The Possible Emergence of Life and Differentiation of a Shallow Biosphere on Irradiated Icy Worlds: The Example of Europa

Michael J. Russell,1 Alison E. Murray,2 and Kevin P. Hand1

Abstract
Irradiated ice-covered ocean worlds with rocky mafic mantles may provide the conditions needed to drive the emergence and maintenance of life. Alkaline hydrothermal springs—relieving the geophysical, thermal, and chemical disequilibria between oceans and tidally stressed crusts—could generate inorganic barriers to the otherwise uncontrolled and kinetically disfavored oxidation of hydrothermal hydrogen and methane. Ionic gradients imposed across these inorganic barriers, comprising iron oxyhydroxides and sulfides, could drive the hydrogenation of carbon dioxide and the oxidation of methane through thermodynamically favorable metabolic pathways leading to early life-forms. In such chemostatic environments, fuels may eventually outweigh oxidants. Ice-covered oceans are primarily heated from below, creating convection that could transport putative microbial cells and cellular cooperatives upward to congregate beneath an ice shell, potentially giving rise to a highly focused shallow biosphere. It is here where electron acceptors, ultimately derived from the irradiated surface, could be delivered to such life-forms through exchange with the icy surface. Such zones would act as “electron disposal units” for the biosphere, and occupants might be transferred toward the surface by buoyant diapirs and even entrained into plumes. Key Words: Biofilms—Europa—Extraterrestrial life—Hydrothermal systems. Astrobiology 17, 1265–1273.

1. Introduction
On Earth, the geochemical utility of life can, in part, be simplified to the hydrogenation of carbon dioxide. Such hydrogenations yield an ever-renewed stock of highly specified organic molecules—the so-called CHNOPS with a typical bonding motif -C–C(H2)–N(H)–C–O (Bernal, 1960; Lassiter, 1986; Fuchs, 1989, 2011). However, the significance of the proton and electron flux must also be appreciated, since those processes are at the root of life’s role in free energy transfer and transformation (Mitchell, 1961; Szent-Györgyi, 1968). Viewed in these terms, life is a mechanism that hastens the flow of “hot” electrons to available electron acceptors (e.g., Steele, 2003; Russell et al., 2003, 2014; Nitschke and Russell, 2011). Here, we suggest that life may have emerged on irradiated icy worlds such as Europa, in part as a result of the chemistry available within the ice shell, and that it may be sustained still, immediately beneath that shell.

2. The Drive to Life on Ice-Covered Ocean Worlds with Rocky Mantles
In cases where ice-covered ocean worlds with rocky cores are subject to surface irradiation and tidal forces, such systems may reach a metastable dynamic state. In these systems, electron-bearing fuels will be produced in serpentinization (rock-water) reactions as salty ocean waters are reduced to hydrogen and formate on gravitation into the primitive ultramafic crust (Windman et al., 2007; Russell et al., 2010; Vance et al., 2016). Primeval (abiotic) methane could be leached concomitantly from the same source (e.g., Watanabe et al., 1983; Sherwood Lollar et al., 2007; McCollom and Donaldson, 2016). Likewise, hydrogen and methane could be entrained convectively to the ocean through widespread and continuous submarine alkaline hydrothermal activity (Hand et al., 2007; Vance et al., 2007, 2016; Vance and Goodman, 2009; Travis et al., 2012; Russell et al., 2014) (Fig. 1). Along...
McDermott et al. (2005) and Kalousova´wamy, 2013). The ice shell is partly based on Showman and tive biosphere (Berisford “Under-Ice Buoyant Rovers for Exploration” of the puta-

standard methods for flying through any existing plumes and produced by high-energy electron radiation from Jupiter (Bolton et al., 2002). In turn, portions of this shallow and buoyant biosphere may be returned to the surface through ice tectonics or sucked into the source regions of water vapor/ice jets on, for example, Europa and Enceladus (Squyres and Croft, 1986; Roth et al., 2014; Lorenz, 2016; Sparks et al., 2016; and McKay et al., 2008). Along with the standard methods for flying through any existing plumes and analyzing the surface, future missions could employ “Under-Ice Buoyant Rovers for Exploration” of the putative biosphere (Berisford et al., 2012, and see Ananthaswamy, 2013). The ice shell is partly based on Showman and Han (2005) and Kalousová et al. (2014). Not to scale.

with methane, the hydrothermal fluids feeding the springs could also have entrained vital nutrients in the form of further reduced volatiles to be expected on a moon such as Europa with a mantle and crust dominated by fayalite (ferrous iron-rich olivine), that is, carbon monoxide, ammonia, and hydrogen sulfide (Fig. 1) (Anderson et al., 1998; Sohl et al., 2002; McDermott et al., 2015; and see Wood et al., 2006; Gaillard et al., 2015). Other entities could be leached into the same hydrothermal fluids, such as the all-important phosphorous (perhaps from dissolution of phosphide) along with the trace metals, including molybdenum, required of all Earthly life (Pasek et al., 2011; Schoepf-Cothenet et al., 2012; Russell et al., 2014; Pasek, 2016).

On Earth, hydrogen, or more precisely its component electrons and protons, is life’s must-have fuel. And, given a supply of carbon dioxide and other, higher potential oxidants such as nitrate, nitrite, sulfate, sulfur, and ferric iron in early mildly acidic oceans, life may have been forced into being in order to resolve these electrogeochemical disequilibria. The best candidate for such interactions would be hydrothermal mounds and sediments comprising ferrous-ferric oxyhydr-oxides and sulfides precipitated where alkaline hydrothermal fluids interfaced acidulous ocean water (Russell et al., 1994, 2003, 2014; Pasek and Greenberg, 2012; Tosca et al., 2016; Haley and Bachan, 2017). Such mounds could have functioned as long-lasting, stably operating electrogeochemical reactors (Russell, 2007). The vectorial proton and redox gradients obtaining at, and near, the surface of the mounds are comparable to those that “energize” life as we know it on Earth (Kelley et al., 2001; Martin et al., 2008; Branscomb and Russell, 2013; Herschy et al., 2014; Branscomb et al., 2017). Moreover, the transition metals required for catalysis—and which are affine with the active centers of metalloenzymes—would also be available in the oxyhydroxides and sulfides constituting the mounds (Nitschke et al., 2013).

It is these physicochemical disequilibria that are, in the alkaline hydrothermal vent model, proposed to be the founding drivers of biogenesis needed to reduce CO$_2$ to simple organic acids, alcohols, and hydrocarbons, to fix nitrogen and to drive other required first-step endergonic reactions that eventuated in cellular life (Russell et al., 2003; Martin and Russell, 2007). We see such worlds as batteries with outputs approaching a volt or so (Russell and Hall, 1997), that drive prokaryotic cells with the same spatiality as natural fuel cells (Mitchell, 1967; Russell, 2007). And the specific iron-bearing minerals dosed with nickel and molybdenum—mainly green rust and lesser mackinawite and greigite—that make up such inorganic layers and micro-conduits constituting the metal-bearing electrodes of the precipitate mound have, it is proposed, the capability to couple the proton and redox gradients to carbon and nitrogen fixation (Génin et al., 2005, 2006, 2008; Nitschke et al., 2013; Barge et al., 2014, 2015a, 2015b; Russell et al., 2014; White et al., 2015; Branscomb et al., 2017; Haley et al., 2017; cf. Młoszewská et al., 2012; Peacock et al., 2016).

3. The Ensuing Biosphere

In comparing active icy worlds such as Europa and Enceladus to our own planet, major differences must be taken into account (Pappalardo et al., 1998; Sotin et al., 2002; Waite et al., 2006, 2017; Nimmo et al., 2007; McKay et al., 2008; Schmidt et al., 2011; Glein et al., 2015). On Earth, the ocean is mostly solar heated. And ice-water associated interfaces are known to support dense congregations of life as a result of (i) Sun-derived energy infiltrating nutrient-bathed sea ice habitats (Fig. 2A, 2B), (ii) dissolved, reduced sulfur sources that drive chemoeutotrophic biofilms in Arctic terrestrial cold-seep formations (Fig. 2C), or (iii) putative detrital organic matter supplies fueling under-ice-shelf ecosystems that even harbor multicellular life (Fig. 2D). On icy worlds, however, the oceans are heated from below, and the ice shells will confer upon the sub-ice ocean the “steady state” characteristics of a giant natural chemostat (Goodman et al., 2004; Glein et al., 2015). Under such conditions, organisms and biological processes could be limited by the availability of oxidants, that is, the compounds needed to “breathe” (Nealson et al., 2002). Iron and manganese oxides and oxyhydroxides, sulfuric acid, sulfates, sulfur, carbonates, and even oxygen itself are possible candidate electron acceptors produced and concentrated on the heavily irradiated surface of certain ice shells (Chyba and Hand, 2001; McCord et al., 2001; Carlson et al., 2002; Zolotov

FIG. 1. Model for the emergence of life on Europa at an alkaline hydrothermal mound (Russell et al., 2014, and see Vance et al., 2016). Also indicated is a hypothesized rapid migration of microbes and nanobes entrained within buoyant thermal plumes toward oxidant-rich areas at the base of the ice lid. These areas act as “electron disposal units” and are derived through subduction of oxidants from the exterior produced by high-energy electron radiation from Jupiter (Bolton et al., 2002). On Earth, hydrogen, or more precisely its component electrons and protons, is life’s must-have fuel. And, given a supply of carbon dioxide and other, higher potential oxidants such as nitrate, nitrite, sulfate, sulfur, and ferric iron in early mildly acidic oceans, life may have been forced into being in order to resolve these electrogeochemical disequilibria. The best candidate for such interactions would be hydrothermal mounds and sediments comprising ferrous-ferric oxyhydr-oxides and sulfides precipitated where alkaline hydrothermal fluids interfaced acidulous ocean water (Russell et al., 1994, 2003, 2014; Pasek and Greenberg, 2012; Tosca et al., 2016; Haley and Bachan, 2017). Such mounds could have functioned as long-lasting, stably operating electrogeochemical reactors (Russell, 2007). The vectorial proton and redox gradients obtaining at, and near, the surface of the mounds are comparable to those that “energize” life as we know it on Earth (Kelley et al., 2001; Martin et al., 2008; Branscomb and Russell, 2013; Herschy et al., 2014; Branscomb et al., 2017). Moreover, the transition metals required for catalysis—and which are affine with the active centers of metalloenzymes—would also be available in the oxyhydroxides and sulfides constituting the mounds (Nitschke et al., 2013).

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Hydrogen peroxide produced in the purest ice regions via radiolysis could subsequently react with hydrogen sulfide and ammonia in the ice, yielding oxidants (e.g., sulfite, nitrate, and nitrite) that are potentially more amenable as acceptors along metabolic pathways than just CO₂ or carbonate (Hand and Brown, 2013; Loeffler and Hudson, 2015; cf. Zolotov and Shock, 2004; Wong et al., 2017). Early in Europa’s history, radiolytically generated oxidized entities may have been subducted toward the ocean through occasional overturn of the ice shell, perhaps such that it produced an initially acidic ocean (Pappalardo et al., 1998; Bolton et al., 2002; Hand et al., 2006; Greenberg, 2010; Pasek and Greenberg, 2012; Kattenhorn and Prockter, 2014; Vance et al., 2016). It is under such conditions that proton and oxidation/reduction gradients imposed across precipitate mounds at submarine alkaline springs (electrons attracted outward, protons in toward the alkaline interior) could potentially have been harnessed through the emergence of metabolism and thereby life, much as thermal gradients can be harnessed to drive the onset of convection (Russell et al., 2003). As one example, given the potentially large flux of radiolytic sulfate, Zolotov and Shock (2003) calculated that sulfate is a strong enough oxidant to accept electrons from both hydrogen and methane, which could then drive the necessary redox gradient across hydrothermal systems at Europa’s seafloor. Nitrate and/or nitrite are even more attractive electron acceptors, as they may be reduced to ammonium in such circumstances, which could be employed to augment the amination of the carboxylic acids (Raulin, 2005; Flores et al., 2016; Russell and Nitschke, 2017). Carbonate (or CO₂) is a lower potential acceptor but has the advantage of also providing further carbon through a variant of the acetyl coenzyme-A pathway (Russell and Nitschke, 2017).

Fed by what may have been a plenitude of reductants (electron donors such as H₂, CH₄, and ferrous iron) from hydrothermal activity, and an ocean with dissolved oxidants providing a geochemical gradient, the first life-forms could potentially follow some of the same metabolic pathways...
known to be at, or near, the root of the earliest life on Earth, that is, acetogenesis and methanotrophy (Russell and Martin, 2004; Nitschke and Russell, 2013; Russell and Nitschke, 2017; cf. Mikucki et al., 2009; Waite et al., 2017). If, during periods of slowed or stalled ice-ocean exchange, \( \text{SO}_4^{2-} \) and \( \text{CO}_2 \) and other electron acceptors were to be rapidly drawn down by participants in the biofilm, the oxidant-limiting conditions would be created and an “oxidant crisis” ensue. Models for transport of material within Europa’s ocean indicate that hydrothermal plumes could be well constrained within the ocean (primarily by the Coriolis force and thermal gradients), leading to effective delivery through the ocean to the ice-water interface (Goodman et al., 2004; Goodman and Lenferink, 2012; Travis et al., 2012; Goodman, 2016). Organisms fortuitously transported from hydrothermal systems to the ice-water interface along with unspent fuels could potentially access a larger abundance of oxidants directly from the ice (Fig. 1) (e.g., Raymond et al., 2008). Importantly, oxidants might only be available where the ice surface has been driven to the base of the ice shell (e.g., Showman and Han, 2005). These sites could be geographically separated from upwelling sites within the ice shell driven by heat from hydrothermalism. Opportunistic life-forms could rely on lateral transport (e.g., ocean currents) along the ice-water interface to reach sites of downwelling convection in the ice that might bring radiolytically produced oxidants to the ocean (Fig. 1).

In such chemostatic conditions, a coevolutionary mutative drive toward lowering the minimal requirement for electron acceptors while recycling electrons would be expected, homologous to dynamic growth in a Winogradsky column (e.g., Schlegel and Jannasch, 2006; Castelle et al., 2015; cf. Fernández et al., 1999; Rinke et al., 2013). This ocean-deep chemostat presents a rather strange and challenging situation in which the long-term supply of useful hot electrons on the one hand, and of oxidants on the other, would be dramatically separated spatially by the \( \sim 100 \text{ km} \) deep ocean desert. Yet carbon as abiotic \( \text{CH}_4 \) and formate exhaled hydrothermally from the crust, as well as in the form of \( \text{CO}_2 \) from melting of the ice shell, could be continually supplied to autotrophic metabolic life-forms. Heterotrophic activity could recycle much of the autotrophic waste and detritus and contribute to a thickening of the ice-bound biosphere, undiluted by sediment—a contrast to our own deep biosphere (Kepner et al., 1998; López-Bueno et al., 2009; Rinke et al., 2013). In these chemostatic conditions, populations could grow asymptotically to a stable, though dynamic, equilibrium (Fernández et al., 1999; De Roos, 2004; Nealon et al., 2005).

Such an evolutionary drive for speciation and potential diversity of metabolisms could create an efficient and durable ecosystem that would continue to draw down nutrients by maximizing the overall cellular electron-to-nutrient flux, thus simultaneously increasing a microbe’s own waste, to be absorbed by nutrients by their adaptable and less discriminating heterotrophic neighbors (cf. Braakman et al., 2017; and see Fernández et al., 1999; Rinke et al., 2013). Typical, rather insoluble, trace elements could also be recycled in organic chelates (cf. Milner-White and Russell, 2008). Thus, a strong effect of electron uptake would be to minimize other waste products through recycling by emerging heterotrophic, fermenting, and symbiotic microbes, and nanobes (Uwins et al., 1998; Rinke et al., 2013; Kuhn et al., 2014; Luef et al., 2015; cf. Stolz, 2017).

The overall effect of this process would be to strongly concentrate any putative cells by many orders of magnitude at these sites. This could be a critical consideration for life detection and the finding of potential biosignatures within Europa’s ice (Hand et al., 2017). An active ice-water interface could reach cell densities of \( 10^3 \) to \( 10^8 \) cells mL\(^{-1} \), comparable to microbial mats or other chemically rich interfaces on Earth (Nealon et al., 2005; Hand et al., 2009) (Fig. 2C). This is considerably higher than cell densities found in the accreditation ice of subglacial Lake Vostok in Antarcctica of \( \sim 10^6 \) cells mL\(^{-1} \), which is perhaps one of the most relevant environmental analogues for Europa that can be found on Earth (Christner et al., 2006). Whether or not cell densities at the ice-water interface are conserved and represented via transport to the surface depends on the variety of potential mechanisms that could deliver basal ice to the surface (see, e.g., Collins and Nimmo, 2009).

Prospects for life detection on ice-covered ocean worlds could be significantly enhanced if the ice-water interface harbors enough redox chemistry to sustain sub-ice shell biofilms (McKay et al., 2008, 2014; Hand et al., 2009, 2017; Shock and Boyd, 2015; Lorenz, 2016; Nimmo and Pappalardo, 2016; Sparks et al., 2016). Detection techniques are itemized in Hand et al. (2017) where, for example, atomic force microscopy as well as deep-UV Raman spectroscopy are considered (Sivakumar et al., 2015; Abbey et al., 2017). It is notable that atomic force microscopes have already been flown on the Phoenix and Rosetta missions (Pike et al., 2011; Bentley et al., 2016).

4. Discussion

That we have not considered methanogenesis as a possible metabolism needs explanation. Of course, methanogens on Earth do need to expel excess electrons, but these are generally borne away physically as methane gas itself, although some do appear to reduce Fe(III) at the same time (Vargas et al., 1998). Be that as it may, it is doubtful if methanogens would have made up a significant portion of the microbial population on Europa or other icy moons given the high concentrations of abiotic methane likely emanating from the reduced mantles (Gaidos et al., 1999, 2009; McDermott et al., 2015; cf. Waite et al., 2017). And they were certainly unlikely to have emerged at an early stage in the emergence of life on such a moon, as conditions would have strongly favored methanotrophy instead, with sulfate, sulfur, and/or ferric iron as oxidants (Nitschke and Russell, 2013; McGlynn, 2017; Russell and Nitschke, 2017; cf. Milucka et al., 2012; Egger et al., 2017).

5. Conclusions

The dynamic communities comprising any sub-ice-shell biosphere could constitute a habitable zone, manifested as microbial mats concentrated around oxidant-rich ice-shell sites at the down-welling regions of thermally unstable regions at the ice-water interface (Goodman et al., 2004). An expectation of this physiochemically dynamic freeze-thaw scenario is that cells would be periodically trapped in the ice, and these communities brought to the surface in a cryogenic state along with their ambient molecules (Showman and Han, 2005; Porco et al., 2006; Spencer et al., 2006; Waite et al., 2006, 2017; Spitale and Porco, 2007; McKay et al., 2008; Roth et al., 2014; Nadeau et al., 2016; Vance et al., 2016; Hand et al., 2017). Thus, along with the standard methods for flying through possible plumes, and deploying landers, future
missions could eventually use robotic capabilities designed for exploring the ice-water interface (Berisford et al., 2012; Ananthaswamy, 2013).

Future missions to search for life on Europa (Hand et al., 2017), a young Enceladus (McKay et al., 2014; Čuk et al., 2016), and other ocean worlds will be tasked with seeking if life emerged afresh elsewhere, independently from Earth where Snowball events were relatively short-lived (Harland, 1964; Kirschvink, 1992; Hoffman and Schrag, 2002; Parkinson et al., 2008; Blanc et al., 2016; Barge and White, 2017). A difference may be that the putative chemostatic biospheres on extraterrestrial, and even extrasolar, icy worlds may, for millions or billions of years, have been dynamically stable long after the emergence of life thereon, supported by serpentinization—life’s mother engine (Russell et al., 1989, 2010; Branscomb and Russell, 2013).

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Address correspondence to:
Michael J. Russell
Planetary Chemistry and Astrobiology Group
Section 3225 MS:183-301
Jet Propulsion Laboratory
California Institute of Technology
4800 Oak Grove Drive
Pasadena, CA 91109-8099
E-mail: mrussell@jpl.nasa.gov

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