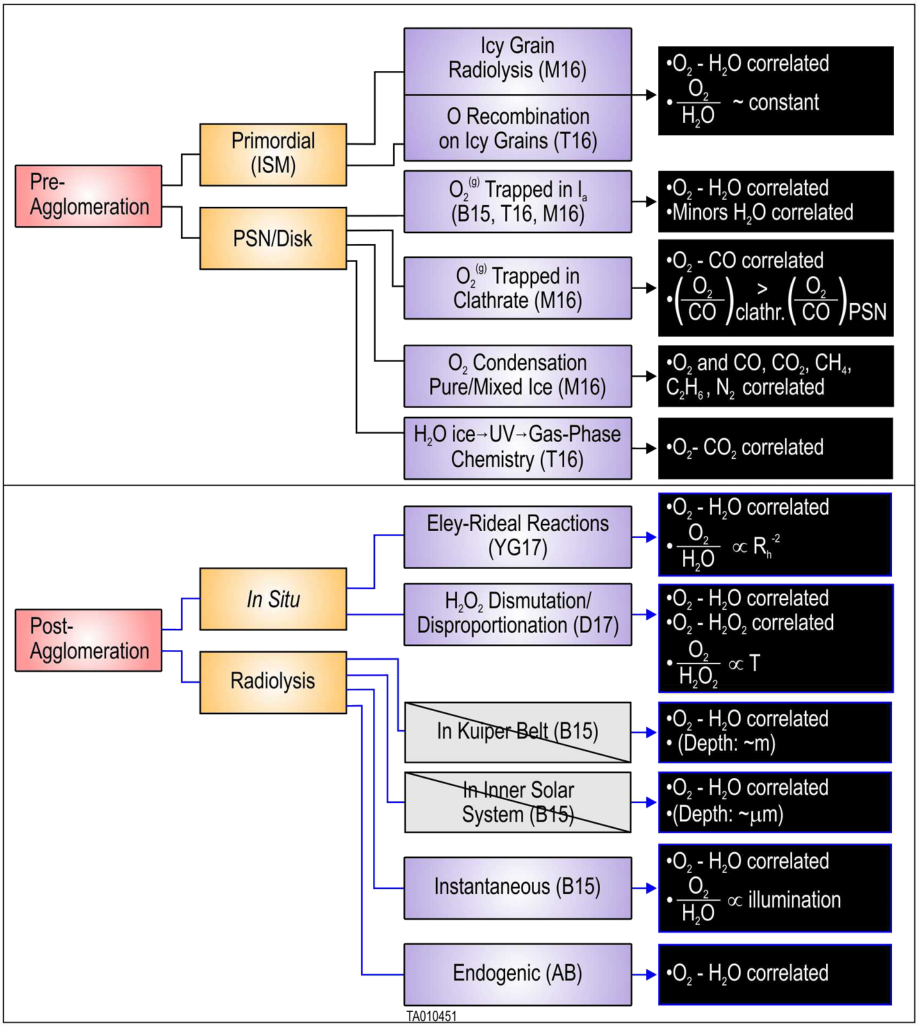

Fig. 1 Proposed explanations for the origin (red and orange), formation mechanisms (purple), and trapping mechanisms (blue) of O_2 from the literature. Implications of the different scenarios to the ROSINA data, i.e. key measurements required to validate the different approaches, are listed in the black boxes. Formation mechanisms in the gray boxes are highly unlikely because of the affected layers would have been removed by erosion since 67P/C-G entered the inner Solar System. References: M16: Mousis et al. (2016b), T16: Taquet et al. (2016), B15: Bieler et al. (2015), M18: Mousis et al. (2018), YG17: Yao and Giapis (2017), D17: Dulieu et al. (2017), AB: Bouquet et al. (2018)

and N_2 would get trapped in clathrates from the gas phase as the disk cools, O_2 would remain trapped from its initial incorporation into the H_2O matrix, maintaining its close association with H_2O (Mousis et al. 2016b). O_2 with an adsorption energy of 1660 K (8.6 kJ/mol) (Laufer et al. 2018; Smith et al. 2015) would be more strongly attached to the ice than N_2 (adsorption energy of 1155 K or 7.2 kJ/mol; Laufer et al. 2018; Smith et al. 2015) and CO (adsorption energy of 1420 K or 7.6 kJ/mol; Laufer et al. 2018; Smith et al. 2015). Ar, with an adsorption energy of 866 K or 7.5 kJ/mol (Laufer et al. 2018; Smith et al. 2015), is even more volatile. PSN formation scenarios do not necessarily require a strong correlation with H_2O, but require a correlation with CO, CO_2, and/or N_2 (Fig. 1). Most recently, Mousis et al. (2018) proposed that an alternative mechanism for O_2 formation is radiolysis of icy grains being cycled between the mid-plane and the upper layers of the disk multiple times. While this turbulent mixing would have allowed the icy grains to undergo stronger GCR irradiation while in the upper layers of the disk, and would explain a strong correlation between O_2 and H_2O, as they point out the timescale needed to make the O_2 in the abundances observed by ROSINA/DFMS exceeds the formation timescale of the comet.

O_2 may have also formed after nucleus accretion, either via radiolysis, or *in situ*. Past radiolysis in the Kuiper-belt seems unlikely to be the main source of O_2 on the comet because the affected layers would be removed by erosion since 67P/C-G entered the inner solar system, and current radiolysis would be indicated by variable O_2/H_2O driven by illumination (Bieler et al. 2015). However, endogenic radiolysis may contribute to the observed O_2 in the coma of 67P. In this scenario, radiation chemistry from an endogenic source, such as decaying radionuclides would produce O_2 homogeneously in the ice of the nucleus. While endogenic radiolysis is unlikely to have produced all the observed O_2 today, it may have significantly contributed to it (Bouquet et al. 2018). *In situ* O_2 formation is possible via water-group ions accelerated by the solar wind and energetic electrons hitting various oxidized surfaces and triggering Eley-Rideal (ER) reactions (Yao and Giapis 2017). Thus, O_2 may be formed on the surface of the nucleus, spacecraft, or the ROSINA/DFMS instrument itself (hyperthermal surface ionization). On the other hand, O_2 formation via the dismutation/disproportionation of H_2O_2 co-sublimating with H_2O was proposed based on laboratory experiments (Dulieu et al. 2017). The ER and the H_2O_2 dismutation/disproportionation reactions, as well as endogenic radiolysis require a strong correlation with H_2O at all times.

This paper reviews the possible O_2 formation mechanisms, as we currently understand them, and evaluates their strengths, weaknesses, and limitations based on the currently available, published *Rosetta* measurements. Sections 2 and 3 provide detailed reviews of pre-agglomeration and post-agglomeration O_2 formation mechanisms from the literature. A comprehensive summary of the current state of knowledge, as well as conclusions are given in Sect. 4. Finally, we suggest future key measurements and data analysis for a deeper understanding of the origin of cometary O_2.

2 Pre-agglomeration Formation and Trapping Scenarios

This section discusses the possibility of O_2 formation in the icy grains precursors of comets. Different scenarios of O_2 formation, proposed both in the ISM and in the PSN, are reviewed.

2.1 O_2 Formation in the ISM

As detailed below, the formation of O_2 can take place in the ISM in dark clouds either through surface reactions on interstellar grains, or via radiolysis and/or photolysis of icy grains.

2.1.1 Exogenic Radiolysis and O_2 Trapping in Icy Grains

Among the possibilities considered, the radiolysis of cometary water ice has attracted significant attention. A first scenario linking the production of O_2 to the ice of the comet nucleus

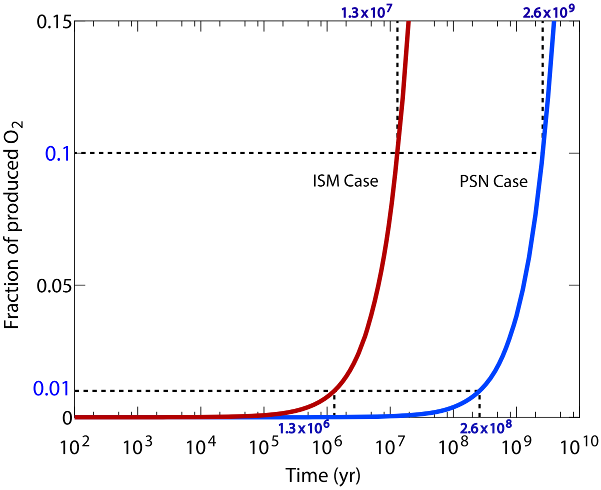

Fig. 2 Time evolution of the fraction of O_2 molecules produced by cosmic rays in icy grains located in various environments (derived from Mousis et al. 2016b). The PSN case (blue curve) considers the irradiation of an icy grain placed at 30 AU in the PSN midplane. The ISM case (red curve) considers the irradiation of an icy grain located in the interstellar medium

was proposed (Bieler et al. 2015). These authors estimated, considering 67P/C-G's thermal history, that any quantity of O_2 formed prior to approach at closer distances to the Sun should have been lost due to outgassing and/or erosion rapidly during the first one or two orbits around the Sun. It was therefore suggested that O_2 must have already been incorporated into 67P/C-G at the time of its formation in the PSN (Mousis et al. 2016b). In this context, radiolysis by Cosmic Ray Flux (CRF) is able to deposit large enough energy doses that create latent tracks in the bulk ice in which O_2 can be formed from the fragments H, O, OH issued from the radiolysis.

The possibility of radiolytic production of O_2 in micron to millimeter-sized icy grains present either in the outer PSN or in the ISM has been investigated by Mousis et al. (2016b). In both cases, the energy available for radiolysis was assumed to be provided by the galactic CRF impacting icy grains. The authors used the energy range and CRF distribution from Yeghikyan (2011) and Cooper et al. (2003) for their calculations, respectively. They also assumed that O_2 is produced by radiolysis of water ice through the chemical reaction

$$2H_2O \longrightarrow 2H_2 + O_2, \tag{1}$$

with an amount of energy needed to alter one H_2O molecule $W_r = 235$ eV (Johnson 1991). Furthermore, the authors assumed that all the energy absorbed by water ice is used to form O_2. Under those circumstances, the time τ needed to reach a given O_2/H_2O ratio in icy grains has been established as follows:

$$\tau = \frac{W_r \cdot N_A}{E_{CR} \cdot M_{H_2O}} \times f_{H_2O} \tag{2}$$

where N_A (mol^{-1}) is the Avogadro constant, M_{H_2O} ($\mathrm{kg\,mol}^{-1}$) is the molar mass of water, E_{CR} ($\mathrm{eV\,kg}^{-1}\,\mathrm{yr}^{-1}$) is the CRF energy dose received by water ice, which depends on the gas number density, and f_{H_2O} is the fraction of altered H_2O molecules, corresponding to two times the fraction of O_2 produced. Figure 2 summarizes the results of the calculations presented by Mousis et al. (2016b) and shows that the timescales needed to produce an O_2 fraction in the 1–10% range in icy grains lying at 30 AU in the PSN midplane are much longer than the lifetime of the PSN ($\sim$ 0.25–2.5 Gyr vs. a few Myr). The CRF energy dose absorbed by icy grains located at this distance from the Sun is within the $\sim (5\text{–}60) \times 10^{16}$ eV kg^{-1} yr^{-1} range, depending on the disk's surface density (between 10 and 10^3 g cm^{-2}; Hersant et al. 2001). We note that the distance of 30 AU was intended as a figure of merit representing the outer part of the disk in Mousis et al. (2016b). It does not quite correspond with where the outermost planets formed because our solar system was more compact, and then relaxed to the current configuration. However, the disk surface density is constant to a good approximation, and so the production rate from GCRs should not vary much inward. Any variation would not be enough to change the conclusion that the production timescale of O_2 in the observed relative abundances is longer than the age of the disk.

Mousis et al. (2016b) also considered the case in which the CRF has supposedly undergone a significant enhancement by a factor of ~ 100 because of a close supernova explosion. Because these events are too brief ($\sim$ a few kyr), such enhancements cannot significantly decrease the time needed to form O_2 in the PSN midplane. Meanwhile, if icy grains have grown to sizes larger than tens of meters in the PSN, then the deepest layers would be more difficult to alter, requiring longer timescales for efficient O_2 formation. Mousis et al. (2016b) also considered the possibility of an icy grain receiving the maximum CRF energy dose estimated by Yeghikyan (2011) ($\sim 1.20 \times 10^{20}$ eV kg^{-1} yr^{-1}), a value corresponding to a surface density of 10^{-3} g cm^{-2}, which is typical of those found in molecular clouds. The authors determined that only $\sim$ 1.3–13 Myr of radiolysis was needed to generate an O_2 fraction in the 1–10% range in icy grains located in environments with such low column densities (see Fig. 2).

Mousis et al. (2016b) considered the radiolysis to be effective because of the different diffusion between the products of the radiolysis reaction. At temperatures encountered in the ISM or the PSN, the diffusion of O_2 in water ice is greatly reduced, which is not the case for H_2 (Johnson 1991). This difference in diffusion disfavors further reactions between O_2 and H_2, and helps to preserve O_2 in the ice. Given this assumption about the effectiveness of the radiolysis, the first consequence of the CRF irradiation of the ice mantles is the creation of latent tracks, i.e. channels void of H_2O molecules but filled with their fragments. These fragments participate in the reconstruction of the ice bulk by forming H_2O molecules (Eq. (3)) which close the open tracks. By doing so, they create cavities playing the role of confinement volumes in which O_2 could be formed by the coupling of two oxygen atoms. Reconstruction can obviously come from the successive addition of two atomic hydrogen to the oxygen atom. However, radiolysis of H_2O ice may create molecules other than H_2 and O_2. The OH radical is produced via the reaction $H_2O \rightarrow H + OH$ (Johnson 1991), which was not considered by Mousis et al. (2016b). The presence of the OH radical opens new chemical routes:

$$OH + OH \rightarrow H_2O + O, \tag{3}$$

$$OH + OH \rightarrow H_2O_2, \tag{4}$$

$$OH + O \rightarrow HO_2 \tag{5}$$

that can be followed by the formation of O_2 according to

$$H_2O_2 + OH \rightarrow HO_2 + H_2O \tag{6}$$

$$H_2O_2 + O \rightarrow HO_2 + OH \tag{7}$$

$$HO_2 + OH \rightarrow O_2 + H_2O \tag{8}$$

The confinement in the cavities makes all these processes possible. The question is how can O_2 survive in these voids? To address this issue, Mousis et al. (2016b) investigated the

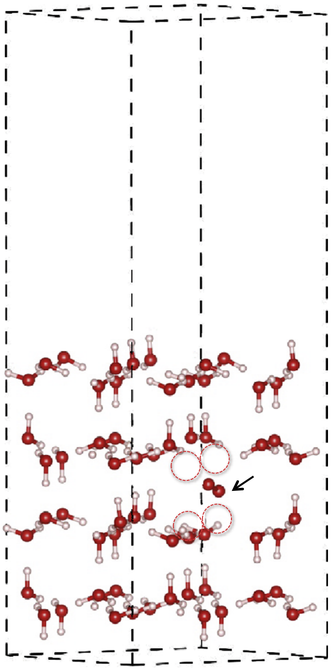

Fig. 3 Optimized crystalline structure for O_2 trapped inside the cavity ($n = 4$). The dashed lines show the unit cell considered in the VASP simulation. A vacuum of 15 Å high is used over the topmost H_2O bi-layer to avoid spurious interactions between adjacent slabs in the periodic treatment. The initial positions of destroyed H_2O are illustrated by the dotted circles. The arrow points to the embedded O_2 molecule

question of the stability of the radiolytically produced O_2 molecules in the water matrix of ice grains. To do so, a sampling of the representative structures of O_2 in solid water ice has been obtained using a strategy based on first principle periodic density functional theory quantum calculations (Lattelais et al. 2011, 2015; Ellinger et al. 2015). These calculations, performed in the case of hexagonal ice *Ih* using the Vienna ab initio simulation package (VASP) (Kresse and Hafner 1993, 1994), show that when 2, 3, or 4 adjacent H_2O molecules were removed from the hexagonal lattice, well defined cavities form with shapes depending on the positions of the dismissed entities. The stabilization energies of the embedded O_2 were found to be in the order of 0.2–0.5 eV, namely the energy between water dimer stabilization and ice cohesion energies. This implies that the presence of O_2 does not perturb the ice structure until its further ejection due to sublimation or abrasion. A typical example of O_2 trapping is illustrated in the case of 4 removed H_2O molecules in Fig. 3. Similar results have been obtained in the case of O_2 stabilization in amorphous ice.

Based on all these considerations, Mousis et al. (2016b) concluded that, even with a strong CRF enhancement due to the presence of a nearby supernova, the radiolysis of icy grains is not fast enough in the PSN to create amounts of O_2 comparable with those observed in 67P/C-G. Instead, they showed that icy grains must be placed in low-density environments such as molecular clouds to enable radiolysis to work efficiently. They also found that the irradiation process favors the stabilization of O_2 molecules in the icy matrix via the development of cavities and is compatible with both amorphous and crystalline ice structures. From this set of constraints, two possible formation scenarios of 67P/C-G in the PSN have been derived by the authors: (1) agglomeration from pristine amorphous icy grains/particles formed in the ISM and (2) agglomeration from multiple guest clathrates including O_2 that formed during the cooling of the disk subsequent to the vaporization of the amorphous icy grains entering the PSN (see Sect. 2.3.2). With the incorporation of O_2 in the cavities created by CRF in the icy matrix, scenario 1 naturally provides an explanation for the strong correlation found between the O_2 and H_2O production rates observed in 67P/C-G's coma (Bieler et al. 2015). However this scenario makes implausible the accretion of 67P/C-G from clathrates and crystalline ices originating from the PSN, as proposed by Mousis et al. (2016a) and Lunine et al. (1991a). A way to reconcile scenario 2 with the strong O_2-H_2O correlation would be to assume that the icy grains (i) initially formed as in scenario 1 and (ii) subsequently experienced an amorphous-to-crystalline phase transition in the 130–150 K temperature range when entering the disk (Kouchi et al. 1994; Maldoni et al. 2003; Ciesla 2014). In this context, all volatiles initially adsorbed by ISM amorphous ice would be released in the PSN gas phase during phase transition. With the cooling of the disk, these volatiles would have been later trapped in the clathrates formed with the crystallized icy grains. O_2 is unique because, in spite of the ice phase transition, this molecule would remain stable within the icy matrix thanks to the strength of the interaction between O_2 and the surrounding H_2O molecules that would remain stable, or eventually increase, upon crystallization.

The exogenous radiolysis scenario makes it possible to rationalize also why H_2O_2 and HO_2 are detected only in very low abundances in 67P/C-G, and O_3 not detected at all. These chemically-related species are formed during radiolysis and are effectively present into the cavities of the cometary ice. Our calculations show that all the oxygenated actors, i.e. H_2O_2, the corresponding radical HO_2, atomic oxygen O, and the OH radical are stabilized within the ice matrix with comparable energies, close to the stabilization energy of water. Due to the confinement situation, the cavity appears as a chemical reactor in which H_2O_2 and HO_2 are converted into O_2 (see reaction network above). It is the formation of O_2 which is at the origin of the failure to observe the reactants leading to its formation. As to O_3, it is so reactive that it will be destroyed by any radical formed in the radiolysis.

2.1.2 Recombination of Oxygen Atoms on the Surfaces of Interstellar Icy Grains

Gas-phase chemistry is not sufficient to account for the observed abundance of interstellar molecules because of the inefficiencies of gas phase routes. Grain-surface chemistry is thus required to explain the observed abundances of water and other molecules, like H_2 or O_2 in molecular clouds (Tielens and Hagen 1982; D'Hendecourt et al. 1985; Hasegawa et al. 1992). Surface O_2 is involved in the chemistry reaction network of water ice (Tielens and Hagen 1982; Cuppen and Herbst 2007), and forms through the recombination of atomic oxygen on icy grain surfaces.

The formation of O_2 in the ISM in dark clouds can take place either through surface reactions on interstellar grains, or via radiolysis and/or photolysis of ice grains. In the case of surface reactions, O_2 is formed through the recombination of atomic oxygen on icy grain surfaces. O_2 efficiently reacts with O to form O_3, and H to form HO_2. The hydrogenation of O_3 is the main destruction process of O_3 and leads to the formation of O_2 along with HO (Mokrane et al. 2009). Formation of O_2 through radiolysis or photolysis takes place when energetic particles and UV photons break bonds triggering chemistry within the icy mantle of the grains, which could possibly lead to the formation of O_2. However, this process seems unlikely for several reasons. First, although UV photolysis produces O atoms that may recombine to form O_2, it also produces H atoms which react with O_2 to reform H_2O. Second, laboratory experiments show that if radiolysis does not occur when water is condensing onto the grain surface, then water radiolysis overproduces H_2O_2 while producing O_2 (Teolis et al. 2006).

Taquet et al. (2016) conducted a parameter study in their astrochemical model to evaluate the formation of O_2 in dark clouds. They varied several chemical and physical parameters with the aim of reproducing the relative abundances of related species (H_2O, H_2O_2, HO_2

and O_3) with respect to O_2 observed in 67P/C-G. The authors were able to reproduce the O_3/O_2 and HO_2/O_2 abundance ratios by introducing an activation barrier of ~ 300 K for the $O + O_2$ and $H + O_2$ reactions. However, under those conditions, H_2O_2 is overproduced by one order of magnitude compared to the observations, suggesting that other chemical processes are at play. In their simulations, Taquet et al. (2016) were only able to reproduce high O_2 abundances, comparable to those measured for 67P/C-G and when the density of H nuclei in the gas phase was very high ($\geq 10^5$ cm^{-3}). Simulations using intermediate temperatures, ~ 20 K, and low cosmic ray flux also favored the formation and survival of O_2, with only a weak impact from visual extinctions. The temperature of ~ 20 K enhances the mobility of oxygen atoms on the surface of the grain, which favors oxygen recombination forming O_2. At the same time, it allows efficient sublimation of atomic hydrogen, limiting the impact of hydrogenation reactions that destroy O_2. The results presented by Taquet et al. (2016) suggest that the physical conditions of ρ Oph A, where Hershel observations revealed the presence of O_2, HO_2 and H_2O_2 gases in proportions consistent with the observations at 67P/C-G, is a favorable environment for the formation and survival of O_2 because of its high density ($\sim 10^6$ cm^{-3}) and warm temperature for a starless core (dust temperature of ~ 20 K). Furthermore, Taquet et al. (2016) showed that O_2 is mostly formed in the innermost layers of the icy mantles and that it is well preserved during the formation of the protoplanetary disk. Contrary to O_2, CO and N_2 mostly form in the outermost layers of the icy mantle. Taquet et al. (2017) detail the impact of layering of the icy mantle during the transition from dark cloud to protoplanetary disk and its consequences to the volatile content of cometary ices. The outer layers of the icy grains are more likely to evaporate in the outer layer of the protoplanetary disk releasing N_2 and CO in the gas phase, while the inner ice layers where most of the O_2 would be trapped remains frozen. N_2 and CO can subsequently freeze out onto ices again once they reach the colder disk mid-plane. As CO is slightly less volatile than N_2, it freezes out more efficiently than N_2, which leads to a low N_2/CO abundance, in agreement with observations made at 67P/C-G (Rubin et al. 2015a). Furthermore, as refreezing is independent of the amount of H_2O in the icy mantle, this would also explain the low correlation of N_2 and CO with H_2O in cometary ices. On the other hand, the inner layer, where most of the O_2 is thought to be trapped in H_2O ice, remains unprocessed, which explains the good correlation between O_2 and H_2O reported by Bieler et al. (2015). The preservation of the inner layers of the icy grain mantles from the dark cloud stage until their incorporation into cometary nuclei is supported by the observation of a distributed source of halogens in the coma of 67P/C-G (Dhooghe et al. 2017). Thus, the scenario of O_2 production and the subsequent evolution of ice during the transition from dark cloud to protoplanetary disk discussed in Taquet et al. (2016) and Taquet et al. (2017) is consistent with observations of other volatiles (such as N_2 and CO) made at 67P/C-G.

2.2 O_2 Formation in the PSN

2.2.1 During Protosolar Collapse/Protoplanetary Disk Formation

Formation of O_2 during protostellar collapse and protoplanetary disk formation was evaluated by Taquet et al. (2016) using an astrochemical model for gas grain chemistry (Furuya et al. 2016). A fluid approach is used to describe the physical evolution of the cloud during its collapse and during the formation of an accretion disk described by the α-viscosity prescription. The fluid parcels are traced with the 2D axisymmetric and semi-analytical model initially developed by Visser et al. (2009). The initial composition of the gas and solid phase of the parent cloud was obtained from a molecular cloud model (Furuya et al. 2015) in

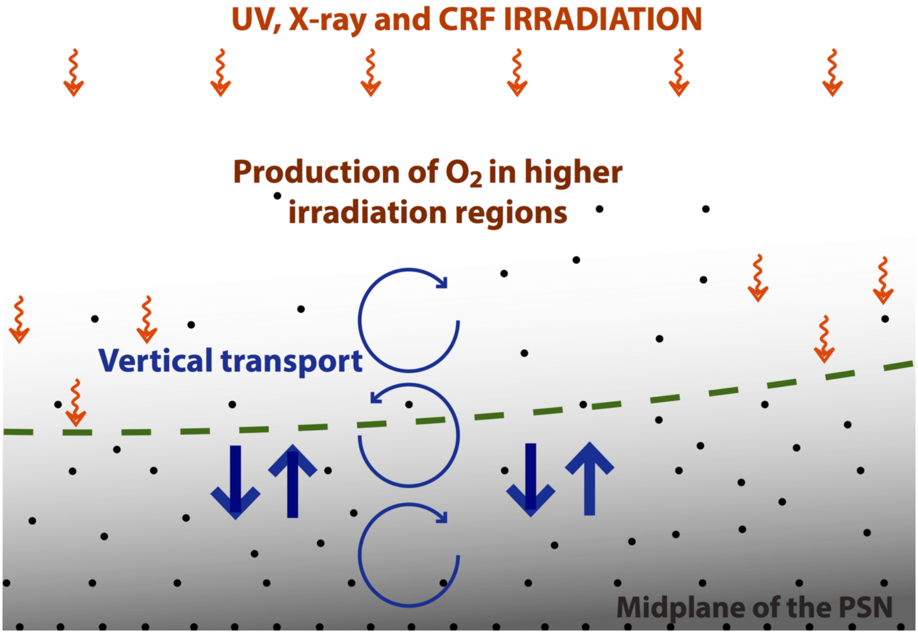

Fig. 4 Illustration of the vertical transport of small icy grains toward disk regions where irradiation is strong and favors the formation of O_2 (figure adapted from Mousis et al. 2018). Grains remain concentrated in the midplane of the disk because of gravitational settling and gas drag

which the amount of O_2 ice is negligible at the onset of the collapse. The authors found that some gaseous O_2 can form (up to $10^{-6}H_2$), but that O_2 trapped in H_2O ice does not form efficiently. Because most of the O-bearing species are in the ices at the onset of the collapse, gaseous O_2 can only form through photodissociation or desorption of H_2O by stellar UV followed by subsequent gas phase reactions. In their simulations, this formation process failed to reproduce the observations of O_2 made in 67P/C-G. They found that the O_2/H_2O ratio in the ice was several orders of magnitude lower, except for a few parcels of the upper layers of the disk where it is higher than 10^{-2}. They also found that O_2 was associated with CO_2 rather than with H_2O because CO_2 ice reformation was more favorable than H_2O reformation.

Taquet et al. (2016) ran another simulation where they modified the initial conditions in order to have a O_2/H_2O ratio of 5% in the ice, comparable to the ratio in 67P/C-G, at the beginning of the collapse. This simulation shows that this ratio is largely preserved, indicating that O_2 produced in an earlier stage, for instance at the molecular cloud stage, would be preserved during the formation of the protoplanetary disk.

2.2.2 During the Vertical Transport of Icy Grains

The O_2 formation in icy grains irradiated during their transport towards the upper layers of the PSN has been investigated by Mousis et al. (2018). In this scenario, the icy grains present in the midplane were lifted toward the upper layers of the disk and dragged down over a large number of cycles, due to turbulent mixing (see Fig. 4). Consequently, these grains spent a non-negligible fraction of their lifetime in the disk's upper regions, where CRF irradiation was stronger than in the PSN midplane.

The computations performed by Mousis et al. (2018) suggest that, even if a significant fraction of the icy particles have followed a back and forth cycle towards the upper layers of the disk over 10 million of years in a static PSN, the amount of O_2 created via radiolysis is at least $\sim$ two orders of magnitude lower than the Rosetta observations, making the proposed mechanism completely negligible if at play. This timespan exceeds by far the formation timescale of 67P/C-G, which has been estimated to range between 2.2 and 7.7 Myr after the formation of Ca-Al-rich inclusions in the PSN (Mousis et al. 2017). They also found that an increase of the CRF up to a factor of $\sim$100 due to a close supernova explosion would not substantially change the O_2/H_2O ratio in icy grains because the timespan of such an event (a few kyr) is too short (Mousis et al. 2016b).

2.3 Different O_2 Trapping Scenarios

2.3.1 Trapping in Amorphous Ice in the PSN Prior to Comet Formation

If O_2 were produced in the molecular cloud prior to the formation of the protosolar nebula itself, might it have been trapped in grains and delivered to the protosolar nebula as the latter formed? Trapping and transport of the pre-nebular molecular oxygen in grains that reach the comet-forming zone in the protosolar nebula is a more complex problem, given the range of environments and the time dependence of processes delivering grains to the disk, along with possible modification of grains as they enter the disk (e.g., Lunine et al. 1991b).

Hence, Taquet et al. (2016) invoke the variable luminosity of low mass stars to construct a scenario in which luminosity outbursts sublimate ice from grains, allowing O_2 to be produced by gas phase cosmic ray energized chemistry, and then frozen out into grains of amorphous ice formed as the stellar luminosity tails off quickly. A series of such luminosity excursions could lead to the production and trapping of O_2 in ice grains directly within the planet-forming disk. However, they discard this disk-origin model for O_2 because, they argue, other species such as N_2 would become trapped with the O_2, which is not consistent with the observed depletion and lack of correlation with H_2O in 67P/C-G, in contrast with O_2's strong correlation (N_2 should be more poorly trapped in amorphous ice than O_2, since the measured binding energy for adsorption of N_2 is about 2/3 that of O_2 (see Introduction), though the key here is the difference in correlation with H_2O). Another concern, not raised by Taquet et al. (2016), is whether the luminosity fall-off and cooling are fast enough to form the amorphous ice required to trap the molecular oxygen.

Taquet et al. (2016) favor a dark cloud site, outside of and perhaps prior to the protosolar nebula, for the chemical production of O_2 from H_2O. Although consistent with the cometary data, the consequent complexities of delivery to the disk including the potential for removal of the O_2 from the ice by even modest heating, must be considered in contemplating a molecular cloud source.

2.3.2 Trapping in Clathrate Hydrate

Trapping of volatile species in nebular clathrate hydrate has been treated by numerous groups over a number of years, but with less attention paid to molecular oxygen until very recently. Tse et al. (1986) prepared a clathrate hydrate with O_2 as the sole "guest" species (the molecule occupying the void or cage site in the water ice H-bonded structure) and found it to induce the so-called structure II clathrate, with 16 small and 8 large cages per unit cell. The dominant clathrate-forming species in the solar nebula, CO and CH_4, both induce structure I clathrate formation (Lunine and Stevenson 1985), but O_2 will incorporate as a secondary guest species in the structure I. Mousis et al. (2016b) numerically computed O_2 incorporation in clathrate in the nebula by considering a two-component gas of O_2 and CO, employing a statistical mechanical formalism first used comprehensively for solar system studies by Lunine and Stevenson (1985), but with molecular interaction (Kihara) parameters from the most recent data sets available. Mousis et al. (2016b) found that the ratio of O_2 to CO in the clathrate hydrate was up to twice that in the coexisting gas phase of the nebula. Given the lack of evidence for direct condensation of the class of volatile species O_2, N_2, and argon as molecular ices, clathrate hydrate may have been an important carrier of molecular oxygen in the protoplanetary disk. This scenario has been ruled out by Mousis et al. (2016b) because it predicts a strong O_2-CO correlation instead of the one observed for O_2-H_2O, regardless the seasons or heliocentric distance of the comet.

2.3.3 O_2 Condensation in the Protosolar Nebula

As mentioned above, direct condensation of O_2 (and other volatiles) in the colder regions of the PSN also needs to be considered in the context of O_2 in comet 67P/C-G. O_2 and other volatiles condensed from the gas phase in the PSN may have incorporated into the forming nucleus if the nucleus was formed in a colder environment than needed for clathration. Pure Ar, N_2, CO, and O_2 condense at similar temperatures ($\sim$ 20–25 K) in the PSN (Fray and Schmitt 2009). Therefore, their similar condensation temperature implies that if direct condensation is responsible for the observed O_2 in the coma of 67P/C-G, then both Ar and N_2 should be present in the nucleus in near-solar proportions.

ROSINA/DFMS measured the abundance of O_2 and other volatiles relative to H_2O in the coma. While it is important to note that measurements of volatile abundances in the coma do not necessarily reflect abundances in the nucleus, they currently are our best estimate of the possible composition of the nucleus. As measured by ROSINA/DFMS, Ar/CO (Balsiger et al. 2015) and N_2/CO (Rubin et al. 2015a) in the coma of 67P/C-G have been found to be significantly depleted compared to the solar abundances, by a factor of $\sim$ 90 and 10, respectively (Mousis et al. 2016b). In addition, N_2 was found to be strongly depleted with respect to CO in three Oort cloud comets (Cochran et al. 2000; Cochran 2002). This depletion implies that Ar and N_2 did not likely form substantial amounts of pure condensates in the PSN where comet 67P/C-G was formed. However, a mixture of pure condensates and clathrates in the nucleus of 67P/C-G is also possible.

O_2 was observed to correlate strongly with H_2O during the six-month approach-phase interval reported by Bieler et al. (2015). If such strong correlation is representative of the outgassing behavior through the entire orbit, then it is likely that either O_2 and H_2O desorb together, or that O_2 is produced from H_2O (see Sect. 3 for details).

3 Post-agglomeration Formation Scenarios

3.1 *In Situ* O_2 Formation Processes

3.1.1 Eley-Rideal Reactions

An alternative hypothesis concerning a class of rarely-considered Eley-Rideal mechanisms (ER) was recently proposed by Yao and Giapis (2017) to explain the presence of O_2 in the coma of 67P/C-G. In these ER reactions, energetic water-derived ions (e.g. H_2O^+, H_3O^+, OH^+, O^+) are accelerated by the solar wind and are pulled back toward the nucleus (or other surfaces). Based on laboratory experiments, when the ionized water-group species collide with oxidized Si/Fe or other mineral surfaces, they abstract an oxygen atom and form an excited precursor state. The dissociation of this precursor state generates energetic O_2^- anions, which are then converted to O_2 by photo-detachment. O_2^- and energetic O_2 produced this way was proposed to account for the O_2 detected in the coma of 67P/C-G (Yao and Giapis 2017). Since O_2 is produced from H_2O on multiple possible surfaces in the proposed ER reactions, the two species must be closely associated at all times, and the O_2^- production rate must be proportional to the accelerated cometary H_2O ion flux. In addition to energetic water-derived ions, O_2 could also be produced in collisions of (1) energetic hydronium ions, (2) energetic neutral water molecules, and (3) excited atomic oxygen (thermal or hyperthermal) on the surfaces of the nucleus, the spacecraft, or the DFMS instrument itself.

While the proposed ER reactions do explain the strong correlation between H_2O and O_2 as reported by Bieler et al. (2015), the energetic water ion flux (Nilsson et al. 2017; Fuselier et al. 2015) seems to be too low to account for the observed high O_2 abundance in the coma of 67P/C-G. Recently, Heritier et al. (2018) concluded that both the integrated energetic cometary water-group ion flux and the maximum fraction of O_2 produced via ER reactions (assuming 100% yield) were insufficient for ER reactions to be the dominant O_2 source. In fact, they estimated that the O_2 production rate by ER reactions is at least 4 orders of magnitude lower than the observed O_2 production rate, even when using the conservative low O_2 concentration of 1%. In addition, Heritier et al. (2018) argue that the energetic water ions that drive ER reactions were anti-correlated with the O_2 density measured by ROSINA/DFMS, at least for March 5–23, 2016. At the same time, Yao and Giapis (2018) argued that “cold” water ions, whose flux is about 100 times that of the “accelerated” water ions (Nilsson et al. 2015) bombarding the spacecraft could produce O_2 in situ. Whether this O_2 would be detected by DFMS is uncertain as the DFMS response under exposure to a low-pressure water plasma containing O_2 is unknown (Yao and Giapis 2018). It is also important to note that Alice has detected O_2 independently of ROSINA (Keeney et al. 2017a), and post-perihelion Alice results indicate that the relative O_2/H_2O decreases with increasing impact parameter above the nucleus (Keeney et al. 2017b). Although the Alice measurements may arguably be affected by spacecraft-produced O_2, the observed O_2/H_2O variation with impact parameter would be unlikely within this framework. Finally, ER reactions require a direct collision with the appropriate atom, which is a low probability process.

3.1.2 O_2 Formation via H_2O_2 Dismutation/Disproportionation

Dulieu et al. (2017) proposed dismutation of cometary H_2O_2 as a source of O_2 observed in the comae of 67P/C-G by ROSINA/DFMS (Bieler et al. 2015) and Halley by the Giotto mass spectrometer (Rubin et al. 2015b). The peroxide is suggested to have a primordial origin, co-produced with water ice on surfaces of interstellar dust grains via hydrogenation reaction of O-bearing species, and transported into the comet-forming regions of the protoplanetary disks (Taquet et al. 2016). The comet’s volatile constituents, including water ice and peroxide, undergo temperature-dependent sublimation during perihelion approach. The peroxide either desorbs as intact molecules, or dismutates as the global reaction

$$2H_2O_2 \rightarrow 2H_2O + O_2. \tag{9}$$

Based on results from their laboratory experiments summarized below, the authors (Dulieu et al. 2017) assert this peroxide-derived O_2 as the source of molecular oxygen detected in the coma of 67P/C-G at abundances ranging from $\sim$ 1–10% relative to H_2O.

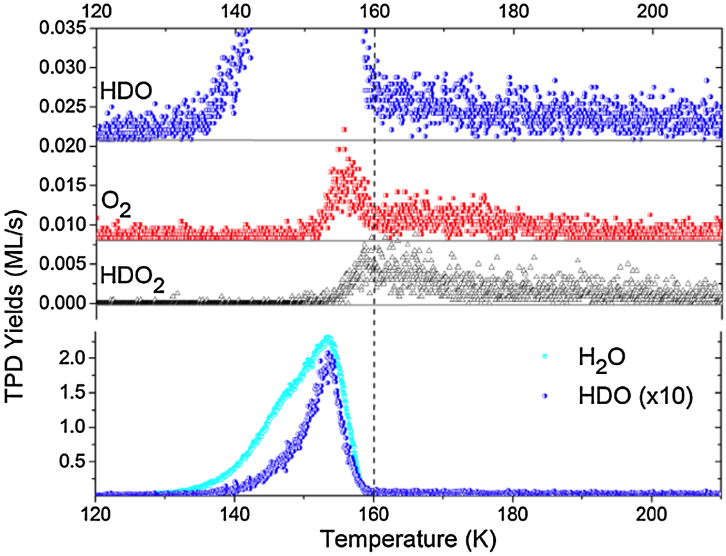

Fig. 5 Desorption rates of O_2, HDO, HDO_2, and H_2O from heating a thin film produced from the reaction of D atoms with O_2 condensed onto the surface of a 25 ML-thick compact amorphous ice. The H atoms are introduced in the deuterated species via isotope exchange. Reproduced from Dulieu et al. (2017)

In the first set of experiments, the authors co-deposited molecular O_2 with an atomic beam of D onto an amorphous silicate substrate held at 10 K. These species condensed and reacted to form a thin film (< 1 ML (monolayer)) of O_2, D_2O, and D_2O_2, which are thermally desorbed and detected with a mass spectrometer when the substrate was heated to > 200 K at 10 $\mathrm{K\,min^{-1}}$. The key result was the presence of O_2 and D_2O desorption peaks at 175 K, accompanying the sublimation of the less volatile D_2O_2. Dulieu and coworkers interpreted the higher temperature O_2 and D_2O peaks as the signature of D_2O_2 dismutation. While a fraction of the D_2O_2 sublimes intact, some are converted to D_2O and O_2 on the surface and released in the gas phase. Above 180 K, the ratio O_2/D_2O_2 is about 0.4; nearly half that of $D_2O/D_2O_2 \sim 1$, and consistent with the stoichiometry of the dismutation reaction.

The second set of experiments was a repeat of the first set, except performed on a 25 ML-thick compact H_2O ice pre-deposited on top of the silicate substrate. A distinct O_2 peak was observed at 155 K, immediately following the main H_2O/HDO desorption. Solid-state isotope exchange led to the conversion of D_2O and D_2O_2 formed via $O_2 + D$ reactions into HDO and HDO_2, respectively. However, it is not clear what fraction of the deuterated species was substituted with H even to form H_2O_2, which is not discussed.

Several differences were noted compared to the first set of experiments: the O_2 peak was observed at 155 K, 20 K lower compared to the first experiments. Further, no concurrent HDO_2 desorption peak was observed with O_2. Instead, the HDO_2 sublimation followed the O_2 peak at 160 K. The authors claim a dismutation origin for the O_2, since they report a HDO desorption rate twice that of O_2 at 155 K. However, this is not consistent with the data in Fig. 3 of their manuscript (reproduced here as Fig. 5) where the HDO rate is about ten times larger compared to O_2. Furthermore, to explain the absence of HDO_2, the authors inferred a highly efficient peroxide dismutation (close to unity) attributed to the high concentration of peroxide that accumulates on the silicate substrate following H_2O sublimation, and the catalytic effect of the substrate favoring peroxide dismutation. Above

160 K, the three species continue to effuse out with O_2/HDO_2 and D_2O/D_2O_2 ratios more consistent with dismutation.

The dismutation process requires the incorporation of primordial peroxide into the cometary nucleus. Though astrochemical models (Tielens and Hagen 1982; van Dishoeck et al. 2013) predict the occurrence of peroxide on interstellar grains, and laboratory experiments support the formation of H_2O_2 via hydrogenation reactions with O-bearing species (Dulieu et al. 2010; Ioppolo et al. 2008; Jing et al. 2011; Oba et al. 2009), an unambiguous detection of solid peroxide in the molecular clouds has not been reported to date. H_2O_2 has been reported in the gas phase, but at a small abundance of 10^{-10} relative to H_2 (Bergman et al. 2011). Smith et al. (2011) analyzed the infrared spectra of several molecular clouds, and placed upper limits on H_2O_2 abundance ($9 \pm 4\%$ relative to water ice) by assessing the possible contribution of the 3.5 μm peroxide feature measured in the laboratory to the 3.47 μm interstellar feature. However, other H_2O_2-specific absorption features expected at 7 and 11.3 μm were not identified, probably due to masking by underlying H_2O and silicate features (Smith et al. 2011). Further, it is not clear if the primordial H_2O_2 can survive the evolution of the dark clouds to protoplanetary disks and be transported unaltered to the comet-forming regions.

It is also challenging to reconcile the highly efficient (50–100%) peroxide dismutation with other laboratory experiments where stable films of pure crystalline H_2O_2 ($\sim 98\%$ purity) is obtained from the isothermal distillation of H_2O-H_2O_2 films at 167 K (Loeffler et al. 2006b). This temperature exceeds the dismutation temperature of 155 K. Using a quartz crystal microbalance, Loeffler and colleagues reported no mass loss (< 0.1 H_2O_2 ML, the detection limit of the microbalance) from a distilled crystalline peroxide film (Loeffler et al. 2006b). Any H_2O_2 dismutation into O_2 and H_2O, which are thermally unstable at 167 K, would have resulted in a mass loss. While we note the use of different substrates (gold vs. silicate), the substrate-promoted dismutation is likely not important for multi-layered peroxide films obtained by Loeffler et al. (2006b).

Finally, H_2O_2 can fragment into O_2 from electron impact in the ionization region of the mass spectrometer (Loeffler et al. 2006a). Also, collision with the chamber walls can dissociate H_2O_2 to O_2. It is unclear if the desorption flux reported by Dulieu et al. (2017) were corrected for fragmentation.

3.2 Post-accretion Radiolysis

One can wonder how radiolysis affected cometary ices over their orbital history during their 4.56 billion-year evolution in the Solar System. Bieler et al. (2015) noted that comets are subject to radiolysis on 3 different timescales: (i) billions of years during their residence in the Kuiper belt, (ii) over a period of a few years when they enter the inner Solar System, and (iii) on very short timescales when they approach perihelion. The authors estimated that the skin depth for producing O_2 is in the range of meters during their residence in the Kuiper belt. However, once a comet migrates towards the inner Solar System, it easily loses surface material over depths reaching several meters during each orbit. This material loss implies that, according to Bieler et al. (2015), no O_2 produced during the Kuiper belt phase is likely to remain in the amount exceeding the percentage level. Radiolysis and photolysis by solar wind and UV flux in the inner Solar System may also produce O_2 at the top micrometer levels of cometary surfaces. Meanwhile, based on measurements of continuous mass loss through outgassing, Bieler et al. (2015) estimated that 67P/C-G's active surface areas lost a depth of several centimeters during their sampling period between September 2014 and March 2015. Because their data show a constant O_2/H_2O ratio during the studied time interval instead of a continuous decrease, the authors ruled out the hypothesis that a recent production by radiolysis or photolysis may be the source of the measured O_2. In addition, Bieler et al. (2015) excluded the possibility of instant creation of O_2 by radiolysis or photolysis because these processes would lead to variable O_2/H_2O ratios as a result of different heliocentric distances and illumination conditions.

3.2.1 Endogenic Radiolysis

A possible source of molecular oxygen in 67P/C-G is radiation chemistry of ice induced by an endogenic source—decaying radionuclides present in the chondritic dust that represents 4/5th of the mass of the comet (Rotundi et al. 2015). Short-lived (^{26}Al, ^{60}Fe) and long-lived (^{40}K, ^{235}U, ^{238}U, ^{232}Th) radionuclides emit energetic alpha particles (helium nuclei), beta particles (electrons), and gamma rays that interact with the surrounding materials, including ice. Assuming an even repartition of the radionuclide-bearing dust, this process would produce O_2 homogeneously within the ice, in conformity with the observation of an O_2 signal correlated with water (Bieler et al. 2015).

Using a production model originally developed for Earth water-rock mixtures (Hofman 1992; Lin et al. 2005a,b; Bouquet et al. 2017), Bouquet et al. (2018) estimated a maximum value of 1% O_2/H_2O produced within 67P/C-G over the age of the Solar System, which is below the 3.8% value derived from the ROSINA/DFMS observations. However, this estimate relies on O_2 production yields from ice irradiation experiments, which are motivated by the need to understand the evolution of icy surfaces exposed to planetary radiation belts (e.g. Europa). These experiments are therefore performed at projectile energies lower than the values relevant to radionuclide decay emissions, and gamma ray irradiation is usually not considered. Additionally, the results of Teolis et al. (2017) indicate that O_2 production yields in ice are higher for low projectile energies and high ice temperatures (> 80 K). Conditions in comet 67P/C-G are therefore unfavorable for O_2 production, as projectile energies are high and the temperature has stayed below 80 K for most of the comet's history (Mousis et al. 2017). For these reasons, the 1% value reported in Bouquet et al. (2018), which uses the highest yields from the literature, is an upper limit.

It should be noted that H_2O_2 is also produced by ice radiation chemistry in a more consistent manner than O_2 (Teolis et al. 2017) regarding projectile energy. The findings of Bouquet et al. (2018) point to the potential for endogenic radiolysis to produce amounts of H_2O_2 on the order of a tenth of a percent compared to water. Such quantities are incompatible with the very low abundance of H_2O_2 detected by ROSINA/DFMS (Bieler et al. 2015), indicating that either production was prevented, or that H_2O_2 was destroyed by a chemical process, possibly producing O_2 (Dulieu et al. 2017).

Endogenic radiolysis cannot account for the abundance of O_2 measured by ROSINA, but it may have produced a non-negligible fraction of it, either directly, or through production and destruction of H_2O_2. This homogenous distribution of O_2 in the ice would fit the observed correlation with water. More laboratory data is required to better constrain this fraction.

4 Conclusions

The presence of large amounts of O_2 in the coma of 67P/C-G continues to be perplexing. While several possible scenarios have been postulated for the formation of cometary O_2, the current state of analysis of the published *Rosetta* data preclude the determination of its dominant source and origin. All O_2 formation mechanisms currently proposed in the literature rely heavily and solely on the only available published O_2 data, which only covers a six-month time interval from *Rosetta's* approach phase (Bieler et al. 2015). This limitation raises the issue of how representative the time interval is for the entire orbit of 67P/C-G, which would be key for deciphering the origin of O_2. Is the O_2-H_2O correlation strong throughout the orbit, or does it change with heliocentric distance? Are there any hemispherical differences between the correlations? Do the large-scale changes or the lack thereof more or less agree with the small-scale changes, and if not, then why? Does the O_2/H_2O ratio remain fairly constant at different orbital segments, or does it change systematically/randomly/hemispherically/with illumination/with temperature? Is the bulk of cometary O_2 produced by one dominant mechanism, or do multiple production mechanisms contribute to the signal? Does the dominant production mechanism change at different parts of the orbit? These are just a handful of questions that need to be answered in order to assess the viability of each scenario reviewed in this paper. Some of the answers most likely lie in the systematic analysis of the *Rosetta* data, and some issues will likely require future missions to address.

If O_2 is primordial, then the O_2/H_2O should remain nearly constant with heliocentric distance, regardless of the hemisphere (see Fig. 1). That is because O_2 and H_2O ices in the nucleus would be physically related. That means that the production rate of O_2 must be related to the production rate of H_2O at all times. When more H_2O is released from the nucleus due to higher sublimation rates, more O_2 is also released, resulting in a nearly constant O_2/H_2O with season, hemisphere, and heliocentric distance. On the other hand, if O_2 has a present-day origin and is produced *in situ*, then the O_2/H_2O is expected to change with the seasons and heliocentric distance. If O_2 is produced *in situ* from water-group ions accelerated by the solar wind hitting various surfaces and triggering ER reactions, then O_2 production would have to depend on: (i) the H_2O production rate, (ii) on the intensity of the solar UV/photoelectrons and the solar wind/energetic electrons, and (iii) dynamic processes in the solar wind including its interaction with the coma (shocks, discontinuities, etc.). UV photons and photoelectrons ionize the cometary H_2O molecules, while the solar wind and energetic electrons drag these water-derived ions back onto the surface, initiating the ER reactions. The H_2O production rate scales with heliocentric distance (R_h) as a function of roughly R_h^{-c2}, where $c2 = 5$ and $c2 = 7$ pre- and post-perihelion, respectively (Hansen et al. 2016). At the same time, the solar wind and solar UV scale with R_h as $\sim 1/R_h^2$. Therefore, the production rate of O_2 should scale with $\sim R_h^{-(c2-2)}$, while the production rate of H_2O is R_h^{-c2}, meaning that the O_2/H_2O ratio should follow a $\sim 1/R_h^2$ dependence. Thus, if ER reactions produce the majority of the observed O_2, then the O_2/H_2O ratio should be several factors (by a factor of ~ 5) higher at perihelion than at 3 AU. Therefore, analysis of the O_2/H_2O over the extent of the mission would be needed to conclude whether or not the ratio changes with cometocentric distance. In addition, ER reactions are independent of the illumination conditions and the nucleus temperature. At the same time, H_2O_2 dismutation/disproportionation reactions are temperature-dependent, and the O_2/H_2O_2 ratio should vary below about 180 K (Dulieu et al. 2017). At $R_h \geq 3$ AU the conditions were ideal for identifying differences in the O_2/H_2O_2 between the two hemispheres due to the different hemispheric temperatures; hence, looking at time periods prior to the inbound equinox and following the outbound equinox may be a good start. We also note that a possible lack of correlation between O_2 and H_2O may occur as a result of H_2O re-condensation onto the nucleus after the more volatile O_2 has already sublimated away. This re-sublimated H_2O would not contain O_2 anymore; hence, would weaken the correlation between O_2 and H_2O.

A potential strong correlation between O_2 and CO, and/or O_2 and CO_2 (hemispheric and/or over a given period along the orbit) would make it more likely that O_2 was formed in the PSN instead of the ISM, and that it is not produced *in situ*. In that case, determining the O_2/CO ratio over time and comparing it to calculations from the clathrate model of Mousis et al. (2016b) could provide more definitive answers as to what phase O_2 is stored in the nucleus. Furthermore, the time scales calculated by Mousis et al. (2016b) may yield a different conclusion about the formation location of icy grains if the GCR flux (H and Fe) were estimated using a different approach, i.e. that of Webber and Yushak (1983). While the Fe flux is lower than the proton flux based on the latter approach, the electronic stopping in H_2O ice is higher, which could potentially make Fe contribute more heavily to O_2 production in icy grains. In future parameter studies, both the issue of GCR flux and the depth-dependency of the O_2 yield (Teolis et al. 2017) will need to be evaluated.

The conundrums created by the discovery of O_2 in 67P/C-G would be readily dismissed as perhaps a peculiarity were it not for the conclusion that 1P/Halley data also show evidence of this molecule in similar amounts (see Sect. 1 Introduction). The inference that 1P/Halley may have been an Oort cloud comet, rather than a Jupiter family object as 67P/C-G, might argue for a widespread occurrence of O_2 in the protoplanetary disk, any other explanation (such as both comets being anomalous) seeming to beg the question. It is thus incumbent upon modelers to focus additional effort on mechanisms for producing this molecule either in the protoplanetary disk, precursor clouds, or in the comet itself. The prospect that a sample of a comet nucleus might be returned to Earth, thanks to the selection for additional development of the CAESAR mission in NASA's New Frontiers program, opens up the possibility of determining how this molecule is incorporated in the ice. Until then, the difficult task of remote sensing of this symmetric molecule or its atomic fragments will have to suffice for additional data.

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