

## Research Paper

# Energy, Chemical Disequilibrium, and Geological Constraints on Europa

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### ABSTRACT

Europa is a prime target for astrobiology. The presence of a global subsurface liquid water ocean and a composition likely to contain a suite of biogenic elements make it a compelling world in the search for a second origin of life. Critical to these factors, however, may be the availability of energy for biological processes on Europa. We have examined the production and availability of oxidants and carbon-containing reductants on Europa to better understand the habitability of the subsurface ocean. Data from the *Galileo* Near-Infrared Mapping Spectrometer were used to constrain the surface abundance of CO<sub>2</sub> to 0.036% by number relative to water. Laboratory results indicate that radiolytically processed CO<sub>2</sub>-rich ices yield CO and H<sub>2</sub>CO<sub>3</sub>; the reductants H<sub>2</sub>CO, CH<sub>3</sub>OH, and CH<sub>4</sub> are at most minor species. We analyzed chemical sources and sinks and concluded that the radiolytically processed surface of Europa could serve to maintain an oxidized ocean even if the surface oxidants (O<sub>2</sub>, H<sub>2</sub>O<sub>2</sub>, CO<sub>2</sub>, SO<sub>2</sub>, and SO<sub>4</sub><sup>2-</sup>) are delivered only once every ~0.5 Gyr. If delivery periods are comparable to the observed surface age (30–70 Myr), then Europa's ocean could reach O<sub>2</sub> concentrations comparable to those found in terrestrial surface waters, even if ~10<sup>9</sup> moles yr<sup>-1</sup> of hydrothermally delivered reductants consume most of the oxidant flux. Such an ocean would be energetically hospitable for terrestrial marine macrofauna. The availability of reductants could be the limiting factor for biologically useful chemical energy on Europa. **Keywords:** Europa—Radiolysis—Oxygen—Habitability—Planetary science. *Astrobiology* 7, 1006–1022.

### 1. INTRODUCTION

WHILE THE MANTRA of “follow the water” has been the call of NASA's search for life beyond Earth, it is really a subset of the mantra “follow the energy.” Life as we know it—that is, all life on Earth—requires just two forms of energy: thermal energy for melting water and chemical

energy for maintaining and regulating processes considered essential for life. Even organisms that directly absorb light, *e.g.*, for photosynthesis, do so as a means of producing utilizable chemical energy, stored in ATP.

The existence of liquid water on any world in our contemporary cold universe ( $2.725 \pm 0.002$  K) is the result of energy production (Mather *et al.*,

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1999). Liquid water implies at least  $6006.8 \text{ J mol}^{-1}$  in order to convert 273.16 K ice to liquid water (Haida *et al.*, 1974). Traditional definitions of the habitable zone have, in part, been restricted to liquid water on the surface of Earth-like planets made possible in part by atmospheric and surface heating from the parent star (Kasting *et al.*, 1993). Such definitions of “surface habitability” cannot (nor were they intended to) take into account two energy sources that may be responsible for maintaining the majority of liquid water in our solar system, if not the universe: tidal and radiogenic energy.

Within the jovian system, the generation of thermal energy through tidal dissipation and radioactive decay (following initial accretional heating) accounts for what are likely our solar system’s three largest oceans. At present, the evidence amassed from the *Galileo* mission leads to the conclusion that liquid water oceans within Europa, Ganymede, and Callisto may harbor a total volume of liquid water 30–35 times that of Earth’s ocean (Spohn and Schubert, 2003).

Despite the fact that these moons likely contain large oceans (Zimmer *et al.*, 2000) and bulk chemical compositions with a suite of biogenic elements (Kargel, 1991; Kargel *et al.*, 2000), the availability of chemical energy may be a limiting factor for habitability. Of the three worlds, the young surface age of Europa [30–70 Myr (Zahnle *et al.*, 2003)] provides some indication that geological processes may be active on a global scale and could serve to help maintain chemical disequilibrium in the ocean. Based on the assumption that no reductant-oxidant chemical pairing could persist on Europa, some workers have argued that the ocean is thermodynamically dead (Gaidos *et al.*, 1999). McCollom (1999), Zolotov and Shock (2003), and Zolotov and Shock (2004), however, analyzed the geochemical possibilities for maintaining chemical disequilibrium in a hydrothermally active euroman ocean and found that energetic niches for microbial life could persist, provided hydrothermal activity is maintained through time. Methanogenesis and sulfate reduction are argued to be viable pathways for life, perhaps supporting  $10^5 \text{ kg yr}^{-1}$  of biomass (McCollom, 1999). By comparison, terrestrial production is  $\sim 10^{14} \text{ kg yr}^{-1}$  globally, with perhaps  $\sim 10^{10} \text{ kg yr}^{-1}$  from hydrothermal vents (McCollom, 1999). Ultimately, however, these systems may be oxidant limited.

But the *Galileo* results (Carlson *et al.*, 1999) and

more recent ground-based results (Spencer and Calvin, 2002) have made a strong case for an oxidant-laden surface on Europa. The predominant source of the oxidants is the radiolytic chemistry that results from the bombardment of the surface ice by energetic electrons and ions trapped within the jovian magnetic field (Johnson *et al.*, 2004). Chyba (2000) and Chyba and Phillips (2001) examined the potential role that surface radiolysis may play in creating an environment of chemical disequilibrium in the putative ocean of Europa. Though their results are contingent on an active surface that delivers surface material to the subsurface, the conclusion is that radiolytically produced oxidants could serve to enhance significantly chemical disequilibrium within the ocean and habitability of the ocean as well.

In the above models, the observed surface age was used to guide calculations for determining the global flux of radiolytic products. Depending on resurfacing mechanisms, the average delivery period for radiolytic products could be considerably longer than the surface age. For this reason, we have explored a wide range of possible delivery periods and examined the resulting oxidant delivery. Here we show that the abundance of oxidants produced in the surface ice suggests that the availability of oxidants is unlikely to be a limiting factor for either abiotic or biological reactions in the subsurface. Delivery of radiolytic oxidants to the ocean could mean the difference between an ocean inhabited by single-celled microbes and one that can support complex, multicellular life forms.

In addition to oxidants, we also experimentally examined the role of radiolysis in the production of reduced single-carbon compounds. Carbon dioxide is, at present, the only form of carbon known to exist on the euroman surface (Johnson *et al.*, 2004). Chyba (2000) and Chyba and Phillips (2001) argued for formaldehyde as a useful radiolytic product in Europa’s ice (at a concentration  $\sim 10^{-6}$  by number relative to water), and Bernstein *et al.* (1995) created methanol in laboratory ices with methane. Here we present laboratory results of  $\text{H}_2\text{O} + \text{CO}_2$  electron irradiation of thin ice films under Europa-like conditions, and we address the implications for oceanic carbon chemistry and habitability. We show that most of the carbon is retained in  $\text{CO}_2$ , while some of the destroyed carbon is sequestered as CO and  $\text{H}_2\text{CO}_3$ . Formaldehyde and

methanol, if present, represent at most a minor species that sequesters a few percent of the destroyed carbon.

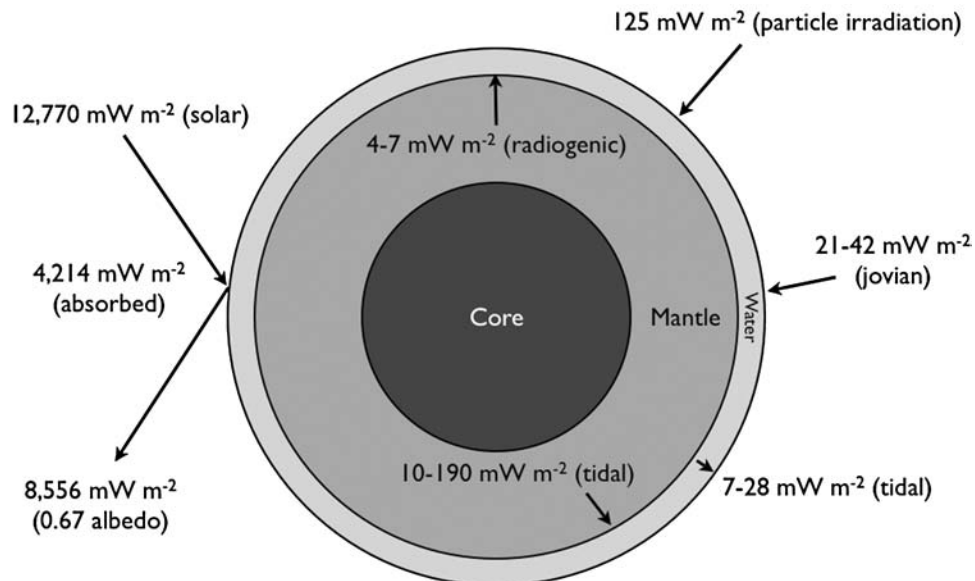
## 2. EUROPA'S SURFACE ENERGY FLUX

The total energetic flux that results from incident ions, protons, and electrons imparts an average of  $125 \text{ mW m}^{-2}$  to the surface of Europa (Cooper *et al.*, 2001). By comparison, the average solar flux is  $12.8 \text{ W m}^{-2}$ , of which  $\sim 60 \text{ mW m}^{-2}$  is due to UV-C (a small portion of which is capable of  $\text{H}_2\text{O}$  photolysis). An additional  $\sim 21$  to  $\sim 42 \text{ mW m}^{-2}$  comes from Jupiter. (This is the combination of reflected and thermal radiation, with the upper limit being set by reflection from the full disk of Jupiter. Since Europa is tidally locked to Jupiter, the sub-jovian hemisphere is the primary beneficiary of this radiation.) By comparison, average insolation over the surface of the Earth is  $\sim 340 \text{ W m}^{-2}$ , with roughly  $240 \text{ W m}^{-2}$  being absorbed by the atmosphere or surface (Wielicki *et al.*, 2005, 1995). Figure 1 shows a diagram that accounts for all known energy sources on Europa.

The solar energy incident on Europa is  $\sim 100$  times that delivered by charged particle irradiation,

but most of the solar flux is reflected back to space (Europa's albedo is  $\sim 0.67$ ). The remaining energy does not penetrate far into the ice and is rapidly reradiated as heat from the  $\sim 70$ – $130 \text{ K}$  surface (Spencer *et al.*, 1999). Only shorter wavelength UV-C photons serve to store energy effectively in the ice by breaking and making new chemical bonds. Note that oceanic photosynthesis cannot strictly be ruled out for young cracks covered by only a thin layer of ice on Europa (Reynolds *et al.*, 1983; Greenberg *et al.*, 2000). This would, of course, be a means for biology to harness the surface energy without any need for radiolytically produced intermediaries.

The population of charged particles is dominated by energetic electrons that can penetrate comparatively deep into the ice layer while exciting and dissociating water into reactive components (*e.g.*, OH, H). More than 80% of the irradiation energy is from electrons that range in energy from a few eV to  $\sim 10 \text{ MeV}$  (Cooper *et al.*, 2001; Paranicas, 2001). In addition, protons and heavier ions create cascades of secondary electrons. The most energetic electrons will penetrate a few to a few tens of centimeters into the ice (Johnson, 1990; Berger *et al.*, 2005). The most energetic ions ( $\text{H}^+$ ) will only penetrate a few millimeters below the surface (Johnson, 1990; Berger



**FIG. 1. The energy budget of Europa.** Sources include external (solar, jovian, particles) and internal (radiogenic, tidal) inputs. Europa's energetic particle flux is  $\sim 0.037\%$  that of Earth's average incident solar flux (Cooper *et al.*, 2001). The solar flux is the flux on the moon's cross-section divided by the total surface area. Numbers for tidal and radiogenic energy are from Squyres *et al.* (1983), O'Brien *et al.* (2002), and Greeley *et al.* (2004).

*et al.*, 2005). Because electrons dominate the charged particle flux and penetrate deeper into the ice than other charged particles, we used electrons in our laboratory simulations of european surface chemistry.

Oxidants in the surface ice of Europa have been constrained by ground-based and spacecraft observations, whereas reductants have not yet been observed. Therefore, we used laboratory experiments to set constraints on the radiolytic production of carbon-containing reductants from compounds observed on the european surface.

### 3. THE SURFACE CHEMISTRY OF EUROPA

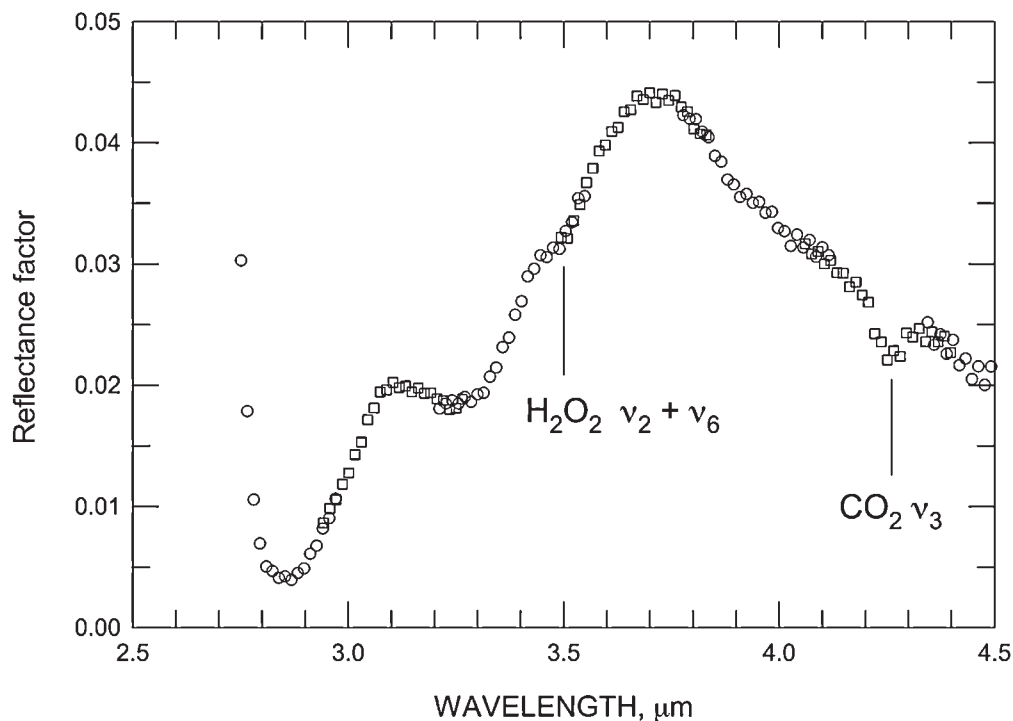
#### 3.1. Inventory of oxidants

The primary observed oxidants on Europa are  $\text{H}_2\text{O}_2$ ,  $\text{O}_2$ ,  $\text{SO}_2$ ,  $\text{CO}_2$ , and the  $\text{SO}_4^{2-}$  anion. Observations from the Near-Infrared Mapping Spectrometer (NIMS) onboard the *Galileo* spacecraft set the surface abundance of radiolytically produced

$\text{H}_2\text{O}_2$  at 0.13% by number relative to  $\text{H}_2\text{O}$  (Carlson *et al.*, 1999). The presence of a thin  $\text{O}_2$  atmosphere ( $\sim 10^{-14}$  bar) on Europa has long been known (Hall *et al.*, 1995), and more recent work indicates that molecular oxygen is trapped in the surface ice of Europa (Spencer and Calvin, 2002). Hand *et al.* (2006) took a detailed look at the ground-based observations of  $\text{O}_2$  and concluded that the 0.3% absorption in the 5771 Å band observed by Spencer and Calvin (2002) suggests an  $\text{O}_2$  abundance of 1.2–4.6%  $\text{O}_2$  by number relative to  $\text{H}_2\text{O}$ , if  $\text{O}_2$  molecules are randomly distributed in the ice.

The surface abundance of  $\text{SO}_2$  is  $\sim 0.3\%$  by number relative to  $\text{H}_2\text{O}$  with a range of 0.1–1.7% constrained by compositional arguments (Crawford and Stevenson, 1988; Kargel *et al.*, 2000; Hand *et al.*, 2006). The dominant reservoir for sulfur on the surface is sulfate, with NIMS observations indicating regions with  $\sim 10\%$  sulfate by number relative to  $\text{H}_2\text{O}$  (Carlson *et al.*, 2005).

Carbon dioxide is present on the surface of Europa with an observed abundance of 0.036% by number relative to  $\text{H}_2\text{O}$ . Figure 2 shows NIMS data and the  $\text{CO}_2$  absorption at  $4.26 \mu\text{m}$  from which this abundance was derived. Previous



**FIG. 2.** *Galileo* NIMS spectrum of Europa showing  $\text{CO}_2$ ,  $\text{H}_2\text{O}_2$ , and  $\text{H}_2\text{O}$  features. A  $\text{CO}_2$  abundance of 0.036% by number relative to  $\text{H}_2\text{O}$  (360 ppm) is estimated using the observed equivalent width ( $\sim 4 \text{ cm}^{-1}$ ), the  $\text{CO}_2$  band strength at 100 K (Gerakines *et al.*, 1995), and the effective path length through the ice ( $\sim 60 \mu\text{m}$ , determined from the observed reflectivity and the absorption coefficient of ice at  $4.26 \mu\text{m}$ ).

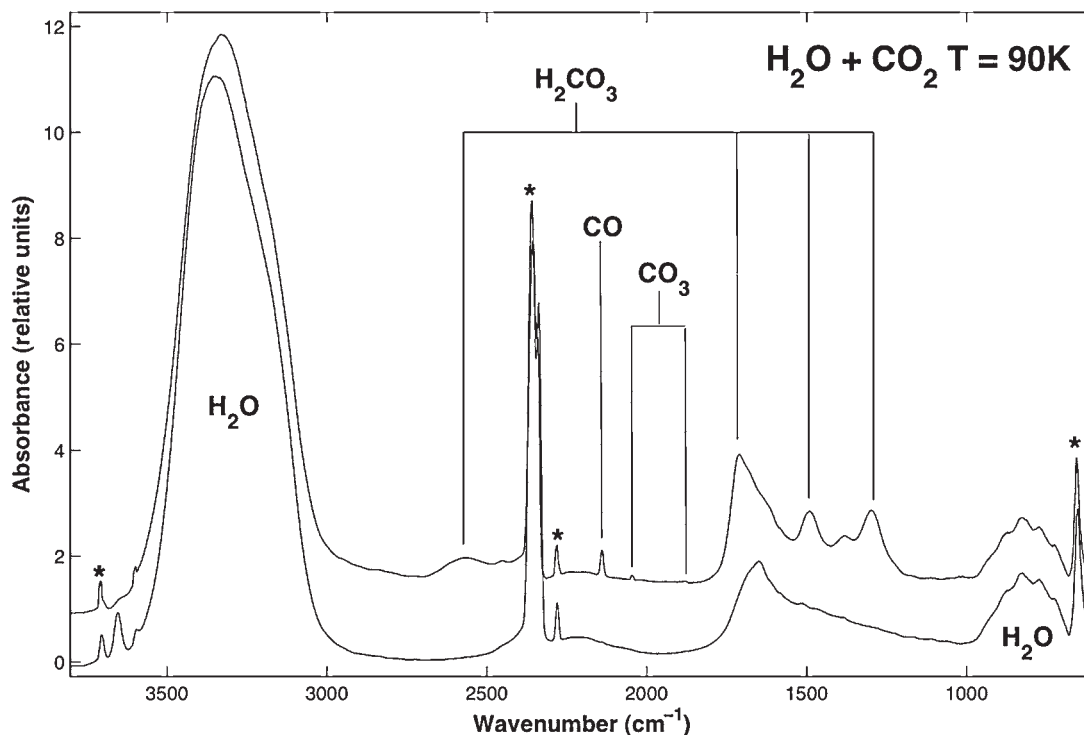


FIG. 3. Spectra of a 1.77  $\mu\text{m}$  film of [2:1]  $\text{H}_2\text{O}:\text{CO}_2$  ice deposited at 50 K and irradiated at 90 K with 10 keV electrons. The bottom spectra shows the film before irradiation and the top spectra shows the film after irradiation. Spectral lines consistent with CO and  $\text{H}_2\text{CO}_3$ —not  $\text{H}_2\text{CO}$ ,  $\text{CH}_3\text{OH}$ , or  $\text{CH}_4$ —are observed in the irradiated spectra. The peaks marked with an asterisk are  $\text{CO}_2$  bands.

workers have used a  $\text{CO}_2$  abundance of 0.08% (Chyba, 2000), but our more recent empirical results show this to be roughly a factor of two too large. However, given a chondritic origin for Europa, the abundance could be as high as 1.23% (Kargel *et al.*, 2000). Carbon monoxide will be produced by  $\text{CO}_2$  radiolysis but has not been detected on Europa, possibly due to CO's extreme volatility and rapid escape from the surface.

### 3.2. Experimentally constrained inventory for reductants

The lack of any observation of reductants on the surface of Europa forces us to consider laboratory simulations as a means of setting constraints on reductants from the surface. It has been proposed that radiolytically produced formaldehyde could be a source of carbon for a subsurface ecosystem on Europa (Chyba, 2000; Chyba and Phillips, 2001). Methanol could also be a useful form of carbon, and several workers have explored methanol in the context of astrophysical ices (Schutte *et al.*, 1993; Bernstein *et al.*, 1995; Moore *et al.*, 1996). However, recent exper-

iments at astrophysical temperatures ( $\sim 5\text{--}20$  K) have shown that formaldehyde is at best a minor product during ion and UV irradiation of  $\text{H}_2\text{O}+\text{CO}_2$  ices (Gerakines *et al.*, 2000; Brucato *et al.*, 1997; Moore and Khanna, 1991). The predominant carbon-bearing products are CO and carbonic acid,  $\text{H}_2\text{CO}_3$ . Nevertheless, as Chyba and Phillips (2001) argued, even small amounts of formaldehyde could help support considerable biomass in the ocean.

We examined the role of high-energy electrons in the radiolytic production of single-carbon species such as  $\text{H}_2\text{CO}_3$ ,  $\text{H}_2\text{CO}$ ,  $\text{CH}_3\text{OH}$ , and  $\text{CH}_4$ . Our primary goal was to set constraints on the production of the reduced species. The configuration of the experiment and vacuum chamber has been described elsewhere (Hand, 2007), but in brief we constructed a  $10^{-9}$  torr vacuum chamber with a He-cryostat cold finger onto which we could deposit thin ice films. A 100 keV electron gun, set to 10 keV, was then used to irradiate the sample while simultaneous acquisition of mid-IR (FTIR) and mass-spectra (RGA) allowed monitoring and analysis of the resulting products.

We examined radiolytic processing of water

and carbon dioxide films at temperatures and pressures relevant to Europa. Figure 3 shows results from 10 keV electron irradiation of a H<sub>2</sub>O+CO<sub>2</sub> (2:1) thin ice film. Water vapor and CO<sub>2</sub> gas were co-deposited at 50 K onto a gold mirror. The final thickness of the film was  $\sim 1.77 \mu\text{m}$ , enough to absorb most of the energy from the 10 keV electrons. After deposition, the film was slowly warmed to 90 K and subsequently irradiated with an electron beam of 100 nA to  $3 \mu\text{A}$ . Spectra were collected at a resolution of  $4 \text{ cm}^{-1}$ , with each spectrum being the co-added average of 1024 spectra collected over a period of approximately 9 minutes. Spectra are presented in units of absorbance, where an averaged pre-depositional spectrum of 3072 spectra has been used in the denominator for calculating absorbance ( $\text{Absorbance} = -\log_{10}(I_{\text{Irradiated}}/I_{\text{Predeposition}})$ , where  $I$  is the intensity of the spectrum). When calculating integrated band strengths for products such as H<sub>2</sub>CO<sub>3</sub>, we used a pre-irradiation-averaged spectrum instead of the pre-depositional-averaged spectrum in the denominator of the absorbance and the absorbance converted to optical depth units.

The lower line in Fig. 3 shows the ice film before irradiation, and the upper spectrum shows the same film after 4 hours of irradiation. The cumulative dose experienced by the film was  $\sim 2 \times 10^{21} \text{ eV cm}^{-2}$ . As can be seen, the major spectral features to emerge are the strong lines at 2570, 2141, 1714, 1485, 1380, and 1298  $\text{cm}^{-1}$ . The CO<sub>2</sub> bands at 2340  $\text{cm}^{-1}$  and 2278  $\text{cm}^{-1}$  persist in the irradiated spectrum. Aside from the 2141  $\text{cm}^{-1}$  band of CO, all of the other bands have been attributed to the formation of H<sub>2</sub>CO<sub>3</sub> (Moore *et al.*, 1991; Schutte *et al.*, 1993; Brucato *et al.*, 1997; Moore and Hudson, 1998; Gerakines *et al.*, 2000).

Consistent with both the UV and ion laboratory results for astrophysical ices, we found carbonic acid and carbon monoxide to be the primary products of H<sub>2</sub>O+CO<sub>2</sub> electron radiolysis of ices at european temperature and pressure. Initially, as shown in Fig. 4, H<sub>2</sub>CO<sub>3</sub> and CO concentrations rose linearly, and the CO<sub>2</sub> concentration decreased slightly. Equilibrium was reached at  $\sim 20 \text{ eV}/16 \text{ amu}$  ( $\sim 10^{20} \text{ eV cm}^{-2}$ ), where production and destruction rates became equal and all four components were in steady state (CO<sub>2</sub>, H<sub>2</sub>O, CO, and H<sub>2</sub>CO<sub>3</sub>).

The initial H<sub>2</sub>CO<sub>3</sub> production rate at 90 K under electron irradiation was  $G = 0.020/100 \text{ eV}$ , compared to 0.028 and 0.030 obtained at 18 K for

proton radiolysis and UV photolysis, respectively (Gerakines *et al.*, 2000). The carbonic acid destruction cross-section for incident 10 keV electrons was  $\sigma_{\text{D}} \sim 10^{-16} \text{ cm}^2$ . Using the three H<sub>2</sub>CO<sub>3</sub> bands of 2626  $\text{cm}^{-1}$ , 1508  $\text{cm}^{-1}$ , and 1307  $\text{cm}^{-1}$ , with corresponding band strengths of  $1.6 \pm 0.08 \times 10^{-17}$ ,  $6.5 \pm 0.6 \times 10^{-17}$ , and  $1.0 \pm 0.02 \times 10^{-17}$  (Gerakines *et al.*, 2000), we found a total H<sub>2</sub>CO<sub>3</sub> production of  $3.24 \times 10^{16}$  molecules per square centimeter. As a fraction of remaining CO<sub>2</sub>, this amounts to a molar ratio of 23.7%. By comparison, the total CO in the ice was  $2.78 \times 10^{16}$  molecules  $\text{cm}^{-2}$ , which led to a CO/CO<sub>2</sub> molar ratio of 20.4%.

The radiolytic destruction of CO<sub>2</sub> generated  $6.22 \times 10^{16}$  atoms of carbon available for synthesis into other compounds. Some of this carbon escaped as CO into the vacuum chamber and was lost from the system. Based on our H<sub>2</sub>CO<sub>3</sub> and CO production, we could account for approximately 97% of the evolved carbon, with roughly equal partitioning into each compound. We found no convincing signatures of H<sub>2</sub>CO, CH<sub>3</sub>OH, or CH<sub>4</sub>. In addition, no signature of carbon suboxide (C<sub>3</sub>O<sub>2</sub>) was found. Interestingly, we saw growth of features at 2044  $\text{cm}^{-1}$  and 1878  $\text{cm}^{-1}$ , which is consistent with the production of the CO<sub>3</sub> radical (Moore and Khanna, 1991; Jacox and Milligan, 1971). Lacking band strengths for these features, we could not quantify the carbon sequestered in this compound.

The combined accounting for carbon residing in CO<sub>2</sub>, CO, H<sub>2</sub>CO<sub>3</sub>, and possible minor species like CO<sub>3</sub> led us to conclude that upper limits for H<sub>2</sub>CO, CH<sub>3</sub>OH, and CH<sub>4</sub> production are in the range of  $\sim 1\%$  of the destroyed carbon or  $\sim 0.5\%$  by number of the remaining CO<sub>2</sub>. On the surface of Europa, this would be  $\sim 4 \times 10^{-4}\%$  H<sub>2</sub>CO by number relative to H<sub>2</sub>O.

Chyba and Phillips (2001) calculated that the upper 1.3 m of gardened regolith on Europa could contain  $5 \times 10^{18}$  molecules of H<sub>2</sub>CO per square centimeter. In that work, however, the CO<sub>2</sub> abundance used was 0.08% by number relative to H<sub>2</sub>O, which led to a 0.16% by number abundance of H<sub>2</sub>CO relative to CO<sub>2</sub> (or  $1.3 \times 10^{-4}\%$  by number relative to H<sub>2</sub>O). Using our new constraint on CO<sub>2</sub> of 0.036% relative to H<sub>2</sub>O leads to  $1 \times 10^{18}$  H<sub>2</sub>CO  $\text{cm}^{-2}$  and a 0.072% abundance of H<sub>2</sub>CO relative to CO<sub>2</sub> (or  $2.6 \times 10^{-5}\%$  by number relative to H<sub>2</sub>O). Our laboratory results show that, in either case, these numbers are within the bounds of our upper limits for H<sub>2</sub>CO.

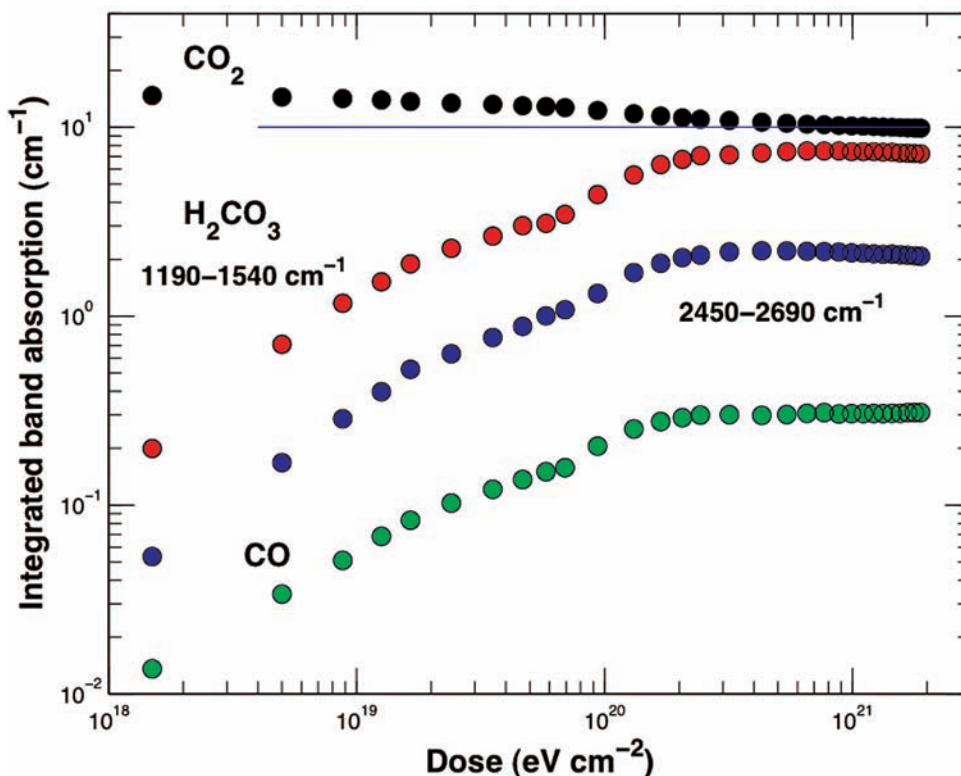


FIG. 4. Integrated band absorptions for  $\text{CO}_2$  and radiolytically produced compounds,  $\text{CO}$  and  $\text{H}_2\text{CO}_3$ , as a function of absorbed dose. Initial production rises linearly with a subsequent plateau as destruction balances production. At  $\sim 20 \text{ eV}/16 \text{ amu}$  (Dose  $\sim 10^{20} \text{ eV cm}^{-2}$ ), all four components approach equilibrium. Results are for the  $2340 \text{ cm}^{-1}$   $\text{CO}_2$  band, the  $2141 \text{ cm}^{-1}$   $\text{CO}$  band, and the  $1190\text{--}1540 \text{ cm}^{-1}$  and  $2450\text{--}2690 \text{ cm}^{-1}$   $\text{H}_2\text{CO}_3$  bands.

With the new  $\text{CO}_2$  results, the conclusion of Chyba and Phillips (2001) that delivery of radiolytically produced  $\text{H}_2\text{CO}$  could support  $\sim 3 \times 10^{23}$  microbial cells must be reduced to  $\sim 1 \times 10^{23}$  cells.

Based on our radiolysis results with  $\text{CO}_2 + \text{H}_2\text{O}$ , we concluded that the surface of Europa is not likely to be a large source of carbon-based reductants for the subsurface ocean. Most of the carbon is in the form of  $\text{CO}_2$ ,  $\text{CO}$ , and  $\text{H}_2\text{CO}_3$ . An important distinction to make here, however, is that the redox state of the initial carbon compound is a critical factor in the resulting carbon chemistry. Laboratory work by the authors has shown polymerization of short-chain alkanes and alkenes in ice, and the production of alcohols,  $\text{CH}_4$ ,  $\text{CO}_2$ , and  $\text{CO}$  (Hand and Carlson, in preparation). Other workers have similarly shown that production of refractory organic material in irradiated ices is possible (Khare *et al.*, 1989; Bernstein *et al.*, 1995; Moore and Hudson, 1998). While radiolysis of  $\text{CO}_2$  may not lead to large quantities of reduced-carbon compounds, exogenous organic material contained within micromete-

orites, comets, and dust particles, if not lost on impact (Pierazzo and Chyba, 2002), could potentially survive radiolysis and be delivered to the ocean in reduced form.

#### 4. CONSEQUENCES OF DELIVERY TO THE OCEAN

The delivery of oxidants to the subsurface ocean could be an important factor for oceanic chemistry and, consequently, the habitability of the ocean. The largest uncertainty, however, is the physical mechanism and timescale for delivery. Therefore, we chose this parameter as a variable and considered the range of delivery rates for these oxidants over a wide range of delivery periods. Here, we define the delivery period,  $\tau_d$ , as the average time it takes for material on the surface of Europa to reach the subsurface ocean. In other words, for a given radiolytic product (*e.g.*,  $\text{O}_2$ ) it will take on average  $\tau_d$  years for that molecule to be transferred to the ocean. Previous work (Chyba, 2000; Chyba and Phillips, 2001)

considered  $\tau_d$  to be roughly equivalent to the observed surface age,  $t_{ice}$ . This may be a fair approximation, but other alternatives are possible. Therefore, we decouple the two parameters in the work presented here.

We have made no restrictions on  $\tau_d$  other than to set an upper limit of 0.5 Gyr. Beyond 0.5 Ga, models for the thermal-orbital evolution of Europa indicate a more tidally active world with a significantly increased heat flux (Hussmann and Spohn, 2004). We have assumed that an increased heat flux would lead to increased ice shell activity. For this reason, we have designated 0.5 Gyr as a sufficient upper limit for our calculations.

Moles of compound delivered per year as a function of delivery period are plotted in Fig. 5a. The total number of moles of each compound is determined by integrating the percent by number abundance constraints through the gardened regolith of the surface. Upper and lower limits for the concentration of various species are shown. Gardening depths,  $d_g$ , are calculated based on Cooper *et al.* (2001),

$$d_g = 10^{-6} g_0 t (1 + t/t_0)^{-0.55},$$

where  $g_0 = 1.2 \mu\text{m yr}^{-1}$  is the initial cumulative growth rate and  $t_0 = 1.7 \times 10^5$  yrs is the mixing timescale. For a given delivery period, the gardening depth is calculated using  $t = \tau_d$ , and the resulting total number of moles of each compound is found. Though gardening depth is a function of surface age, it is an appropriate conservative integration depth for us to use because resurfacing mechanisms such as cryovolcanism will only serve to increase the depth of the layer of radiolytically processed material. For long delivery periods, the gardening depth is likely a very conservative underestimate for this depth.

The number of moles delivered to the ocean per year,  $\eta_i$ , is then found by dividing the total number of moles of compound  $i$  by the delivery period,

$$\eta_i = \frac{A d_g \varepsilon_i}{\tau_d}.$$

Here,  $A$  is the surface area of Europa, and  $\varepsilon_i$  is the concentration of each compound throughout the gardened layer in units of moles per cubic meter.

If the delivery period is comparable to the ob-

served surface age of 30–70 Myr (Zahnle *et al.*, 2003), then the ocean on Europa receives between  $8 \times 10^8$  and  $5 \times 10^9$  moles per year of  $\text{O}_2$ . If the delivery period is 10 Myr, the flux lies between  $2 \times 10^9$  and  $9 \times 10^9$  moles per year. Even at  $\tau_d = 500$  Myr, the flux lies between  $3 \times 10^8$  and  $1 \times 10^9$  moles  $\text{O}_2$  per year. These numbers are comparable to the contemporary  $\text{O}_2$  flux of  $7 \times 10^9$  moles  $\text{yr}^{-1}$ , which results from photolysis in Earth's upper atmosphere. Photosynthesis on Earth, by comparison, yields  $\sim 10^{16}$  moles per year (Walker, 1977).

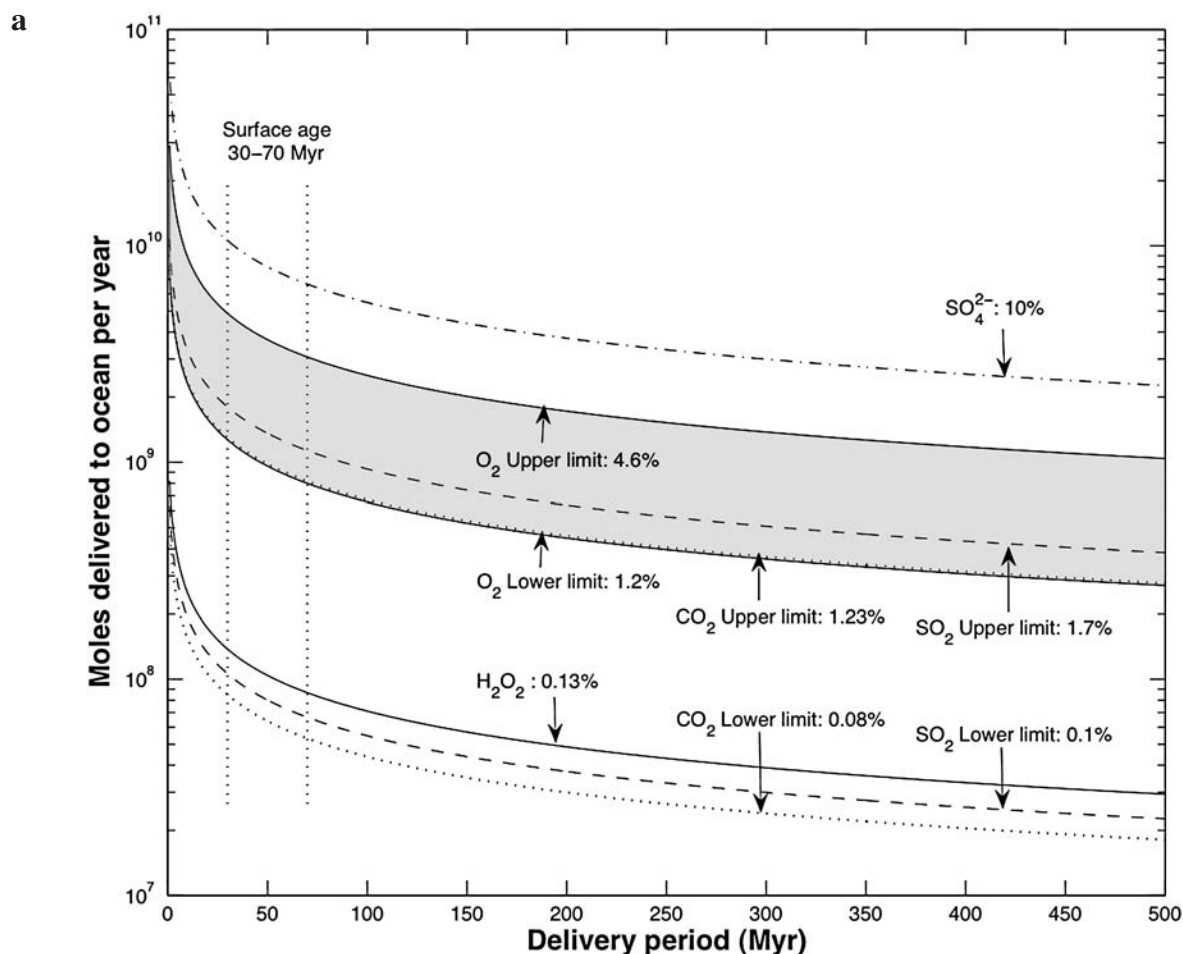
Figure 5b shows our calculation of the integrated molarity of  $\text{O}_2$  and  $\text{H}_2\text{O}_2$  in a 100 km thick global ocean. Our results are for 1 Gyr of integration over the delivery period—*e.g.*, for  $\tau_d = 100$  Myr the ocean would have received the gardened surface reservoir of oxidants ten times. To explore the upper limits on concentration, we have considered here a scenario in which radiolytically produced oxidants are delivered to an ocean with no chemical sinks. Next, we consider the role of reductants from a geologically active seafloor.

#### 4.1. Abiotic sinks for surface oxidants

McCullom (1999) examined the possibility of hydrothermally derived reductants on Europa as a mechanism for driving methanogenesis. With regard to reduced ocean hydrothermal fluid, the reductants  $\text{CH}_4$ ,  $\text{H}_2$ ,  $\text{H}_2\text{S}$ , and  $\text{Fe}^{2+}$  are present at 4.9, 12.0, 33.3, and 0.30 mm concentration. The terrestrial hydrothermal flux is  $3 (\pm 1.5) \times 10^{13}$  kg of seawater per year (Elderfield and Schultz, 1996), and the european flux, according to McCullom (1999), is  $\sim 10^{-3}$  that of Earth. This leads to delivery fluxes of  $1.5 \times 10^8$ ,  $3.6 \times 10^8$ ,  $1.0 \times 10^9$ , and  $9 \times 10^7$  moles per year for  $\text{CH}_4$ ,  $\text{H}_2$ ,  $\text{H}_2\text{S}$ , and  $\text{Fe}^{2+}$ , respectively.

As an added check on these estimates, we calculated a european hydrothermal flux by using the terrestrial oceanic heat flux of  $3.2 \times 10^{13}$  W (Stein and Stein, 1994) and the mid-ocean ridge heat flux of  $2 (\pm 1) \times 10^{12}$  W (Elderfield and Schultz, 1996) as scaling factors for Europa's hydrothermal fluid flux. For total european ocean heat fluxes ranging between  $1.74 \times 10^{11}$  and  $5.1 \times 10^{12}$  W (corresponding to 6.5–190 mW  $\text{m}^{-2}$ ), we found a fluid flux range of  $1.5 \times 10^{11}$  to  $4.8 \times 10^{12}$  kg  $\text{yr}^{-1}$ . Using terrestrial hydrothermal fluid concentrations for  $\text{H}_2\text{S}$ ,  $\text{CH}_4$ , and  $\text{H}_2$  from Elderfield and Schultz (1996) and Kelley *et al.* (2001) leads to  $\sim 10^9$ ,  $\sim 10^7$ ,

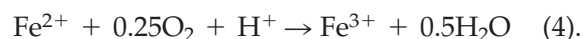
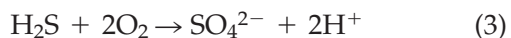
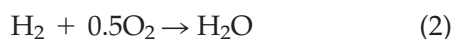
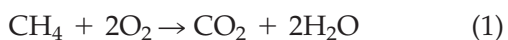




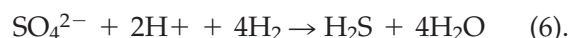
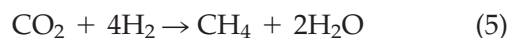
**FIG. 5.** (a) Moles per year of radiolytically produced oxidants delivered to the subsurface ocean of Europa. The delivery period,  $\tau_d$ , is the average time it takes for material on the surface of Europa to reach the ocean. While the surface age falls between 30–70 Myr (Zahnle *et al.*, 2003), the delivery period could be considerably longer depending on ice shell structure and resurfacing mechanisms (see text). The abundances of compounds are given in percent by number abundance relative to water. Upper and lower bounds on abundances are set by empirical constraints or compositional models. (b) Oxygen molarity of a 100 km global ocean on Europa, assuming no oxygen sinks. For a given delivery period the flux is integrated over 1 Gyr.

and  $\sim 10^8$  moles per year of each compound, respectively. These are comparable to the values of McCollom (1999).

To build up oxidants in Europa's ocean, the annual flux of radiolytically produced oxidants must compensate for the hydrothermally delivered reductants. The reductant-oxidant pairing could be accomplished with the following representative reactions, proceeding abiotically (McCollom and Shock, 1997):



The total O<sub>2</sub> needed to compensate these reactions, based on the reductant fluxes given above, is  $2.5 \times 10^9$  moles per year. As McCollom (1999) has shown, the temperature and pressure dependence of the above reactions largely determines the reaction thermodynamics. Here we have assumed all reactions move to the right in order to maximize oxidant consumption. The oxidants CO<sub>2</sub> and SO<sub>4</sub><sup>2-</sup> could also react with available reductants via



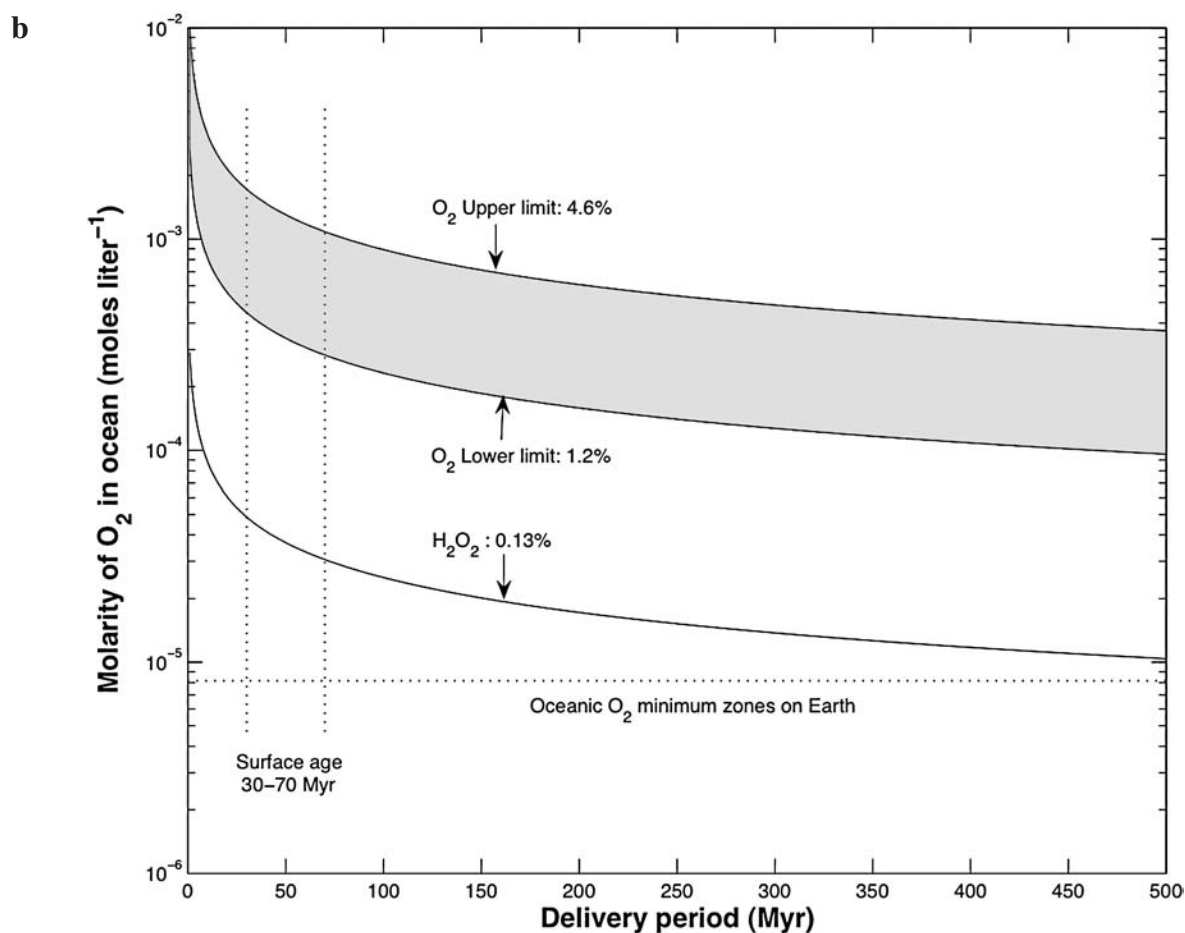


FIG. 5. (cont'd)

The sinks for the sulfate anion and carbonate anion can include precipitation of anhydrite ( $CaSO_4$ ) and carbonate ( $CaCO_3$ ). Both compounds have enhanced solubility at lower temperatures, but precipitation would have to be complete in order to consume as much of the surface oxidants as possible. Taking the McCollom (1999) hydrothermal flux of  $1.5 \times 10^9$  moles per year of  $Ca^{2+}$ , we found that much of the carbon could be consumed via precipitation. The delivery of sulfate, however, is large enough to accommodate anhydrite precipitation for the full range of delivery periods examined here.

Figure 6 shows our calculation of the  $O_2$  molarity of the ocean with the added condition of  $2.5 \times 10^9$  moles per year of  $O_2$  consumed by hydrothermally delivered reductants. As in Fig. 5b, we have limited our integration to only the past 1 Gyr on Europa. We have treated the  $H_2O_2$  delivery as part of the total  $O_2$  delivery, since  $H_2O_2$  decays to  $O_2$  on geologically short timescales [with a half-life of  $\sim 10$  yrs (Chyba and Phillips,

2001)]. To compensate the reductants completely with  $O_2$  and  $H_2O_2$ , the delivery timescale can be no greater than 107 Myr. For the lower limit of  $O_2$  abundance, the delivery period must be less than 11 Myr. In both cases, once the delivery period is short enough and the net flux of  $O_2$  is positive, then the  $O_2$  concentrations in the ocean rise rapidly.

Shown in Fig. 5b and Fig. 6 is the dissolved  $O_2$  concentration found in terrestrial oceanic oxygen minima zones. This concentration of  $O_2$  has been found sufficient for some terrestrial oceanic metazoans (Childress, 1968; Childress and Seibel, 1998). The work of Childress (1968) was on the small (35–125 mm in length) crustacean *Gnathophausia ingens*. Considering  $O_2$  in Europa's ocean, we concluded that, for the high-end surface concentration of 4.73% by number, the delivery period can be as long as 105 Myr and still surpass concentrations in terrestrial  $O_2$  minima zones. For the low-end surface concentration of 1.33% by number abundance, the delivery period

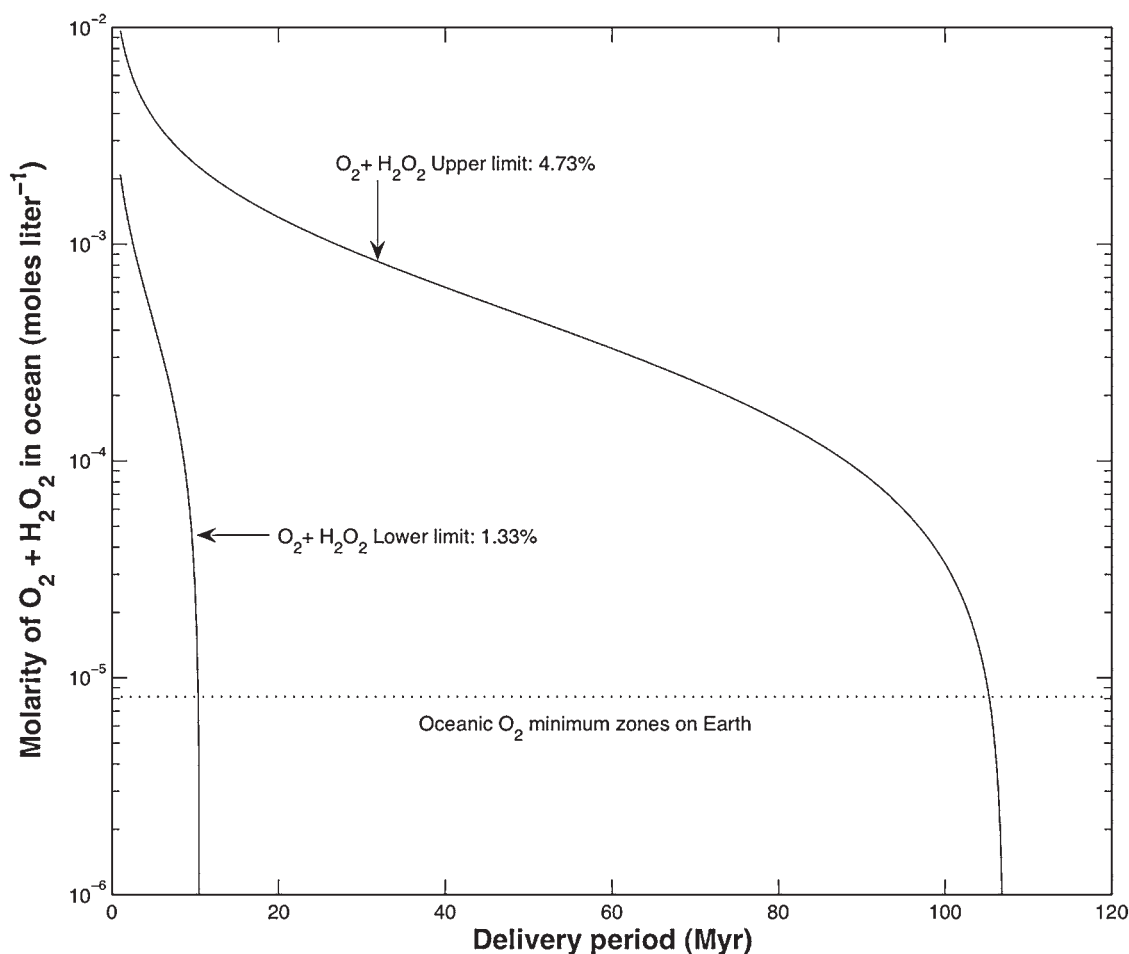


FIG. 6. Oxygen molarity (with  $\text{H}_2\text{O}_2$  added) of a 100 km global ocean in which  $2.5 \times 10^9$  moles per year of  $\text{O}_2$  are consumed by the hydrothermally delivered reductants  $\text{CH}_4$ ,  $\text{H}_2$ , and  $\text{H}_2\text{S}$ . Here we show oceanic concentrations that would result from low (1.33% by number abundance relative to  $\text{H}_2\text{O}$ ) and high (4.73% by number abundance relative to  $\text{H}_2\text{O}$ ) surface concentrations of  $\text{O}_2 + \text{H}_2\text{O}_2$ . For the high end, delivery periods as long as 105 Myr will still result in  $\text{O}_2$  concentrations that surpass those found in terrestrial  $\text{O}_2$  minima zones. For the low end, the delivery period needs to be 10 Myr or less in order to reach this level. Even with sinks added, the oxygen concentration of Europa's ocean can exceed levels comparable to that of Earth's ocean surface waters [ $\sim 250 \mu\text{M}$  (Millero, 2005)]. If the  $\text{O}_2 + \text{H}_2\text{O}_2$  abundance in the surface ice is 4.73% by number relative to  $\text{H}_2\text{O}$ , then ocean concentrations of  $250 \mu\text{M}$  are exceeded for delivery periods less than  $\sim 68$  Myr. For the lower surface abundance of 1.33% by number relative to  $\text{H}_2\text{O}$ , delivery periods of  $\sim 7$  Myr or less are required to exceed  $250 \mu\text{M}$   $\text{O}_2$ .

must be 10 Myr or less in order to surpass such concentrations. In other words, if the delivery period is less than  $\sim 100$  Myr and the surface  $\text{O}_2 + \text{H}_2\text{O}_2$  concentration is in the range of a few percent by number abundance relative to  $\text{H}_2\text{O}$ , then the ocean of Europa will contain enough dissolved oxygen to support organisms comparable to the macrofauna found in Earth's oceanic  $\text{O}_2$  minima zones.

The availability of dissolved oxygen is largely responsible for the diversity of large, complex species in our ocean. Regions of Earth's ocean are  $\sim 3\%$  supersaturated with  $\text{O}_2$  [ $\sim 250 \mu\text{M}$ , at  $15^\circ\text{C}$

and  $\sim 0.1$  kPa (1 atm) (Millero, 2005)]. On Europa, the cold water and increased pressure results in higher  $\text{O}_2$  saturation levels. For euroman ocean conditions of  $\sim 270$  K and 10–100 MPa,  $\text{O}_2$  saturation will be  $\sim 50$  mM (Lipenkov and Istomin, 2001). This is much greater than needed by terrestrial organisms. On Europa, surpassing dissolved  $\text{O}_2$  levels comparable to saturation levels for Earth's ocean occurs for delivery periods less than  $\sim 7$  Myr and  $\sim 68$  Myr, for the low-end and high-end values of surface  $\text{O}_2 + \text{H}_2\text{O}_2$ , respectively. In other words, for the high-end value, if the delivery period is the same as the surface age,

then Europa's ocean could well have enough dissolved oxygen to support any known marine macrofauna.

In all cases of accounting for sinks we concluded that the delivery of the sulfate anion will likely serve as the largest oxidant reservoir for aqueous chemistry in the European ocean. Though  $O_2$  and  $CO_2$  could be largely consumed by endogenous reductants, there is a minimum of  $\sim 2 \times 10^9$  moles per year of sulfate delivered to the ocean. Achieving sulfate concentrations comparable to those of Earth's ocean [ $2.86 \times 10^{-2}$  moles  $kg^{-1}$  (Kelley *et al.*, 2001)] would require delivery periods of  $< 51$  Myr. In dissolved form, the  $SO_4^{2-}$  and  $HSO_4^-$  would buffer the ocean with chemically useful oxidants, and it would be sulfate chemistry that dominates the ocean.

## 5. DISCUSSION

While radiolytic processing of the upper few millimeters of the surface occurs on short geological timescales [ $< 10^2$  to  $10^3$  yrs (Johnson, 2004)], considerable debate exists as to whether any of the surface oxidants do indeed reach the putative subsurface ocean. Without such surface-to-subsurface cycling, the available free energy will be largely limited to geologically leached or out-gassed oxidants such as  $CO_2$  and  $SO_4^{2-}$  (Zolotov and Shock, 2003; Zolotov and Shock, 2004). Our understanding of the geology of Europa is restricted to surface observations and thus remains poorly constrained. There is, at present, no evidence for contemporary resurfacing (Phillips *et al.*, 2000). Nevertheless, only  $\sim 15\%$  of Europa has been imaged at  $< 1$  km per pixel, and thus our ability to detect changes is limited by the available data (Schenk *et al.*, 2004).

Due to a lack of any evidence for contemporary activity to which relative ages can be tethered (*e.g.*, active plumes), the only definitive statement that can be made about resurfacing of the ice shell is that  $\sim 30$ – $70$  Ma much of the cratering record was erased from the surface (Zahnle *et al.*, 2003). Erasing of the cratering record does not strictly imply delivery of new material to the surface or delivery of surface material to the subsurface. We explore these relationships in this section. Above, we left the delivery period as a free variable. Here our goal is to provide order-of-magnitude estimates for the delivery period by

considering a few simplified models for surface processes.

The need to decouple the delivery period from the surface age is best explained by providing an example of how the two timescales could differ significantly. Considering cryovolcanism as a resurfacing process on Europa, a comparison can be made to snowfall in Antarctica and the delivery of material on the surface of the Antarctic ice sheet to subglacial lakes. In both cases, melting at the base of the ice drives delivery of surface material. One millimeter of unit density ice deposited on the surface causes roughly one millimeter of unit density ice to melt from the bottom. Over time, material that was buried on the surface reaches the ice-liquid interface. The delivery period is regulated by surface deposition, which in turn is directly related to the observed surface age. The period of delivery, however, can be much different from the surface age. For instance, the surface age of the Antarctic ice sheet is essentially zero (new snow and winds cover the surface on the timescale of  $\sim 1$ – $10$  yrs), and yet the bottom of the ice sheet contains material  $\sim 0.5$  Myrs old (Petit *et al.*, 1999). The surface age and the delivery period are off by five to six orders of magnitude. If cryovolcanism were the primary process for resurfacing on Europa, then the surface age could be a misleading proxy for the delivery period.

We have considered two possible models for cryovolcanism on Europa. The first has to do with sublimation of ice along warm ridges as a source for new surface material deposited elsewhere on the surface. In the second model, we have made a potentially erroneous comparison to the plumes on Enceladus and have scaled the surface deposition to Europa. This comparison may be inherently flawed due to the lack of knowledge as to what is happening on the south pole of Enceladus. Workers have proposed, however, that the plumes are evidence of a geyser releasing subsurface material (Porco *et al.*, 2006; Spencer *et al.*, 2006). More to the point, whether the plume material is from a subsurface liquid water reservoir is of little significance for our present calculation. The important aspect is that some of the plume material is redeposited on the surface of Enceladus, burying some of the older material and moving it closer to the ice-water interface.

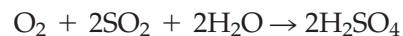
Sublimation from ridges is essentially muted cryovolcanism. Models for double-ridge formation based on strike-slip faulting argue for fric-

tional heating and “thermal upwarping” as a means by which the ridges are raised (Nimmo and Gaidos, 2002). Such heating causes sublimation along the ridges. On the low end, ridge temperatures of  $\sim 130$  K lead to sublimation and subsequent deposition of  $1 \mu\text{m yr}^{-1}$  (Fagents *et al.*, 2000). Higher temperatures (*e.g.*, 150 K) raise this rate by nearly three orders of magnitude. If half the surface area of Europa is sublimating while the other half is accreting, then global deposition rates are in the range of  $0.5\text{--}500 \mu\text{m yr}^{-1}$ . This implies a delivery time of  $2 \times 10^6$  to  $2 \times 10^9$  yrs for each kilometer of ice shell thickness. Obviously, the upper end of a few billion years would imply little to no delivery of surface material. The lower end implies relatively rapid delivery of surface material. For an ice shell of 4 km thickness (Hand and Chyba, 2007), surface material would be delivered in 8 Myr. Similarly a 10 km or 20 km shell would imply delivery in 20 Myr or 40 Myr, respectively. By these estimates, a 35 km thick ice shell yields a delivery time of 70 Myr, which is consistent with the upper-end estimates for the surface age (Zahnle *et al.*, 2003).

Approaching cryovolcanism from a different angle, we used the recent *Cassini* observations of the South Polar region of Enceladus (Spencer *et al.*, 2006) as a rough guide for what could occur on an active Europa. The south pole ice geyser on Enceladus allows  $150\text{--}350 \text{ kg s}^{-1}$  of water to escape (Hansen *et al.*, 2006). Kargel (2006) estimated that the actual amount of water ejected could be  $\sim 840 \text{ kg s}^{-1}$ , which implies that  $\sim 500 \text{ kg s}^{-1}$  is eventually redeposited. The new terrain on Enceladus is restricted to the southern hemisphere, or about a quarter of the moon’s surface area ( $2 \times 10^{11} \text{ m}^2$ ). Using a surface area this large means that our numbers for redeposition will be a conservative low-end estimate. We calculated a mass source rate to surface area renewed of  $\sim 2.5 \times 10^{-9} \text{ kg m}^{-2} \text{ s}^{-1}$ . This would lead to  $\sim 100 \mu\text{m yr}^{-1}$  of material on the surface, or 10 Myr for delivery through each 1 km of ice shell thickness. This result is consistent with our previous calculations based on ridge sublimation.

If deposition of material onto the surface of Europa lies in the range of tens to hundreds of microns per year, then the delivery period for a shell of thickness 10 km or less would be  $< 100$  Myr. This is for the case of resurfacing dominated by cryovolcanism. If fractures or melt-through events were to allow direct communication of the surface with the subsurface, then delivery peri-

ods could be significantly shorter (Carr *et al.*, 1998; Chyba, 2000). One counter argument to this has been that fractures and melt-through events will cause outgassing and loss of the radiolytically produced surface compounds (Zolotov and Shock, 2004). We argue that, while degassing may occur, most of the oxidants do not escape (Fagents *et al.*, 2000; Carlson *et al.*, 2005). Instead, they are redeposited and trapped in the surface ice in colder regions. The presence of molecular oxygen in the solid phase on the surface of Europa is itself a puzzle (Baragiola and Bahr, 1998; Johnson, 1999). Recently, Hand *et al.* (2006) argued that mixed clathrates of  $\text{O}_2\text{-CO}_2\text{-SO}_2$  could solve the trapping problem. While  $\text{O}_2$  may be released to the atmosphere, the higher temperatures will also promote the reaction of  $\text{O}_2$  to sulfate and carbonate, with chemical pathways such as



These compounds would collect in the ice while  $\text{H}_2\text{O}$  sublimates. Such surface chemistry during warming could, in part, explain the observations of hydrated sulfate material in the hummocky low-lying matrix terrain of chaos features and the absence of such material on the surface of intact “raft” blocks. The matrix material would have been warmed to a greater degree than the tops of the ice rafts. Carlson *et al.* (2005) proposed a similar mechanism to explain the formation of concentrated sulfate hydrate lag deposits on the flanks of double ridges. While molecular  $\text{O}_2$  may evolve out of the ice or water during warming, Europa retains its  $\text{O}_2$  atmosphere, and the gaseous  $\text{O}_2$  may be redeposited in solid phase elsewhere on the surface. In addition, some of the  $\text{O}_2$  in the region of fracturing or melt-through will be sequestered into other oxidants. Nevertheless, the case of oxidants escaping can be treated as another line in Fig. 6. For instance, if the surface abundance of  $\text{O}_2 + \text{H}_2\text{O}_2$  is 4.73% by number relative to  $\text{H}_2\text{O}$  and 75% of the oxygen and peroxide escapes during resurfacing, then the amount delivered to the ocean would be comparable to that of the line for 1.33% by number abundance  $\text{O}_2 + \text{H}_2\text{O}_2$ .

For an ice shell thicker than  $\sim 10$  km, several workers have argued that convection, as opposed to conduction, will be the primary mechanism for heat transport (McKinnon, 1999; Pappalardo *et*

*al.*, 1998). In such models, a brittle ice lid of a few kilometers thickness overlies a thick ductile layer in which convective plumes rise and fall. Plumes could serve as a useful delivery mechanism for oxidants within the ice shell (Barr *et al.*, 2002; Barr and Pappalardo, 2003). As warm material from the base of the ice moves upward, regions of downwelling could entrain material from the base of the brittle layer. Calculations of plume velocities ( $\sim 10$ s of cm per year) lead to rise times for plume material on the order of tens to hundreds of thousands of years (Barr and Pappalardo, 2003). This is short compared to the timescales found for delivery via cryovolcanism. Thus, if material were to be cryovolcanically transported through a 3–10 km brittle layer in tens of millions of years, then transport from the brittle-ductile layer interface could be relatively rapid (Barr *et al.*, 2002).

In all of the above models, a reasonable order of magnitude estimate for transport of material through the ice shell is tens of millions of years. Delivery periods could be longer ( $\sim 10^9$  yrs) if ridge sublimation is limited to temperatures of 130 K or less, but this seems unlikely given that daytime average equatorial surface temperatures reach  $\sim 130$  K (Spencer *et al.*, 1999). Our estimates for the delivery period are independent of, but consistent with, the surface age as constrained by crater counts (Zahnle *et al.*, 2003). This is interesting because these two timescales do not necessarily need to agree. The fact that these estimates agree suggests that delivery periods in the range of 10–100 Myr are appropriate for Europa.

One possible interpretation of the observed surface age is that 30–70 Ma Europa experienced resurfacing; since that time it has been cooling and the thickness of the ice shell increasing. This may have been the last time surface oxidants were transferred to the subsurface. Zolotov and Shock (2004) argued that in the present epoch there is no effective mechanism by which oxidants are delivered to the ocean. This could be the case, but if Europa was active in the past, then the question arises whether delivery in the past could serve to maintain chemical disequilibrium through to the present. In other words, how long could  $O_2$  in the ocean persist at biologically useful levels if the last delivery occurred 30–70 Ma and no new material has since reached the ocean?

With  $2.5 \times 10^9$  moles per year of  $O_2$  consumed by reductants for 30–70 Myr,  $O_2$  levels in Europa's ocean would need to have started with

$1.1 \times 10^{-4}$  to  $1.4 \times 10^{-4}$  moles per liter to achieve contemporary concentrations of  $8 \times 10^{-5}$  moles per liter (comparable to terrestrial  $O_2$  minimum zones and capable of supporting macrofauna). Maintaining an ocean with  $1.1 \times 10^{-4}$  to  $1.4 \times 10^{-4}$  moles per liter would have required delivery periods of  $<90$  Myr prior to the last resurfacing and delivery event. This is considerably longer than the surface age. If the delivery period is equivalent to the surface age, then contemporary  $O_2$  concentrations are between  $\sim 10^{-3}$  and  $\sim 10^{-4}$  moles per liter, well within the range of being able to support any terrestrial macrofauna, not just those found in the oxygen minima zones on Earth.

## 6. CONCLUSION

We have shown that even with hydrothermal sinks and long delivery periods, the ocean on Europa could reach dissolved oxygen levels capable of supporting terrestrial marine macrofauna. At a minimum, the abundance of sulfate supplied from the surface could lead to sulfate buffers in the form of mineral precipitation (*e.g.*, anhydrite). Zolotov and Shock (2004) argued that abiotic reactions would consume radiolytic oxidants, which would leave little geochemical energy available for life. We found that, for delivery periods of less than  $\sim 100$  Myr, the flux of  $O_2$  and  $H_2O_2$  will more than compensate for hydrothermal reductants, given the level of hydrothermal activity predicted by McCollom (1999) and our own scaling of the terrestrial flux to the European system. Reduction of sulfate—a key metabolic pathway for terrestrial deep ocean ecosystems and one explored by Zolotov and Shock (2004)—would be an obvious niche for European biota, which would likely not be limited by the availability of oxidants. Contrary to the work of Gaidos *et al.* (1999), we have found that the limiting factor for chemical energy on Europa could be the availability of reductants, not oxidants.

We have shown that few, if any, reductants are produced through radiolysis of  $CO_2$  with water. Carbon dioxide is found to be present on the surface of Europa at 0.036% by number relative to water (360 ppm). If  $CO_2$  is the primary initial form of carbon on Europa, then radiolysis would serve to partition the carbon into reservoirs of  $CO_2$ , CO, and  $H_2CO_3$  with an approximate ratio of [5:1:1]

for the three species, respectively. Reductants such as formaldehyde may account for some of the radiolytically processed carbon, but based on our mass balance analysis, the abundance of such reductants is less than 1% of the observed surface abundance of CO<sub>2</sub>. This experimental result is consistent with the calculations of Chyba and Phillips (2001), but it implies that delivery of radiolytically produced reductants is a few orders of magnitude lower than geologically supplied reductants (McCullom, 1999).

The availability of geologically supplied reductants is a function of seawater cycling with the mantle. This, in turn, is a function of tidal dissipation in the mantle. Partitioning of tidal energy in the ice layer and mantle through time is, therefore, a critical parameter for discerning the availability of both reductants and oxidants on Europa. Empirical constraints on tidal dissipation in the mantle and on seawater cycling through the oceanic crust could greatly enhance our understanding of the reductants and oxidants available for a putative European biosphere. Along with surface spectroscopy for compositional information, gravity and altimetry data on a future mission could help resolve these outstanding questions.

## ACKNOWLEDGMENTS

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## ABBREVIATIONS

NIMS, Near-Infrared Mapping Spectrometer.

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