

HABITABILITY AND PLANETARY REDOX

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Abstract

This paper reviews results of Solar System explorations and telescope observations of geologically-active icy bodies (Europa, Enceladus, and Ceres) and Mars, where liquid waters are, or were, present. In particular, we focus on the availability of both reductants and oxidants as well as water chemistry on these planetary bodies. This paper also proposes an idea of “planetary redox”—a planetary-scale system that can generate a redox and pH gradient through geohydrological cycles. Based on the understandings of planetary redox on Europa, Enceladus, and Mars, we discuss about bioavailable energy on these bodies and science targets in future missions. Knowledge on the presence or non-presence of life in these habitable worlds would shed light on the conditions where life could emerge on early Earth.

Key words: Habitability, Astrobiology, ocean worlds, Mars, Solar System explorations, Europa, Enceladus, Ceres

1. Introduction

Planetary habitability can be defined as a planetary-scale system that develops and maintains ingredients of life—liquid water, organic matter, and energy—and provides them to life continuously through hydrogeochemical cycles over geological time. Owing to Solar System explorations, we have found lines of geophysical (e.g., induced magnetic fields [1]; gravity [2,3]; shape and libration [4–6]) and geological evidence (e.g., valley networks [e.g., 7,8], deltas [e.g., 9]; evaporates [e.g., 10,11]) for the long-term existence of liquid water on multiple Solar System bodies. These bodies include Mars, Europa, Ganymede, Callisto, Enceladus, Titan, Ceres, and Pluto. The number of such planetary bodies having liquid water would increase when spacecrafts acquire detailed observational data of large icy bodies in the outer Solar System, such as Triton and trans-Neptune objects.

Despite the findings of liquid water, availability of energy and organic matter on these Solar System bodies had been poorly constrained until early 2010's. This is the case because both of reductants and oxidants, which generate bioavailable chemical energy, and organic matter are, or were, usually trace in aqueous environments on these planetary bodies. Thereby, in order to reveal availability of energy and organic matter, spacecrafts or rovers need to directly collect liquid

water samples or sediment samples and to perform in-situ chemical analyses remotely, which was technically challenging.

Since early 2010's, however, recent space missions have provided much observational data on chemistry, which are essential to constrain the availability of energy and organic matter beyond Earth. NASA's Cassini spacecraft directly collected plume materials erupted from the subsurface ocean of Enceladus during the flybys [e.g., 12]. On Mars, NASA's Mars Science Laboratory Curiosity rover landed on paleolake sediments within Gale Crater and drilled them for in-situ chemical, mineralogical, and organic analyses [e.g., 13].

In the present paper, we provide a review on results from these recent Solar System explorations and observational data on chemistry of these planetary bodies and discuss the available energy and organic matter there. First, we describe a general view on a planetary-scale system that can provide chemical energy to life in Sec. 2. Next, we discuss both of the oxidants and reductants available on the planetary bodies in Sec. 3. Based on the observational data obtained by recent space missions, such as Cassini, Curiosity, and Dawn, we review water chemistry and possible redox reactions in icy bodies and on Mars in Sec. 4. Finally, we summarize this paper in Sec. 5.

2. Planetary redox

Life is a dynamic-equilibrium system that is composed of complex organic matter having functions (e.g., protein and DNA for Earth's life). Since the complex organic matter having functions is thermodynamically unstable, they are gradually metamorphosed or decomposed, or oxidized on Earth, over time. This results in loss of functions and, eventually, a termination of a life system (i.e., death). To avoid metamorphose and decomposition, life needs to continuously recreate the complex organic matter that consists themselves. The recreation processes require continuous chemical energy and supply of building materials of the complex organic matter, such as bioessential elements.

Either on terrestrial planets (e.g., Earth and early Mars) or geologically-active icy bodies (e.g., Europa and Enceladus), a planetary-scale system having hydrogeochemical cycles can provide chemical energy

and building materials to life (Fig. 1) [14]. In the atmospheres or on the surfaces, solar UV/visible light and high-energy particles (solar winds and cosmic rays) dissociate H_2O , which results in irreversible escape of produced H and consequent production oxidants (such as O_2 and H_2O_2) (Fig. 1) [e.g., 15–17]. If the surface contains sulfur or nitrogen, the surface oxidation involves acidification through formation of acids, such as SO_4^{2-} and NO_3^- . On the other hand, water-rock reactions on seafloor or within the subsurface provide both reductants, such as H_2 , and alkaline, such as Na^+ , Mg^{2+} , and Ca^{2+} , to the hydrospheres [e.g., 18–21]. In addition to these “secondary” oxidants/reductants that are formed by in situ chemical reactions, planetary bodies could possess “primordial” oxidants/reductants (see Sec. 3 for details), which were originally contained in building materials of the planetary bodies and avoided from dissociation during accretion and evolution. Both of the primordial and secondary oxidants/reductants are transported and mixed through hydrological cycles and atmospheric circulations on the planetary bodies, which generate a redox and pH gradient near the surface (Fig. 1).

We call this dynamic planetary-scale system that can create a redox gradient as “planetary redox”. Using a redox disequilibrium in the planetary redox, chemoautotrophic life can acquire chemical energy (chemical affinity) to recreate the complex organic matter by producing thermodynamically stable molecules (metabolic products) [14]. In other words, the thermodynamically stable molecules formed by life through reactions of available reducing and oxidizing

molecules are predictable. These thermodynamically stable molecules can be treated as potential biomarkers. For instance, H_2 (reductant) and CO_2 (oxidant) are available in the subsurface ocean of Enceladus [22]. The measured abundances of $\sim 1\%$ of H_2 and $0.3\text{--}0.8\%$ of CO_2 relative to H_2O are in a redox disequilibrium [22]. The thermodynamic calculations show that CH_4 is thermodynamically more stable than the mixture of H_2 and CO_2 [22]; accordingly, CH_4 can be a biomarker of this icy moon [22]. On Titan’s surface, photochemically-produced H_2 (reductant) and C_2H_2 (oxidant) can be recombined to thermodynamically-stable CH_4 , which is a potential biomarker of Titan’s life [23]. Thereby, knowledge on the planetary redox is critical to predict potential biomarkers and quantitative biomass on planetary bodies for future missions that aim to find extraterrestrial life.

3. Oxidants and reductants in Solar System bodies

Depending on the formation process of planetary bodies, combinations of available oxidants and reductants are different. They are also changed over geological time even on a single planetary body depending on the evolution of the planetary body. In this section, we review the chemical compounds of the primordial and secondary origins of both oxidants and reductants available on the planetary bodies (Fig. 2).

Primordial reductants: The primordial reductants include organic matter, CH_4 , and NH_3 contained originally in icy planetesimals and proto-planets (Fig. 2). Organic matter in icy planetesimals is considered to

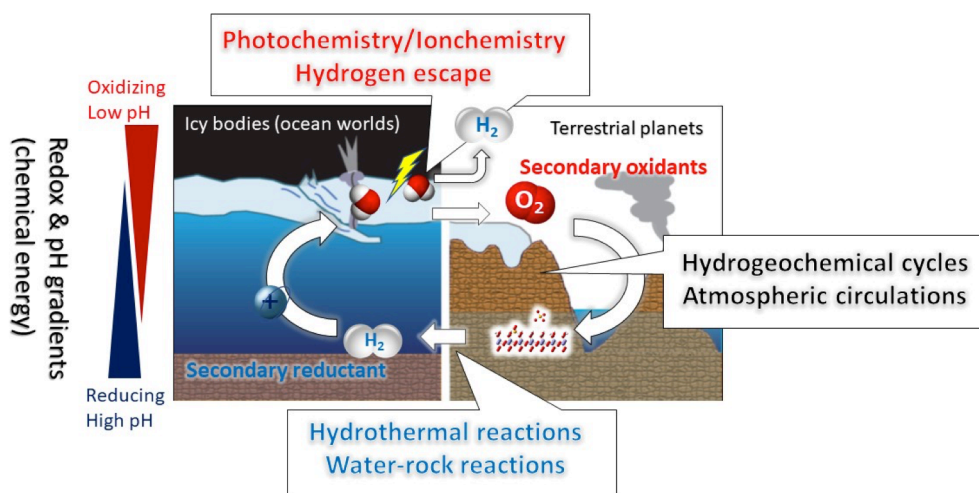


Figure 1. A conceptual image of “planetary redox” on icy bodies and terrestrial planets that possess liquid water. The planetary redox is defined as a planetary-scale system that can generate oxidants and reductants continuously and can provide them to life through hydrological cycles. On planetary surfaces, including atmospheres, oxidants and acids can be produced by photochemical/ionchemical reactions and subsequent hydrogen escape to the space. In subsurface or on seafloor, reductants and alkaline can be provided from rocks through hydrothermal reactions. These chemical compounds are transported by global-scale hydrological cycles and atmospheric circulations, generating redox and pH gradients in hydrospheres. Chemoautotrophic life on Earth uses these redox disequilibria generated in the planetary redox in order to acquire energy. See the main text for the details.

have been generated from polymerization of simple organic molecules, such as aldehyde and ammonia, in the circumplanetary disk through radiogenic heating [24–26]. Organic synthesis would have also proceeded through heating events induced by large-scale impacts [27]. These primordial reductants could survive during the accretion if a planetary body did not experience very high temperatures ($> \sim 1000$ °C).

The undifferentiated rocky interiors of Enceladus suggest that they did not experience the high temperatures (rock melting) [3], implying that primordial reductants are available in these planetary bodies. In fact, Enceladus' plume erupting from its subsurface ocean contains a significant level of CH_4 , NH_3 , and other organic matter [12]. Since their abundances are comparable to those in comets (i.e., icy planetesimals), Enceladus' CH_4 , NH_3 , and, at least, some of organic matter may be primordial [12]. Primordial organic matter would also exist in an early ocean of Ceres given its chemical and mineralogical similarities to C-type asteroids [e.g., 28]. The widespread occurrence of NH_4 -bearing phyllosilicate on Ceres [29] suggests that its early ocean would have contained primordial NH_3 [28].

On Mars and Earth, the primordial reductants of organic matter would have been decomposed in magma oceans during the accretion (e.g., giant impacts) [30]. Although the primordial reductants would have lost from the terrestrial planets, decomposition of organic matter in magma ocean results in formation of their

primordial atmosphere [e.g., 31]. If the magma ocean contains metallic iron, the primordial atmosphere should have contained high abundances of reductants, H_2 and CH_4 . In a giant impact, fragments of a metallic Fe core of an impactor would have also reduced the atmosphere-surface system through re-entering to the terrestrial planet [32]. These atmospheric reductants would have been eventually lost through H_2 escape to the space over 0.1–1 billion years [33].

It is unclear whether Europa possessed the primordial reductants, such as organic matter. Primordial CH_4 and NH_3 would not have been contained in the planetesimals that formed Europa due to relatively high temperatures (~ 150 K) around Europa-forming regions in the circum-Jovian disk [34]. During the accretion stage of Europa, impact velocity of icy planetesimals onto proto-Europa in the circum-Jovian disk would be too low (~ 2 km/s) to decompose primordial organic matter (as well as other primordial NH_3 and CH_3OH) [36–38]. Long-lived radiogenic heating and tidal heating may be able to increase the interior temperatures sufficient to decompose the primordial organic matter on Europa [e.g., 39]. Detailed gravitational data and revealing the existence of metallic Fe core on Europa are a key to understand whether Europa has experienced high temperatures and whether primordial organic matter is available on this icy moon.

Secondary reductants: Hydrogen molecule (H_2) is the important secondary reductant available on the

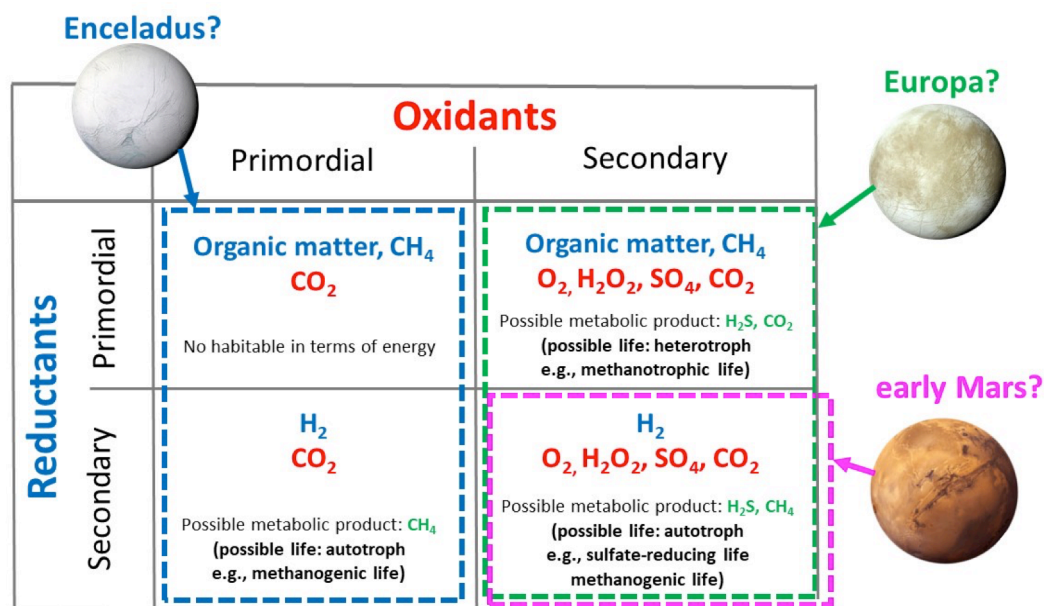


Figure 2. A comparison of the primordial and secondary reductants/oxidants available on the planetary bodies in the Solar System. Possible metabolic products and types of life (e.g., heterotroph/autotroph) are also shown. Enceladus possesses the primordial oxidant of CO_2 , contained in icy planetesimals, and secondary reductant of H_2 , formed by hydrothermal reactions (the blue broken square). On Europa, secondary oxidants of O_2 , H_2O_2 , and SO_4 are available on the surface; whereas, it is unconstrained whether primordial matter and/or secondary reductant of H_2 are available (the green broken square). On early Mars, both of primordial reductants and oxidants would have been decomposed in the early stage of its evolution (i.e., magma ocean). The secondary reductants (H_2 and H_2S) and oxidants (H_2O_2 , O_2 , SO_4 , CO_2 , ClO_3 , and ClO_4) are suggested to have been available on early Mars (the pink broken square). See the main text for the details and references.

planetary bodies that possess liquid water (Fig. 2). H_2 is generally formed through hydrothermal alterations of Fe(II)-bearing rocks, such as olivine and pyroxene, as a product of formation magnetite in serpentinization [e.g., 40]. To produce H_2 through water-rock reactions efficiently, reaction temperatures need to be, at least, $\sim 100^\circ\text{C}$ [e.g., 41].

The Fe(II)-bearing minerals are considered to be commonly contained in rocky interiors of icy bodies, regardless of the degree of differentiation of rocks. If the rocky interior is undifferentiated (i.e., no rock melting), and if its composition is similar to unaltered chondritic rocks (composed mainly of Fe-Mg-rich olivine and pyroxene), as suggested for Enceladus [21,42], hydrothermal alterations of Fe(II)-bearing minerals, together with metallic iron, should result in production of high levels of H_2 [21,43]. Such hydrothermally-generated H_2 has been found on Enceladus [22]. If the rocky interior is differentiated through rock melting, the seafloor rocks would be composed mainly of basaltic rocks that have less Mg and Fe than undifferentiated chondritic rocks. Hydrothermal alterations of basaltic rocks on the seafloor can also generate H_2 [e.g., 18], although the abundance of H_2 production would be lower than those of undifferentiated chondritic rocks.

Similar to icy bodies, H_2 is an important secondary reductant on Mars [e.g., 19,44]. Hydrothermal alterations of mafic basaltic crusts would have generated H_2 through serpentinization of Fe(II)-bearing minerals and Fe(II) oxidation on early Mars [19]. Given the collision-induced absorption of H_2 in the atmosphere, its formation is also important to keep the surface temperature above freezing point of water on early Mars [45,46]. Mineralogical evidence for hydrothermally-altered crustal rocks (i.e., the existence of serpentine and phyllosilicates) has been found on Mars through remote sensing [e.g., 47,48]. Although these remote-sensing data suggest the occurrence of hydrothermal alterations and serpentinization on early Mars, one possibility that may inhibit the efficient H_2 production is the presence of abundance CO_2 in the fluids [e.g., 49,50]. Effective formation of carbonate mineral would reduce the number of available Fe^{2+} for oxidation and could inhibit efficient H_2 production [49], which could have happened on early Mars [50].

Another key secondary reductant on early Mars is Fe^{2+} ion. Fe^{2+} can be provided through water-rock reactions by surface water (i.e., chemical weathering). Although hydrothermal alterations in the subsurface can also provide Fe^{2+} into groundwater, its concentrations would be very low [51]. This is the case because pH of hydrothermal fluids that interact with mafic rocks tend to be alkaline, and because Fe^{2+} tend to be incorporated into the solid phase (i.e., minerals) under alkaline pH conditions [51]. Since pH of the surface water is suggested to be circumneutral to acidic owing to a CO_2 -rich atmosphere and volcanic SO_4 on

early Mars, chemical weathering of surface rocks could have provided Fe^{2+} to rivers and lakes more efficiently than hydrothermal alterations [51–53].

Primordial oxidants: As for icy bodies, such as Enceladus, the major primordial oxidant would be CO_2 , originally contained in icy planetesimals as ice (Fig. 2). Observations of comets suggest that CO_2 contents in icy planetesimals would have reached as 1–5 % relative to H_2O [54]. In addition to CO_2 , primordial O_2 formed in molecular clouds can be contained in icy planetesimals [55]. However, due to the high volatility of O_2 , primordial O_2 would be available only in cold regions of the protoplanetary disk (e.g., 20–40 K).

Secondary oxidants: Various secondary oxidants, including O_2 , O_3 , H_2O_2 , SO_4 , ClO_3 , and ClO_4 , have been found or suggested on icy bodies and Mars (Fig. 2). Spacecraft and telescope observations show the presence of photochemically or ionchemically-produced, high-Eh oxidants of O_2 , O_3 , and H_2O_2 in the current atmosphere of Mars [17]. These high-Eh oxidants are also found in the tenuous atmosphere and surface of Europa [e.g., 56]. On Europa, surface sulfate acid (H_2SO_4) is also found [57]. These H_2SO_4 considered to be generated by high-energy particle irradiations onto mixtures of H_2O and S [e.g., 58]. On Mars, perchlorate salts, such as $\text{Ca}(\text{ClO}_4)_2$, have been found through in-situ chemical analyses for the surface soils [e.g., 59]. These perchlorates would be generated through photochemical reactions of HCl and oxidative radicals, such OH and O, in the atmosphere [e.g., 17]. Since $\text{ClO}/\text{ClO}_2/\text{ClO}_3$ are intermediates to form ClO_4 from Cl [60], the presence of reactive chlorate is also suggested on early and current Mars [61,62].

Figure 2 compares the above-mentioned primordial and secondary reductants/oxidants available on the planetary bodies in the Solar System. In addition to the photochemical and hydrothermal reactions that form the secondary oxidants/reductants shown in Fig. 2, volcanic activity and bolide impacts could be additional sources of reductants and oxidants. Owing to the reducing mantle of Mars compared with Earth, magma formed by partial melting of Martian mantle would contain an oxidant of CO_2 and reductants of H_2 and H_2S [e.g., 45,63]. Cometary and asteroidal impacts would also provide both of oxidants (such as CO and CO_2) and reductants (such as H_2) through shock heating of organic matter and evaporates in target rocks [e.g., 64–66]. Catalytic reactions in impact-induced plumes and in planetary atmosphere may have converted impact-induced CO, CO_2 , and H_2 into a reductant of CH_4 [67–69].

As for the combination of the primordial oxidant of CO_2 and primordial reductant of organic matter or CH_4 , life would be unable to acquire sufficient energy because the chemical reactions would not proceed under the P-T conditions of aqueous environments of icy bodies and terrestrial planets (Fig. 2). In order for

life to acquire sufficient energy (e.g., ATP synthesis for Earth's life), a planetary system needs to provide continuously the secondary oxidants, or secondary reductants, or both, to life (Fig. 2).

If only primordial oxidants or primordial reductants are available on a planetary system, this system would lose habitability when the primordial oxidants or reductants are consumed by life. As discussed below in Sec. 4.1, this situation could occur on Enceladus in future. Sustainable bioavailable chemical energy over geological time would be supported by continuous formation of both of the secondary oxidants and reductants. This can be achieved, for instance, on Europa, early Mars, Titan, and Earth in the Solar System (see Sec. 4 below).

4. Water chemistry, planetary redox, and habitability

This section summarizes the recent results of spacecraft and rover observations for water chemistry and redox states of the hydrospheres on the icy bodies and terrestrial planets in the Solar System. Based on the idea of planetary redox described in Secs. 2 and 3, we also discuss the habitability in terms of bioavailable chemical energy on these planetary bodies.

4.1. Ocean worlds

Several geologically-active icy bodies in the outer Solar System are known to possess subsurface oceans beneath the icy crusts [e.g., 1–4]. These icy bodies having the oceans are called as “ocean worlds”. Together with tidal heating for some of icy moons around gas giants, short-/long-lived radioactive nuclides and exothermic serpentinization are heat sources to form and maintain the subsurface oceans [e.g., 39,70]. The water chemistry in the subsurface oceans have been investigated directly through in-situ analyses of plume materials erupting from the oceans (e.g., Enceladus) and indirectly through non-ice materials, such as salts, on the surface (e.g., Ceres and Europa) by recent space explorations [22,42,57,71].

Enceladus and Ceres: The in-situ analyses for plume materials by the Cassini spacecraft have revealed that Enceladus' ocean contains sodium chloride [72], simple and complex organic molecules [73], nanosilica and H_2 formed by hydrothermal activity within the rocky core [22,74], and primordial CO_2 and NH_3 [12]. To form nanosilica and H_2 within Enceladus, hydrothermal reactions at temperatures ≥ 100 °C are required [21,74]. Complex organic matter found in Enceladus' plume has aromatic compounds and amine functions in its structure [73,75]. To explain a series of the in-situ observations, geochemical models suggest that Enceladus has a mildly-saline ($\sim 1\%$ of NaCl), reducing ($\sim 1\text{--}3\%$ of dissolved H_2), and alkaline (pH 9–11) ocean [21,72,74,76–78]. In Enceladus' ocean, hydrothermally-produced H_2 and primordial CO_2 are in redox disequilibrium [22].

Similar water chemistry has been proposed for an

early subsurface ocean of Ceres based on the global appearance of serpentine, NH_4 -bearing phyllosilicate, and Mg carbonate minerals on the surface [28,29,42]. These secondary minerals are considered to have been generated in an early subsurface ocean of Ceres, which was initially formed due to short-lived radiogenic heating [42,79,80]. The secondary minerals have appeared on the surface upon freezing of the early ocean and subsequent sublimation of the surface ice [42]. To form both NH_4 -bearing phyllosilicate and Mg carbonate, oceanic pH of Ceres would have been 7–10 [28]. The appearance of aliphatic hydrocarbons on Ceres' surface suggests that in-situ organic synthesis proceeded within the reducing early ocean through hydrothermal reactions [81].

On Enceladus and Ceres, water-rock reactions with the chondritic rocks results in formation of reducing and alkaline oceans [21,43]. Water-rock reactions with ultramafic chondrite rocks lead to generation of alkaline-pH fluids (pH $\sim 9\text{--}13$) [43] and formation of dissolved H_2 through oxidation of metallic Fe and Fe(II)-bearing minerals in association of serpentinization [21,22].

On Enceladus, the major oxidant is the primordial CO_2 (Fig. 2). Using the secondary reductant of H_2 formed by hydrothermal reactions, CH_4 -producing autotrophic life (methanogenic life) could acquire sufficient energy to maintain biological activities, e.g., synthesis of ATP, in Enceladus [22] (Fig. 2). This means that CH_4 is a potential biomarker on this icy moon. As described in Sec. 3 above, one important issue for continuous habitability on Enceladus is that bioavailable energy would be lost when the primordial CO_2 is consumed by life. Solar UV irradiation on Enceladus' surface and Saturn's E-ring particles could generate secondary oxidants; however, their concentrations in the ocean are very low based on the plume compositions [12]. In addition, the secondary oxidants need to be provided into the ocean continuously for sustainable habitability; however, it is unclear whether prolonged and continuous resurfacing has been promoted on Enceladus. Some theoretical studies suggest that Enceladus' current geological activity started in the recent past and could be short-lived [e.g., 82]; whereas, others propose that prolonged ocean and geological activity on Enceladus [e.g., 83,84].

Given the fact that Earth's life uses available energy in environments as much as possible, the fact that both H_2 and CO_2 coexist in Enceladus' ocean may raise a fundamental question on the habitability; that is, why the chemical energy is unused by life if it exists in Enceladus? One possible idea to explain this is that another factor, such as availability of bioessential metal, limits the bioactivities within Enceladus. In particular, Earth's methanogen requires Ni for an active center of enzyme [85]; however, the concentration of dissolved Ni^{2+} in Enceladus' ocean would be low given the high

pH. Another possibility is that Enceladus is habitable—satisfying the availability of ingredients for life—but it supports no life. This may imply that Enceladus would not meet the conditions for the emergence of life. If Enceladus is habitable and lifeless, it would provide unique insights into the conditions for the emergence of life on planetary bodies, including Earth.

Europa: The existence of sodium/magnesium chloride and sulfuric acid (H_2SO_4) [e.g., 57,86,87] on Europa's surface implies that its ocean may be more oxidizing and circumneutral pH than those of Enceladus and Ceres [88,89]. Sulfuric acid on the surface of Europa's trailing hemisphere is considered to be generated through UV and/or high-energy particle irradiations onto mixtures of H_2O ice and S [57]. Through resurfacing of the icy crust on Europa, the surface sulfuric acid would be supplied into the ocean, providing acidity [15,16]. The provided sulfate would be consumed through hydrothermal sulfate reduction if oceanic pH is low (< 7) and basaltic rocks appear on Europa's seafloor [89]. In contrast to the sulfate-rich trailing hemisphere, sodium/magnesium chloride appears in the leading hemisphere, especially in geologically-active chaotic terrains [57]. The chaotic terrains are suggested to be formed by eruption of subsurface liquid water reservoir and represent the subsurface oceanic composition [e.g., 90]. The existence of sodium/magnesium chloride in the chaotic terrains suggests that the major dissolved species of Europa's ocean would be Na^+ , Mg^{2+} , and Cl^- .

Why is the water chemistry different between Europa and Enceladus? One important factor that determines the water chemistry on an icy body is the rock composition of seafloor [89]. Water-rock reactions with differentiated basaltic rocks tend to result in lower pH, whereas those with undifferentiated chondritic rocks lead to alkaline pH [89]. In order to generate basaltic rocks on the seafloor, the rocky mantle needs to experience high temperatures sufficient to cause rock melting ($\sim 1500^\circ\text{C}$ or greater), which might have been achieved for Europa due to strong tidal heating with Jupiter and radiogenic heating [39]. Another important factor is effective formation of acids and oxidants through UV and high-energy irradiations onto the icy surface. On Europa, Jupiter's strong magnetosphere accelerates electrons and protons of solar winds. These high-energy particles are irradiated onto Europa's surface, forming a variety of oxidants and acid, H_2SO_4 , O_2 , O_3 , and H_2O_2 [15,16]. Lastly, H_2 escape from the subsurface ocean is another important factor to determine the redox state of the ocean. Through effective resurfacing and eruption of oceanic water induced by strong tidal force of Jupiter, dissolved H_2 in the ocean would have been irreversibly lost to the space, resulting in oxidation and acidification of the ocean [88]. Owing to Europa's size and massive Jupiter, formation of basaltic seafloor rocks and high-energy

particle irradiations may have occurred on Europa effectively than small Enceladus orbiting around less massive Saturn. Although no data on H_2 escape from Europa is available, its globally young surface implies that efficient resurfacing could have induced loss of substantial amounts of H_2 from the subsurface ocean [88].

If an oxidizing ocean occurs on Europa, it is essential for habitability in terms of the availability of energy in the subsurface ocean (Fig. 2). When the primordial reductant of organic matter is available, CO_2 would be a potential metabolic product of heterotrophic life through oxidation of primordial organic matter on Europa (Fig. 2). If the secondary reductant of H_2 are formed through hydrothermal reactions on the seafloor, H_2S could be a metabolic product of sulfate-reducing autotrophic life using a secondary oxidant of SO_4 (Fig. 2). An experimental study indicates that abiotic sulfate reduction proceeds only at $\text{pH} < 7$ [89]. Thus, if the water chemistry of Europa's ocean is circumneutral to alkaline, H_2S in the ocean would be a promising biomarker. These biogenic H_2S could be supplied to the surface through ice crust convection, and then, could be recycled back to SO_4 through the oxidation on the surface. One issue on habitability on Europa would be whether continuous supply of surface oxidants occurs over geological time. Active and continuous resurfacing of the icy crust is crucial for sustainable habitability on Europa, which could be science targets in future missions.

4.2. Terrestrial planets

The oceanic chemistry and planetary climate on terrestrial planets can be recorded in sedimentary rocks (e.g., evaporates, clays, and salts) and geological features (e.g., valley networks, deltas, fans, and gullies). Unlike the ocean worlds, we can reveal their time evolutions based on geochemical analyses for sedimentary rocks and geomorphic analyses for geological features on both Earth and Mars in the Solar System (Fig. 3).

Earth: On Earth, the redox state of the ocean-atmosphere system has shifted from reducing to oxidizing at around 2.4–2.3 billion years ago (Ga), which is called the Great Oxidation Event or GOE [e.g., 91–93] (Fig. 3). The GOE is evidenced by a positive excursion of carbon isotope [e.g., 94], deposition of Fe oxides [e.g., 95–97], mass independent fractionation of sulfur [e.g., 98], and oxidative weathering of redox sensitive elements [e.g., 99,100]. Although the trigger for the GOE is still in debate, this may have been caused by cyanobacterial blooming in response to a dramatic climate change [e.g., 97,101–104] and/or a decline of a degassing flux of reducing gases [e.g., 105,106]. The second oxidation in Earth's history occurred at around 0.7–0.6 Ga, which is called the Neoproterozoic Oxidation Event or NOE [e.g., 92,93] (Fig. 3). These two oxidation events in Earth's history

seems to coincide with Snowball Earth events [107] (Fig. 3). The redox states of the ocean-atmosphere system would have been also linked to biological evolution (i.e., the emergences of Eukaryotes and multicellular life) [97] (Fig. 3), although the mechanisms for the linkages remain poorly constrained based on factual evidence.

Mars: Unlike Earth, Mars had possessed abundance of liquid water on the surface only around 3.8–3.5 Ga, evidenced by the occurrence of valley networks, deltas, lake sediments, Al phyllosilicates, and sulfate deposits [e.g., 47,48,108] (Fig. 3). These geological features and secondary minerals can be formed through prolonged (e.g., $> 10^3$ years) hydrological cycles. Formation models of valley networks, Al phyllosilicates, and hyposaline paleolake water on early Mars suggest that they would have been generated in relatively short-term (e.g., $\sim 10^4$ – 10^6 years) warm and wet climate periods during 3.8–3.5 Ga [8,109,110]. This implies that in 3.8–3.5 Ga, Mars may have been generally cold and dry, punctuated by episodic warming periods driven by emission of greenhouse effect gas and/or changes in orbital forcing [108–110] (Fig. 3).

Although warm and wet climates were short-lived compared to Earth, Mars would have experienced a dramatic change in pH and redox states of the hydrosphere at around 3.5 Ga [48,111,112] (Fig. 3).

High-resolution remote sensing data suggest that pH of surface water on early Mars would have been circumneutral at 3.8–3.6 Ga based on widespread occurrence of phyllosilicates [48,111]. At around 3.5 Ga, pH of the surface water would have changed to highly acidic, based on the occurrence of sulfate-silica mineral assemblages [52,111]. After 3.4 Ga, the occurrence of surface water becomes only transient (Fig. 3). The surface was covered with thin, oxidizing soil layers [48].

At Gale Crater, NASA's Curiosity rover has investigated lacustrine sediments to reveal the paleo-environment of closed-basin lakes developed in early Hesperian (~ 3.7 – 3.5 Ga) [13,113,114]. According to the mineralogical and chemical compositions of the lake sediments [e.g., 113,114], pH of early Gale lakes is suggested to have been circumneutral to weakly alkaline [110,115]. The water chemistry of the early lake is suggested to have been Na-Cl type and mild salinity (~ 0.3 – 1 %) [110]. This composition is similar to those of closed-basin lakes developed in semiarid climate zones on Earth [110,116].

The Curiosity rover has found that Gale's lacustrine sediments preserve redox disequilibria in the secondary minerals (e.g., existence of Fe (hydro)oxides and Fe smectite) [110,113,117]. One suggested idea for the disequilibria is a redox stratification within the early Gale lake [117]. In this scenario, shallow-surface lake

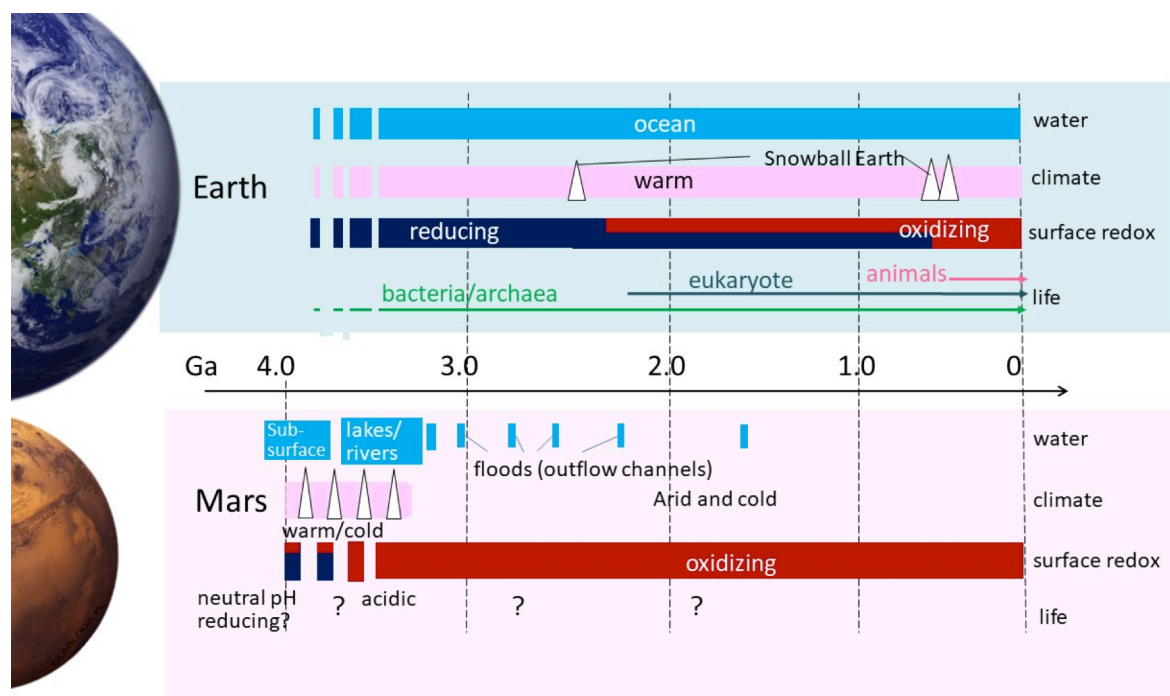


Figure 3. A comparison of evolution of aqueous environments on Earth and Mars. Earth's climate has been generally warm to support oceans on the surface. Earth has experienced two-step oxidations of the atmosphere-surface system; that is, the Great Oxidation Event (GOE) at around 2.4 Ga and the Neoproterozoic Oxidation Event (NEO) at around 6 Ga. In the GOE, the atmospheric O_2 levels rose to ~ 0.1 – 1 % of the present atmospheric level; whereas, the deep oceans remained as reducing. After the NOE, the entire of the oceans has been oxidized. This redox shift seems to link to dramatic climate changes (i.e., Snowball Earth: white triangles) and evolution of life (the three arrows). On Mars, abundant surface water was available only at around 3.8–3.5 Ga. During this period, climate is suggested to have been generally cold, punctuated by episodic warming. The redox states and pH of surface environments have evolved dramatically from 3.8 to 3.4 Ga, characterized as large-scale acidification and oxidation at around 3.5 Ga. See the main text for the details and references.

water contained high levels of oxidants, such as O_2 and oxychlorides, formed by atmospheric and surface reactions induced by Solar UV light [61,62,117–119]. Photo-oxidation of Fe^{2+} in the shallow lake water is another source of oxidants [112]. From the bottom of the lakes, reducing and alkaline groundwater could have upwelled, providing secondary reductants (such as H_2 and Fe^{2+}) into the lakes [19,50,51]. Authigenic deposition of green rust—a precursor of magnetite in the lake sediments—would have also generated H_2 upon its formation within the early lakes [120]. If the redox stratified lake formed at Gale on early Mars, both of the oxidants from the atmosphere and reductants from the subsurface would have been available at the redox boundary within the lake.

Alternative interpretation of the redox disequilibria in Gale’s sediments is a post-depositional intrusion of oxidizing and acidic fluids into the reducing lacustrine sediments [110,113]. In this scenario, the original lake environments were reducing [110,113]. A later transient rewetting event would have supplied oxidizing and acidic fluids to the subsurface sediments and would have partly oxidized the sediments by forming Fe(III) (hydro)oxides [113]. In fact, the lake sediments contain Ca sulfate veins [13]. The in-situ K-Ar dating for the Ca sulfate veins suggests that oxidative and acidic post-depositional alteration may have occurred in a much later period (e.g., ~2 Ga) [121], although the formation mechanisms of oxidizing and acidic water are unclear. If the latter scenario of intrusion of oxidizing and acidic fluids is the case, secondary oxidants could have been accumulated within the surface ice and soils [17]. A transient warming on early Mars could have melted oxidizing ice and have driven redox interactions in aqueous environments [110].

Through pyrolysis analyses for Gale’s lacustrine sediments, the Curiosity rover also found organic matter [e.g., 122–124]. The organic contents in Gale’s sediments are generally very low (in order of 100–300 ppb.) [122]; however, organic matter with order of ppm levels were found in ~3.5-Ga mudstone of Gale’s lake sediments [123]. The organic matter in the mudstone contains high levels of sulfur as thiophenic and thiol compounds, and 5% carbon as organic sulfur molecules [123]. This characteristic of the organic matter is distinct from those in carbonaceous chondrites, Enceladus’ plume, or Earth’s sediments [123]. The stable isotope analysis for pyrolyzed organic matter shows that there were multiple sources of organic matter in Gale’s sediments, including exogenic inputs from meteorites as well as in situ organic synthesis on early Mars [124]. NASA and ESA’s Mars Sample Return (MSR) missions may provide the detailed structure and chemical compositions of organic matter preserved in the ancient lake sediments at Jezero Crater deposited in ~3.8 Ga.

After the periods of circumneutral pH and relatively

reducing aqueous environments, Mars would have experienced acidification and oxidation [111]. At Meridiani Planum, Mars Exploration Rover, Opportunity, has found large amounts of Fe sulfate, jarosite, in the middle to late Hesperian sediments, possibly at around 3.5 Ga [125]. Jarosite is thermodynamically stable only at low pH 2–4 [52], strongly suggesting the occurrence of highly acidic surface water at ~3.5 Ga [52]. Such highly acidic water may be generated by photo-oxidation of Fe^{2+} ions induced by solar UV light [112]. Massive depositions of sulfate minerals, together with silica deposits, are found widespread on Martian surface in the age of 3.5–3.0 Ga through remote sensing [111]. The sulfate-silica mineral assemblages are usually formed via chemical weathering by highly acidic water [126].

After the oxidation and acidification at around 3.5 Ga, the redox boundary would have moved downward in deep subsurface on Mars [e.g., 19,44]. Secondary oxidants on the surface could be transported to reducing subsurface through infiltration and movement of surface fluids [127]. Although liquid water became thermodynamically unstable on the surface of Mars after the middle Hesperian (~3.5 Ga), it still can exist as liquid in the subsurface owing to high pressures and temperatures due to geothermal heating [19,47]. These suggest that deep subsurface hydrosphere would be central of biosphere, if exists, after ~3.5 Ga on Mars.

If life exists on the oxidizing surface of today’s Mars, they could live only in localized “hot spots”, where reductants are available. These hot spots include the locations where upwelling of deep reducing groundwater could occur. Previous studies proposed that upwelling of deep groundwater might occur seasonally along with fractures of bedrocks within impact craters, where recurring slope lineae [e.g., 128]—dark streak features appeared seasonally on steep slopes—can be found on current Mars [129]. Another possibility of supply of reductants to the surface is destabilization of CH_4 clathrate hydrate in permafrost [e.g., 130,131]. Spikes of ppb levels of CH_4 are observed at Gale Crater by the Curiosity rover [e.g., 132]. According to the atmospheric circulation model, CH_4 that generated the spikes is likely to originate from a permafrost area near Gale Crater [131]. A comparison of a measured duration of a CH_4 spike and results of photochemical models suggests that atmospheric CH_4 needs to be consumed very rapidly through unknown processes near the surface [131]. These two localized hot spots on current Martian surface—recurring slope lineae and permafrost areas—could be science targets for future landing missions.

5. Conclusions

The present paper proposed an idea of planetary redox—a planetary-scale system that can provide chemical energy to life through geohydrological cycles—developed in the icy bodies and on the

terrestrial planets in the Solar System. Based on the results of recent explorations by spacecrafts and rovers, we discussed the availability of primordial and secondary reductants/oxidants on these planetary bodies.

In the subsurface oceans of Enceladus and early Ceres, both of the primordial and secondary reductants (i.e., organic matter and H_2) would have been abundant; whereas, primordial CO_2 would be the only major oxidant. Given the existence of reducing and organic-rich aqueous environments, Enceladus and Ceres might be suitable for chemical evolution of organic matter in hydrothermal environments over geological time. Because of low production capacity of secondary oxidants, these icy bodies would have lost habitability when primordial CO_2 is consumed by autotrophic life.

On the other hand, Europa and early Mars would be capable of generating both of the secondary reductant and oxidants. If the primordial organic matter is available on Europa, heterotrophic life could emerge in the subsurface ocean. One major issue for Europa's habitability is the occurrence of continuous resurfacing of icy crust that guarantees to provide the surface oxidants to the subsurface ocean. On current Mars, the biosphere, if exists, could have been located in deep subsurface, because the redox boundary would have been moved downward after the surface oxidation and acidification, and because liquid water would be also available in subsurface. If we seek for living life on oxidizing Martian surface, we need to access to localized "hot spots", where subsurface reductants could be upwelled seasonally (e.g., upwelling of deep groundwater or permafrost melting).

The origin-of-life problem may be unsolvable on Earth because of lack of the geological records of Hadean Earth. On the other hand, geological records at around 4 Ga are abundant on Mars [e.g., 44]. On Europa and Enceladus, direct sampling of subsurface oceanic water would be possible through capturing plume materials by spacecrafts and in-situ analyses by landers [e.g., 133–136]. Findings of the presence or non-presence of life on these Solar System bodies would provide unique insights into the conditions required for the origin of life on Earth.

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