Europa

The Production of Oxidants in Europa’s Surface

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ABSTRACT

The oxidants produced by radiolysis and photolysis in the icy surface of Europa may be necessary to sustain carbon-based biochemistry in Europa’s putative subsurface ocean. Because the subduction of oxidants to the ocean presents considerable thermodynamic challenges, we examine the formation of oxygen and related species in Europa’s surface ice with the goal of characterizing the chemical state of the irradiated material. Relevant spectral observations of Europa and the laboratory data on the production of oxygen and related species are first summarized. Since the laboratory data are incomplete, we examine the rate equations for formation of oxygen and its chemical precursors by radiolysis and photolysis. Measurements and simple rate equations are suggested that can be used to characterize the production of oxidants in Europa’s surface material and the chemical environment produced by radiolysis. Possible precursor molecules and the role of radical trapping are examined. The possibility of oxygen reactions on grain surfaces in Europa’s regolith is discussed, and the earlier estimates of the supply of O₂ to the atmosphere are increased. Key Words: Europa—Oxygen—Ice—Chemical kinetics. Astrobiology 3, 823–850.

INTRODUCTION

The putative subsurface ocean on Europa is of interest to astrobiologists as an environment that might be able to sustain life processes. Given the presence of oxygen, carbon, sulfur, and, possibly, nitrogen, organisms dependent on conventional carbon-based biochemistry may be feasible. However, the presence of aerobic life processes may be contingent on the transport of oxidants or oxygenated species formed at the surface to an ocean that is covered by a substantial thickness of ice (Chyba, 2000; Kargel et al., 2000; Chyba and Hand, 2001; Cooper et al., 2001). Although oxygen has been detected in Europa’s very thin atmosphere and oxidants have been observed as trapped species in its icy surface, their transport to a subsurface ocean presents considerable thermodynamic and kinetic challenges.

It is generally agreed that the radiolysis of ice by energetic ions and electrons trapped in the Jovian magnetosphere produces the oxygen and peroxide seen in Europa’s icy surface (e.g., Johnson et al., 2003). This occurs because the bombarding particles chemically alter the ice and decompose it, producing molecular hydrogen and oxygen.

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The hydrogen readily escapes from the surface material and, in turn, from Europa's atmosphere because of the low gravitational field. The options for oxygen are the release into the tenuous atmosphere, where it is retained because of its high molecular mass, and retention in the ice lattice as homogeneously dissolved oxygen, as trapped bubbles of oxygen, or as an oxidized trace species. Because of the preferential loss of hydrogen, oxygen-rich species are formed preferentially in Europa's surface ice (Johnson and Quickenden, 1997; Madey et al., 2002). Therefore, oxygen, peroxide, and oxidized sulfur and carbon have been detected as trapped species (e.g., Johnson et al., 2003).

The production and trapping of such species in the surface layers are, of course, not sufficient for our purposes, as indicated schematically in Fig. 1. Radiolysis can occur to depths of the order of tens of centimeters because of the penetration of the energetic component of the incident radiation (Cooper et al., 2001; Paranicas et al., 2001). Mixing of these radiolytic products to greater depths occurs because of meteoroid bombardment (Cooper et al., 2001). This bombardment also produces a porous regolith (Buratti, 1995) composed of sintered grains (Grundy et al., 2001), which increases the effective radiation penetration depth. In addition, the atmospheric O\textsubscript{2} permeates pore space in the regolith. Therefore, oxygen gas in the porous regolith can be trapped by the collapse of pores on meteoroid impact or can react on grain surfaces well below the typical radiation penetration depth. Finally, macroscopic mass transport of trapped species by crustal subduction (Prockter and Pappalardo, 2000) must occur. Because of the temperature gradient, relevant species must be stable in the ice at temperatures well above Europa's surface temperature (80–110K) and at higher pressures. The subduction process effectively is a macroscopic mass transport pump, which is needed to carry oxidants to Europa's ocean.

As a first step, we focus in this paper on the chemical processes leading to the formation of oxygen and related oxidants in Europa's regolith. The goal is to characterize the chemical state and stability of the irradiated surface material. We first summarize the spacecraft and telescopic observations of oxygen and related species at Europa. Next we summarize the laboratory data on the radiolysis and photolysis of ice. Because data are not available for all incident species and incident energies, we concentrate on the descriptions of the chemistry of formation of molecular oxygen. The focus on oxygen is not because this is the species delivered to a subsurface ocean, but because understanding the chemistry of its formation in ice is key to describing the chemical state and stability of Europa's irradiated surface material. We then use the data to correct previous estimates of the production rate of oxygen at Europa and suggest experiments in order to characterize the chemical state of the irradiated surface that leads to the production of O\textsubscript{2}.

**OBSERVATIONS**

**Molecular oxygen**

Tenuous oxygen atmospheres have been reported at both Ganymede (Hall et al., 1998) and Europa (Hall et al., 1995) based on Hubble Space Telescope (HST) observations. The detection of molecular oxygen was indirect. That is, two lines (135.6 and 130.4 nm) due to excited O were observed in emission, and their ratio (~1.9) suggested that the excited atoms were produced by electron impact dissociation of molecular oxygen. In addition, two well-known transitions for interacting pairs of O\textsubscript{2} molecules, \( ^1\Delta_g + ^1\Delta_g \leftrightarrow ^3\Sigma_g^- + ^3\Sigma_g^- \), were observed in the reflectance spectra of Ganymede (Calvin et al., 1995; Spencer et al., 1995) and Europa (Spencer and Klesman, 1995).
2001; Spencer and Calvin, 2002) using ground-based telescopes and the HST. These absorption bands cannot be due to atmospheric O\textsubscript{2} because very high pressures or very long line-of-sight columns of O\textsubscript{2} would be required.

The positions of the two signature absorptions for dimer O\textsubscript{2}, at 577.2 nm and 627.5 nm, respectively (Landau et al., 1962; Cooper et al., 2003a), suggest that the O\textsubscript{2} is locally quite dense (Calvin et al., 1996, 2003). Therefore, these bands were suggested to be due to inclusions of O\textsubscript{2} trapped within Ganymede’s icy surface (Calvin et al., 1996; Johnson and Jesser, 1997). It is seen from Table 1 that although the atmospheric and surface reservoirs of O\textsubscript{2} are coupled, the oxygen content in the surface ice is the largest. The observed O\textsubscript{2}-dimer band shapes and relative band depths are distorted from solid or liquid O\textsubscript{2} (Johnson, 1999). At Ganymede, where spatial resolution was obtained using the HST, both the position of the band minimum and its shape vary with latitude (Calvin and Spencer, 1997). Therefore, care must be taken when comparing the peak positions of the bands seen in the discovery spectrum at Ganymede with those of solid or liquid oxygen. This spectrum is a hemispherical average of spectral features that vary in their peak positions and band shapes. It was obtained by ratioing Ganymede’s reflectance to that of Callisto (Spencer et al., 1995), which we now know exhibits a weak solid-like O\textsubscript{2} feature. It was recently shown that O\textsubscript{2} is also trapped in Europa’s icy surface (Spencer and Klesman, 2001; Spencer and Calvin, 2002). However, the solid-like O\textsubscript{2} feature at Europa is much weaker than that at Ganymede (577.2 nm band depth \(\sim 0.3\%\) vs. \(\sim 1.8\%\)). This could be due to the fact that Europa’s surface scatters light more efficiently in the visible, leading to shorter path lengths (Johnson and Jesser, 1997). It could also be due to competing chemical processes (Calvin et al., 1996; Johnson and Quickenden, 1997).

### Ozone and peroxide

Related to the oxygen observations, the Hartley band of O\textsubscript{3} has been tentatively identified in the ultraviolet (UV) reflectance spectra of Ganymede and in the icy satellites of Saturn (Noll et al., 1996, 1997). O\textsubscript{3} trapped within the icy surface would be consistent with the presence of trapped oxygen exposed to radiolysis (Johnson and Quickenden, 1997). The presence of trapped O\textsubscript{3} supports the interpretation that the dimer-O\textsubscript{2} observations are due to inclusions of oxygen trapped in the ice. However, the shape of the O\textsubscript{3}-like feature also varies significantly with latitude at Ganymede (Hendrix et al., 1999a) and is highly distorted. Based on the band shape, the presence of an additional absorbing species was inferred. This was initially suggested to be trapped OH (\(\sim 0.28 \mu\text{m}\)) (Noll et al., 1996), but may more likely be due to organic molecules (Johnson, 2001). This O\textsubscript{3}-like feature is superimposed on a very broad UV absorption extending from about 0.4 \(\mu\text{m}\) to shorter wavelengths seen on all of the icy satellites. The broad UV absorption has been attributed to another radiolytically produced oxidant, H\textsubscript{2}O\textsubscript{2} (Carlson et al., 1999a; Hendrix et al., 1999b), but may also include absorption by trapped HO\textsubscript{2} and OH (Taub and Eiben, 1968; Johnson and Quickenden, 1997). Identification of specific radiolytic products in the UV is difficult because the bands are very broad and overlap. The presence of H\textsubscript{2}O\textsubscript{2} trapped in Europa’s ice was confirmed by a band in the infrared observed using the Near Infrared Mapping Spectrometer (NIMS) on the Galileo spacecraft (Carlson et al., 1999a). Remarkably, the amount seen in the infrared is roughly consistent with the amount suggested by the decrease in reflected light in the UV.

### Table 1. Global Oxidant Inventory

<table>
<thead>
<tr>
<th>Reservoir</th>
<th>Oxidant</th>
<th>Column density ((10^{16}\text{ mol/cm}^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atmosphere(^1)</td>
<td>O\textsubscript{2}</td>
<td>(~0.10)</td>
</tr>
<tr>
<td>Regolith (gas)(^2)</td>
<td>O\textsubscript{2}</td>
<td>(~10^{-5})</td>
</tr>
<tr>
<td>Trapped in ice (1 mm at unit density)(^3,4)</td>
<td>O\textsubscript{2}</td>
<td>(~50)–(~500)</td>
</tr>
<tr>
<td></td>
<td>H\textsubscript{2}O\textsubscript{2}</td>
<td>(~400)</td>
</tr>
</tbody>
</table>

\(^1\)Based on Hall et al. (1995, 1998).

\(^2\)Estimated using average regolith depth of \(~1\) m.

\(^3\)Europa band depth approximately one-sixth that in Calvin et al. (1996), who give 0.1–1% concentration on Ganymede.

\(^4\)For comparison, sulfur species on the trailing hemisphere: [SO\textsubscript{2}] \(~300\) [sulfate], or \(~1,000 \times 10^{16}\text{ mol/cm}^2\).
Whereas \( \text{H}_2\text{O}_2 \) is observed in ice at Europa at \( \sim0.13\% \) level, the \( \text{O}_3 \)-like UV feature seen at Ganymede is not obvious at Europa (e.g., Fanale et al., 1999). This again may be due to the fact that less trapped \( \text{O}_2 \) is seen in reflectance at Europa than at Ganymede. That is, since \( \text{O}_2 \) is a precursor of \( \text{O}_3 \), the factor of \( \sim6 \) reduction in \( \text{O}_2 \) means that the identification of this broad feature superimposed on other broad UV bands is problematic. However, the absence of the \( \text{O}_3 \)-like feature could also be due to the presence of sulfur species that strongly compete for excess oxygen (Johnson and Quickenden, 1997).

**Summary: space observations**

Although each of the individual identifications of suggested products of water radiolysis or photolysis (\( \text{OH}, \text{H}_2\text{O}_2, \text{O}_2, \text{O}_3 \)) has some uncertainty, the reflectance spectra taken as a whole give a fairly clear, self-consistent picture. The irradiated surfaces of the icy satellites contain trapped molecules that would be expected from radiolysis or photolysis of an icy surface (Johnson and Quickenden, 1997). Indeed, \( \text{OH} \) is a suggested precursor of \( \text{H}_2\text{O}_2 \), which is a suggested precursor of \( \text{O}_2 \), which in turn is a precursor of \( \text{O}_3 \). However, the separation into amounts of individual species based on the absorption in the UV identifications remains difficult. Therefore, the observed band of trapped \( \text{H}_2\text{O}_2 \) in the infrared and the pair of bands in the visible of a condensed form of \( \text{O}_2 \) are critical, as they confirm the presence of radiolytically produced oxidizing molecules in Europa’s icy surface.

Consistent with the above, oxygen-rich molecules derived from the radiation processing of an ice containing sulfur (\( \text{SO}_2 \) and a sulfate) and carbon (\( \text{CO}_2 \) and a carbonate) have been identified (see, e.g., Johnson et al., 2003). The sulfate has been suggested to be a hydrated salt mineral (McCord et al., 1999) or a hydrated sulfuric acid (Carlson et al., 1999b, 2002). The latter is an efficient oxidant that is also refractory. Together these observations indicate that volatile and refractory oxidizing molecules are readily formed by radiolysis and photolysis in Europa’s surface material. If indeed that material can be delivered to Europa’s putative subsurface ocean, a source of free energy may be available for potential biological activity. Here we consider the formation of molecular oxidants by radiolysis with emphasis on \( \text{O}_2 \).

**RADIOLYTIC PRODUCTION: LABORATORY DATA**

**Introduction**

In this section we review the laboratory data leading to the production of oxygen and related species by radiolysis and photolysis of ice. We first compare the data for production of oxygen by incident ions, electrons, and UV photons. This is followed by a review of the data on the loss of hydrogen, which is the other principal product of radiation-induced decomposition of ice. We then consider the evidence that certain proposed species, such as peroxide or trapped \( \text{O}_2 \), might be precursors to molecular oxygen formation in ice. Some of these data have been summarized earlier, but with a very different emphasis. Here the goal is to motivate the development of chemical models for describing irradiated ice, models that can be used to suggest new experiments and to interpret data. Individuals familiar with the data can go directly to the modeling section, in which rate equations are developed and used to interpret aspects of the diverse database.

**Molecular oxygen**

Gas-phase \( \text{O}_2 \) has been produced by irradiating low temperature ice using UV photons, low-energy (eV) electrons, keV ions and electrons, and MeV ions (see, e.g., reviews by Johnson and Quickenden, 1997; Delitsky and Lane, 1998; Johnson, 1990, 1998, 2001; Strazzulla, 1998; Baragiola, 2003; Johnson et al., 2003). In spite of the considerable differences in excitation density and penetration depth for these incident particles, the results exhibit important similarities. Here we summarize the principal findings. We first note that the efficiency of this process in pure ice is likely to be lower than estimates based on very early measurements of the production of \( \text{O}_2 \) in ice (see, e.g., Hart and Platzman, 1961) because of low levels of contaminants in those early experiments (Baragiola and Bahr, 1998; Moore and Hudson, 2000). Therefore, trace species can be important in determining the \( \text{O}_2 \) production rates from Europa’s icy surface and will be discussed shortly.

In studying the ability of energetic plasma particles to eject (sputter) molecules from ice, a process occurring on small Outer Solar System bodies, Brown, Lanzerotti, and co-workers (Brown...
et al., 1982, 1984) found that, at temperatures relevant to the surface of Europa, H$_2$ and O$_2$ were important components of the ejecta. They then used those data to predict the presence of a radiolytically generated O$_2$ atmosphere on Europa (Johnson et al., 1982). The production efficiency for gas-phase O$_2$ was found to be strongly temperature dependent, as seen in Fig. 2a for MeV He$^+$ ions incident on ice and Fig. 2b for keV Ar$^+$ ions on ice. In Fig. 2 the production rate is given as a yield, which is the number of molecules ejected per incident ion (i.e., O$_2$ production rate divided by the flux of incident particles: photons, electrons, or ions). Yields are typically measured at a low incident particle flux so that sample heating does not occur. The yield versus temperature shown in Fig. 2 appears to increase exponentially with $T$ over a range of temperatures. Although this is not an Arrhenius dependence, rough activation energies can be extracted over narrow ranges of $T$ (e.g., Fig. 2a, inset). These are of the order of 0.01–0.07 eV (Table 2). Such values are much smaller than those for diffusion of vacancies or trapped species in ice (Livingston et al., 2002), but are comparable to the reported activation energies for H$^+$ or H diffusion in ice, as noted earlier (Johnson and Quickenden, 1997). The lowest energies are also comparable to the enthalpy difference between amorphous solid water and crystalline ice (Ayotte et al., 2001). Therefore, the estimated energies are likely related to H$^+$ and H transport or to hydrogen bond re-orientation. It has also been shown that as the temperature is increased above ~80–100K morphological changes occur that can affect the reaction kinetics and give incorrect activation energies. This is especially so when using measurements of average quantities, such as yields, rather than directly extracting rate constants by measuring transients (Selby, 2003). In addition, the activation energies can be representative of the competing (destruction) processes, rather than the formation processes (e.g., Matich et al., 1993) as discussed in the model section.

The measured O$_2$ production rates (yields) were also found to be fluence dependent, where fluence is the radiation flux $\times$ the time or the total number of particles per unit area onto the ice. Multiplying the fluence by the incident particle energy and dividing by the average penetration depth gives the energy per unit volume, often called an average dose. As seen in Fig. 3, the O$_2$ yield versus fluence rises from zero, implying that a single ion incident on a fresh surface does not efficiently produce and eject oxygen. This is the case even for an incident 1.5 MeV Ne$^+$ for which the excitation density along the ion path is high. However, it is seen in Fig. 3 that with increasing irradiation time individual impacting ions produce and eject O$_2$ with increasing efficiency as the material is chemically altered. At large fluences the yield appears to saturate, indi-

![Fig. 2](image_url)

**Fig. 2.** a: Yield for D$_2$ and O$_2$ at saturation (steady state) from 1.5 MeV He$^+$ on D$_2$O ice versus the temperature of the ice (adapted from Brown et al., 1982). Inset: D$_2$ yield minus the constant yield at low $T$ versus $1/\hbar T$, giving an average activation energy of 0.03 eV. b: Yield of O$_2$ at saturation versus temperature for incident 30 keV Ar$^+$ ions (adapted from Baragiola et al., 2003).
cating that destruction processes are in a rough steady state with formation processes. The yields shown in Fig. 2 are purportedly those after saturation, although full saturation is often approached slowly. The slope of the O$_2$ yield versus fluence, shown in Fig. 3, increases with increasing temperature, giving the activation energies in Table 2. These values are similar to those obtained from Fig. 2. For energetic ions that fully penetrate the film, as in Fig. 2a and 3a, the yield versus fluence can exhibit a second rise at higher fluxes for which the radiation track cores begin to overlap. This increase also depends on temperature and exhibits similar activation energies (Reimann et al., 1984). The strong dependence on temperature is at first surprising, since the energy density deposited by a 1.5 MeV Ne$^+$ produces transient temperatures in the track core that are much higher than the ambient material temperature. Therefore, track temperature (local excitation density) alone does not determine the O$_2$ yield.

For all incident particle types and energies, the measured fluence dependence is found to be stable over laboratory time scales. That is, for experiments carried out at high vacuum, the yield returns to the value it had when the beam was turned off. This indicates that the irradiated ice is "permanently" altered (Reimann et al., 1984). Thus a relatively stable chemical state is created that is favorable for O$_2$ production. This could be the formation of a particular trapped radiation product in ice that acts as a stable precursor or is due to the altered chemical and physical state of the irradiated ice. Trapped O, H$_2$O, and HO$_2$ (Matich et al., 1993; Johnson and Quickenden, 1997; Sieger et al., 1998) have been proposed as stable precursor species.

Using isotopically labeled H$_2$O, Benit and Brown (1990) showed that considerable transport of O occurs along the ion track when an energetic heavy ion penetrates an ice sample. Because of this, the O$_2$ yield was found to depend on sample thickness. Therefore, for thin ice samples the

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**Table 2. Oxygen and Peroxide Production**

<table>
<thead>
<tr>
<th>Radiation</th>
<th>Product</th>
<th>T (K)</th>
<th>$E_a$ (eV)</th>
<th>Percent at saturation</th>
<th>$G$ (product/100 eV)$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>He$^+$</td>
<td>O$_2$</td>
<td>300</td>
<td>0.008</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ne$^+$ (30 MeV)$^3$</td>
<td>O$_2$</td>
<td>300</td>
<td>0.0016</td>
<td></td>
<td></td>
</tr>
<tr>
<td>He$^+$ (6 MeV)$^3$</td>
<td>O$_2$</td>
<td>300</td>
<td>0.008</td>
<td></td>
<td></td>
</tr>
<tr>
<td>He$^+$ (29 MeV)$^3$</td>
<td>O$_2$</td>
<td>300</td>
<td>0.0016</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H$^+$ (80 keV)$^4$</td>
<td>O$_2$</td>
<td>70</td>
<td>0.0002</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H$^+$ (200 keV)$^5$</td>
<td>O$_2$</td>
<td>120</td>
<td>0.0007</td>
<td></td>
<td></td>
</tr>
<tr>
<td>He$^{2+}$ (1.5 MeV)$^6$</td>
<td>O$_2$</td>
<td>50 (100)</td>
<td>0.03</td>
<td>(0.7–4) x 10$^{-4}$</td>
<td></td>
</tr>
<tr>
<td>Ne$^+$ (1.5 MeV)</td>
<td>O$_2$</td>
<td>7</td>
<td>10–15$^c$</td>
<td>0.03</td>
<td></td>
</tr>
<tr>
<td>Ar$^+$ (0.1 MeV)$^9$</td>
<td>O$_2$</td>
<td>30–140</td>
<td>&lt;0.01–0.04</td>
<td>0.006–0.08</td>
<td></td>
</tr>
<tr>
<td>e (30–100 eV)$^{10}$</td>
<td>O$_2$</td>
<td>120</td>
<td>0.02–0.03</td>
<td>0.005–0.007</td>
<td></td>
</tr>
<tr>
<td>hv (10.2 eV)$^{11}$</td>
<td>O$_2$</td>
<td>50 (100)</td>
<td>0.03</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H$^+$ (1 MeV)$^{12}$</td>
<td>H$_2$O$_2$</td>
<td>16 (77)</td>
<td>0.1 (&lt;0.01)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>+ 10% CO$_2$</td>
<td>77</td>
<td>0.1</td>
<td>0.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>+ 10% O$_2$</td>
<td>77</td>
<td>0.1</td>
<td>0.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H$^+$ (30 keV)$^{13}$</td>
<td>H$_2$O$_2$</td>
<td>16 (77)</td>
<td>0.22 (0.38)</td>
<td>0.098 (0.086)</td>
<td></td>
</tr>
<tr>
<td>C$^+$ (30 keV)</td>
<td>H$_2$O$_2$</td>
<td>16 (77)</td>
<td>1.7 (2.2)</td>
<td>0.23 (0.34)</td>
<td></td>
</tr>
<tr>
<td>N$^+$ (30 keV)</td>
<td>H$_2$O$_2$</td>
<td>16 (77)</td>
<td>1.6 (1.4)</td>
<td>0.21 (0.11)</td>
<td></td>
</tr>
<tr>
<td>O$^+$ (30 keV)</td>
<td>H$_2$O$_2$</td>
<td>16 (77)</td>
<td>1.4 (4.0)</td>
<td>0.26 (0.15)</td>
<td></td>
</tr>
<tr>
<td>Ar$^+$ (30 keV)</td>
<td>H$_2$O$_2$</td>
<td>16 (77)</td>
<td>2.2 (2.0)</td>
<td>0.11 (0.06)</td>
<td></td>
</tr>
</tbody>
</table>

$^a$References are as follows: 1Lefort (1995); 2Ghormley and Stewart (1956); 3Baverstock and Burns (1976); 4Baragiola et al. (1999); 5Baragiola and Bahr (1998); 6Brown et al. (1982) (ion does not stop in sample); 7Benit and Brown (1990) (ion does not stop in sample); 8Reimann et al. (1984) (ion does not stop in sample); 9Baragiola (2003); 10Sieger et al. (1998) (steady-state value); 11Westley et al. (1995) (steady-state value as no fluence dependence seen); 12Moore and Hudson (2000); 13Gomis et al. (2003).

$^b$G values are for escaping O$_2$. For H$_2$O$_2$ and O$_2$ formation, both of which require multiple events, yields after saturation are used. In a few cases yields are obtained by melting the sample. Values in parentheses are those at another temperature.

$^c$Percent of film eroded as O$_2$ molecules for long-term irradiation.
“saturated” yields change slowly with fluence. More importantly, O from water molecules at a considerable depth into the sample contributed to the O\textsubscript{2} ejected from the surface. Since there was no observed diffusion of the O\textsubscript{2} in ice at the ambient temperature (7K) over the time for their experiment, they concluded that the oxygen transport and production are stimulated by the incident ions. The transport was suggested as being due to percolation/diffusion along the damaged and transiently heated tracks (Reimann et al., 1984; Benit and Brown, 1990). They also found that in fully eroding (sputtering) thin ice films, the total amount of O\textsubscript{2} produced required about 10–15% of the D\textsubscript{2}O molecules in the films at T = 7K. On warming irradiated samples, some O\textsubscript{2} formed at depth is found to remain trapped for experimentally relevant times (see, e.g., Hart and Platzman, 1961; Benit and Brown, 1990; Baragiola and Bahr, 1998).

Matich et al. (1993) detected luminescence in 77K H\textsubscript{2}O and D\textsubscript{2}O ice from newly formed and excited O\textsubscript{2}. They suggested that the O\textsubscript{2} is formed from the interaction of a freshly produced, mobile O interacting with a previously produced and trapped O or H\textsubscript{2}O\textsubscript{2}. They favored the former. In matrix isolation studies of peroxide irradiated by UV photons luminescence from newly formed excited O\textsubscript{2} was seen. However, the oxygen was formed from mobile O (greater than ~30K in Kr lattice) interacting with O trapped as H\textsubscript{2}O-O (Khriachtchev et al., 2000). These studies also suggest that trapped O, possibly in the form H\textsubscript{2}O-O, may be an important precursor.

In Fig. 4a, the O\textsubscript{2} yield for low-energy electrons plotted as a function of electron energy exhibits an apparent “threshold” at ~10 eV (Orlando and Sieger, 2003). Although the uncertainties are large, the authors suggested there may be a lower threshold, ~6 eV, corresponding to a very small cross section for O\textsubscript{2} production (~10\textsuperscript{−20} cm\textsuperscript{2}). This could be associated with an excitation at the ice surface. Bulk ice exhibits very weak absorption at photon energies below ~6 eV, but exhibits a strong absorption that, depending on the ice structure, begins at about 7.3 eV with a peak at ~8.6 eV. This
is followed by a peak in absorption at $\sim$10 eV. The results in Fig. 4a show that there is a dramatic increase in the production of O$_2$ at $\sim$10 eV, which is the onset of secondary electron production in the bulk (Orlando and Sieger, 2003).

For incident fast ions, the yield at a given temperature was found, after a small fluence, to be independent of whether the sample was crystalline or amorphous ice (Brown et al., 1982). However, using low-energy electrons the yields were found to be smaller for an initially crystalline ice (Orlando and Sieger, 2003). Since very low doses of ion radiation (a few eV per molecule) can convert crystalline ice to amorphous ice at low temperatures (Leto and Baratta, 2003), the damage produced by the penetrating ions used by Brown et al. (1982) affected the O$_2$ yield. The structural damage produced may create trapping sites, cause changes in the electronic relaxation pathways, or enhance percolation.

The temperature dependence of the O$_2$ yield is shown in Fig. 5 for electrons incident on initially amorphous (Fig. 5a) and initially crystalline (Fig. 5b) ice. A small decrease in efficiency is seen in both cases at $\sim$120–130K, where Ic forms from amorphous ice and pore collapse occurs (Rowland et al., 1991). This is followed by an increasing yield with increasing $T$ and then by a more dramatic drop near $\sim$160K where Ih forms. During the transition to Ih trapped molecules have been shown to escape efficiently from ice samples (Ayotte et al., 2001). A large drop in the yield is also seen in Fig. 2b for incident Ar$^+$ ions.

In modeling the dramatic decreases in the yield in Figs. 2b and 5 care must be taken. That is, the time for crystallization of an amorphous sample (Baragiola, 2003), even allowing for the large uncertainties, is $<30$ min at $\sim$145K and becomes $<1$ min at 160K. Therefore, pulsed radiolysis experiments should be carried out at these temperatures, and the transients observed. Since the time for conversion from amorphous to crystalline ice can be shorter than the experimental times at $>145$K, the results are not comparable to those for which the chemical state of the ice at a given fluence is stable over experimental times. Below we focus on the data below $\sim$140K.

We have emphasized processes initiated by the electronic excitations and ionizations produced. However, momentum transfer collisions, which are the dominant energy loss process for low-energy ions, also produce dissociations, defects, and O$_2$ in ice (Bar-Nun et al., 1985). The relative efficiency of momentum transfer and electronic processes for producing O$_2$ needs further study. As the penetration depths are much smaller when
the former dominates, the produced O₂ likely escapes readily.

**H₂ formation and loss: correlation with O₂**

The production of O₂ from a low temperature ice by radiolysis correlates with the formation and loss of H₂ (or D₂ from D₂O ice) (Reimann et al., 1984). D₂O is used to reduce the background in mass spectrometry studies. The yields of O₂ from D₂O and H₂O ices were shown to be comparable. However, the total yields from D₂O were about 10% less (Reimann et al., 1984), consistent with H (D) transport being important. It is seen in Fig. 3 that D₂ is promptly produced and lost from the D₂O ice. At higher fluence, the D₂ yield is seen to exhibit a dependence like that for O₂. For the 1.5 MeV Ne⁺ ions, which fully penetrate the ice sample, the D₂ yield eventually decreases since D₂ is produced and escapes from the full thickness of the film.

Because of H₂ (D₂) loss the surface region of the irradiated ice becomes depleted in H (D) relative to O favoring the formation of oxygen-rich species. The change seen in the ratio of H (D) to O in the irradiated ice is small. An irradiated film (~100 nm) remains stoichiometric to better than 2% (Brown et al., 1980) and in the near surface region Auger spectroscopy suggests only a slight oxygen enhancement due to irradiation by keV electrons (Rye et al., 1978). Sieger et al. (1998) suggested a precursor concentration of the order of a percent. Such concentrations are an order of magnitude smaller than the steady-state concentration of dissociated H₂O (Table 2).

Using infrared spectroscopy the damaged H₂O concentrations at low temperatures in the saturation regime are about 10% over the irradiated volume (Benit et al., 1987; Watanabe et al., 2000; Gomis et al., 2003). This fraction is the ratio of the dissociation cross section to the effective cross section for recombination to H₂O as discussed later. At a 10% concentration most H₂O will have a neighbor that is dissociated.
At temperatures above ~40K it is seen in Fig. 2 that the D₂ and O₂ yields exhibit the same temperature dependence, suggesting a correlation between D₂ and O₂ loss. H₂ (D₂) can be formed by reactions between diffusing hydrogen from dissociated water or directly [i.e., H₂O* → H₂ + O (e.g., Kimmel and Orlando, 1995); H₂O* → (H + OH)cage → H₂ + O (e.g., Matich et al., 1993); H₂O* + e → H₂ + OH (e.g., Williams et al., 1996)]. Subtraction of the nearly constant D₂ yield in Fig. 2a gives the Arrhenius plot in the inset. Since molecular hydrogen readily escapes at these temperatures, it is the H₂ (D₂) formation process that has an activation energy of ~0.03 eV/molecule. The fact that slopes of the yields for H₂ and O₂ above ~40K are similar suggests that H₂ (D₂) formation and loss is the rate-limiting step in determining the production and loss of O₂ at these temperatures.

Although the data at low T in Fig. 2a have considerable uncertainties, below about 20–40K the D₂ production is roughly independent of temperature, but the O₂ yield continues to decrease with decreasing temperature. Radiolytically produced D₂ is mobile and can escape above ~15–20K (Watanabe et al., 2000), but O₂ is immobile at such temperatures, and the incident He⁺ ions are much less efficient at causing percolation than the incident Ne⁺ discussed earlier.

The production of H₂ (D₂) from ice has also been studied using low-energy electrons and UV photons at very low temperatures. In the former studies, absolute yields were not obtained, but there appeared to be a threshold at ~6.3 eV (Fig. 4b). This is roughly the threshold for excitation of a surface state (Khusnatdinov and Petrenko, 1992), and the threshold for peroxide production is close to this value. The efficiency for H₂ (D₂) production increases around ~11 eV with a second steep rise at ~17 eV (Kimmel et al., 1994). The O₂ and D₂ yields versus electron energy in Fig. 4 exhibit some similarity in the threshold region, although the uncertainties are large and the sample temperatures different. Measuring the H₂ (D₂) and the O₂ ejecta simultaneously over a range of temperatures, as in the Ne⁺ experiments, would be instructive.

Using 9.8 eV photons at low T (12K) Watanabe et al. (2000) measured the D₂ ejected and trapped in ice. They obtained a cross section for production of D₂ (Table 2) at low fluences that is ~10–20% of the total absorption cross section with significant uncertainties. They also found that the equilibrium damage fraction in the sample was ~10–20% of the D₂O molecules, but the equilibrium production of D₂ was about an order of magnitude smaller, ~1–2% at their temperatures. They suggested that the D₂ is formed at grain interfaces and cracks and on the surfaces of pores. In a mixed ice, D₂O + CO, exposed to UV photolysis, D₂ and CO₂ formation are correlated (Watanabe and Kouchi, 2002). The D₂O dissociates to produce D₂ plus O, and this transiently mobile O reacts with CO to produce CO₂.

**Precursor state and peroxide**

In order to produce O₂ from low temperature ice, it appears that the ice sample must lose hydrogen and form trapped, oxygen-rich, reactive species. The efficiency of production also appears to be affected by the level of defects and damage in the ice, consistent with the suggestion that the hydrogen-bonding network is important in the production of O₂ via availability of trapping sites, new electronic relaxation pathways, or the nature of the bonding of precursors. Here we briefly examine the possible role of the suggested precursor molecules H₂O₂ and HO₂. We note that H₂O₂ might not readily dissolve in ice, possibly accounting for its low abundance in some experiments. It appears to be heterogeneously distributed in the form of microcrystals (Gurman et al., 1967). If H₂O₂ does act as a precursor, the formation of aggregates could affect the dimer absorption bands (Cooper et al., 2003a) and affect the production and stability of O₂ (Cooper et al., 2003b).

The results of Gerakines et al. (1996), in which ice at ~10K is irradiated by UV photons, confirm that H₂O₂ forms in ice from two OH after a build-up of trapped OH. They monitored the band associated with H₂O-HO (Langford et al., 2000), in which the HO is bound to water with 0.24 eV. Therefore, they might only be monitoring a subset of the trapped OH seen in earlier experiments (e.g., Taub and Eiben, 1968). The H₂O₂ concentration in ice reaches a steady-state level at fluences of about 10¹⁸ photons/cm² (Gerakines et al., 1996). As seen in the model section, this gives an estimate of the H₂O₂ photodestruction cross section of the order of 10⁻¹⁸ cm². Similarly, HO₂ begins to be seen in absorption at about a few times 10¹⁷/cm² shortly after they begin to detect H₂O₂. The absolute yields were not measured.

Westley et al. (1995) detected H₂ and O₂ pro-
duced by Lyman-α (9.8 eV) radiation of ice, but found no fluence dependence for fluences greater than $\sim 10^{17} \text{cm}^{-2}$. They also saw small amounts of H$_2$O$_2$ by programmed thermal desorption of the sample, but made no quantitative evaluation. Comparing their lowest fluence for the production of O$_2$ with the result of Gerakines et al. (1996) for peroxide suggests that H$_2$O$_2$ and HO$_2$ are probably not important precursors of O$_2$. In UV photolysis of H$_2$O$_2$ using 6.4 eV photons the production of O$_2$ was not observed (Vaghjiani et al., 1992), and the excitation of an irradiated ice, which presumably contained some peroxide, by 3.7 eV photons did not produce O$_2$ (Baragiola et al., 2003). Direct excitation of matrix-isolated H$_2$O$_2$ at low temperature also did not yield O$_2$, but the production of a mobile O that reacted with trapped O (H$_2$O-O) did give O$_2$ (Khriachtchev et al., 2000).

Irradiating with 200 keV protons at temperatures of 40–129K, Bahr et al. (2001) found only about 0.001–0.02% H$_2$O$_2$ using programmed thermal desorption as compared with earlier experiments that suggested larger values (e.g., Table 2). Using infrared absorption Moore and Hudson (2000) found a $G$ value of $\sim 0.1$ for incident MeV protons at low temperature, but the signal in the observed band became negligible at 80K, suggesting that H$_2$O$_2$ was not being formed. They also found that adding O$_2$ significantly increased the production efficiency of H$_2$O$_2$. That is, that the amount of peroxide was affected by the amount of trapped oxygen. Based on the matrix isolation studies (Khriachtchev et al., 2000), dissociated mobile O might trap as H$_2$O-O, which on excitation converts to H$_2$O$_2$. Therefore, even if H$_2$O$_2$ is not the precursor, the peroxide and trapped oxygen concentrations will be related.

Although molecular oxygen was not a product of photolysis of matrix isolated H$_2$O$_2$, it was a product of photolysis at 266 nm (4.66 eV) of peroxide dimers in an argon matrix: $2 \text{H}_2\text{O}_2 \rightarrow 2 \text{H}_2\text{O} + \text{O}_2$ (Engdahl and Nelander, 2002). This decomposition was thought to be due to the considerable distortion of the bonds in the dimer. Therefore, the configuration or distortion by the lattice of peroxide or any other precursor molecule in the ice may be critical (Sieger et al., 1998). In addition, more recent experiments show that $G$ values for the production of H$_2$O$_2$ by 30 keV incident ions are significant, as are the steady-state ratios of H$_2$O$_2$/H$_2$O (Gomis et al., 2004). Ratios of the order of 0.2–4% were found at 16K and 77K in the irradiated regions, with incident H giving the smallest fraction and incident O the largest (Table 2). At these concentrations, peroxide molecules might segregate, forming inclusions (Gurman et al., 1967; Cooper et al., 2003b). Since the amount of trapped peroxide also competes with the amount of trapped O, studies are needed to describe the chemical state of the solid produced by radiolysis. This will be critical in describing the fate of the irradiation products at Europa. In particular, the chemical composition favorable for producing O$_2$ needs to be determined, as does the importance of trapped O, H$_2$O$_2$, HO$_2$, or peroxide dimers as precursors.

Other species

In the model below, we will refer to atomic and molecular species trapped in ice. Such species are often discussed in the literature on radiolysis and photolysis (for summaries, see Matich et al., 1993; Johnson and Quickenden, 1997). Trapped OH, O, H$_2$O$_2$, and HO$_2$ have been discussed and/or measured by a variety of techniques (absorption and luminescence spectroscopy, electron spin resonance, programmed thermal desorption, etc.). Care must be taken when using these data as results for ice samples formed below $\sim 160$K or those exposed to penetrating ion beams likely have numerous defects, voids, and grain interfaces so that a variety of trapping sites and trap depths exist. Therefore, when a particular band for a trapped species (e.g., OH) disappears with increasing temperature, it could be due to a change in the nature of the trapping as well as to loss of the species by reaction.

Although H is discussed below, we do not distinguish it, in these simple models, from H$^+$ trapped as the hydronium ion, H$_3$O$^+$, which would mean that there are corresponding negative ions present. Therefore, below we refer to the various species as if they are neutral, although this might not be the case. Although trapped electrons are detected only over a narrow range of temperatures ($\sim 100–120$K), negative ions must be important over a broad range of temperature.

We also note that SO$_2$ and a sulfate, and CO$_2$ and a carbonate, appear to be trapped species in Europa’s icy surface. Under radiolysis each of these can dissociate directly, giving O$_2$. However, with the exception of the sulfate, their densities are less than 1%, so they are not relevant sources of O$_2$. However, their presence is indicative of the
preference for forming oxygen-rich molecules in Europa’s ice and can affect the efficiency of production of $O_2$ and $H_2O_2$.

MODELS FOR FORMATION OF $O_2$

Introduction

Based on the data described above, the yields for incident electrons and ions are found to be nearly linear in fluence at the lowest fluences for which $O_2$ is detected. In addition, the relevant alterations of the ice samples by radiolysis appear to be stable and independent of the beam flux. Remarkably, this is the case both for low-energy electrons that make only a single excitation for each impact and fast ions that make a density of excitations along their path through the solid. This suggests that $O_2$ is produced and trapped in the initial events and then caused to escape from the solid by the subsequent radiation, or that a stable chemical alteration of the ice is required before the radiation can produce and eject $O_2$.

Because H produced by the dissociation of water molecules can attack trapped $O_2$ and any precursor oxidants, the loss of H is important. This occurs by the production and loss of hydrogen molecules, as discussed, leaving a surface that is slightly rich in O relative to H. The $O_2$ production mechanism could be direct excitation of a particular precursor species, or it might not be specific. That is, a new OH or O produced by the incident radiation could react with the H-depleted solid, producing $O_2$. This would occur more efficiently as the ratio of O to H in the near surface region increased.

In their early work, W.L. Brown and colleagues assumed that processes similar to those used to describe radiolysis of liquid and gaseous $H_2O$ could be used to describe the radiolysis in ice. The low activation energy that they found was assumed to be associated with diffusion of some mobile radical species in ice, such as H or O, or, possibly, diffusion of the $O_2$ molecule itself. Based on their studies of ejection from isotopically labeled $D_2O$ samples, they concluded that the $O_2$ is formed in the track of a single ion and then ejected by subsequent ions (e.g., Benit and Brown, 1990). More recently, trapped species have been suggested as precursors. These are either subsequently excited by the incident radiation or attacked by newly produced mobile species. We consider a simple model that incorporates all of these processes and can be used to organize and interpret the experimental data. We also discuss its relationship to more complete models. In this discussion, much of which is in the Appendix, we consider the standard radiation products that have been often described. However, in a solid, the excited electron cloud produced by absorption can overlap a number of lattice sites. Therefore, their relaxation pathways and/or product species could be very different from those that have been traditionally considered in the literature on radiolysis and photolysis.

Precursor model

The column density of a precursor species, $N_p$, formed in ice by incident radiation can be calculated using a simple model. In this model cross sections are used for the production, $\sigma_p$, and destruction, $\sigma$, of the precursor. $O_2$ is then formed by excitation of the precursor or by reaction of a newly formed radical with the precursor. This is also described using a cross section, $\sigma_{O_2}$. For incident electrons having a small penetration depth, the $O_2$ produced is assumed to rapidly diffuse to the surface and escape (Sieger et al., 1998). More generally, we define $N$ as the column density of $H_2O$ from which the incident radiation can produce and eject $O_2$. A pair of rate equations gives both $N_p$ and the production rate of oxygen, $dN_{O_2}/dt$. That is,

$$H_2O + \text{radiation} \rightarrow \text{precursor;}$$
$$\text{precursor + radiation} \rightarrow O_2$$

giving

$$dN_p/dt = \sigma_p \phi N - \sigma \phi N_p$$ (1)
$$dN_{O_2}/dt = \sigma_{O_2} \phi N_p$$ (2)

In Eq. 1 $\phi$ is the incident flux, and the total precursor destruction cross section can be written as $\sigma = \sigma_p' + \sigma_{O_2}$, with $\sigma_p'$ accounting for precursor destruction processes other than the formation of $O_2$. Solving Eqs. 1 and 2, and assuming $N$ is nearly constant (~10% level as discussed), the fraction of precursors, $c_p$, in the affected column after time $t$ is obtained (Appendix):

$$c_p = N_p/N = [\sigma_p/\sigma] [1 - \exp(-\sigma \Phi)]$$ (3)

Here $\Phi = [\phi t]$ is the fluence (flux $\times$ time), which
is the number of particles (photons, electrons, or ions) incident on the surface per unit area. Using \( c_p \) in Eq. 2, the \( O_2 \) yield, \( Y \), at any fluence can be written in terms of the yield at steady state, \( Y_\infty \):

\[
Y = \frac{dN_{O_2}}{dt}/\phi = \sigma_{O_2} c_p N = Y_\infty \left[1 - \exp(-\sigma \Phi)\right] \tag{4a}
\]

\[
Y_\infty = \left[\sigma_p \sigma_{O_2} / \sigma\right] N \tag{4b}
\]

If we also account for the reduction in the density of water molecules in the initial column \( N \), these forms change only slightly. The size of the two parameters \( Y_\infty \) and \( \sigma \) can be obtained by fitting the yield versus fluence data, such as that shown in Fig. 3.

For the low-energy electron data, Sieger et al. (1998) showed that the ratio, \([Y/Y_\infty]\), for a given incident electron energy is independent of temperature over a narrow range of temperature. Therefore, the destruction cross section, \( \sigma \), in Eq. 4a is roughly independent of \( T \) and can be estimated from the \([Y/Y_\infty]\) curve. Sieger et al. (1998) found a precursor destruction cross section \( \sigma = 0.8-3.0 \times 10^{-16} \text{ cm}^2 \) for incident electron energies from 30 to 100 eV. This is of the order of the electron impact ionization cross section for \( H_2O \).

Based on the above model, the lack of an observed fluence dependence for fluences down to \( \sim 10^{17} \text{ h}v/\text{cm}^2 \) in the Lyman-\( \alpha \) irradiation of ice (Westley et al., 1995) can be examined. The lowest fluence used implies that the precursor destruction cross section for Lyman-\( \alpha \) is of the order of the Lyman-\( \alpha \) absorption cross section in ice \( \sim 0.9 \times 10^{-17} \text{ cm}^2 \).

Sieg et al. (1998) also assumed that \( \sigma_p' = 0 \). This would mean that the precursor is only destroyed by production of \( O_2 \) (i.e., \( \sigma = \sigma_{O_2} \)). That is unlikely since suggested precursors can be destroyed by reaction with \( H \) and other radicals. Their assumption would also mean that the cross section for production of \( O_2 \) from a precursor, \( \sigma_{O_2} \), is large. This would be surprising and appear to contradict some of the data discussed above. Instead, we assume that \( \sigma \) is not equal to \( \sigma_{O_2} \) and the total destruction cross section, \( \sigma \), is of the order of the ionization or absorption cross section.

Having obtained \( \sigma \), the measured temperature dependence for production of \( O_2 \) is contained only in \( Y_\infty \). Over a narrow range of \( T \), one can write \( Y_\infty(T) \approx Y_\infty \exp(-E_a/kT) \) and obtain the estimated of the activation energies in Table 2. If \( \sigma_p' \neq 0 \), as discussed, then \( \sigma_p \) and \( \sigma_{O_2} \) in Eq. 4b cannot be obtained separately from the data for \( Y_\infty \) unless an independent measure of \( c_p \) is obtained. Such a measurement is critical for describing the chemical state of the irradiated surfaces.

The observed temperature dependence of \( Y_\infty \) is contained in \( \sigma_{p'} \), \( \sigma_{O_2} \), or \( N \). Here \( N \) is the “depth” from which newly formed \( O_2 \) can reach the surface and escape given as a column density of \( H_2O \). The physical depth is obtained by dividing the column density \( N \) by the molecular number density of the ice. Assuming that in the low-energy electron experiments \( N \) is independent of temperature and is about three monolayers (Sieger et al., 1998), the measured \( Y_\infty \) gives \( [\sigma_{O_2} \sigma_{p'}/\sigma] \sim 0.5-2.0 \times 10^{-18} \text{ cm}^2 \) over the electron impact energy range. At 110–120K, this ratio was found to be proportional to \((E - E_o)\) for \( E > E_o \sim 10 \text{ eV} \), again assuming fixed \( N \) (Orlando et al., 1998; Orlando and Sieger, 2003).

In the following section we first consider a precursor, like peroxide, that typically forms from two dissociation events. We use this to show under what circumstances such a model does not violate the observed linearity of the \( O_2 \) yield data with fluence. Following that, we relate the simple precursor model above to the case where trapped O is the precursor. We then use the model for trapped O to examine the effect of the trap density on the production of \( O_2 \). The density of traps (defects) is determined by the sample formation temperature and the subsequent radiation damage. Finally, we consider the escape depth, \( N \), for penetrating radiation within the precursor model. These discussions are supported by more detailed rate equations in the Appendix.

Precursor: trapped peroxide

The proposed precursor peroxide is typically formed from products of two dissociation events: i.e., \( 2H_2O \rightarrow 2H + 2OH \rightarrow H_2 + H_2O_2 \). This was confirmed in low temperature ice (Gerakines et al., 1996). It is also possible that a dissociation producing a trapped O, followed by an excitation event, can produce peroxide: \( 2(H_2O + h\nu) \rightarrow H_2 + H_2O-O + h\nu \rightarrow H_2O_2 + H_2 \) (e.g., Khriachtchev et al., 2000). The \( O_2 \) yield versus fluence for incident electrons is reasonably well fit by the yield expression above for fluences greater than \( \sim 10^{14} \text{ /cm}^2 \). Therefore, it has been suggested that
any precursor species must be formed in a single event. Using a model in the Appendix in which the precursor is formed by two events, we show this is not necessarily the case. Precursor formation, if it is fast, could involve two dissociation events and give the measured fluence dependence. Although we consider peroxide here, these conclusions apply to other possible precursors.

In the example in the Appendix, H$_2$O is dissociated to H + OH according to the cross section $\sigma_d$. The reactions of two OH units to form H$_2$O$_2$ (rate constant, $k_{2OH}$) and 2 H to form H$_2$ ($k_{2H}$) compete with the recombination of H and OH to H$_2$O ($k_{H,OH}$). If $k_{2H}$ is much greater than $k_{2OH}$, then H$_2$ loss dominates at low fluences as expected (Appendix). Steady state requires, not surprisingly, that the rate for forming H$_2$O$_2$ is roughly equal to the rate for forming H$_2$. Finally, it is seen in the Appendix that the low H$_2$O$_2$ concentrations suggested by experiment imply that $k_{H,OH} >> (k_{2H} k_{2OH})^{0.5}$. Such sizes are reasonable.

The set of rate equations in the Appendix that use number densities of species is integrated as solutions that combine the rate of production of freshly produced mobile species with previously produced trapped species. We show in the Appendix that the O$_2$ yield versus fluence can be written in a form similar to that in Eq. 4a but with a small offset due to the two-step precursor formation process:

$$Y \approx Y_\infty(T) \left[1 - \exp(-\sigma \Phi) - (\sigma/\sigma_r)\right];$$

for $\Phi >> \sigma_r^{-1}$ (4c)

Here $\sigma$ is again the precursor destruction cross section, but $\sigma_r = (2\sigma_{2OH} + \sigma_{H,OH})$ is the effective cross section for loss of OH by formation of H$_2$O$_2$ and H$_2$O. The corresponding expression for $Y_\infty(T)$ is given in the Appendix.

The form for the yield versus fluence in Eq. 4c is consistent with the low-energy electron measurements if $(\sigma/\sigma_r) << 1$ and if $\sigma_r >> \Phi^{-1} \approx 10^{-14}$ cm$^2$. Such sizes are indeed possible. What is required is that, at the relevant temperatures (50–110K), the interaction length associated with $\sigma$ is more than a few molecular layers (greater than ~10 Å). A cross section that is likely to be large above ~20K is $\sigma_{H,OH}$, which describes the mean distance for diffusion of mobile H before it reacts. Since $\sigma$, discussed earlier, is of the same order of magnitude as the H$_2$O dissociation cross section, $\sigma_d$, then the precursor concentration, $c_p$, (in this case H$_2$O$_2$) is roughly proportional to $[\sigma_{2OH}/\sigma_{H,OH}] << 1$ (Appendix).

Based on the above, a two-step precursor formation process could be consistent with the electron data, contrary to the statements in Sieger et al. (1998), Orlando et al. (1998), and Orlando and Sieger (2003). Experiments are needed to determine the relevant cross sections. Below we consider a precursor formed in a single excitation event.

**Precursor: trapped O**

O$_2$ can be formed, for instance, by diffusion of a transiently mobile O to a previously formed and trapped O or to the production of O near the site of a previously produced and trapped O (Match et al., 1993; Johnson and Quickenden, 1997). We refer to this as the Match–Johnson–Quickenden (MJQ) model and note that O + OH $\rightarrow$ O$_2$ + H can also give molecular oxygen.

Trapped O as H$_2$O–O was in fact seen to be a precursor to O$_2$ when attacked by a mobile O in a Kr matrix (Khriachtchev et al., 2000). Therefore, O trapped as H$_2$O–O was also suggested as a precursor in ice (Johnson, 2001). Before proceeding we note that the examination of the MJQ model in Sieger et al. (1998) was incorrect. They considered two mobile interacting species whose lifetimes were long compared with the bombardment rate, rather than a new mobile O interacting with a previously trapped O. Although this has not been corrected, recently they added O trapped as H$_2$O–O as a possible precursor (Orlando and Sieger, 2003). O trapped as H$_2$O–O is seen in matrix isolation studies, as discussed above, but it has not yet been identified in ice, and, like OH, it may trap in a number of ways.

The MJQ model is essentially the following. Formation of H$_2$ + O is followed by loss of H$_2$ and trapping of O (O$_1$). A subsequent dissociation or excitation event can lead to the destruction of O$_1$ by reaction with, for instance, H or by conversion to H$_2$O$_2$. However, if this dissociation event also leads to H$_2$ + O, a mobile O is produced that can react with O$_1$ with an interaction length that depends on $T$. This results in the formation of O$_2$ [O + O$_1$ $\rightarrow$ O$_2$] giving a net production of 2 H$_2$ and 1 O$_2$. In the Appendix the relevant rate equations (Eqs. A1c–A3c) are con-
The density of trapping sites, \( n_v \), was not explicitly accounted for. However, in the discussion of both the experimental data and models, trapping sites have been assumed to be important. It has been demonstrated repeatedly that the density of defects, voids, and interfaces decreases as the temperature of formation of the ice increases. However, the efficiency of production of \( O_2 \) is the opposite; it increases with increasing \( T \). Therefore, the oxygen yield varies in a manner that is the inverse of the trap density over a range of temperatures. For penetrating ions in which the energy density deposited is high and \( O_2 \) might be formed in a single track, a simple explanation has been given. As the density of traps for \( O_2 \) is reduced and the temperature increases, the \( O_2 \) produced can diffuse to the surface and escape more efficiently, limiting back reactions on further irradiation. This is examined in the next section. However, such a process does not affect the low-energy electron yields for which the penetration depth is small and the formed \( O_2 \) escapes readily at the measurement temperatures. In Eqs. A1c, A1c’, A3c, and A10 in the Appendix, we again use a simple set of rate equations for trapped and mobile \( O \) in order to determine the role of the trap density, \( n_v \), on the production of a precursor species. The conclusions apply to any model based on a trapped precursor.

In the MQJ model, mobile \( O \) can be trapped forming \( O_t \) (described by \( k_{O,t} n_t \)) and can react with previously trapped \( O \) to form \( O_2 \) (\( k_{O,O} \)). In addition, it can react at other sites, and \( O_2 \) can be destroyed by mobile reactive species such as \( H \) (\( k_{H,O} n_{H,t} \)). Mobile \( H \) can also react with other trapped species (\( k_{H,R} n_{H,R} \)). Incorporating these reactions, Eq. A10 in the Appendix gives a steady-state yield, \( Y_{\infty} \). When the density of traps is large, the steady-state yield is given in Eq. A5c:

\[
Y_{\infty} = \left( \sigma_d' \sigma_d / \sigma_d \right) \left[ \left[ k_{O,O} k_{H,R} n_t / [k_{H,O} k_{O,t} n_t] \right] N \right]
\]  

Here \( \sigma_d' \) and \( \sigma_d \) are the dissociation cross sections that determine the production of \( H \) (\( H + OH \)) and \( O \) (\( H_2 + O \)) by the incident radiation. Comparing the result in Eq. 5 with \( Y_{\infty} \) in the simple precursor model in Eq. 4b, the dissociation cross sections in Eq. 5 are now scaled by a ratio of the reaction rates.

It is seen in Eq. 5 that the steady-state yield, \( Y_{\infty} \), depends inversely on the density of traps, \( n_t \). That is, there are competing destruction processes for trapped \( O \) (\( O_t \)). Therefore, in order to form \( O_2 \) a mobile \( O \) competes with mobile \( H \) to find a trapped \( O \) before it becomes trapped. In this way, the increasing \( O_2 \) yield correlates with the reduction in the trapping sites with increasing temperature of formation. The small activation energies discussed earlier would be related to the re-orientation of the lattice binding leading to the reduction in trap density. At relatively high \( T \) the density of traps becomes small, so that only the
sample surface or grain interfaces might act as traps, accounting for the observed drop in the yield at high $T$. For this reason, it is important to determine if the yield for $T$ greater than $\sim 150K$ depends on the incident flux, $\phi$. Since other quantities in the expression for $Y_e$ could also be temperature dependent, experiments are needed. These would likely be pulsed radiolysis experiments in which the transients are studied rather than the steady-state yields. However, the available data for lightly ionizing radiation do suggest that the $O_2$ yield depends inversely on trap density, as in the model above.

Escape from depth

The quantity $N$ in Eq. 1 is the “depth” given as a molecular column density from which $O_2$ formed below the surface can percolate to the surface and escape. It can be converted to a physical depth by dividing by the molecular number density of the ice. In the case of the low-energy electrons, the depth below the surface at which ionizations and excitations are produced is small. However, for fast ions that penetrate many monolayers, this is not the case. Below we examine $N$ in Eq. 1.

Although it has long been understood that two excitations events are required to produce $O_2$ (e.g., Brown et al., 1982; Reimann et al., 1984), the precursor model suggests that at saturation (steady state) any new event can produce $O_2$ from the steady-state density of trapped precursors. Therefore, one might expect the yield at saturation to be nearly linear in the excitation cross section. This is the case for the low-energy electrons, and it was initially assumed to be the case for the fast ions (Brown et al., 1980; Reimann et al., 1984). However, Baragiola et al. (2003) showed that the total sputtering yield in the saturation region at temperatures greater than $\sim 100K$, which is dominated by decomposition (Brown et al., 1982), is proportional to the square of the electronic energy deposition per unit path length in the solid, $(dE/dx)_e$. Assuming that the production and destruction cross sections in $Y_x$ in Eq. 4b roughly scale with $(dE/dx)_e$, then their ratio $[\sigma_p \sigma_{O_2}/\sigma]$ also roughly varies as $(dE/dx)_e$. If this is the case, then the observed quadratic dependence implies that the depth, $N$, from which $O_2$ can be mobilized to escape, must also depend on the excitation density, $(dE/dx)_e$. This is consistent with the observation that the $O_2$ yield depends on thickness for samples thinner than the ion penetration depth (Reimann et al., 1984; Benit and Brown, 1990). Therefore, the percolation depth for escape, $N$, is a critical factor in comparing yields for penetrating radiation with those for non-penetrating radiation, like the low-energy electron and low-energy ion data. It is also seen that percolation and trapping can be included within the simple model considered here.

Model summary

We have examined the simple precursor model introduced by Sieger et al. (1998) to explain their electron data. We have shown how it can be generalized and derived from an integration of the appropriate chemical rate equations, with the cross sections and total column density containing the reaction rates and the physics of diffusive transport. Therefore, the parameters can have very different meanings from those initially assumed. The equations are useful when there are fast processes, which go to completion in times much shorter than the time between particle impacts, and slow processes, associated with species that are assumed to be trapped between particle impacts. This separation allowed us to examine those models proposed for precursor formation and destruction due to reacting mobile species formed from dissociation events. Further, from the size of the onset of the linearity of the yield versus fluence we can place constraints on the role of nonlinear processes, such as those that might be associated with the formation of a precursor like peroxide.

With these extensions, this simple model is useful for approximating the full rate equations in the temperature region for which the yields depend on the fluence (dose) and not on the dose rate. Based on the assumptions in the model, this implies temperatures at which precursor species are stable over experimental times. At the highest temperatures for the yields shown in Fig. 4a, this might not be the case. This should be tested experimentally. In this regard, it is puzzling that experiments have shown that the absorption bands associated with certain trapped species, such as OH and trapped electrons, “disappear” at $\sim 100–120K$ (see, e.g., Johnson and Quickenden, 1997), whereas the $O_2$ yield data indicate that relevant precursor species must be stable to $\sim 140K$. Therefore, the proposed $O_2$ production processes can only be distinguished by directly determining the chemical state of the irradiated ice.
It may be the case that a particular precursor is not required, as mentioned earlier. Rather, after a sufficient level of oxidation a newly produced O or OH can react in the oxygen-rich lattice producing \( \text{O}_2 \) in a pseudo-first-order process. This can be tested experimentally. Indeed, trapped \( \text{O} \) and peroxide may be changed into one another as in the matrix isolation experiments (Khriachtchev et al., 2000). Therefore, their relative concentrations versus temperature and dose should be studied.

In the model considered here, it is seen that the parameters in \( Y_x \) must account for the strong temperature dependence. Since the number of bulk trapping sites decreases with increasing \( T \) as the ice sample is annealed, one might expect that the precursor concentration would decrease. We suggest that the observed temperature dependence is determined by the competition between the availability of trapping sites and mean interaction distances of a mobile species such as \( \text{O} \) and \( \text{H} \). That is, the \( \text{O}_2 \) yield varies inversely with the density of traps over a range of temperatures. In the simple model above, this effect is included indirectly as shown using the more detailed equations in the Appendix.

**EUROPA**

**Oxygen and peroxide production at Europa:**

\( G \) values

The dependence of the yield on the thickness of the ice sample for highly penetrating ions suggests that the \( \text{O}_2 \) yield is roughly related to the amount of energy deposited in the sample. Therefore, the amount of \( \text{O}_2 \) produced and lost from ice in steady state is often given as a \( G \) value, the number of molecules produced per 100 eV deposited in Table 2. In applying these \( G \) values to the planetary environment care must be taken, since the yields are temperature, fluence, and excitation density dependent. They also are affected by the presence of other proton scavengers known to be present in Europa’s ice.

The \( G \) values for peroxide in Table 2 are those for production at low fluence, but the \( G \) values for \( \text{O}_2 \) are for the production and escape of gas-phase oxygen at saturation. Therefore they depend on the formation and destruction cross sections in the model above. Such \( G \) values can be used to describe the steady-state source of the ambient \( \text{O}_2 \) atmosphere at Europa, but are not helpful in determining the ability to produce and trap \( \text{O}_2 \) at depth into the icy surface. Over the time scales of the experiments, some \( \text{O}_2 \) is seen to remain trapped and is not destroyed by radicals. Typically, there are a number of trapping sites, and recent estimates of the activation energy for an \( \text{O}_2 \) molecule trapped in a substitutional site (Hori and Hondoh, 2002) suggest that it can be trapped for times comparable to the time required for the conversion of amorphous ice into Ih (Ayotte et al., 2001). The stability of \( \text{O}_2 \) inclusions has not been studied.

To understand the relationship between the \( G \) values for \( \text{O}_2 \) in Table 2 we note that fast light ions and electrons lose their energy predominantly by producing ionizations and excitations. The ionization events produce secondary electrons that can result in further ionizations. The number of ionization events, \( N_i \), produced by a fast light ion stopping in a water ice is, \( N_i = E_0/W \), where \( E_0 \) is the initial energy and \( W \) is the average energy expended per ionization event, \( \sim 27 \text{eV} \) in water ice. Therefore, radiolysis by fast ions is often described as the net effect of the shower of electrons set in motion by the incident ion. In this manner, the \( G \) values for production of \( \text{O}_2 \) from ice by energetic light ions and electrons can be roughly estimated as the sum of the effects of all the secondary electrons using the yield, \( Y_\text{e} \), for \( \sim 10–100 \text{eV} \) electrons. That is, if we ignore the percolation depth, \( N \), we can write the number of \( \text{O}_2 \) produced as the number of ionization events times \( Y_\text{e} \), which already has in it the destruction processes. That is, \( G \sim N_iY_\text{e}/E_0 \sim Y_\text{e}/W \sim 0.006 \text{O}_2/100 \text{eV} \).

This estimate of \( G \) is seen to be an order of magnitude larger than the keV proton value for \( \text{O}_2 \) in Table 2 but is much smaller than the \( G \) value for energetic \( \text{Ne}^+ \). These differences from the simple estimate are consistent with the observation that the yield in the saturation regime for penetrating ions varies nonlinearly with excitation density. The difference from the keV proton \( G \) value is likely due to the inability of \( \text{O}_2 \) to escape from depth before destruction. On the other hand, the larger \( G \) value seen using MeV \( \text{Ne}^+ \) is likely due to the high density of excitation. This can result in more efficient production of \( \text{O}_2 \) increased production of damage sites for forming \( \text{O}_2 \), and/or increased transport (percolation) along the transiently heated track. That is, the ability of the formed \( \text{O}_2 \) to percolate to the surface during ion
bombardment plays an essential role in determining the measured yields as discussed above. This effect needs to be evaluated for a planetary surface subject to particle fluxes that are many orders of magnitude smaller than those used in the laboratory.

In the absence of O\(_2\) yields for all of the relevant ions and energies, an estimate of the total supply of O\(_2\) can be obtained using the \(G\) values in Table 2. For the energetic oxygen and sulfur ions we use \(G\) values for neon and argon ions. These are lower bounds as the data were obtained at temperatures much lower than the surface temperatures at Europa (80–110K). For the fast, penetrating electrons and protons, we use the value for 200 keV protons in Table 2. For the heavy ions we used the Ne\(^+\) and Ar\(^+\) values. For comparison we also give an estimate using the \(G\) values obtained from the low energy electron data and the total ionization, as discussed above.

The \(G\) values are combined in Table 3 with the electron and ion energy flux at Europa. Although there is some deflection of the flow due to induced fields, the net energy flux to the surface is not reduced much from these values (Paranicas et al., 2002). In fact, locally produced pick-up ions, which are formed from the ejecta and accelerated to the surface, can contribute (Ip, 1996). Further, although \(G\) values are typically independent of the incident angle, the loss of O\(_2\) is a surface process and is enhanced with angle. That is, the number of O\(_2\) produced within the escape depth increases with increasing angle to the normal (steeper than the inverse cosine). This enhancement is \(\sim 2.5-4\) (Jurac et al., 2001). Ignoring such corrections, the total production rate calculated (2.3–6.2 \(\times 10^9\) O\(_2\)/cm\(^2\)/s) is a lower bound to the actual production rate from the icy regions of Europa’s surface. Recent modeling of the O\(_2\) atmosphere suggest that such a source rate is required (Shematovich and Johnson, 2001).

Earlier estimates of the O\(_2\) source rate were incorrect because O\(_2\) production was assumed to be a fixed fraction of the H\(_2\)O sputtering yield. At the ambient temperature an ejected H\(_2\)O sticks efficiently (Smith and Kay, 1997) to the surface of neighboring grains in the porous regolith, reducing the sputtering yield for H\(_2\)O (Johnson, 1989). This reduction does not apply to the O\(_2\) fraction of the yield, enhancing its relative importance to H\(_2\)O. Here we assume that all of the gas-phase O\(_2\) produced can contribute to the ambient atmosphere, even if it is produced at a grain surface that is at some depth into the porous regolith.

Finally, Europa’s surface is not pure ice everywhere. That is, much of the trailing hemisphere is a hydrated sulfuric acid containing small amounts of sulfur and SO\(_2\), and the leading hemisphere contains low levels of carbon, CO\(_2\), and carbonates. Sodium and potassium atoms are sputtered from the icy regions (e.g., Leblanc et al., 2002). O\(_2\) production from surfaces containing these species has not been measured. C and S are both proton scavengers, and the other species can be sources of O as discussed, so that the O\(_2\) yield from such regions could be enhanced. However, there can also be competing processes that might reduce these rates. In fact, recent HST observations suggest that the O\(_2\) might not be produced uniformly across Europa’s surface (McGrath et al., 2000). The analysis of these observations is preliminary and is not simple since the observed

<table>
<thead>
<tr>
<th>Species</th>
<th>Implantation Energy flux</th>
<th>Oxygen production</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(10^9/(\text{cm}^2\text{s}))</td>
<td>(10^9) keV/(cm(^2)/s)(^{(1)})</td>
</tr>
<tr>
<td>H (&gt;10 keV)</td>
<td>0.015(^{(1)})</td>
<td>12</td>
</tr>
<tr>
<td>O (&gt;10 keV)</td>
<td>0.015(^{(1)})</td>
<td>1.8</td>
</tr>
<tr>
<td>S (&gt;10 keV)</td>
<td>0.009(^{(1)})</td>
<td>3.0</td>
</tr>
<tr>
<td>Electrons</td>
<td>62</td>
<td>0.43 (3.7)(^{b})</td>
</tr>
<tr>
<td>Plasma (&lt;10 keV) (13.7 amu)</td>
<td>~1.3(^{(2)})</td>
<td>1.0</td>
</tr>
<tr>
<td>Total</td>
<td>79</td>
<td></td>
</tr>
<tr>
<td>UV photons (&gt;6.4 eV)</td>
<td>46</td>
<td></td>
</tr>
</tbody>
</table>

\(^{a}\) References are as follows: \(^{1}\)Cooper et al. (2001) [similar results in Paranicas et al. (2002)]; \(^{2}\)Mauk et al. (1996).

\(^{b}\) Using \(G\) for 200 keV protons (upper bounds in brackets are based on the low-energy electrons data as a model for the secondary electrons produced).

\(^{c}\) Using \(G\) for 1.5 MeV Ne\(^+\) at 7K, a rough lower bound.
emissions depend on the local plasma properties. However, the efficiency of O\textsubscript{2} production in contaminated ices needs to be studied.

**Porous regolith: \textsubscript{O}2 interactions on grain surfaces**

Although the O\textsubscript{2} atmosphere is principally produced in the near surface layers and is eventually lost to space, it also permeates Europa’s porous regolith. The porosity, \(p\) (void space), of the regolith is uncertain (Buratti, 1995). It has been estimated to be the most compact surface in the Outer Solar System, \(p \approx 0.25\) on the trailing hemisphere and \(p \approx 0.79\) on the leading hemisphere (Buratti and Veverka, 1983), and the most porous surface, \(p \approx 0.96\) globally (Domingue et al., 1991; Domingue and Hapke, 1992). These large differences are due to the uncertainties in the amount of backscattered light at small phase angles and on the photon absorption properties and grain sizes. The more compact surface is likely correct.

Grain sizes, \(r\textsubscript{g}\), of the order of 100 \(\mu\text{m}\) have been suggested (Hansen and McCord, 1999, 2000; Geissler et al., 1998). Europa’s regolith differs significantly from the lunar regolith, which is a sand-like surface of individual grains. Analysis of the thermal inertia of Europa’s surface (Grundy et al., 2001) suggests that the ice grains are sintered, forming a fairy castle-like structure. Sintering can occur thermally or due to the incident radiation. In addition, ices doped with acids and alkalis in the laboratory can be powdery solids with the impurities primarily found at grain interfaces.

The porous regolith affects the above estimates of the oxygen production in three ways. First, for isotropic bombardment the mean distance, \(d\), into the surface at which an incident ion or photon strikes a grain surface is \(d \approx (8/9)r\textsubscript{g}/(1 - p)\). Using the above value for \(r\textsubscript{g}\) then \(d \approx 0.2\) m if the porosity is very large: \(p \approx 96\%\). Therefore, desorbed molecules can come from a considerable depth and will interact with grain surfaces. Even for much lower porosities the effective sputtering yields can be significantly modified (Johnson, 1989). As discussed above, the yields for ejected H\textsubscript{2}O, which sticks onto neighboring grains at the ambient temperatures, are reduced, but those for ejected O\textsubscript{2} are not. This enhances the relative importance of the O\textsubscript{2} yields.

Finally, the surfaces and interfaces of the sintered grains in Europa’s porous surface are places where low temperature chemistry involving the ambient oxygen can occur at depths that are well below the nominal penetration depth of the incident radiation. The relative importance of such chemistry is roughly indicated by the ratio of the total surface area in the regolith to the area of Europa’s visible surface. Using the porosity and grain size above and a regolith depth, \(d\textsubscript{r}\), of the order of a meter, then this ratio is large: \(\approx 3(1 - p)\textsubscript{d}\textsubscript{r}/r\textsubscript{g}\), which is \(\approx 10^3 - 2 \times 10^4\) for average porosities of 96\% and 25\%, respectively. Therefore, the gas-phase O\textsubscript{2} molecules below the visible surface interact frequently with the grain surfaces. In this way a very large volume of the subsurface could be altered chemically even if it is not directly exposed to the radiation.

From the overlying structures seen in the high-resolution images of Europa’s surface by the Galileo spacecraft (e.g., Prockter and Pappalardo, 2000), it is clear that the youngest surfaces are redder. The reddening in the visible has been attributed to the presence of sulfur in the ice (McEwen, 1986; Johnson et al., 1988; Calvin et al., 1995; Carlson et al., 1999b). The amount of reddening in the spectra of the surface material decreases with age, and the surface materials appear to become brighter with age. This might occur by the slow accumulation of a frost over-layer or by radiolysis (Carlson et al., 2002; Johnson et al., 2003). Radiolysis preferentially converts the sulfur in the ice to sulfur dioxide or sulfuric acid, both of which have flat spectra in the visible. In regions where the radiation does not directly penetrate, the O\textsubscript{2} permeating the regolith can oxidize the sulfur at the surfaces of the icy grains and at grain interfaces. Similarly, the carbon seen in the ice on Europa’s leading hemisphere (e.g., Carlson et al., 2004; Johnson et al., 2003) can be oxidized by radiolysis in the near surface layers or by reactions on the grain surfaces at depth in the regolith by the ambient O\textsubscript{2}. The meteoroid bombardment that produces the regolith also exposes fresh surfaces for oxidation and can cause the collapse of pores, leading to the trapping of oxygen. In this manner, both refractory and volatile oxidants can be formed and trapped in the subsurface ice for potential delivery to Europa’s subsurface ocean.

**SUMMARY**

The presence of a thin oxygen atmosphere and oxidants trapped in Europa’s surface ice (e.g., Johnson et al., 2003), combined with the possible
presence of a subsurface ocean (e.g., Carr et al., 1998), have made Europa an exciting target for future space exploration. The molecular oxidants produced by radiolysis and photolysis could be species needed for carbon-based biochemistry in Europa’s putative subsurface ocean. However, there has been no model for the formation, trapping, and transport of relevant oxidants.

In this paper we have reviewed the space observations and laboratory studies related to the chemistry of formation of oxidants in ice by the incident radiation. Because the laboratory data are incomplete, we examined the rate equations for formation of oxygen and related species by radiolysis and photolysis. We showed how such equations can be simplified to the analytic model that was used for fitting the fluence and temperature dependence of the O_2 yield produced by low-energy electrons (Sieger et al., 1998). In deriving the analytic model from the more complete rate equations, the competition between formation and destruction processes can be studied, as can the role of trapping sites, escape from depth, and temperature history. These equations also allowed us to put incident photon, electron, and ion data on a similar footing for the first time.

The model can be used to suggest measurements that are needed to describe the chemical state of the irradiated ice and to interpret new laboratory data. We showed that if reactions are fast, the yield data could be consistent with a precursor being formed by two events, as is the case for peroxide. However, we favor trapped O as a precursor, as initially suggested by Matich et al. (1993) for production of excited O_2. Such a species, if present, could be detected spectroscopically, as can trapped O_2 through bands activated by lattice perturbations (Cooper et al., 2003a).

The available oxygen yield data were used to compare G values for different incident particles. These were then used to estimate the oxygen production in the radiation environment at Europa. The lower bounds were consistent with the production rates obtained from a recent model of Europa’s atmosphere. The porosity of the regolith was also considered. It not only affects the relative sputtering yields for O_2 and H_2O, but also provides an enormously increased surface area on which the ambient gas-phase oxygen can react with species in the ice. That this might be occurring is consistent with the change in reflectance associated with surface aging. Such reactions could also convert ambient molecular oxygen into other more refractory species that remain trapped on subduction of Europa’s crust.

Although radiolysis produces a stable, chemically altered surface in the laboratory, the particle flux to Europa’s surface is many orders of magnitude lower. Therefore, annealing can be effective at temperatures that are much lower than those typically found experimentally. Below about 120K the annealing times appear to be long (e.g., Baragiola, 2003) so that laboratory data can often be directly applied to Europa’s icy surface. However, account has to be taken of the synergism between the UV and the energetic plasma, as discussed earlier (Johnson and Quickenden, 1997).

Transient surface melting might initiate life processes, but subduction of oxidants to the putative ocean is likely to be required if biochemistry is to occur at Europa (Chyba and Hand, 2001). Although the temperature versus depth into Europa’s regolith is not well known, below the regolith the temperature and pressure apparently increase with depth. At some depth (approximately kilometers) either very warm ice or an ocean exists (Ruiz and Tejero, 2000). Therefore, chemically refractory oxidants are likely to be required in order to survive subduction to the warmer subsurface regions. Trapped species, if delivered downward, can become mobile and will segregate forming inclusions (Johnson and Jesser, 1997). Indeed, peroxide appears to segregate in ice (Gurman et al., 1967), and these inclusions may remain relatively stable until the peroxide is dissolved in the putative ocean. The volatiles seen in reflectance, such as O_2, SO_2, and CO_2, will also segregate. But at the higher temperatures they could also diffuse through the bulk, react, or percolate into the regolith atmosphere. Therefore, the observation of the trapped volatiles in Europa’s surface ice is of interest primarily because it suggests that oxidants are present. The formation of oxygen-rich molecules follows the preferential loss of hydrogen. However, the surface is in a local steady state with implanted H, O, and S from the plasma and the loss to space. Since the plasma flux to the surface can be variable, this balance can also vary. Indeed temporal changes in reflectance have been reported (Domingue and Hendrix, 2004).

Based on the models for formation of O_2 ex-
examined in this paper, additional experiments are needed to determine the chemical state of irradiated ice at low fluences. Of immediate interest is the identification of stable molecular precursors required for the formation of O$_2$. Based on the available laboratory data, individual peroxide molecules trapped in the ice do not appear to be the principal precursors, but trapped O (Matich et al., 1993) remains a viable candidate. Although the data suggest that the local hydrogen-bonding network is important in the production of O$_2$, the effect of the formation temperature and radiation damage on the structure need to be measured. It is also important to describe quantitatively the relationship between H$_2$ loss and the formation of O$_2$ and H$_2$O$_2$ over a range of temperatures and fluences. Finally, one would like to determine the steady-state densities of biochemically interesting molecules formed by radiolysis in an ice containing sulfur and carbon at Europa’s surface temperatures, and then determine their stability with increasing temperature and pressure. Such experiments still need to be carried out. Here we have presented a model that brings together the various laboratory data and now can be used to consider the formation trapping and transport of relevant oxidants at Europa.

**APPENDIX**

**Introduction**

In this Appendix we examine rate equations that describe various aspects of the radiolysis or photolysis of ice. These equations need to be understood if one is to be able to calculate the formation, trapping, and transport of oxidants. The emphasis is on the formation of molecular oxygen. We integrate these equations over the escape depth of O$_2$ to give the simplified rate equations discussed in the text in which number densities are replaced by column densities (e.g., Eqs. 1 and 2). In this way we can examine the relationship between the rate constants and the effective precursor formation and destruction cross sections extracted from data. We first consider a precursor, such as H$_2$O$_2$, that is formed from two excitation events. This bears on the observed linearity of the oxygen yield versus fluence. We then consider the equations for trapped versus a transiently mobile species. We use a reaction between a mobile and trapped O as an example, although O + OH can also give oxygen. Finally, we examine the possible dependence of the O$_2$ formation process on the density of traps (defects, voids, and grain boundaries) as a function of temperature. The results are discussed in the text.

For clarity, all possible radiolytic species are not included in the discussion below. Therefore, potentially important products such as HO$_2$ and the charged species (e.g., H$_3$O$^+$, the trapped electron, etc.) are missing. In each section we attempt to make a point related to production of O$_2$ and other oxidants by using a subset of the products rather than attempt a complete description with many unknown rate constants.

**Fast versus slow processes**

To describe the O$_2$ production rate from a precursor such as H$_2$O$_2$, we first use a simple but instructive set of rate equations to describe the formation of H$_2$O$_2$. We then relate these to the simplified rate equation for the precursor in the text, Eq. 1, and show how the postulated precursor formation cross section, $\sigma_p$, is related to the H$_2$O dissociation cross section, $\sigma_d$, by the reaction rates.

Using the reactions:

\[ \text{H}_2\text{O} + \text{radiation} \rightarrow \text{H} + \text{OH} \quad (\sigma_d) \]

\[ \text{H} + \text{H} \rightarrow \text{H}_2 \quad (k_{2\text{H}}) \]

\[ \text{H} + \text{OH} \rightarrow \text{H}_2\text{O} \quad (k_{\text{H,OH}}) \]

\[ \text{OH} + \text{OH} \rightarrow \text{H}_2\text{O}_2 \quad (k_{2\text{OH}}) \]

the reaction pathways are described by:

\[ \text{H}_2\text{O} + \text{radiation} \xrightarrow{\sigma_d} \text{H} + \text{OH} \]

\[ \text{OH} \xrightarrow{k_{2\text{OH}}} \text{H}_2\text{O}_2 \]

\[ \text{OH} \xrightarrow{k_{\text{H,OH}}} \text{H}_2\text{O} \]

\[ \text{H}_2 \]

\[ \text{H} \]

This approach allows us to incorporate the observed linearity of the oxygen yield versus fluence into the model.
The corresponding rate equations in an irradiated volume are

\[
\frac{dn_{\text{OH}}}{dt} = \sigma_d \phi n - 2k_{\text{OH}} n_{\text{OH}} n_{\text{OH}} - k_{\text{H,OH}} n_{\text{H}} n_{\text{OH}} \quad (A1a)
\]

\[
\frac{dn_{\text{H}}}{dt} = \sigma_d \phi n - 2k_{\text{H}} n_{\text{H}} n_{\text{H}} - k_{\text{H,OH}} n_{\text{H}} n_{\text{OH}} \quad (A2a)
\]

\[
\frac{dn_{\text{H}_2\text{O}_2}}{dt} = k_{\text{H,OH}} n_{\text{OH}} n_{\text{OH}} - \text{destruction processes} \quad (A3a)
\]

Here \( \sigma_d \) is the dissociation cross section, \( \phi \) is the radiation flux, and \( n \) is the molecular number density of ice, with \( n_{\text{OH}} \) and \( n_{\text{H}} \) the density of dissociation products OH and H, respectively. The rate constants \( k_{\text{OH}} \), \( k_{\text{H}} \), and \( k_{\text{H,OH}} \) describe the reactions above. In this model, the H\(_2\) formed is assumed to escape for temperatures above about 20K. We do not distinguish between trapped species and mobile species, although in fact that distinction is important as discussed in the next section. That is, any OH produced at low temperature by one ion would likely be trapped prior to interacting with an OH produced by a subsequent ion. At higher temperatures this can break down, as discussed in the text. We first relate the above set of equations to Eq. 1 in the text and then consider precursor destruction processes.

Equation 1 in the text is obtained by solving these equations together and then by integrating over a depth \( \Delta c \). Here \( \Delta c \) is the smaller of the penetration depth of the particle and the O\(_2\) escape (percolation) depth. Assuming the molecular density of ice, \( n \), is constant with depth, \( \Delta c n = N \) in Eq. 1. Comparing Eq. 1 with Eq. A3a, the precursor formation rate, \( \sigma_p \phi N \), is equivalent to \( k_{\text{H,OH}} n_{\text{OH}} n_{\text{OH}} \Delta c \). Assuming that the processes in Eqs. A1a and A2a are fast, then the steady state is readily obtained. In addition, if \( k_{\text{H}} \gg k_{\text{OH}} \), there is preferential loss of H\(_2\) at short times as suggested by the laboratory data. If steady state is reached the production of H is equal to that of H\(_2\)O\(_2\) using only the equations above. Further, one obtains

\[
[k_{\text{H,OH}} n_{\text{OH}} n_{\text{OH}}] \Delta c \to [f_p \sigma_d] \phi N \quad (A4)
\]

with

\[
f_p = 0.5/[1 + 0.5 k_{\text{H,OH}}/(k_{\text{H}} k_{\text{OH}})^{0.5}] \quad (A5a)
\]

Therefore, the precursor formation cross section, \( \sigma_p \), in Eq. 1 is a fraction, \( f_p \), of the total dissociation cross, \( \sigma_d \). Since laboratory data suggest the H\(_2\)O\(_2\) fraction in an irradiated ice is small, then \( k_{\text{H,OH}} \gg (k_{\text{OH}} k_{\text{H}})^{0.5} \), which is likely, giving \( f_p \to [(k_{\text{OH}} k_{\text{H}})^{0.5}/k_{\text{H,OH}}] \).

**Trapped versus mobile species**

To examine the fluence dependence discussed in the text we note that trapped OH and freshly produced, transiently mobile OH can be treated as different species (e.g., Matich et al., 1993). Therefore, assuming no trapping of H, the OH rate equation above would be replaced by two equations: one for the trapped species, \( n_{\text{OH trap}} \), and the other for the freshly produced mobile species, \( n_{\text{OH}} \). Assuming the reaction of two mobile OH units is unlikely and that peroxide is formed from the interaction of a trapped OH with a subsequently produced OH, an expanded set of equations is obtained:

\[
\text{OH} + \text{trap} \to \text{OH} \quad (k_{\text{OH,OH}})
\]

\[
\text{OH} + \text{OH}_t \to \text{H}_2\text{O}_2 \quad (k_{\text{OH,OH}_t})
\]

\[
\text{H} + \text{OH}_t \to \text{H}_2\text{O} \quad (k_{\text{H,OH}_t})
\]

then the reaction pathways are described by

\[
\begin{align*}
\text{H}_2\text{O} + \text{radiation} & \quad \text{H} + \text{OH} \\
\text{trap} \quad k_{\text{OH,OH}} & \quad \text{OH} \quad k_{\text{OH,OH}_t} \\
\text{OH} \quad k_{\text{H,OH}} & \quad \text{H}_2\text{O} \quad k_{\text{H,OH}_t} \\
\end{align*}
\]

The resulting set of equations is:

\[
\frac{dn_{\text{OH}}}{dt} = \sigma_d \phi n - k_{\text{H,OH}} n_{\text{H}} n_{\text{OH}} - k_{\text{OH,OH}_t} n_{\text{OH}} n_{\text{OH}_t} \quad (A1b)
\]

\[
\frac{dn_{\text{OH}_t}}{dt} = k_{\text{OH,OH}_t} n_{\text{OH}} n_{\text{OH}_t} - k_{\text{H,OH}_t} n_{\text{H}} n_{\text{OH}_t} \quad (A1b')
\]

\[
\frac{dn_{\text{H}}}{dt} = \sigma_d \phi n - 2k_{\text{H}} n_{\text{H}} n_{\text{H}} - k_{\text{H,OH}} n_{\text{H}} n_{\text{OH}} - k_{\text{H,OH}_t} n_{\text{H}} n_{\text{OH}_t} \quad (A2b)
\]
where \( n_1 \) is the trap density in the irradiated ice. At low \( T \) we can assume \( n_1 \) is large so that \( dn_1/dt \sim 0 \), simplifying the set of equations. If the precursor of interest is trapped \( \text{O} \), as discussed in the text, then a similar set of equations can be constructed for \( \text{O} \) and \( \text{O} \) is the trap density in the irradiated ice. At low \( T \) on the average. Therefore, between impacts only species trapped at defects, pores, or grain surfaces are assumed to be present, as suggested by the lack of a dependence on the incident beam flux. In this limit the rate of change of trapped OH roughly simplifies to:

\[
dn_{\text{OH}_t}/dt = 2 k_{\text{H},\text{OH}_t} n_{\text{H}} n_{\text{H}} - 2 k_{\text{OH},\text{OH}_t} n_{\text{OH}} n_{\text{OH}_t},
\]

It is seen that the production of peroxide depends on the loss of \( \text{H} \) by formation of \( \text{H}_2 \), as discussed, and at steady state the production rate for peroxide equals the rate of formation of \( \text{H}_2 \) in these equations.

Treating the mobile and trapped species separately, we can further simplify the rate equations and obtain the precursor model used in the text. That is, integrating over the relevant depth, \( \Delta x \), the densities are replaced by column densities. The rate constants, \( k_i \), are then related to effective cross sections, \( \sigma_i \). In this way cross sections are given as an interaction length for each freshly produced mobile radical: \([k_i n_i] \rightarrow [\sigma_i \phi]\). The \( \text{trapped} \) OH column density, \( N_{\text{OH}_t} \), and peroxide production rate can be estimated from “linear” rate equations:

\[
dN_{\text{OH}_t}/dt = [\sigma_4 \phi] N - 2 [\sigma_{2\text{OH}} \phi] N_{\text{OH}_t} - [\sigma_{\text{OH},\text{OH}} \phi] N_{\text{OH}_t} \quad (A6a)
\]

\[
dN_{\text{H}_2\text{O}_2}/dt = [\sigma_{2\text{OH}} \phi] N_{\text{OH}_t} - \sigma N_{\text{H}_2\text{O}_2} \quad (A6b)
\]

Here \( \sigma_4 \) is again the dissociation cross section, and the destruction processes in Eq. A3b are contained in \( \sigma \). The second and third terms on the right in Eq. A6a are the loss of \( \text{OH} \) due to the production of \( \text{H}_2\text{O}_2 \) and \( \text{H}_2 \): In the integration of Eq. A1b’ [2 \( k_{\text{OH},\text{OH}_t} n_{\text{OH}} \) becomes \( 2 \sigma_{2\text{OH}} \phi \), and \( k_{\text{H},\text{OH}_t} n_{\text{OH}} \) becomes \( \sigma_{\text{OH},\text{OH}} \phi \). Therefore, the density and the interaction length of mobile \( \text{H} \) are contained in \( \sigma_{\text{OH},\text{OH}} \). If \( \text{H}_2\text{O}_2 \) is indeed the precursor, then in Eq. 2 in the text \([\sigma_p \phi N]\) is becomes \( [\sigma_{2\text{OH}} \phi N_{\text{OH}_t}] \) from Eq. A6b. Accounting for precursor destruction, which can give back two \( \text{OH} \), and treating \( \text{H}_2 \) can both be included in the integrated model via the \( \sigma_i \) values.

The simplified set of equations above allows us to examine the relative time (fluence) scales for precursor formation (in this case \( \text{H}_2\text{O}_2 \)). Solving Eqs. A6a and A6b, the column density of \( \text{OH} \) and the concentration of precursors versus fluence, \( c_p \), can be obtained. Using the column of \( \text{H}_2\text{O}_2 \) produced as the precursor column, \( N_p \), in Eq. 2, then \( \text{O}_2 \) yield can be obtained. The results can be compared with the results from Eqs. 1 and 2 in the text. The average precursor (\( \text{H}_2\text{O}_2 \)) concentration over the column depth of water molecules, \( N \), is:

\[
c_p = f_p (\sigma_i/\sigma)\left[1 - \exp(-\sigma \Phi)\right] - (\sigma/\sigma_t)\left[1 - \exp(-\sigma_r \Phi)\right], \quad (A7)
\]

with

\[
f_p = 2\sigma_{2\text{OH}}/(\sigma_r - \sigma), \quad (A5b)
\]

In these equations, \( \sigma_r = (2\sigma_{2\text{OH}} + \sigma_{\text{H},\text{OH}}) \) and \( \sigma_r/\sigma_t < 1 \).

It is seen that the precursor concentration with time, \( c_p \), depends on two rates, the reaction rates that determine \( \sigma_i \) and the destruction rates in \( \sigma \). As in Eq. 4a the yield can be written as:

\[
Y = \sigma_{\text{O}_2} c_p N, \quad (A8)
\]

If \( \sigma_i \) and \( \sigma \) are comparable, then the yield at small...
fluence is quadratic in $\Phi$. However, if $\sigma_{t} > > \sigma_{r}$ then the linear dependence on fluence is obtained with a small shift in the fluence, as shown in Eq. 4c in the text. Further, the steady-state yield is now:

$$Y_{\infty}(T) = \sigma_{O_{2}} [f_{p} \sigma_{d}] N/\sigma$$  \hspace{1cm} (A9)

That is, $\sigma_{r} \rightarrow [f_{p} \sigma_{d}]$ as in Eq. A4, and the temperature dependence for the incident electron data must be contained in $[\sigma_{O_{2}}/\sigma_{p}]$ or in the ratio $[\sigma_{O_{2}} \sigma_{OH}]/\sigma_{H,OH}$.

For comparison with their precursor model, Sieger et al. (1998) examined the possibility of obtaining the $O_{2}$ precursor by considering reactions for a density of diffusing dissociation products, as in Eqs. A1 and A2, rather than a trapped product interacting with a freshly formed dissociation product. Based on the above, the lowest fluence at which $O_{2}$ is first detected experimentally sets a limit on the time scale for mobile–mobile reactions.

Effect of trap density

Equations A1b, A1b’, A2b, and A3b can be approximately solved assuming that the $dn_{OH}/dt$, $dn_{H}/dt$, and $dn_{t}/dt$ are very small on the average as discussed above. In order to examine the role of the trap density, $n_{t}$, which can depend on the temperature and method of formation, and on the radiation history of the ice, we use the slightly simpler precursor model. In this model the $O_{2}$ produced directly by dissociation traps forming a precursor. $O_{2}$ is then formed when a freshly produced $O$ or other species reacts with a trapped oxygen atom, $O$:

$$\begin{align*}
H_{2}O + \text{radiation} &\rightarrow H_{2} + O \\
O + \text{trap} &\rightarrow O_{t} \quad (\sigma_{d}) \\
O + O_{t} &\rightarrow O_{2} \quad (k_{O_{t}O_{t}})
\end{align*}$$

The reaction pathways for the oxygen species are:

$$\begin{align*}
H_{2}O + \text{radiation} &\rightarrow \sigma_{d}' \rightarrow O_{t} \\
H_{2} + O &\rightarrow \sigma_{d} \rightarrow O_{t} \\
R &\rightarrow \sigma_{O,R} \rightarrow \sigma_{d} \rightarrow O_{t} \\
O &\rightarrow k_{O_{t}O_{t}} \rightarrow O_{2} \\
H(k_{H,Oh}) &\rightarrow OH_{t} \\
\end{align*}$$

We assume, for simplicity, both $H_{2}$ and $O_{2}$ escape from depth $\Delta x$ after formation. We also allow mobile $H$ to react with $O_{t}$ ($k_{H,Oh}$), removing trapped $O$ and both the mobile $H$ and $O$ to be removed by other reactants, $R$ (e.g., $OH$ or contaminants). This leads to a simplified set of equations not directly involving $OH$ or peroxide:

$$\begin{align*}
dn_{O}/dt &= \sigma_{d}' \phi n - k_{O_{t}O_{t}} n_{O} n_{t} - k_{O,O_t} n_{O} n_{R} \\
&\quad - k_{O,O_t} n_{O} n_{t} \\
&\quad - k_{O,O_t} n_{O} n_{R} \\
dn_{O}/dt &= k_{O_{t}O_{t}} n_{t} n_{O} - k_{O,O_t} n_{O} n_{t} \\
&\quad - k_{H,O_t} n_{H} n_{O_t} \\
dn_{H}/dt &= \sigma_{d} \phi n - k_{H,O_t} n_{H} n_{O_t} \\
&\quad - k_{H,R} n_{H} n_{R} \\
dn_{O_{2}}/dt &= k_{O_{t}O_{t}} n_{O} n_{t}
\end{align*}$$

These equations, of course, act in parallel with the equations above for $OH$, and mobile $OH$ may react with trapped $O$ to form $O_{2}$. Here we focus only on mobile $O$.

Since the diffusion of $H$ and $O$ are fast and the density of traps is large, the $n_{H}$ and $n_{t}$ averaged over the bombardment rate can be taken, very roughly, as time independent. Further, if we assume the number of trapped $O$, $n_{O_{t}}$, is small compared with the number of sites at which $H$ can react, then $n_{H} \sim [\sigma_{d} \phi /k_{H,R} n_{R}]$. For a low radiation flux, $\phi$, $n_{H}$ is small, on the average, as assumed. Since the $O_{2}$ yield, $Y_{O_{2}}$, is equal to $[(dn_{O_{2}}/dt)/\Delta x/\phi]$ with $\Delta x$ the escape depth, then the steady-state yield, $Y_{\infty}$, can be obtained analytically:

$$Y_{\infty}/[\sigma_{d}' \ N] = 1 + ((q - 1) - [(q - 1)^2 \\
+ 8 \ q \ \delta]^{0.5})/4 \ \delta$$  \hspace{1cm} (A10)

$$q = [k_{O_{t}O_{t}}(n_{t} + n_{R})]/(k_{O,O_t} n_{H}/(\sigma_{d}' \ phi \ n) \ k_{O,O_t})$$

$$\delta = 0.5 \ [1 + n_{t}/(n_{t} + n_{R})]$$

We note that for $n_{t}$ large, $q$ can be large. Assuming that $q \gg 1$ and $n_{t} \gg n_{R}$ then Eq. A10 becomes:

$$Y_{\infty}/[\sigma_{d}' \ N]/q = (\sigma_{d}' \ N) (\sigma_{d}'/\sigma_{d})$$

$$[k_{O,O_t} k_{H,R} n_{R}]/[k_{H,Oh} k_{O,O_t} n_{t}]$$  \hspace{1cm} (A5c)
Comparing with $Y_\infty$ in the simple precursor model in Eq. 4b, then $\sigma \to [(k_{H,O} n_{H})/\phi] \to [\sigma_d n_{H} k_{H,O}]/[k_{H,R} n_{R}]$. In addition, the product $[\sigma_0 \sigma_d] \to [\sigma_d \sigma_d'] [k_{O,O} n]/[k_{O,1} n_1]$. That is, the dissociation cross sections are modified by reaction rates.

Quite remarkably, it is seen in Eq. A5c that the steady-state yield, $Y_\infty$, can depend inversely on the density of traps, $n_T$, in the temperature and flux regimes for which the approximations are relevant. That is, if there are competing destruction process for trapped O, then at high trap density a mobile O must find a trapped O before it becomes trapped or before mobile H destroys the O$_2$. In this way the increasing O$_2$ yield with increasing $T$ can be related to the change in the trapping density, $n_T$, with the formation temperature of the ice sample. As the temperature increases and the density of traps in the bulk decreases, the surface and grain interfaces become the only trapping sites.

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**ABBREVIATIONS**

HST, Hubble Space Telescope; MJQ, Matich–Johnson–Quickenden; NIMS, Near Infrared Mapping Spectrometer; UV, ultraviolet.

**REFERENCES**


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