

Life in Ice-Covered Oceans

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Recent evidence for salt-water oceans beneath the ice crusts of Europa and Callisto (1, 2) has bolstered speculation that these satellites of Jupiter may harbor life (3,4). Attention has focused on Europa. The geology and young age of its surface (5,6) and the predicted heat flow from radiogenic decay and tidal dissipation (7,8) suggest a geologically active interior and liquid water at shallow depths. To assess the plausibility of life on Europa and suggest which kinds of organisms are most likely to inhabit this ocean, we must look at the fundamental requirements for life on Earth.

In addition to liquid water and a supply of suitable chemical elements, organisms on Earth require a source of energy for metabolism, growth, maintenance, and reproduction. This energy is derived primarily from sunlight through photosynthesis (in certain bacteria or the bacterially-derived chloroplasts in plants) or photorespiration (in archaea living in salty environments); a very small proportion is derived from geothermally driven chemical disequilibria. The chemical products of this activity span a range of oxidation potentials that drive a cascade of intermediate oxidation-reduction (redox) reaction pairs (see the figure). Organisms on Earth exploit these thermodynamically-favored reactions as energy sources, and combinations of oxidants and reductants support various metabolic lifestyles. Before the evolution of photosynthesis, organisms could not use sunlight directly, and life on Earth depended on abiotic sources of chemical energy in the form of disequilibrium concentrations of redox reactants driven by hydrothermal activity, solar ultraviolet radiation, electrical discharges, and impacts (9). All these redox pairs are depleted by abiotic reactions and biological activity, and without an external energy source such as sunlight (or internal geothermal energy), chemical equilibration will ultimately extinguish all life. This thermodynamic reality imposes severe constraints on any biota on Europa that is based on chemical energy.

If an ocean exists on Europa, it is physically and chemically isolated by an ice crust 10-100 km in thickness (1). We have to go back far into Earth's climatic history to find a possible analogy for this situation. Kilometer-

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thick ice may have entombed Earth's oceans during "snowball" episodes of global glaciation, which are believed to have persisted for

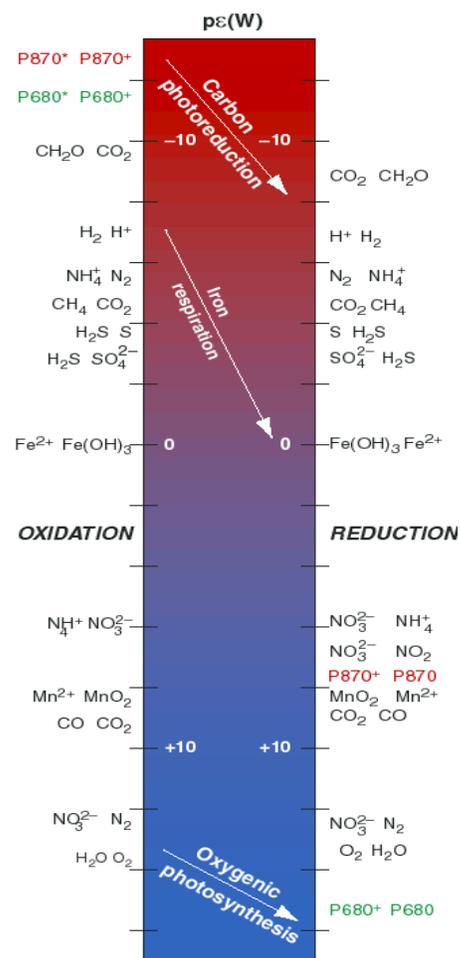
5-50 million years (My) during the Proterozoic (about 2500 to 543 My before present) until the buildup of atmospheric CO₂ from volcanoes created a greenhouse effect strong enough to melt the ice (10).

Without photosynthesis or contact with an oxidizing atmosphere, an isolated subsurface ocean will approach chemical equilibrium and annihilate any ecosystems dependent on redox gradients unless there is a substantial alternative (for example, geothermal) energy source. The terrestrial ocean circulates through the hydrothermal systems of mid-ocean spreading ridges in ~10 million years (11) and would equilibrate with the chemistry of basaltic magmas on that (geologically short) time scale. Biological activity would only accelerate the process of equilibration, ensuring its own destruction by consuming the limited supply of oxidants. Hydrothermal alteration and weathering would likewise drive the equilibration of oceanic and silicate crust chemistry on Europa. Thermodynamics-driven extinctions would ensue on both Europa and a "snowball" earth. Under Europa's permanent ice crust they may have been terminal.

Hydrothermal vents have been cited as potential analogs to life on Europa, because they do not receive sunlight and appear to be isolated from other ecosystems. The vent ecosystems, however, depend almost exclusively on oxidants (SO₄²⁻, O₂ and CO₂) dissolved and transported from the surface to the deep ocean (12): More than 99% of the energy available to vent biota is from sulfate reduction, sulfur oxidation, and aerobic metabolism (13). Without oxidants from the surface ocean, organisms would have to rely on low-energy methanogenesis and elemental sulfur reduction. The flux of available energy from these reactions in the most active vent fields is only ~5 x 10⁻³ ergs cm⁻² sec⁻¹ (14): For comparison, the mean primary production in the upper ocean (15) is equivalent to a biological energy flux of ~10 ergs cm⁻² sec⁻¹, and this is only 0.01% of the total energy available in sunlight. It is unclear that such low energy fluxes could support extensive life on the sea floor.

Life may persist, however, if a flux of oxidants into the subsurface ocean can be maintained. To understand how this might happen, we must compare the geology and atmosphere of Europa with that of a "snowball" Earth.

The thermodynamics of life. Organisms harvest energy by coupling energetically favorable pairs of oxidation and reduction half-reactions. Reactions of common inorganic substrates are plotted according to



their redox potential pe at 1 atm, pH = 7 and 25°C (41). $[Fe^{2+}]$ is taken to be 10⁻⁵ M. Water and protons are not shown in the equations. Only redox reaction pairs with a negative net redox potential can provide energy. The primary donors of Photosystem I (P870) and II (P680) are strong reducers in their excited state and are used to fix carbon. In the oxidative (rest) state only P680 is capable of oxidizing water, producing oxygen.

Residual disequilibrium would persist in an ice-covered ocean to the extent that turnover in the ice crust can introduce oxidants into the ocean. Diffusion of gases through low-temperature ice is essentially zero (16). On a "snowball" Earth, turnover of the ice sheet and transport of oxygen to the ocean could occur through sublimation and thermally driven transport of water vapor from the equator to the poles or through

ablation by winds. These processes cannot occur on Europa, and yet its surface appears to be only 10-100 Myr old (1, 17), however, this may be an underestimate (8). Solid-state convection, predicted in an ice crust thicker than about 10 km, would explain the age and

much of the morphology of the surface (5). Europa lacks an atmosphere suitable for photochemistry, but ultraviolet photolysis and radiolysis of ice by jovian magnetospheric ions generate hydrogen (which escapes from the weak gravity), molecular oxygen, hydrogen peroxide (18), and hydroxide radicals within the ice (19). An estimated oxygen production rate of $10^9 \text{ cm}^2\text{sec}^{-1}$ (20) maintains a tenuous but detectable oxygen atmosphere (21). If the flow of molecular oxygen from surface ice to the atmosphere is much slower than its subsequent loss by sputtering and solar wind pickup, a larger reservoir, perhaps $\sim 10^{22} \text{ cm}^2$, may be stored in a "solid-state atmosphere" within the ice (19,22). In theory, continuous transport of this oxygen reservoir to the interface with a reducing ocean could provide an energy flux of $\sim 3 \times 10^{-4} \text{ ergs sec}^{-1}\text{cm}^2$, although the oxygen-impregnated outer crust is relatively rigid and brittle and may only be infrequently subsumed into the interior. Regardless, the estimated energy available from this process is three orders of magnitude lower than levels known to support ecosystems on Earth.

Thus, a mechanism to continuously supply significant oxidants for life in Europa's ocean is lacking. The continuity of life on a snowball Earth would have been insured by at least two near-surface niches where liquid water was available for organisms capable of converting sunlight into biological energy. Water with little or no ice cover would be found in continental hot springs like the Yellowstone and Mammoth calderas or over shallow rifting zones like Iceland. Also, liquid water inclusions form around sediment particles heated by the sun at shallow depths in sublimating ice (24), and bacteria capable of carrying out photosynthesis at the low light levels found beneath several meters of ice (3, 25) would support a food chain in these environments.

In contrast, the surface of Europa is highly unlikely to support any type of life requiring liquid water. Surface temperatures are less than 128 K (26), and the water melting point is reached only at depths exceeding $\sim 20 \text{ km}$, whereas sunlight penetrates to depths of tens of meters only (27). Cracks in the crust are also unlikely to allow sunlight to reach an interior ocean for even brief periods (28), contrary to earlier suggestions (3). Large impacts may puncture the ice shell (29) but these events are likely to be transient and rare throughout most of the satellite's history. Transient brines could occur over diapiric plumes of warm ice (5,30), but individual diapirs form on time scales of $< 10^5$ years (31) and any brines freeze by conductive cooling in $\sim 10^3$ years, brief periods relative to the turnover time of the ice crust. It seems unlikely that such bodies of water, isolated and subsequently frozen for at least 10^7 years, could perpetuate a global biosphere.

We are left with geochemical reactions such as methanogenesis and elemental sulfur reduction as the main driving forces for potential life on Europa. These reactions have

been proposed as the basis for metabolism on the primitive Earth (32), particularly for ecosystems in subsurface refugia protected from the sterilizing effects of large impacts (33, 34), and as an energy source for life on other Solar System bodies (14, 35). They may also be the last resort for life in ice-covered oceans. The energy source is a "geothermocouple" created when the direction of a redox reaction at high temperature is opposite to that at low temperature but the latter is kinetically inhibited, creating disequilibrium (35). Biological catalysis of the low-temperature reaction then extracts useful energy from the geothermal gradient. Energy will be available as long as the temperature differential persists and there is a flux of re-actants (typically compounds of carbon, sulfur, hydrogen, and iron) through the high- and low-temperature regimes.

The C, S, and H compounds are replenished over long periods of time from gases released by the crust ("outgassing") or by hydrothermal circulation. In contrast, iron, involved in many geochemical reactions, requires replenishment of chemically active rock from the mantle by volcanism or tectonics. Otherwise, the iron in the reaction zone will be completely oxidized, geochemical reactions will halt, and any dependent biology will be extinguished. Hydrothermal alteration at terrestrial mid-ocean ridges would proceed to completion in less than 10^3 years in the absence of new crust continuously created by seafloor spreading.

On a snowball Earth, plate tectonics, volcanism, and submarine hydrothermal activity would continue unabated. The geodynamics of Europa are completely unknown. It has been suggested that the satellite may have a metal core and silicate mantle (36) with an estimated heat flow from the metal silicate interior 10 to 30% that of the Earth (8) and comparable to that of Mars (37), which has experienced significant extrusive volcanism in the past (38, 39). It is plausible, but not established, that episodic volcanism and hydrothermal activity may also occur at an ocean-mantle boundary on Europa.

Hydrothermal alteration of Earth's upper mantle and crust oxidizes iron to produce the reductant hydrogen. Outgassed carbon equilibrates under conditions that produce the oxidant CO_2 . Subducted carbonates are also outgassed as CO_2 . Biology can then exploit the energy made available by the methanogenesis reaction $\text{CO}_2 + 4\text{H}_2 \rightarrow \text{CH}_4 + 2\text{H}_2\text{O}$. The hydrothermal production of hydrogen would cease once oxidation of the crust was complete, but plate tectonics has effectively "buffered" the oxidation state of the crust with that of the mantle (40). On Europa, methanogenesis may not be a viable energy source even if volcanic and tectonic activity are present, because its mantle, without the subduction of oxidants, could be more reducing than Earth's crust, and the 1- to 2-kbar pressure at the water-silicate boundary will shift the gaseous CO_2 - CH_4 equilibrium

(at a given oxygen fugacity) to higher temperatures. Hydrothermal activity will then produce abundant hydrogen, but carbon will outgas as methane, rather than as CO_2 . Likewise, sulfur would appear as sulfide rather than as oxidants such as elemental sulfur or sulfur dioxide (41). It thus appears likely either methanogenesis or elemental sulfur reduction would be able to support life on Europa.

The above considerations illustrate that nearly all metabolic life-styles on the present Earth will be denied to organisms inhabiting an ice-covered ocean on Europa because soluble oxidants will not be produced or transported into the water column. Geochemical energy could power a relatively feeble ecology but requires volcanic resurfacing or plate tectonics. Even if Europa's interior is geologically active, energy-generating reactions such as methanogenesis and sulfur reduction used by terrestrial organisms will not be available to hypothetical life-forms because carbon and sulfur will be outgassed as reduced, rather than oxidized, species.

This severe paucity of oxidants cautions against expectations that diverse, thriving life will be found in a European ocean. The only plausible oxidants may be oxidized metals such as ferric iron. The low-temperature reduction of Fe_2O_3 by hydrogen, methane or (hydrogen) sulfide is thermodynamically favorable especially under local conditions of low $[\text{Fe}^{2+}]$ or acidic pH (42). These reactions might support a simple ecology within hydrothermally weathered rock percolated by ocean water containing dissolved H_2 , CH_4 and H_2S . Hydrogen-, methane-, and sulfur-oxidizing bacteria are ubiquitous on the Earth (43) and two groups of mineral iron-reducing bacteria are known (44). Among the latter are bacteria that use hydrogen as a reductant. These organisms may metabolically resemble those that could function in a European biogeochemical cycle.

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