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Amino acid synthesis in Europa's subsurface environment

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Abstract: It has been suggested that Europa's subsurface environment may provide a haven for prebiotic evolution and the development of exotic biotic systems. The detection of hydrogen peroxide, sulfuric acid, water, hydrates and related species on the surface, coupled with observed mobility of icebergs, suggests the presence of a substantial subsurface liquid reservoir that actively exchanges materials with the surface environment. The atmospheric, surface and subsurface environments are described with their known chemistry. Three synthetic schemes using hydrogen peroxide, sulfuric acid and hydrocyanic acid leading to the production of larger biologically important molecules such as amino acids are described. Metabolic pathways based on properties of the subsurface ocean environment are detailed. Tidal heating, osmotic gradients, chemical cycling, as well as hydrothermal vents, provide energy and materials that may support a course of prebiotic evolution leading to the development or sustenance of simple biotic systems. Putative organisms may employ metabolic pathways based on chemical oxidation–reduction cycles occurring in the putative subsurface ocean environment.

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Key words: amino acids, chemoautotrophs, Europa, hydrocyanic acid, hydrogen peroxide, redox cycles, sulfuric acid.

Introduction

Europa is one of 65 satellites of Jupiter identified thus far (Bennett *et al.* 2007). The four largest of the Jovian satellites (Io, Callisto, Ganymede and Europa) are referred to as the Galilean Satellites because they were discovered by Galileo in 1610. The innermost of these, Io, is the most volcanically active body in the solar system (Jakosky 1998). Europa, the second Galilean satellite from Jupiter, has a dense core and an ice crust that may be underlain by a liquid water ocean (Greenberg *et al.* 2002). Ganymede, the third Galilean satellite, has scars from giant impacts but shows near complete resurfacing (Bennett *et al.* 2007). Finally, Callisto, the fourth satellite, seems to be heavily cratered and undifferentiated, thus preserving evidence of its early history (Anderson *et al.* 1998). With a size slightly smaller than our Moon, Europa is the smallest of the four Galilean satellites.

In the mid 1940s Kuiper showed that Europa's crust was composed of water and ice (Bennett *et al.* 2007). The Pioneer and Voyager fly-by missions in the 1970s verified Kuiper's prediction and added more detailed information about Europa. In 1995, the Galileo mission began gathering more detailed images and measurements within the Jovian satellite system, providing the information needed to shed light on Europa's history, current conditions and future. Europa resides in the temperature region of the Solar System where water ice and other volatiles become stable over the age of the solar system. The composition and chemistry of the surface and subsurface environments are of interest because recent information gathered on Europa suggests that subsurface water reservoirs are likely to exist under the icy surface (Anderson *et al.* 1997; Carr *et al.* 1998; Kivelson *et al.* 2000). Moreover, evidence suggests that the moon is internally active (Kivelson *et al.* 2000). It is, therefore, possible that the mix of chemicals in the presence of water and available energy sources may produce a prebiotic evolutionary pathway that could potentially lead to the development and persistence of life. This paper describes the surface, subsurface and atmospheric environments on Europa and details plausible synthetic schemes leading to the production of amino acids from simple organic or inorganic reactants. The potential of the subsurface environment to host exotic biotic is also examined.

The environment of Europa

Prior to the Galileo mission, the only information known about Europa was that it was a small ice-covered satellite of Jupiter with a very shiny surface covered by pale curved and linear markings. The Galileo mission provided evidence of a young, thin, cracked and ruptured ice shell that appears to be moving slowly over the surface of a putative briny ocean

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Table 1. *Some atmospheric and surface properties of Europa*

Property	Value
Surface pressure[a]	1.0×10^{-10} bars
Atmospheric O_2 mole fraction[a]	95%
Atmospheric H_2 mole fraction[a]	1%
Primary atmospheric gases[a]	O_2 followed by H_2, H_2O and various sulphur compounds
Surface temperature[b]	−145 °C
Equatorial radius[b]	1569 km
Mean density[c]	3.01 g cm^{-3}
Surface composition[a,c]	Mostly water ice
Distance from the Sun[b]	7.8×10^8 km

[a] Data taken from Chela-Flores (2001).
[b] Data taken from Pappalardo *et al.* (1999).
[c] Data taken from JPL-Galileo website (2007).

that is approximately 100 km deep (Jakosky 1998). The Galileo Spacecraft also detected an ionosphere above Europa's surface when its radio transmission to Earth was deflected by electrons due to Europa's position between Galileo and Earth during the transmission. Intense radiation, along with the proximity of Jupiter, has created the ionosphere where active dissociation of atmospheric species occurs. An ionosphere is a layer of charged particles (ions and electrons) found in the upper levels of a given atmosphere just inside the exosphere. An ionosphere is created when gas molecules in the atmosphere become ionized due to encounter with incoming solar radiation. The Hubble Space Telescope detected oxygen emissions, a clear indication of the presence of a thin atmosphere above the Europan surface (Hall *et al.* 1995). Some of Europa's most important atmospheric and surface parameters, determined to date, are shown in Table 1.

The atmospheric environment

On Earth, photosynthetic organisms generate and maintain a 21% oxygen atmosphere. However, it is unlikely that this is the case on Europa. It appears that purely non-biological processes produce Europa's thin oxygen atmosphere (Chela-Flores 2001). Europa's icy surface is exposed to sunlight and is impacted by dust and charged particles trapped within Jupiter's intense magnetic field. Combined, these processes cause some of the frozen water ice on the surface to vaporize producing water vapour as well as gaseous fragments of water molecules. After the water vapour molecules and molecular fragments in the form of molecular ions or radicals are produced, they undergo a series of chemical reactions that result in the production of molecular hydrogen and oxygen. The low molecular weight of hydrogen gas allows its molecules to escape into space, while the heavier oxygen molecules accumulate to form a thin atmosphere that extends approximately 200 km above the surface (Cooper *et al.* 2003). The oxygen gas slowly leaks into space and its concentration in the atmosphere is maintained via the continuous decomposition of water vapour in the atmosphere. NASA's Hubble Space Telescope detected the presence of oxygen in Europa's atmosphere when it determined a series of oxygen emissions on Europa (Leblanc *et al.* 2002). In Europa's thin atmosphere, the ionosphere layer is caused by both the Sun's ultraviolet radiation and by energetic particles trapped in Jupiter's strong magnetic field (the magnetosphere). It is likely the charged particles in Jupiter's magnetosphere are hitting Europa's icy surface with great energy, causing sputtering of the surface and knocking atoms of water molecules off the moon's surface in order to generate the ionosphere (Johnson *et al.* 2003). The density of electrons in Europa's ionosphere is about 10 000 electrons per cubic centimetre, significantly lower than the average density of 20 000 to 250 000 electrons per cubic centimetre found in Jupiter's ionosphere (Johnson *et al.* 1998). This indicates that Europa's ionosphere is tenuous; nonetheless, it is strong enough to be called an ionosphere.

The surface environment

Europa has been described as the smoothest object in the Solar System (Jakosky 1998). This is due to the presence of a global ice shell that covers the surface of the moon. On the surface are a series of dark bands or cracks that appear to criss-cross. The largest of these cracks is estimated to be about 20 km across and contains a central band of lighter material. These dark cracks are thought to have been produced under the influence of tidal forces (Greenberg *et al.* 2003) or volcanic eruptions or geysers located within the moons subsurface (Greeley *et al.* 2000). The eruptive sites intermittently release water onto Europa's surface. The water then freezes and, as a result, erases the traces of impact craters (Greeley *et al.* 2000). Another factor contributing to the observed appearance of the outer surface is the activity of the plumes. It is likely that if liquid water reaches the surface via volcanic eruptions, the material venting from the subsurface to the surface creates vapour clouds (Greenberg *et al.* 2003). Salty minerals contained within these vapour clouds (such as sulphates and carbonates) may show up as dark areas on the surface of the moon (Leblanc *et al.* 2002). Thus if there is a subsurface ocean or liquid water reservoirs that exchange materials with the surface, the ocean is likely to be a salty one. Direct sampling and analysis of Europa's surface has not occurred yet but extensive spectral measurements taken from orbit have provided a wealth of information. These spectral measurements only sampled the uppermost layers of the surface (McCord *et al.* 1998; Carlson *et al.*1999a, b; Dalton 2003). The surface of Europa consists of what seems to be slushy ice sheets and very few craters. The presence of only a few craters on the surface suggests that the surface is relatively young, perhaps only about 30 million years old (Jakosky 1998). As a result of the sunlight reflecting off of its icy crust, Europa is considered to be one of the brightest objects in the Solar System. Figure 1 is an image of Europa's smooth and shiny surface that shows the dark criss-crossing bands. The dark bands on Europa's surface may indicate past volcanic eruption and potential eruption of gases and rocky matter from the moon's interior (Greeley *et al.* 1998). These features coupled with the cracks and slushiness of the icy surface suggest that liquid water

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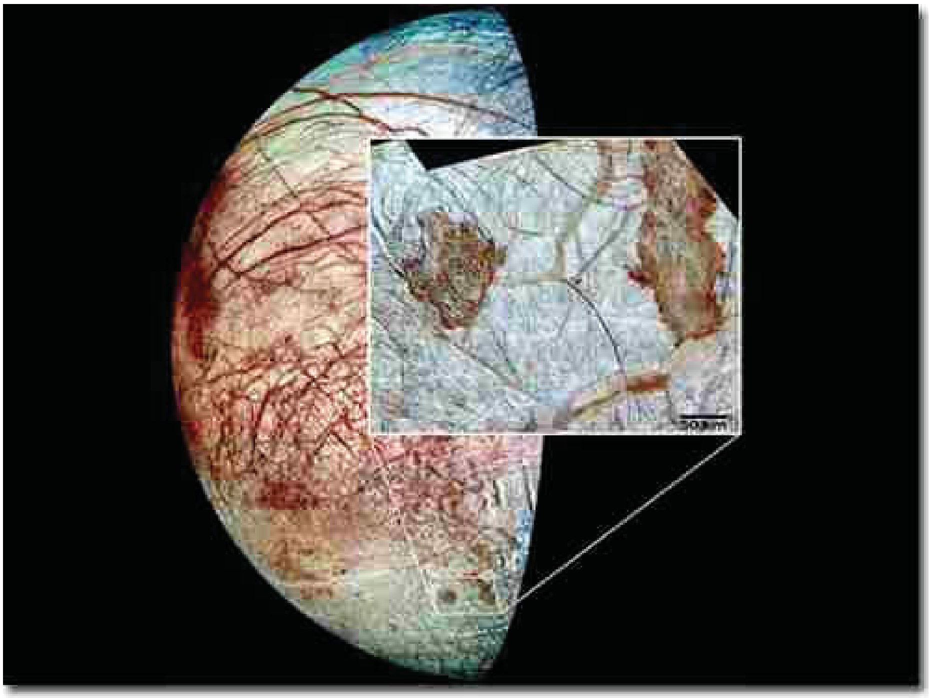

Fig. 1. Europa's surface and an enlargement of the Thrace region (from the JPL Galileo website).

existed underneath the icy crust when eruptions first began. In addition, Europa has ridges indicating the surface crust was separated and injected with some type of substance (Greeley *et al.* 2000). Other ridges present on the surface are known as the youngest ridges and these have central fractures, synchronized knobs and irregular dark patches. These particular characteristics indicate cryovolcanism, surface changes due to eruptions of gases and ice (Figueredo *et al.* 2003).

Europa's external surface has two additional prominent features: its impact craters and broken ice. The diameter of the largest impact crater is approximately 30 km. The crater lodged into the crust, spreading debris onto the surrounding terrain. The limited number of craters on the surface, however, qualifies Europa as an active surface because craters are evidence of old terrain. Europa's surface icy crust reveals fractures indicated by dark, linear, curved and wedged-shaped bands. Some of the fractures have parted the crust into sections up to a diameter of 30–50 km. The areas between the sections contain a mixture of icy slush contaminated with rock debris. In addition, certain sections appear to have rotated and diffused into new alignments (Greenberg 2002).

Europa's surface has been divided into geologic units (Figueredo *et al.* 2003). The geologic units are distinguished by their physical features and approximate time of formation. The five primary terrain types now recognized in the Galileo images of Europa are as follows: plains chaos, bands, ridges and crater materials (Greeley *et al.* 2000; Figueredo *et al.* 2003). Most terrains are the visible results of internal activity. The surface terrains are instrumental in driving the dynamic exchange of materials and energy that occurs between the subsurface and surface environments allowing for a reasonable setting for prebiotic evolution (Greenberg & Geissler 2002). Figueredo *et al.* (2003) described the basic characteristics of these terrains:

1. *Plains*. These are the most common surface type. Plains consist of three divisions: a) ridged plains, (b) smooth plains or (c) undifferentiated.
   (a) Ridged plains vary in size, orientation and cross-cutting intersections and are considered to be the oldest and most identifiable surface feature.
   (b) Smooth plains are the result of volcanic activity and thus tend to be dark. They are considered to be the youngest and occur in circular to unevenly shaped areas.
   (c) Undifferentiated ridges are not very visible and are thought to be a mixture of both ridged and smooth plains.
2. *Chaos*. Chaos terrains are among the youngest surface features. They are characterized by high material mobility because of rotation and tilting of blocks and are distorted and cracked. The surface in areas of chaos terrains appears as fractured sections of pre-existing materials that have been initiated by internal activity such as hydrothermal vents or a different heat source.
3. *Bands*. Bands were probably the ending phase of ridges and may have arisen due to breakage of crust whereby they occupied gaps. Bands are bright and have slice-shaped regions.
4. *Ridges*. Ridges may have been formed due to volcanic activity or pieces broken from the crust. They are either

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straight or curved and have single or double intersecting divisions.

5. *Crater material*. Crater materials consist of brim and miscellaneous material.

The subsurface environment

High-resolution images from the Galileo spacecraft have validated that Europa's hard surface crust consists of 'mobile icebergs' with a layer of something softer under it that has been affecting the external surface features (Carr *et al.* 1998). Magnetometer measurements of changes in the magnetic field carried out by the Galileo spacecraft are consistent with the presence of a near-surface layer of electrically conducting material (Kivelson *et al.* 2000). The most reasonable conducting layer consistent with observed measurements and properties would be a briny global ocean beneath the ice layer. Thus, Europa's slushy ice surface is thought to be floating over a global subsurface ocean.

It is likely that Europa is internally active and that its crust may have liquid water warm enough to sustain simple life in the dark underneath the global ice shell. Europa may be internally heated by two unique phenomena. Fractional warming may be caused by the decay of radioisotopes within the core. This process is unlikely to contribute much to internal heating because it is a limited process based on Europa's formation theory (Greeley *et al.* 2000; Greenberg *et al.* 2003). Frictional warming (tidal heating) is the other scenario that produces heat. Due to the attractive forces of Jupiter, the tidal bulges on Europa cause the surface to expand and contract slightly during each orbit and shift from side to side. This produces frictional heat as the layers of Europa's internal material rub against one another. This causes the surface to fracture. When large fractured blocks move around the icy crust, it causes heat to build up inside. The heat could melt the ice on the surface forming a liquid ocean or subsurface liquid reservoirs beneath the moon's icy surface.

Greenberg & Geissler (2002) suggest that tidal heating is the dominant internal heat source that keeps the ocean liquid while allowing crustal melt and thickness variability. The visible markings on Europa could be a result of internal global expansion where the ice crust could have fractured, filled with water and frozen (Greenberg & Geissler 2002). The 'wandering' of surface icebergs causes heat build-up underneath the surface due to friction between the masses. Increased salinity and acidity cause an increase in the highest density of liquid water at a lower temperature allowing for the plausibility of heavier liquid water to exist near the 'ocean bottom'. Recently, however, a controversy arose when some authors suggested that the ocean environment is alkaline due to the presence of a substantial amount of ammonia dissolved in the ocean water (for example, Bains (2004)). In a given column of ocean water, denser water (containing more solutes) will sink to the bottom while increasingly lighter water will fill the upper portions of the column. Within the column, the density gradient increases downward and is dependent upon the amount of solutes found in the water. The higher the concentration of dissolved salts in the water, the higher the density and the larger the magnitude of the freezing point depression will be. The most common salt in Europa's putative ocean is thought to be magnesium sulphate (Dalton 2003). Thus, estimation of the freezing point of ocean water containing a given concentration of salt can be approximated by ignoring the presence of other solutes and using the formula (Brown *et al.* 2002)

$$\Delta T_f = iK_f m. \tag{1}$$

Equation (1) reflects the fact that a more concentrated solution results in a greater change in freezing temperature. In Eq. (1), ΔT_f is the change in freezing point between the solution and pure solvent, i is the van't Hoff factor defined as measured over the calculated ΔT_f, K_f is the molal freezing-point-depression constant for the solvent (water in this case) and m is the molality of the solution given as the number of moles of solutes per kilogram of solvent. In the absence of any information about the actual value of i for a solution, it is customary to use the ideal value in calculations by noting the number of ions per formula unit of salt (Brown *et al.* 2002). For example, since both NaCl and $MgSO_4$ consist of two ions per formula unit, the ideal value for i for either of these salts is 2.The units of K_f are °C/m. For water, the value of K_f is 1.86 °C/m, meaning that a 1 molal salt solution of water will freeze 1.86 °C lower than pure water (Brown *et al.* 2002). Using the above formula, one can calculate the freezing temperatures that will correspond to a certain salt concentration. $\Delta T_f = T_{\text{pure}} - T_{\text{solution}}$ is the difference between the normal freezing temperature of the pure solvent and the freezing temperature of the solution. Thus, $T_{\text{solution}} = T_{\text{pure}} - \Delta T_f$. The T_{pure} value refers to the freezing point of pure water, which does not change much with changes in pressure. Levine (1988) shows that for a pressure increase from 1 to 100 atm, the freezing point of pure water is only lowered by 0.75K. This value is obtained by applying the Clapeyron equation for solid–liquid equilibrium in the case of water. Brown *et al.* (2002) showed that at a pressure of 4.58 torr (0.0013 atm) the freezing temperature of pure water is 0.0098 °C. At pressures lower than the value of 4.58 torr, however, water sublimes due to the fact that values below this pressure fall below the triple point of water on its phase diagram and would, therefore, correspond to transitions between solid and gas (Brown *et al.* 2002). The very low pressure on Europa's surface explains why the presence of liquid water is unlikely. The various freezing temperatures for the ocean's salty water depending on the salt concentrations are given in Table 2.

Table 2 clearly demonstrates that while the presence of ammonia significantly impacts the lowering of the freezing point, only at relatively high salt concentrations does the freezing temperature of the ocean water decrease significantly below zero. Dean (1992) reports that at an NaCl concentration of slightly above 23 % by mass in a water solution, the saturation temperature of sodium chloride dehydrate ($NaCl.2H_2O$) is attained causing the solution to freeze at −21.13 °C. Any solutions of higher NaCl concentration

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Table 2. *Freezing ocean water temperature per given concentrations of salt or ammonia*

Salt Concentration	$T_{solution}$ for an NaCl dominated ocean (°C)	$T_{solution}$ for an $MgSO_4$ dominated ocean (°C)	NH_3 concentration (moles per kg of water)	$T_{solution}$ for an NH_3 dominated ocean(°C)
100 mg l^{-1}	−0.00636	−0.000833	0.01	−0.0186
500 mg l^{-1}	−0.0318	−0.00420	0.1	−0.1860
1 g l^{-1}	−0.0636	−0.00833	1	−1.8600
5 g l^{-1}	−0.318	−0.0420	5	−9.3000
10 g l^{-1}	−0.636	−0.0833	10	−18.600
50 g l^{-1}	−3.18	−0.420	25	−46.500
100 g l^{-1}	−6.36	−0.833	50	−93.000

will start to freeze at temperatures that are gradually closer and closer to zero. Dean (1992) reports that at an NaCl concentration of slightly above 26% by mass a water solution freezes at 0 °C. The temperature of maximum density (T_{max}) for water at different pressures (p in atmospheres) is given by an empirical equation reported by Dean (1992):

$$T_{max} = 3.98 - 0.0225(p - 1). \quad (2)$$

Using Eq. (2), one can calculate the temperature of maximum density for water at various depths in Europa's putative ocean by knowing the pressure at the given depth and taking into consideration the fact that Europa's gravity is about one-tenth that of Earth. This can be done by applying the formula $p = \rho g h$. In this formula, p is the pressure, ρ is the density of the liquid medium, g is the gravitational acceleration and h is the column depth. The pressure obtained by this formula can be added to the pressure exerted by the global ice cover from above to give the total pressure at the desired depth. For instance, for a total pressure of 10 atm, Eq. (2) gives a temperature of maximum density of approximately 3.78 °C. Thus, if the ocean is deep enough so that near its bottom a pressure of say 200 atm is exerted on the surroundings, Eq. (2) gives a T_{max} of approximately −0.498 °C. Models of Europa's interior show that beneath a thin crust of water ice Europa may have oceans that are at least 50–100 km deep. If the upper value of this prediction is taken, and an average density of salty water of 1200 kg m^{-3}, a pressure of 1160.6 atm is obtained. If we consider an added 10 atm exerted by the ice from above, a total pressure of 1170 atm is obtained. Using these values, Eq. (2) gives a T_{max} of approximately −22.34 °C. Thus, a concentrated salt-water ocean of say 80 km depth will have liquid water at the bottom. The presence of liquid water enhances the survival of numerous species of microorganisms as it allows for mobility and mixing of nutrients and energy sources. In addition, the water of maximum density (containing the maximum number of dissolved substances) will sink to the bottom of the ocean making the near-ocean-bottom environment the most feasible for microorganisms to thrive. Based on data obtained by the Voyager spacecraft, gravity and magnetic field measurements, radio Doppler data and images gathered by the Galileo spacecraft, a plausible depiction of Europa's internal structure is now possible. Based on external gravitational field and magnetic field measurements conducted by the Galileo spacecraft, an exclusively water–ice interior has been excluded for Europa (Anderson *et al.* 1997). In addition, the measurements are consistent with a metallic core surrounded by a rocky mantle that is engulfed by a global ocean beneath a surface ice layer. The densities of ice and water are about 0.9 and 1.0 g cm^{-3}, respectively, but may vary depending on the temperature and solute content. Anderson *et al.* (1998) estimated a density of 3.0 g cm^{-3} for Europa's interior, which suggests at least the presence of rock.

Chemical composition

On Europa's surface and in the atmosphere, oxygen, hydrogen, hydrogen peroxide, hydrogen cyanide, magnesium, sulphur, nitrogen, methane and sodium have been detected in varying abundances (Johnson *et al.* 1998; McCord *et al.* 1998; Carlson *et al.* 1999a; Leblanc *et al.* 2002; Johnson *et al.* 2003; Cooper *et al.* 2003). These chemical precursors form a variety of compounds that in turn provide a wealth of chemical reactions (Johnson *et al.* 2002). On Earth, these reactions occur routinely; however, in low temperature and pressure environments such as at Europa, these reactions may proceed over an extended period of time due to the low temperatures in the atmosphere and on the surface (Masterton & Hurley 2001). This, however, may not be true for reactions under the icy surface. Of the known chemicals on Europa, water, hydrogen, oxygen, hydrogen peroxide, sulphur, sulphuric acid, sulphur dioxide and potassium appear to be in abundance (Brown 2001).

Both hydrogen gas (H_2) and oxygen gas (O_2) are found in the atmosphere of Europa (Cooper *et al.* 2003). Magnesium sulphate ($MgSO_4$), sulphuric acid (H_2SO_4) and its hydrates are also abundant on the surface of the satellite in varied amounts (Greenberg *et al.* 2003). These chemical species initiate a rich chemistry in all three regions of Europa – in the atmosphere, on the surface and beneath the surface.

The evidence that H_2SO_4 hydrates exist on Europa is consistent with UV spectroscopic measurements (Carlson *et al.* 1999a). Hydrates refer to compounds surrounded by water molecules, frozen in this case, in various amounts, which constitutes the majority of the surface of Europa. One of the elements of interest is sulphur, because of its origin and

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Table 3. *Europa's chemical inventory*

Compounds or Elements	Chemical Formula	Detected or inferred in	Comments	Reference
Ice-water	H_2O	Lower surface areas	Abundant	Reported by most authors
Water vapour	H_2O	Surface/atmosphere	Forms due to irradiation of H_2O	Johnson *et al.* (1998)
Oxygen gas	O_2	Atmosphere	End product of radiolysis of H_2O	Cooper *et al.* (2003)
Hydrogen peroxide	H_2O_2	Surface	Surface combination of radicals	Carlson *et al.* (1999a)
Sulphuric acid	H_2SO_4	Surface/subsurface	End product of radiolysis of S and H_2O	Carlson *et al.* (2002)
Elemental sulphur	S_x	Surface/subsurface	Jovian, Ioan or internal volcanic origin	Carlson *et al.* (1999b)
Sulphur dioxide	SO_2	Surface/subsurface	Oxidation product of sulphur	Carlson *et al.* (2002)
Carbon dioxide	CO_2	Surface/subsurface	Low abundance	Johnson *et al.* (1998)
Hydrogen cyanide	HCN	Surface/subsurface	Produced via radiolysis of organics	Johnson *et al.* (1998)
Hydrogen sulphide	H_2S	Surface/subsurface	Produced via radiolysis of H_2SO_4	Carlson *et al.* (2002)
Ammonia	NH_3	Near surface	Abundant	Brown *et al.* (1988)
Methane	CH_4	Surface/subsurface	Low abundance	Strazzulla (1998)
Sodium	Na	Surface/atmosphere	Trace element in atmosphere	Leblanc *et al.* (2002)
Potassium	K	Surface/atmosphere	Trace element in atmosphere	Brown (2001)
Magnesium	Mg	Surface/atmosphere	Trace element in atmosphere	Johnson *et al.* (1998)
Magnesium sulphate	$MgSO_4$	Surface/ subsurface	Minor impurity in ice	McCord *et al.* (1998); Dalton (2003)
Metal oxides/ hydroxides	$MO_x(OH)_y$	Surface/subsurface	May provide raw materials for metabolism	Johnson *et al.* (1998); McCord *et al.* (1998)
Organics	Multiple	Surface/subsurface	Inferred	Johnson *et al.* (1998)

its stability under irradiation; sulphur may have been implanted from the Jovian plasma (Carlson *et al.* 2002), from Io or brought to the surface from the interior via volcanic processes (Anderson *et al.* 1998).

Greenberg *et al.* (2003) inferred the presence of H_2SO_4, SO_2 and sulphur polymers on the Europan crust, and while cracks are believed to form under pressure, tectonic movement or an upwelling of volcanic or warm geyser emissions, these cracks are filled with ice or liquid water from below creating a new lesion in the surface (Chandler & Hecht 2002). This surface expression would be two dark bands and a possible bright white median of pure ice, accounting for the appearance of the triple bands (Greenberg *et al.* 2003). On the other hand, sulphur deposits on the surface may have been brought about by this upwelling to produce sulphate salts (Carlson *et al.* 2002).

Radiolysis of such evaporate salt minerals also produces MgO, CaO, K_2O, Na_2O, KOH, $Mg(OH)_2$, $Ca(OH)_2$ and NaOH (Carlson *et al.* 2002). These compounds are very likely to form under favourable conditions and, therefore, may exist on Europa. Although these reactions may occur on the surface, their progress may be at a sedentary rate due to the low temperatures (Masterton & Hurley 2001). Table 3 lists the known chemicals detected near the surface thus far on Europa.

Chemical synthesis on Europa

Europa resides inside Jupiter's huge magnetosphere. Thus, Europa's icy surface is subject to continuous bombardment by energetic ions and electrons. This bombardment yields radiolysis and photolysis products such as oxygen gas and peroxides on and near the surface (Carlson *et al.* 1999a; Leblanc *et al.* 2002; Johnson *et al.* 2003). The radiolysis also causes the cycling of sulphur species between sulphuric acid, sulphur dioxide and sulphur polymers, with sulphuric acid being about 50 times as abundant as the other forms of sulphur (Carlson *et al.* 1999b). Photolysis of water on the surface yields OH radicals that react with methyl and methylene radicals to produce CO. Alternatively, OH radicals produced may combine to produce hydrogen peroxide as shown in reaction (3) below. Further reaction of the CO produced with OH radicals yields CO_2. The CO and CO_2 produced may undergo limited exchange between the surface and subsurface environment. The presence of water in the surface environment plays an important role in the fabric of reactions leading to products of biological importance. One of the most significant roles that water plays is the production of hydroxyl radicals. This is due to the fact that OH radicals are very reactive precursors for organic synthesis.

Based on the chemical inventory detected or inferred on Europa thus far (Table 3), numerous reactions may occur that result in the production of products useful in organic synthesis. Such products may serve as precursors for the synthesis of biologically important molecules or serve as useful metabolic end products. Plausible reactions that are made possible due to the presence of their ingredients and conditions in the Europan environment are summarized in Table 4.

Synthesis of amino acids

Amino acids from hydrogen peroxide via carboxylic acids

Radiation hitting the surface water-ice may generate hydroxyl radicals ($OH^{\bullet}$). The subsequent recombination of

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Table 4. *Plausible reactions in the European environment*

Possible reactions with known reactants on Europa	Energy yielding reactions for microbes under Earth conditions which are possible in the European subsurface environment
$N_2+3H_2 \rightarrow 2NH_3$	$H_2+NO_3^- \rightarrow NO_2+H_2O$
$NH_3+H_2O \rightarrow NH_4^+ + OH^-$	$4H_2+NO_3^- +2H^+ \rightarrow NH_4^+ +3H_2O$
$2NH_3+Mg \rightarrow Mg(NH_3)_2$	$4FeS_2+15O_2+H_2O \rightarrow 2Fe_2(SO_4)_3+2H_2SO_4$
$H_2S+H_2O \rightarrow HS^- +H_3O^+$	$4H_2+CO_2 \rightarrow CH_4+2H_2O$
$2H_2S+O_2 \rightarrow 2S+2H_2O$	$4\ H_2+SO_4+2H \rightarrow 4\ H_2O+H_2S$
$Na_2O+2H_2O \rightarrow 2NaOH+H_2O_2$	$4FeCO_3+10H_2O \rightarrow 4Fe(OH)_3+(CH_2O)+3HCO_3^- +3H^+$
$MgO+H_2O \rightarrow Mg(OH)_2$	
$Na_2O+2H^+ \rightarrow 2Na^+ +H_2O$	$2Fe^{2+} + \frac{1}{2}O_2+2\ H^+ \rightarrow 2Fe^{3+} +H_2O$
$MgO+2H^+ \rightarrow Mg^{2+} +H_2O$	$H_2S+2O_2 \rightarrow SO_4^{2-} +2H^+$
$NaOH+H_2O \rightarrow Na^+ +OH^-$	$CO_2+H_2O \rightarrow CH_4+2H_2O$
	$SO_2+3H_2 \rightarrow H_2S+2H_2O$

hydroxyl radicals produces hydrogen peroxide:

$$OH^\bullet + OH^\bullet \rightarrow H_2O_2. \tag{3}$$

Carlson *et al.* (2002) indicated that sulphuric acid, sulphur dioxide and sulphur allotropes are part of Europa's radiolytic sulphur cycle. The detection of SO_2 locked in the ice (Johnson *et al.* 1998) on the surface can explain the production of SO_3 via radiolysis (Bugaenko *et al.* 1993). SO_3 is rapidly converted to sulphuric acid in the presence of water. The synthesis of sulphuric acid via this route is shown in reactions (4) and (5) below. In reaction (4), $h\nu$ stands for high-energy photons:

$$SO_2 + h\nu + O \rightarrow SO_3, \tag{4}$$

$$SO_3 + H_2O \rightarrow H_2SO_4. \tag{5}$$

The presence of acid in the surface environment along with the presence of water, carbon dioxide and simple hydrocarbons (Table 4) will inevitably lead to the production of some aldehydes and carboxylic acids (Chyba 2000). Among the simplest of these will be acetic acid. Acetic acid may also be produced from simple alkynes when exposed to basic H_2O_2:

$$H_3C\text{–}C \equiv C\text{–}CH_3 + H_2O_2/OH^- \rightarrow 2H_3C\text{–}\overset{\overset{\displaystyle O}{\|}}{C}\text{–}OH. \tag{6}$$

The acetic acid produced by radiolysis or via reaction (6) can be used to produce biologically important macromolecules such as amino acids. In the slushy ice/briny ocean environment, ammonia is abundant so that if the carboxylic acid is halogenated and exposed to water in the mixture, and this encounter is followed by ammonolysis, an amino acid is produced (Solomons 1996):

$$RCH_2COOH \xrightarrow[2.H_2O\ 3.NH_3]{1.X_2/P_4 \text{ or } S_x \text{ surface}} R\text{–}C\text{–}H(NH_3)^+COO^-. \tag{7*}$$

* 1 means first step is treatment with X_2/P_4 or S_x followed by $2.H_2O$, and then $3.NH_3$

The X_2 in reaction (7) is a halogen such as chlorine or bromine. Depending on the nature of the alkyl group (R), reaction (7) can generate a variety of amino acids. Thus, it is very likely that amino acids are found in the European subsurface environment. Amino acids self-assemble under slightly acidic conditions in the presence of a catalyst producing peptides by forming amide bonds between the carboxyl group of one and the amino group of another (Solomons 1996). The formation of the amide bond is accompanied by the loss of water.

Amino acids from hydrogen cyanide via alpha amino nitriles

The detection of hydrogen cyanide on Europa's surface as a possible product of the radiolysis of organics (Johnson *et al.* 1998) allows for another synthetic possibility. The HCN may react with simple aldehydes in the presence of ammonia to give an alpha-amino nitrile (Solomons 1996):

$$HCN + \text{aldehyde} + NH_3 \rightarrow RC - C \equiv \underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle NH_2}{|}}{N}} \tag{8}$$

If the alpha-amino nitrile produced in reaction (8) is exposed to an acidic environment and a heat source, it produces an alpha-amino acid. In addition, if the product of reaction (8) obtains a heat source and mixes with the acetic acid produced by radiolysis or via reaction (6), an alpha-amino acid is produced:

$$R\text{–}\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle NH_2}{|}}{C}}\text{–}C \equiv N \quad + H^+ + \text{heat} \rightarrow R\text{–}\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle NH_3^+}{|}}{C}}\text{–}COO^- \tag{9}$$

Amino acids from hydrocyanic acid via UV photon-assisted self-assembly

The HCN detected on Europa's surface (Johnson *et al.* 1998) may self-combine in aqueous solutions present on the surface to form amino acids with the assistance of UV photons (Miller 1998):

$$3\ HCN + 2H_2O + h\nu \rightarrow CH_2CO_2HNH_2 + CN_2H_2. \tag{10}$$

In addition to glycine, reaction (10) yields cyanamide (CN_2H_2), which can link amino acids together as the first step in the formation of proteins (Abbas & Schulze Makuch 2002). Reaction (10) may occur as all its components are present in the Europa surface environment but is limited to the requirement of surface liquid water and an abundance of photons.

Plausible metabolic pathways in the Europa subsurface

Metabolism refers to the collective sum of useful reactions that occur in a cell to produce useful work for an organism

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(McMurry 2004). Depending on their environmental conditions, organisms employ various strategies to accomplish the task. The organism usually adapts to the environmental conditions by evolving in a manner that allows it to utilize the suitable raw materials that are available in its environment. For example, anaerobic bacteria living in oxygen depleted environments employ metabolic pathways that do not require oxygen. One of the most common strategies employed by organisms is the coupling of reactions whereby available energy generated from a spontaneous reaction can be used to drive a desirable but, otherwise, non-spontaneous reaction. On Europa, a simple but useful reaction that is likely to occur is:

$$S + O_2 \rightarrow SO_2 \quad \text{where } \Delta G^{\circ} = -300.1\ \text{kJ}. \tag{11}$$

with ΔG° being the free energy under standard conditions. Reaction (11) is spontaneous and energy-yielding under standard conditions. Elemental sulphur is implanted on Europa's surface from Io (Jakosky 1998). In the subsurface environment, hydrothermal vents may produce elemental sulphur. Schulze-Makuch & Irwin (2002) discuss several chemical metabolic pathways that may constitute chemical cycling by hypothetical chemotrophs in Europa's putative ocean. For instance, instead of reaction (11), the sulphur produced at a hydrothermal vent near the reducing ocean bottom may donate electrons to iron (III) in an alternative pathway:

$$S + 6Fe^{3+} + 4H_2O \rightarrow HSO_4^- + 6Fe^{2+} + 7H^+ \quad \Delta G^{\circ} = -250.5\ \text{kJ}. \tag{12}$$

Reaction (12) was reported by Lovely (1991) as being the metabolic pathway employed by several species of microorganisms in acidic environments on Earth. The importance of reaction (12) becomes obvious when one considers the fact that its products may explain some of the observed sulphuric acid on the surface. The hydrogen sulphate (HSO_4^-) produced in reaction (12) may ultimately lead to the production of sulphuric acid that may seep to the surface through cracks in the ice shell. Under standard conditions, reaction (12) yields 2.6 eV per mole of elemental sulphur. The reduction of Fe(III) may alternatively be coupled to the oxidation of H_2 produced by hydrothermal vents:

$$2Fe^{3+} + H_2 \rightarrow 2Fe^{2+} + 2H^+ \quad \Delta G^{\circ} = -148.61\text{kJ}. \tag{13}$$

Both reactions (12) and (13) produce H^+ thus further increasing the acidity of the putative ocean. Schulze-Makuch & Irwin (2002) list several examples of species on Earth that employ reaction (13) as an energy source. These include *Pseudomonas* sp. and *Shewanella putrefaciens*. Another reaction that is likely to occur near the ocean floor in areas of hydrothermal vents is the methanogenesis reaction employed by methanogens on Earth:

$$4H_2 + CO_2 \rightarrow CH_4 + 2H_2O \quad \Delta G^{\circ} = -130.8\text{kJ}. \tag{14}$$

Reaction (14) is a common and early metabolic pathway employed by primitive chemoautotrophs on Earth. The reactants in reaction (14) are both produced by hydrothermal vents.

Discussion

A life-sustaining environment requires a suite of biogenic elements, which include carbon, hydrogen, oxygen, nitrogen, phosphorous, sulphur and other elements. Europa's surface appears to consist predominately of water ice. However, metabolic pathways of microbial life on Europa might employ the oxidants that are produced due to the heavy doses of lethal radiation that surround Jupiter (Chyba 2000). The radiation might cause chemical reactions to occur on its surface, and thus provide a fuel for life. A global ice cover has been projected to be at least several kilometres thick (Figueredo *et al.* 2003). If the ice is as thick as projected it would be impossible for sunlight to penetrate it, and thus photosynthesis cannot be a source for chemical reactions for subsurface life in a liquid ocean. If hydrothermal vents are present at the bottom of the putative ocean, they will emit some light that is likely to be insufficient to drive photosynthesis (Van Dover *et al.* 1994). In addition, the heavy doses of radiation on the surface will make the surface environment prohibitive for the survival of organisms (Marion *et al.* 2003).

There has been speculation that Europa has hydrothermal vents on its seafloor resembling those on Earth (Irwin & Schulze-Makuch 2003). If present, hydrothermal vents could serve as a possible energy source. Nevertheless, for life to thrive oxidants are needed so that coupling between oxidation and reduction can generate energy needed to do useful cellular work. Oxidants generated at the surface would need to migrate through cracks in the ice in order to get to the ocean environment where they can be coupled with reduced chemical species produced in hydrothermal vent areas. However, the thickness of the ice makes it very challenging for oxidants to reach the subsurface environment.

The presence of heat, water and organic molecules suggest that Europa's ocean may be a suitable environment for hosting life. The possibility of life is attributed to two major factors. One is the bombardment of radioactive waves that create radical molecules. The other factor is the putative thermal vents at the lower surface of Europa's ocean. It is, however, not likely for life to exist on the surface because of Europa's unforgiving surface environment. The surface environment is unforgiving due to the heavy doses of radiation it receives, and its near vacuum pressure and very low temperature (Table 1). It is unlikely that organisms use light as a source to metabolize, since very little light is provided through Europa's daylight to begin with. In addition, the light must also pass through the thick ice that covers the oceans of Europa. Therefore, it is important to look at the lower surface of the ocean where no light exists. Chemolithoautotrophs are microbes that live on earth in the dark in environments that lack oxygen. They are capable of colonizing inorganic aqueous habitats that furnish their requisite reductant, a nitrogen source, carbon dioxide and other

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Table 5. *Potential energy sources in Europa's ocean*

Energy source	Mechanism of energy generation	Type of organism able to utilize it	Likelihood on Europa
Sunlight	Drives photosynthesis	Phototrophic	Unlikely due to thick surface ice cover
Hydrothermal vents	Thermal energy	Thermotrophic	Moderate
Tidal heating and convection cells	Kinetic energy	Kinetotrophic	Moderate
Ocean ionic potential	Osmotic gradients	Osmotrophic	Likely due to the high salinity of the ocean
Chemical energy	Coupling of redox reactions	Chemotrophs	Very likely due to abundance of raw materials
Other	Magnetic or gravitational	Magnetotrophic gravitotrophic	Unlikely

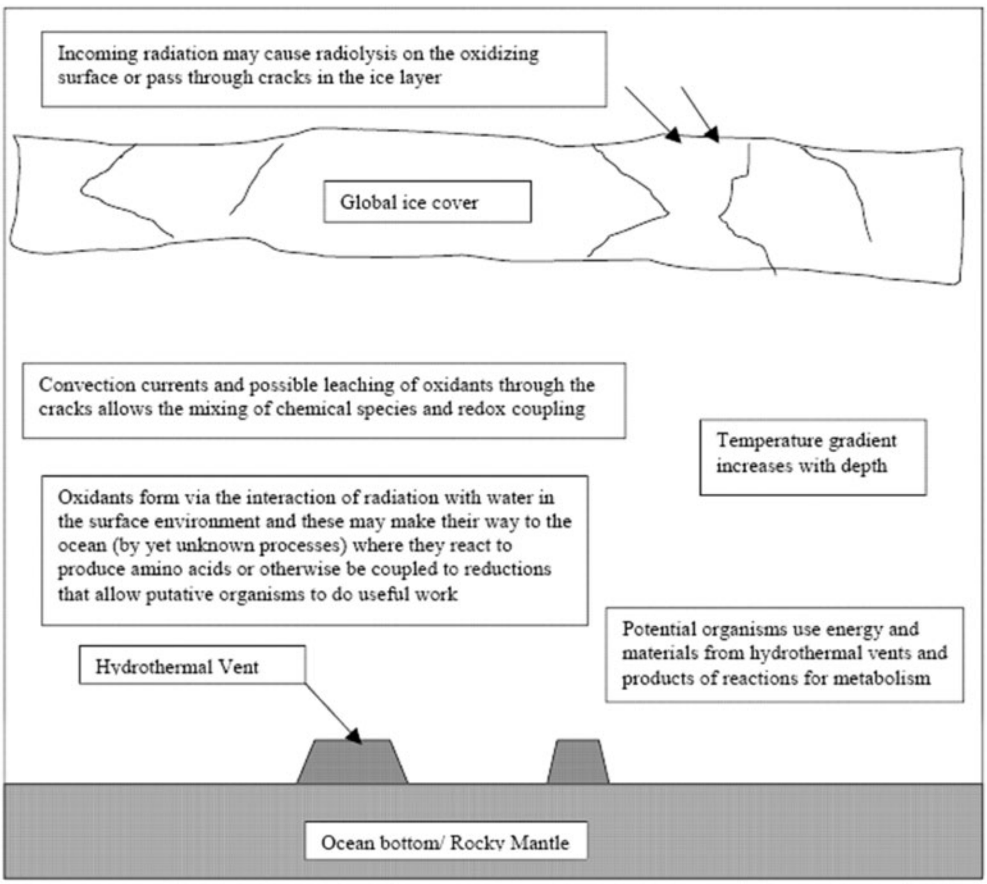

Fig. 2. Europa's Ocean Environment. Radiation from Jupiter's magnetosphere hits the cold surface producing oxidants that may seep through unknown mechanisms to the upper layers of the subsurface. The outermost layer is a global ice shell with visible cracks and channels as have been determined from images of the surface.

essential mineral nutrients (Dawes 1986). These microbes are also anaerobic, which means that they do not use oxygen as their final electron acceptor. Instead they may use species such as nitrate as the electron acceptor to make adenosine triphosphate (ATP) (Dawes 1986). Under Europa's conditions, the microbes would need to live near thermal vents where reduced compounds are present in the ecosystem (Herbert & Codd 1986). While microorganisms would be able to use reduced inorganic sulphur and other minerals to make energy, the microbes would still require the need of an oxidant to oxidize iron, sulphur compounds, ammonia or nitrite for biosynthesis (Dawes 1986). This is where the radiation on Europa's surface plays a role. According to Chyba (2000), it is possible that the radiation might cause the ice to melt and chemical reactions to occur that would provide several fuels such as formaldehyde. Furthermore, the interaction between the radiation and water would provide the oxidants necessary for the microorganisms to use. Not only would it provide oxidants but also other simple compounds that would be easily metabolized by microorganisms. One molecule of importance would be carbon dioxide, which might be an important carbon source for biosynthesis reactions to build the cellular structures of putative chemotrophic organisms. However, the conditions on and near the surface are likely be detrimental to the microorganisms, since radiation can be lethal to them. Therefore, the oxidants would simply have to descend into the lower part of the ice layer where dynamic flux mixes them into the ocean environment allowing

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microorganisms to flourish in vast amounts. If chemolithotrophic microbes are present in Europa, it is possible that other higher forms of microorganisms might also be present (Irwin & Schulze-Makuch 2003). Chemoautotrophs could represent the food base for a functional ecosystem with several trophic levels in the subsurface environment. Europa's subsurface ocean could, in this case, resemble the primitive ocean that harboured prebiotic evolution and early life forms on Earth. The potential energy sources that may yield energy to certain types of organisms and the likelihood of these mechanisms to occur in Europa's putative ocean environment are described in Table 5.

Future missions to Europa will enhance our understanding of the chemistry occurring in both the atmospheric, surface and subsurface environments and may give direct proof of the presence of a global ocean. With detection reagents efficiently packaged and miniaturized as immunosensor chips in analytical panels, antibody microarrays could serve as a means of detection and identification of biological remnants *in situ* during exploratory missions. Specific antibodies could also be used for affinity concentration of potential biomarkers obtained from sample return missions (Tang 2007). The likely ocean environment and the possible resources available for putative organisms are described in Figure 2.

Conclusions

This paper details plausible atmospheric, surface and subsurface chemistry likely to occur on Europa. Since Europa's atmospheric and surface processes are largely dominated by oxygen, water and hydrogen peroxide chemistry, chemistry based on these three synthetic schemes leading to the production of amino acids are presented and evaluated: Two synthetic schemes are based on hydrocyanic acid and are likely to occur as both require precursors and reagents that are likely to exist in the Europan environment. Two metabolic pathways are described: the first one is based on the coupling of reactions to produce available energy; the second is based on the decomposition of carboxylic acids. Most species included in the reactions described above were obtained from detection and predictions made by Carlson, Johnson, Leblanc, McCord and others (Carlson *et al.* 1999a, b; Leblanc *et al.* 2002; Johnson *et al.* 1998, 2002, 2003; McCord *et al.* 1998). The subsurface ocean may provide a haven for life due to the existence of liquid water, heat sources and chemicals needed for metabolism and growth. Future missions to Europa will enhance our understanding of the chemistry occurring in both the atmospheric, surface and subsurface environments.

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