A model for low-temperature biogeochemistry of sulfur, carbon, and iron on Europa

Mikhail Y. Zolotov
Department of Geological Sciences, Arizona State University, Tempe, Arizona, USA

Everett L. Shock
Department of Geological Sciences, Arizona State University, Tempe, Arizona, USA
Department of Chemistry and Biochemistry, Arizona State University, Tempe, Arizona, USA

Received 6 October 2003; revised 19 April 2004; accepted 26 April 2004; published 5 June 2004.

[1] Galileo spacecraft data obtained from Jupiter’s ice-covered satellite Europa suggest the existence of a subsurface water ocean. The formation of this ocean is a direct consequence of early igneous and hydrothermal processes that may have facilitated oxidation through H$_2$ and CH$_4$ escape. These processes could have led to a moderately alkaline sulfate-carbonate ocean and a moderately oxidized magnetite-bearing silicate mantle. When the ocean formed, low-temperature chemical disequilibria involving oceanic sulfate, bicarbonate, and ferrous minerals in underlying rocks could have provided multiple energy sources for chemotrophic organisms. Potential metabolic processes include oxidation of ferrous iron, sulfides, native sulfur, methane, hydrogen, and organic compounds, as well as reduction of water, sulfate, bicarbonate and carbonate ions (methanogenesis and acetogenesis), native sulfur, and ferric iron. If they occurred, these reactions would have provided close coupling for biogeochemical cycles of S, C, and Fe in the ocean. Periodic supplies of fresh rocks and/or aqueous fluids at the oceanic floor could drive these cycles throughout the satellite’s history, including the present epoch. Signs of chemical disequilibria in the ocean would indicate chemical sources of energy for metabolism but should not be considered as indicators of life. In turn, observational signs of low-temperature redox equilibration among sulfur and carbon species would be suggestive of ancient life. INDEX TERMS:
6218 Planetology: Solar System Objects: Jovian satellites; 1060 Geochemistry: Planetary geochemistry (5405, 5410, 5704, 5709, 6005, 6008); 1030 Geochemistry: Geochemical cycles (0330); KEYWORDS:
Europa, ocean, mantle, life


1. Introduction

[2] Deep below the Earth’s surface and at the ocean floor, the geochemistry of S, C, and Fe is connected through a variety of pathways mediated by chemotrophic microorganisms [Stevens, 1997]. These organisms do not need light and gain metabolic energy from reduction-oxidation (redox) reactions that proceed slowly if life is not involved. Participation of chemotrophic organisms in the oxidation of ferrous minerals, sulfides, native sulfur, dissolved hydrogen, and organic compounds, as well as in the reduction of ferric iron, sulfate, and oxidized carbon species, provides coupling of biogeochemical cycles. Could similar cycling occur on the icy Jovian satellite Europa?

[3] The idea of life on Europa, first proposed by Consolmagno [1975], gained some support from tidal heating models that demonstrated the possible existence of an unfrozen water layer beneath the icy shell [Cassen et al., 1979]. Reynolds et al. [1983] first discussed the habitability of Europa’s seafloor hydrothermal systems, as well as photosynthesis at the icy surface. These two possibilities for life remained unexplored until Galileo data provided stronger arguments for an electrolytic water layer [e.g., Carr et al., 1998; McCord et al., 1999; Pappalardo et al., 1999; Kivelson et al., 2000].

[4] Despite early considerations by Reynolds et al. [1983] and some more recent suggestions, the possibility for photosynthetic life at Europa’s cold surface seems to be equivocal. At surface temperatures (80–123 K [Spencer et al., 1999]), brine pockets cannot exist in the ice. Intensive irradiation by electrons, protons, and heavy ions that also leads to the formation of strong oxidants (e.g., H$_2$O$_2$ and O$_2$) [Carlson et al., 1999a; Spencer and Calvin, 2002; Cooper et al., 2001; Johnson et al., 2003] seems likely to sterilize the surface. Alter-
natively, life in Europa, if it exists, may be supported by
chemical sources of energy somewhere in the subsurface
where liquid water and nutrients are also available. In
such a case, supplies of reactants from the icy surface
and/or from the silicate mantle could be required.

[5] Although the differentiated interior of Europa
[Anderson et al., 1998] implies intensive exchange of
mass and energy between aqueous solutions and minerals
during ocean-forming processes, there was not enough
radioactive heat to maintain such an exchange through-
out history and to keep an ocean unfrozen. Since the
history of variations in tidal activity is unknown, it is
not clear if volcanic and tectonic activity in the mantle
has maintained such exchanges. However, the Laplace
resonance among orbits of Io, Europa, and Ganymede
could have caused periodic oscillations and abrupt
increases in tidal heat production in Europa’s mantle
[e.g., Ojakangas and Stevenson, 1986; Hussmann and
Spohn, 2004]. Note that a global resurfacing several tens
of millions of years ago could have been caused by an
increased production of tidal heat in the mantle. As for
the present epoch, tidal heating may or may not cause
volcanic [e.g., Geissler et al., 2001] and hydrothermal
processes.

[6] If tidal heat is produced in the silicate mantle,
hydrothermal systems could operate at the oceanic floor
and, by analogy with terrestrial seafloor systems [Kelley
et al., 2002], could support several metabolic processes.
In fact, McCollom [1999] and Zolotov and Shock [2003b]
demonstrated numerically that hydrothermal processes in
underlying igneous rocks on Europa could provide chem-
ical energy for methane-generating (methanogens) and
sulfate-reducing organisms, either of which could utilize
dissolved H2 formed through water reduction.

[7] In terrestrial oceanic sediments and igneous rocks
exposed at the ocean floor, microorganisms live in
locations that are not related to hydrothermal systems,
and many organisms do not need O2 for metabolism [e.g.,
Parkes et al., 1994; Fisk et al., 1998; Orphan et al.,
2002; D’Hondt et al., 2002; Furnes et al., 2002]. By
analogy with low-temperature terrestrial microbial com-
munities, Jakosky and Shock [1998] proposed that chem-
ical redox disequilibria between the ocean and underlying
rocks could provide chemical sources of energy for
metabolic reactions. In particular, redox disequilibria
between oceanic sulfate and ferrous minerals in underly-
ing rocks could provide chemical sources of energy
[Zolotov and Shock, 2000a, 2003b]. Although distinct
metabolic pathways in the European ocean have been
considered [e.g., Gaidos et al., 1999; McCollom, 1999;
Kargel et al., 2000; Chyba, 2000; Schulze-Makuch and
Irwin, 2002; Zolotov and Shock, 2003b; Marion et al.,
2003], global biogeochemical cycling in the ocean, bot-
tom sediments, and underlying rocks has not been dis-
cussed. In this paper, we examine low-temperature chemical
disequilibria that could provide energy for metabolic reac-
tions and analyze possible coupling and completion of S, C,
and Fe cycles in an oxidized sulfate-carbonate ocean. Our
analysis is based on (1) suggestions about ocean-forming
processes; (2) observational data that can provide informa-
tion about oceanic chemistry; (3) thermodynamic stability
calculations for major aqueous and solid species of S, C, and
Fe; and (4) a review of low-temperature metabolic reactions
used by chemotrophic microorganisms.

2. Chemical Aspects of Ocean-Forming
Processes on Europa

[8] According to the gas-starved disc model of Canup
and Ward [2002], the Galilean satellites formed from
a mixture of water ice and a rocky component that accu-
mulated from the surrounding solar nebula rather than
condensing in a high-pressure Jovian subnebula. P- and
D-type asteroids that are abundant in the outer asteroid
belt and Trojan groups and are presented by a moderately
processed material are better compositional analogs for
icy Galilean satellites than C-type asteroids [McKinnon
and Zolensky, 2003], which are generally considered as
parent bodies of heavily aqueously altered carbonaceous
chondrites. An ordinary chondrite composition rather than
one like carbonaceous chondrites is also consistent with
the satellite’s moments of inertia [Kuskov and Kronrod,
2001]. It follows that the majority of the components that
formed the Galilean satellites were reduced, and anhy-
drous material in which sulfur was present as FeS; Fe
was in Fe-Ni metal, FeS, and Mg-rich silicates; and carbon
was in high-molecular weight organic polymers
[McKinnon and Zolensky, 2003]. Note, however, that
altered and oxidized asteroidal material could also be
part of the initial mixture: Cruikshank et al. [2001] do
not exclude the presence of serpentine in the Trojan
asteroid Hektor.

[9] On Europa, melting of ice in the outer parts of the
satellite could have occurred at late stages of accretion
when the release of impact energy increased [Stevenson
et al., 1986]. Subsequent warming of the interior driven by
radioactive decay resulted in melting of ice and outward
migration of water. This process could have limited
aqueous alteration and oxidation of central parts of the
satellite. However, subsequent heating made alteration and
oxidation of outer parts of the body unavoidable. Some-
what similar processes could have occurred during aque-
ous alteration of parent bodies of chondrites and were
driven by radioactive decay of short-lived radionuclides
[e.g., Zolensky and McSween, 1988; Grimm and McSween,
1989; Brearley and Jones, 1998]. On Europa, magmatic
processes that supplied reduced material to upper horizons
of the mantle accompanied global redistribution of mate-
riał during differentiation and core formation. Hydrother-
mal fluids that formed at the mantle-ocean boundary
would have affected the composition of the primordial
ocean.

[10] Oxidation of Europa’s mantle was driven by fast and
pervasive reactions of water with metallic iron, ferrous
silicates, and ferrous iron in magmas followed by H2
production and escape [Zolotov and Shock, 2001c, 2003a].
Coincident with oxidation of the mantle, the composition
of ocean-forming fluids would have evolved from sulfide-rich
to sulfate-carbonate-bearing solutions [McKinnon
and Zolensky, 2003; Zolotov and Shock, 2003a]. Formation
of sulfates in CI and CM carbonaceous chondrites is usually
associated with profound aqueous oxidation of sulfides in
parent bodies of these meteorites [e.g., Zolensky
and McSween, 1988; Brearley and Jones, 1998], although some
sulfates (epsmite) in Cl chondrites were redeposited in veins after the meteorites arrived on Earth [Gounelle and Zolensky, 2001]. On Europa, analogous aqueous oxidation of sulfides could have occurred during differentiation of the satellite and would have required H₂ escape [Zolotov and Shock, 2001c, 2003a]. The high water-to-rock ratio on Europa would have led to more profound oxidation compared with carbonaceous chondrites.

[11] If Europa’s mantle was oxidized beyond the quartz-fayalite-magnetite (QFM) and Ni-NiO buffers [Zolotov and Shock, 2001b, 2001c], hexavalent sulfur should be present in magmas and igneous rocks [Carroll and Webster, 1994]. Recently, McKinnon and Zolensky [2003] proposed the presence of anhydrite (CaSO₄) in Europa’s oxidized mantle on the basis of stability relations developed for Io by Lewis [1982]. If so, oceanic sulfate could have been derived through aqueous alteration of sulfate-bearing igneous rocks. Since low temperatures permit higher solubilities of sulfates, high-temperature hydrothermal activity is not required to supply sulfates from the rock into the ocean.

[12] High-temperature processes associated with differentiation also imply transformation of accreted chondritic-type organic compounds into carbon oxides, CH₄, and graphite early in the satellite’s history. In addition, both CO₂ and CH₄ could have been produced through hydrolytic disproportionation of carbon [Helgeson et al., 1993; Price and DeWitt, 2001] in the chondritic organic polymers, followed by graphitization of organic residue as the temperature increased. In subsequent igneous processes, graphite could have been oxidized to carbon oxides upon magma upwell- ing, a process proposed for other planetary bodies [e.g., Fogel and Rutherford, 1995]. In hydrothermal processes, CO is easily converted with water to CO₂ and H₂(aq), which escapes [McCollom and Seewald, 2003; Zolotov et al., 2003]. Over time, oxidation of Europa’s mantle would have increased the fraction of CO₂ in volcanic gases and ocean-forming fluids. Carbon dioxide is the major carbon species in terrestrial volcanic gases and would predominate in Europa’s counterparts owing to the Earth-like oxidation state proposed for the satellite’s mantle [Zolotov and Shock, 2001c]. The greater solubility of CO₂ in water, compared with CH₄ and CO, and non-acidic pH values favored accumulation of oxidized carbon species (HCO₃⁻ and CO₃²⁻) in the ocean. In addition to H₂ loss, preferential escape of CH₄ and CO (if they survived hydrothermal oxidation) would have contributed to oxidation of fluids and mantle minerals. Note that nitrogen should also have escaped, which may have limited the habitability of the ocean.

[13] Cooling of ocean-forming fluids hosted in chondritic-type ultrabasic rocks would have led to an alkaline ocean [Rosenberg et al., 2001; Zolotov and Shock, 2003b]. In fact, aqueous weathering of ultrabasic rocks leads to solutions with pH of 10–12 [e.g., Barnes et al., 1982]. However, alkaline pH values of 11–12, which are observed in terrestrial Na₂CO₃-saturated “soda” lakes and are discussed as analogs for Europa [Sleep et al., 2001; Kempe and Kazmierczak, 2002], seem unlikely because of a deficiency of Na in the ocean [Zolotov and Shock, 2001a]. Dilution of alkaline fluids in a vast volume of oceanic water, partially formed from melted ice, would lower the pH. Both primordial and present-day oceans on Europa could have a moderately alkaline pH of ~8–9, similar to the terrestrial value of ~8.2.

3. Reservoirs and Speciation of S, C, and Fe in Europa’s Ocean and Underlying Rocks and Sediments

3.1. Sulfur

[14] Sulfur, which is at least in part bonded with O, has been detected on Europa’s surface with ground and Galileo UV spectrometry [Noll et al., 1995; Hendrix et al., 1998]. Furthermore, the sulfate (SO₄²⁻) group has been detected in the non-ice surface material with Galileo near-infrared spectrometry [McCord et al., 1999; Carlson et al., 1999b]. The association of the hydrated sulfate group (in sulfate salts and/or sulfuric acid) with disrupted surface areas indicates an endogenic source for the sulfur, likely from an underlying ocean [McCord et al., 1999; Fanale et al., 2000]. Although sulfate observed in the non-ice material can form through irradiation of reduced sulfur species at the satellite’s surface [Carlson et al., 1999b, 2002], concentrations of reduced sulfur species (e.g., HS⁻ and H₂S) in oceanic water may be low owing to low solubilities of sulfide minerals (FeS and FeS₂) at low temperature. Therefore traces of reduced sulfur species delivered from oceanic water to the surface may not account for observed near-infrared spectra in disrupted areas. Instead, magnesium sulfate is highly soluble in water at low temperatures, and spectra of frozen Mg sulfate solutions are consistent with Galileo spectra of the non-ice material [McCord et al., 2002]. In fact, epsomite (MgSO₄·7H₂O) is stable with respect to both irradiation and dehydration in experimental models of Europa’s icy surface [McCord et al., 2001]. It follows that the satellite’s subsurface and ocean may contain sulfate, as widely adopted [McCord et al., 1999, 2002; Fanale et al., 2000; Kargel et al., 2000; Zolotov and Shock, 2001a]. Although strong observational evidence for an endogenic origin of surface S⁶⁺-bearing compounds is lacking, endogenic formation of sulfates is a logical consequence of aqueous oxidation of sulfides on water-bearing bodies that experienced internal heating and H₂ escape (see section 2). In this paper, we assume that oceanic water contains sulfate.

[15] Although Galileo magnetometer data [Kivelson et al., 2000] are consistent with the presence of ions in the ocean, they do not indicate very high conductivity and ionic strength of Europa’s ocean [e.g., Greeley et al., 2003], and oceanic water is not likely to be a brine saturated with Mg sulfate [Zolotov and Shock, 2001a; McKinnon and Zolensky, 2003]. In fact, saturation would require a lower brine-to-ice ratio (a few percent) than is estimated for the water shell (see results of freezing calculations by Kargel et al. [2000] and Zolotov and Shock [2001a]). However, it is likely that a sulfate-bearing ocean is saturated with respect to sparingly soluble Ca sulfates (e.g., gyspum, CaSO₄·2H₂O) that can be present in chemical sediments at the oceanic floor [Zolotov and Shock, 2001a]. Native sulfur that forms in radiolytic processes on the surface [Carlson et al., 1999b] should also settle to the oceanic floor through local or global melting of the icy shell. In addition to slightly soluble sulfates and native sulfur, secondary sulfides can be present.
in sediments. In mantle igneous rocks, sulfur can be present either in sulfates or in sulfides (see section 2).

[16] Figure 1a contains a plot of log $H_2$ fugacity ($f$) versus pH, which allows us to illustrate stability relations in the S-H-O system at the temperature and pressure of Europa's oceanic floor. Some reactions between sulfur compounds depend only on pH, and vertical lines separate the stability fields for those compounds. Other reactions depend only on redox potential (as quantified by $fH_2$ and activity ($a$) of dissolved $H_2$), yielding horizontal lines separating stability fields. Most reactions between sulfur compounds depend on both pH and $fH_2$, leading to lines with positive or negative slopes. The lines between stability fields of aqueous species represent equal activities of those species. The boundaries of the field representing the stability of native sulfur ($S^0$) depend on the total amount of dissolved sulfur, which in this case is assumed to be $1.7 \times 10^{-2}$ mol (kg H$_2O$)$^{-1}$ (see caption for Figure 1a). At the pH of $\sim$7 to $\sim$10, $SO_4^{2-}$ is the dominant aqueous form of oxidized sulfur, and $HS^-$ is the dominant form of reduced sulfur. Native sulfur is not likely to coexist stably with sulfate, especially at moderate bulk sulfur abundances. The assumed presence of sulfate constrains the lower limit of the oxidation state of oceanic water. Sulfate and bisulfate (HSO$_4^-$), which can be easily formed from $SO_4^{2-}$ if the pH is low enough, exist stably at $fH_2 < \sim 10^{-6}$ and $aH_2(aq) < \sim 10^{-9}$, depending on the pH.

[17] Similar diagrams can be generated for other chemical systems; for example, a diagram for the Fe-H-O system is superimposed on the diagram for the S-H-O system in Figure 1b. By placing one stability diagram over the other, it can be seen that magnetite is only stable with $HS^-$, which means that it would be unstable in the presence of any of the other sulfur compounds. Likewise, goethite is stable in the presence of sulfate and has a small range of stable coexistence with $HS^-$ at very high pH. In contrast, aqueous ferrous iron (Fe$^{2+}$) can coexist stably with all forms of sulfur, depending on the pH and $fH_2$. The occurrence of aqueous ferric iron (Fe$^{3+}$) is limited to very acidic and very oxidized (low $fH_2$) conditions. Of course, superimposed

Figure 1. Equilibrium speciation of S and Fe as functions of log $H_2$ fugacity ($f$) and pH at the conditions of the oceanic floor on Europa (0°C, 1375 bar). Corresponding log activities ($a$) of dissolved $H_2$ are presented on the right axes. Calculations were performed with the SUPCRT92 program [Johnson et al., 1992] with thermodynamic data for aqueous species from Shock et al. [1989, 1997]. (a) Speciation in the S-H-O system. Stability fields of sulfate and bisulfate (HSO$_4^-$) represent pH-$fH_2$ conditions in sulfate-rich oceanic water. The stability field of native sulfur ($S^0$) is for bulk sulfur content of $1.7 \times 10^{-2}$ mol (kg H$_2O$)$^{-1}$. This value is numerically equal to $aSO_4^{2-}$ in equilibrium with gypsum from Zolotov and Shock [2001a]. The stability field of $S^0$ becomes broader with increasing bulk sulfur content [see Zolotov and Shock, 2002]. (b) Speciation in the Fe-H-O system (solid lines) superimposed on the speciation in the S-H-O system from Figure 1a (dotted lines). The bulk Fe content is $1.4 \times 10^{-9}$ mol (kg H$_2O$)$^{-1}$. This value corresponds to Fe$^{2+}$-FeOOH equilibrium at the $fH_2$, set by equal activities of $SO_4^{2-}$ and $HS^-$ at pH 10. Divalent iron is a likely form of iron in both oceanic water and pore solutions. (c) Speciation in the Fe-S-H-O system superimposed on the speciation in the S-H-O system from Figure 1a (dotted lines). Bulk Fe content is $3.5 \times 10^{-10}$ mol (kg H$_2O$)$^{-1}$, and bulk S content is $1.7 \times 10^{-2}$ mol (kg H$_2O$)$^{-1}$. The Fe abundance is chosen to match conditions of the FeOOH-FeS$_2$ equilibrium at pH 10. The ovals may represent conditions in pore fluids and oceanic water. The arrows schematically show mixing pathways in the vicinity of the oceanic floor.
diagrams do not show relations in the combined chemical system, and the contrast can be dramatic, as revealed by comparing Figures 1b and 1c. In Figure 1c, stability relations are shown in the Fe-S-H-O system. Note that fields of pyrite (FeS₂) and ferrous monosulfide (FeS) stability appear in the combined chemical system, and in this case, no stability field for magnetite exists owing to the relatively high total abundance of sulfur. At one set of conditions or another, pyrite coexists with native sulfur (low pH), goethite (high pH), FeS (very high pH and fH₂), and sulfate (a broad pH range and a limited fH₂ range). Goethite appears to be stable only in the stability field of sulfate.

3.2. Iron
[18] The non-acidic and anoxic nature of Europa’s oceanic water implies that dissolved iron occurs in the divalent form, as illustrated in Figures 1b and 1c. However, the oceanic abundance of iron is likely to be limited by precipitation of ferric and ferrous minerals in weathered rocks and chemical sediments. By way of a terrestrial analogy, these minerals would be ferrous sulfides (e.g., pyrite), ferrous oxyhydroxides (e.g., goethite), and clays. In frozen oceanic water on the satellite surface, ferrous iron could be oxidized radiolytically, providing a source of Fe³⁺. If the icy shell recycles, the ferric iron either precipitates in the form of hydroxides or becomes reduced to Fe²⁺. Reduction pathways for ferric iron may include formation of Fe²⁺ and pyrite (see Figure 1c). Fe³⁺ in the ocean depends on the pH, the oxidation state (fH₂), and bulk Fe and S contents.

[19] Since the formation of sulfate-bearing fluids requires oxidation of the mantle well beyond the QFM buffer [Zolotov and Shock, 2001b, 2003b], magnetite should be abundant in fresh igneous rocks. Likewise, magnetite can be present in hydrothermally altered mantle rocks. In fact, aqueously altered carbonaceous and ordinary chondrites [Brearley and Jones, 1998] and terrestrial serpentinites are rich in magnetite that is the product of iron oxidation by water. Although magnetite can coexist with sulfates in hydrothermal fluids, at lower temperatures it becomes unstable in contact with oceanic sulfate as illustrated in Figures 1b and 2. At high sulfur content and high fH₂, pyrite is stable instead of magnetite, while goethite can be stable at low S content and low fH₂ (see Figure 1c). Hematite is unstable with respect to goethite at these conditions. Ferrous silicates (e.g., fayalitic olivine), if some of them survived oxidation in the mantle, are stable at higher fH₂ than magnetite, and they are out of equilibrium with oceanic sulfate as well (see Figure 2). It follows that there may be a potential for conversion of ferrous silicates, magnetite, and FeS to goethite and/or pyrite at the oceanic floor.

3.3. Carbon
[20] Carbon dioxide observed on the surface of Europa [McCord et al., 1998] can form through radiolysis of cosmogenic organic material and carbonates [Cooper et al., 2001; Johnson et al., 2003] and can also arrive from the interior. In the latter case, CO₂-bearing ice may represent frozen oceanic water delivered to the surface through the icy shell. The presence of oxidized carbon species in Europa’s oceanic water is consistent with the predominance of sulfate over sulfides, as can be seen in Figure 3, which contains the same S-H-O diagram shown in Figure 1a together with the stability relations in the C-H-O chemical system. The stability fields of oxidized carbon species (CO₂(aq), HCO₃⁻, and CO₃²⁻) overlap the stability fields of sulfate and bisulfate. Therefore a sulfate-bearing ocean would contain oxidized carbon, if equilibrium among S and C compounds is attained. Oxidized carbon species can also be stable at more reduced conditions than sulfate. Note that

Figure 2. Stability fields for iron minerals in comparison with stabilities of sulfate and bicarbonate as functions of temperature and fH₂ at pH 10 and 1375 bar. The stability fields of iron sulfides are not shown. At 0°C, fayalite and magnetite are unstable with respect to sulfate and bicarbonate. Cooling of hydrothermal fluids, in which SO₄²⁻ and HCO₃⁻ coexist with magnetite, creates potentials for magnetite oxidation coupled with reduction of SO₄²⁻ and HCO₃⁻.

Figure 3. Speciation in the C-H-O system as a function of log fH₂ and pH at the conditions of oceanic floor on Europa (0°C, 1375 bar). The speciation is superimposed on the speciation in the S-H-O system from Figure 1a (dotted lines). The ovals show conditions proposed for pore fluids and oceanic water.
methane and sulfate do not coexist stably anywhere in this
diagram and that methane is also not in equilibrium with
native sulfur at the conditions proposed for Europa and used
to construct this diagram. Since organic compounds require
higher \( f_{H_2} \) than does \( CH_4(aq) \) to reach a metastable
equilibrium with oxidized carbon species, they are unstable
with respect to sulfate and native sulfur but can coexist with
HS\(^-\) and \( H_2S(aq) \). Comparisons of the C-H-O stability
diagram with \( Fe-H_2O \) and \( Fe-S-H-O \) diagrams (Figures 1b
and 1c) demonstrate that \( FeS \) and \( magnetite \) are unstable
with respect to oxidized carbon species. Likewise, at low
temperature, ferrous silicates are unstable in the presence of
oxidized carbon (see Figure 2).

[21] The non-acidic pH of Europa’s oceanic water sug-

gests that oxidized carbon occurs as \( HCO_3^- \) and/or \( CO_3^{2-} \).

Although a high pH would allow higher bulk carbon

content, the carbon abundance in solution could be limited

by precipitation of \( Ca-Mg-Fe \) carbonates.

[22] Although it is unlikely that organic species

extracted into a primordial ocean survived to the present,

there are several possible sources for reduced carbon in

water and sediments. Throughout the satellite’s history,

cosmogenic (meteoritic or cometary) organic material

could reach the ocean [Chyba and Phillips, 2001;

Pierazzo and Chyba, 2002] through periodic recycling

of the icy shell and penetrating impacts. Organic

compounds formed in impact events [e.g., Borucki et al.,

2002; Gerasimov et al., 2002] may condense on the

surface and eventually penetrate into the ocean. At

the ocean floor a limited amount of simple organic com-

pounds (\( CH_4, \) formate, and methanol) can form from

inorganic species (\( H_2, \) \( CO_2 \), and \( CO \)) during hydrothermal

mineral-catalyzed reactions [e.g., Salvi and Williams-

Jones, 1997; McCollom and Seewald, 2001, 2003;

Voglesonger et al., 2001; Charlou et al., 2002]. There

is also a thermodynamic drive for formation of larger

organic compounds when hydrothermal fluids mix with

oceanic water [Shock and Schulte, 1998] and when

trapped magmatic gases cool during silicate volcanism

at the oceanic floor [Zolotov and Shock, 2000b]. In

the present-day ocean, organic compounds can coexist

metastably with oxidized carbon species owing to low-
temperature inhibition of redox reactions. Likewise,

without life, organic compounds can coexist with sulfate,

native sulfur, and ferric iron compounds.

4. Chemical Disequilibria as Sources for
Metabolic Energy for Nonphotosynthetic Life

[23] On Earth, microbial life is detected in the deep
continental subsurface [Stevens and McKinley, 1995;
Pederson et al., 1997; Chapelle et al., 2002], in the depths
of ocean trenches [Kato et al., 1997; Li et al., 1999],
and beneath the ocean floor [e.g., Parkes et al., 1994; Hinrichs
et al., 1999; Furnes et al., 2002; D’Hondt et al., 2002]. The
subsurface biosphere has been estimated to contain a
significant part (up to 50% [Whitman et al., 1998]) of
Earth’s biomass. Although subsurface microorganisms gain
metabolic energy from redox reactions that do not require
photons, it is thought that the majority of subsurface
organisms consume organic compounds and/or oxygen that
are products of photosynthesis. Therefore not all terrestrial

subsurface organisms could be considered as analogs for

Europa.

[24] At low temperatures, many redox reactions are

sluggish, and oxidized species (\( O_2, \) \( SO_4^{2-}, \) \( CO_2, \) \( NO_3^-, \)

\( NO_2^-, \) \( Fe^{3+}, \) and \( Mn^{4+} \)) can coexist metastably with

reduced aqueous (e.g., \( H_2, \) \( H_2S, \) \( Fe^{2+}, \) \( CH_4, \) formate,

acetate, methanol, and other organic solutes) and solid

compounds (e.g., ferrous silicates, oxides and sulfides,

native sulfur, organic matter, and \( Mn^{2+} \) oxides), as illus-

trated in Figure 4. Microorganisms take advantage of

these disequilibria and gain metabolic energy by catalyz-

ing reactions that are otherwise inhibited. Some of the

major metabolic reactions used by terrestrial microorgan-

isms are listed in Table 1.

[25] In dark oxic environments, such as shallow
continental ground waters, the deep open ocean, and seawater-
rock (or sediment) interfaces, many organisms gain

metabolic energy by oxidizing ferrous iron (in volcanic

glass, silicates, oxides, and sulfide minerals), dissolved

\( H_2S, \) sulfides, methane and organic compounds, and native

sulfur as illustrated by reactions (1)–(9) in Table 1. Deeper

in the continental subsurface and beneath the

ocean floor, where \( O_2 \) is unavailable, microorganisms gain

energy through anaerobic respiration, where ferric iron,
nitrate, nitrite, sulfate, \( CO_2, \) native sulfur, and \( MnO_2 \) are

used as electron acceptors, while dissolved \( H_2S, \) methane,

organic compounds, sulfides, native sulfur, ferrous iron,

and \( Mn^{2+} \)-bearing species can be electron donors (reac-

tions (10)–(24)).

[26] At anoxic conditions, aqueous oxidation of ferrous

minerals occurs via dissociation of water molecules and

release of \( H_2S, \) as exemplified by net reactions

\[
1.5Fe_2SiO_3(\text{fayalite, in olivine}) + H_2O \rightarrow Fe_2O_3(\text{magnetite}) + 1.5SiO_2(aq) + H_2(aq) \tag{25}
\]

\[
3FeSiO_3(\text{ferrosilite, in pyroxene}) + H_2O \rightarrow Fe_3O_4 + 3SiO_2(aq) + H_2(aq) \tag{26}
\]

\[
FeS(\text{ferrous monosulfide}) + 4H_2O \rightarrow Fe_3O_4 + 3H_2S(aq) + H_2(aq). \tag{27}
\]

Low-temperature formation of \( H_2 \) by reactions like (25) and

(26) is observed during aqueous alteration of ultramafic

rocks (serpentinitization) [Abrajano et al., 1990; Sano et al.,

1993; Charlou et al., 2002]. Although reactions (25)–(27)

are energetically favorable in open systems where \( H_2 \) is

removed, no organisms are known to gain energy from

<table>
<thead>
<tr>
<th>( O_2 )</th>
<th>( SO_4^{2-} )</th>
<th>( SO_4^{2-} )</th>
<th>( S^0 )</th>
<th>( CO_2 )</th>
<th>( CO_2 )</th>
<th>( Fe^{3+} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( H_2 )</td>
<td>( HS^- )</td>
<td>( S^0 )</td>
<td>( HS^- )</td>
<td>( CH_4 )</td>
<td>( \text{Organic} )</td>
<td>( \text{solutes} )</td>
</tr>
</tbody>
</table>

**Figure 4.** Major pairs of oxidized and reduced chemical

species that coexist metastably in low-temperature aqueous

systems. Chemotrophic organisms gain metabolic energy by
catalyzing slow or inhibited reactions among oxidized and

reduced chemical species.
### Table 1. Major Microbial Metabolic Processes Involving S, C, and Fe

<table>
<thead>
<tr>
<th>Metabolic Process</th>
<th>Example of Net Reaction</th>
<th>Reaction</th>
<th>Example of Organism or Genus&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Aerobic Reactions</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Oxidation of ferrous silicates, oxides, and sulfides</td>
<td>$1.5Fe_2O_3 + 0.5SO_2(aq) \rightarrow Fe_3O_4 + 1.5SO_2(aq)$</td>
<td>(1)</td>
<td>Thiobacillus ferrooxidans</td>
</tr>
<tr>
<td></td>
<td>$3FeS + 2O_2(aq) \rightarrow 3S^2 + Fe_2O_4$</td>
<td>(2)</td>
<td>Thiobacillus ferrooxidans</td>
</tr>
<tr>
<td></td>
<td>$FeS_2 + 3.5SO_2(aq) + H_2O \rightarrow 2SO_2^2^- + Fe^2^2 + 2H^+$</td>
<td>(3)</td>
<td>Thiobacillus ferrooxidans</td>
</tr>
<tr>
<td></td>
<td>$Fe_3O_4 + 0.5SO_2(aq) + 1.5H_2O \rightarrow 3FeOOH$</td>
<td>(4)</td>
<td>Thiobacillus ferrooxidans</td>
</tr>
<tr>
<td>Oxidation of H$_2$(aq)</td>
<td>$H_2(aq) + 0.5O_2(aq) \rightarrow H_2O$</td>
<td>(5)</td>
<td>Acidovorax facilis</td>
</tr>
<tr>
<td>Oxidation of methane</td>
<td>$CH_4(aq) + 2O_2(aq) \rightarrow CO_2(aq) + 2H_2O$</td>
<td>(6)</td>
<td>Methylomonas</td>
</tr>
<tr>
<td>Oxidation of organic compounds</td>
<td>$CH_3COO^- + H^+ + 2O_2(aq) \rightarrow 2CO_2(aq) + 2H_2O$</td>
<td>(7)</td>
<td>Pseudomonas</td>
</tr>
<tr>
<td>Oxidation of aqueous sulfides</td>
<td>$HS^- + 2O_2(aq) \rightarrow SO_2^2^- + H^+$</td>
<td>(8)</td>
<td>Thiobacillus</td>
</tr>
<tr>
<td></td>
<td>$S^2 + 2O_2(aq) \rightarrow SO_2^2^- + 2H^+$</td>
<td>(9)</td>
<td>Sulfobolus acidocaldarius</td>
</tr>
<tr>
<td><strong>Anaerobic Reactions</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Methanogenesis</td>
<td>$HCO_3^- + H^+ + 4H_2(aq) \rightarrow CH_4(aq) + 3H_2O$</td>
<td>(10)</td>
<td>Methanobacterium</td>
</tr>
<tr>
<td></td>
<td>$CO(aq) + 3H_2(aq) \rightarrow CH_4(aq) + H_2O$</td>
<td>(11)</td>
<td>Methanobacterium</td>
</tr>
<tr>
<td></td>
<td>$4HCOO^- + H^+ \rightarrow 3CO_2(aq) + CH_4(aq) + H_2O$</td>
<td>(12)</td>
<td>Methanococci</td>
</tr>
<tr>
<td></td>
<td>$CH_3OH(aq) + H_2(aq) \rightarrow CH_4(aq) + H_2O$</td>
<td>(13)</td>
<td>Methanosphaera stadtmanae</td>
</tr>
<tr>
<td>Holoacetogenesis</td>
<td>$2HCO_3^- + H^+ + 4H_2(aq) \rightarrow CH_3COO^- + 4H_2O$</td>
<td>(14)</td>
<td>Acetobacterium woodii</td>
</tr>
<tr>
<td>Coupled sulfate reduction-H$_2$ oxidation</td>
<td>$SO_2^2^- + H^+ + 4H_2(aq) \rightarrow HS^- + 4H_2O$</td>
<td>(15)</td>
<td>Desulfosarcina</td>
</tr>
<tr>
<td>Coupled sulfate reduction-organic carbon oxidation&lt;sup&gt;b&lt;/sup&gt;</td>
<td>$SO_2^2^- + 4HCOO^- + H^+ \rightarrow HS^- + 4HCO_3^-$</td>
<td>(16)</td>
<td>Desulfobacter</td>
</tr>
<tr>
<td>Coupled sulfate reduction-methane oxidation&lt;sup&gt;c&lt;/sup&gt;</td>
<td>$SO_2^2^- + CH_4(aq) \rightarrow HS^- + HCO_3^- + H_2O$</td>
<td>(17)</td>
<td>–</td>
</tr>
<tr>
<td>Coupled methane oxidation-water reduction</td>
<td>$CH_4(aq) + 3H_2O \rightarrow HCO_3^- + H^+ + 4H_2(aq)$</td>
<td>(18)</td>
<td>a methanogen</td>
</tr>
<tr>
<td>Coupled oxidation of native sulfur-Fe$^{3+}$ reduction&lt;sup&gt;d&lt;/sup&gt;</td>
<td>$S^2^- + 6Fe^{3+} + 4H_2O \rightarrow SO_2^2^- + 6Fe^{2+} + 8H^+$</td>
<td>(19)</td>
<td>Acidithiobacillus ferrooxidans</td>
</tr>
<tr>
<td>Coupled reduction of native sulfur-H$_2$ oxidation</td>
<td>$S^2^- + H_2(aq) \rightarrow H_2S(aq)$</td>
<td>(20)</td>
<td>Acidianus (thermophilic)</td>
</tr>
<tr>
<td>Coupled reduction of native sulfur-methane oxidation</td>
<td>$4S^2^- + CH_4(aq) + 2H_2O \rightarrow 4H_2S(aq) + CO_2(aq)$</td>
<td>(21)</td>
<td>Halobacterium</td>
</tr>
<tr>
<td>Coupled reduction of native sulfur-organic carbon oxidation</td>
<td>$4S^2^- + CH_3COO^- + 2H_2O \rightarrow 4H_2S^- + 3H^+ + 2CO_2(aq)$</td>
<td>(22)</td>
<td>Desulforomacina acetoxidans</td>
</tr>
<tr>
<td>Disproportionation of native sulfur</td>
<td>$4S^2^- + 4H_2O \rightarrow SO_2^2^- + 3HS^- + 5H^+$</td>
<td>(23)</td>
<td>Desulfoarcus sulfoxigens</td>
</tr>
<tr>
<td>Reduction of ferric iron&lt;sup&gt;e&lt;/sup&gt; ⊃</td>
<td>$Fe(OH)_3 + 0.5H_2(aq) + 2H^+ \rightarrow Fe^{2+} + 3H_2O$</td>
<td>(24)</td>
<td>Acidithiobacillus SH</td>
</tr>
</tbody>
</table>

<sup>a</sup>The names of organisms are from Brock et al. [1994], except the organism for reaction (18) is from Hinrichs et al. [1999]; the organism for reaction (19) is from Brock and Gustafson [1992]; the organism for reaction (23) is from Finster et al. [1998]; and the organism for reaction (24) is from Bridge and Johnson [2000].

<sup>b</sup>Organic acids, alcohols, and aromatic compounds could be electron donors in the process of biologic sulfate reduction.

<sup>c</sup>Although no known organism uses methane for sulfate reduction, the overall process (17) is probably mediated by coexisting methanogens (operating in reverse) and sulfate-reducing organisms [Hinrichs et al., 1999; Boetius et al., 2000; Orphan et al., 2002].

<sup>d</sup>This process occurs favorably in acidic environments.

<sup>e</sup>Organic compounds and sulfur (reaction (19)) also reduce ferric iron.

these pathways. However, H$_2$ could be involved in several biological reactions.

[27] Release of H$_2$ into fluids that contain CO$_2$, CO, formate, and methanol creates the potential for methano-
genesis via net reactions (10)–(13). Aqueous abiotic synthesis of methane is inefficient even at temperatures $>200^\circ$C [Berndt et al., 1996; McCollom and Seewald, 2001; 2003], allowing catalysis by enzymes in methanogens that populate both low-temperature and hydrothermal anoxic environments [Zinder, 1993; Stevens and McKinley, 1995; Chapelle et al., 2002]. Likewise, abiotic reduction of sulfate by H$_2$(aq) (reaction (15)) is inhibited in the lower-temperature regions of hydrothermal systems where H$_2$S, HS$^-$, and SO$_4^{2-}$ coexist metastably [Malinin and Khatarov, 1969; Ohmoto and Lasaga, 1982]. Under these conditions, microorganisms mediate sulfate reduction.

[28] Thermochemical reduction of sulfate through reactions involving organic compounds is also inhibited below $\approx 200^\circ$C [Goldhaber and Orr, 1995], and there is no geological evidence for abiotic sulfate reduction below 110$^\circ$C [Noth, 1997]. In organic-rich sediments, sulfate reduction occurs through microbial oxidation of organic carbon, as exemplified by reaction (16). Anaerobic oxidation of methane coupled with sulfate reduction (reaction (17)) occurs through a two-step metabolic pathway, which is not well understood [e.g., Valentine and Reeburgh, 2000; Orphan et al., 2002]. It is proposed that first, a methanogen operating in reverse (reaction 18) oxidizes CH$_4$, leading to formation of H$_2$ [Zehnder and Brock, 1979; Hinrichs et al., 1999] as well as organic by-products of incomplete methane oxidation (formate and acetate). Second, the H$_2$ and/or organic compounds released are used by sulfate-reducing bacteria [e.g., Boetius et al., 2000]. Pyrite often forms as a result of biological sulfate reduction in H$_2$- and organic-rich environments [Berner, 1984; Canfield, 1989].

[29] Native sulfur that often forms at seafloor hydrother-
mal vents through oxidation of magmatic sulfides can be biologically oxidized with O$_2$, ferric iron (reactions (9) and (19)), and nitrate; reduced with H$_2$(aq), methane, and organic compounds (reactions (20)–(22)); or even disproportionated (reaction (23)). Microbial reduction of ferric iron species (e.g., amorphous hydroxides by reaction (24)) occurs in organic-rich sediments and other reduced environments where organic compounds and H$_2$(aq) are electron donors [Lovley, 1997; Vargas et al., 1998]. Several types of organisms usually compete for electron donors and accep-
tors. For these reasons, the biogeochemical cycles of S, C, and Fe in the Earth’s subsurface are closely interconnected.

5. Potential Metabolic Reactions at the Bottom of Europa’s Ocean

[30] As the preceding discussion indicates, several redox disequilibria involving oceanic water, minerals, and organic compounds create the potential for energy-yielding reactions. Disequilibria at mineral surfaces could involve interfaces of relatively reduced minerals (FeS, ferrous silicates, magnetite, and native sulfur) and sulfate-carbonate oceanic water, as well as interfaces of oxidized minerals (e.g., goethite) and reduced aqueous species (H₂, HS⁻, and CH₄). In the aqueous phase, disequilibria could exist among solutes abundant in oceanic water and reduced species formed in pore spaces. Although it is not likely that pore solutions completely equilibrate with rocks at low temperature, elevated concentrations of H₂(aq) and HS⁻ can be expected in pore fluids as a result of abiotic water reduction by ferrous minerals (reactions (25) and (26)) and dissolution of sulfide minerals, respectively. If life exists, pore fluids may also contain reduced solutes of biologic origin (e.g., HS⁻, CH₄, organic acids, and alcohols). Ovals in Figures 1c and 3 illustrate the difference in oxidation states that may exist between pore fluids and oceanic water. The conditions for pore solutions are chosen to be in equilibrium with pyrite at pH of about 7–10, and oceanic water is chosen to be in the stability fields of SO₄²⁻, CO₃⁻, pyrite, and goethite at the same pH range. Fluid mixing, and contact of minerals with solutes, would lead to contrasting redox environments at the oceanic floor that could be used by chemotrophic organisms to gain metabolic energy through enzymatic catalysis.

[31] Exposure of igneous rocks on the ocean floor creates the potential for oxidation of ferrous iron in minerals (silicates, FeS, and magnetite), exemplified by anoxic downstream flow, oceanic water, sulfate, and bicarbonate (or CO₃⁻) become unstable with respect to reduced minerals, solutes in pore fluids, and organic compounds, if they are present. This creates potentials for reduction of water, sulfate, and bicarbonate and corresponding oxidation of ferrous iron, sulfides, and reduced carbon. In the upstream flow, oceanic water mixes with reduced fluids formed through abiotic and biologic processes of mineral dissolution and oxidation and biologically catalyzed reduction of sulfate and bicarbonate. Redox disequilibria in the mixing zone provide chemical sources of energy for organisms that oxidize H₂, HS⁻, organic carbon species, and ferrous iron. Potential distribution of reduced solutes in the whole ocean mass implies that energy for metabolism could be available far away from the oceanic floor. Circulation of water is also the major driving force for cycling of elements in sequential oxidation and reduction processes. Mobility of solutes creates conditions for coupling of biogeochemical cycles and linking of abiotic and biologic processes.

[32] Periodic supply of fresh mantle rocks to the oceanic floor is needed for the biogeochemical cycling to persist over long periods. Evidently, the supply should be faster than chemical equilibration of altered rocks with oceanic water. Both volcanism and vertical tectonic movements could supply fresh rocks. Equilibration of long-exposed igneous rocks with oceanic water, which is unlikely without life, should cause termination of biologically mediated processes. In sections 5.1 and 5.2 we discuss major abiotic and biologic processes in the Europan ocean that are summarized in Table 2.

5.1. Oxidation of Ferrous Minerals and Reduction of H₂O, SO₄²⁻, and HCO₃⁻

[33] Exposure of igneous rocks on the ocean floor creates the potential for oxidation of ferrous iron in minerals (silicates, FeS, and magnetite), exemplified by anoxic...
conversion of magnetite to goethite with water, sulfate, and bicarbonate as electron acceptors:

$$\text{Fe}_3\text{O}_4 + 2\text{H}_2\text{O} \rightarrow 3\text{FeOOH} + 2\text{H}^+ + 0.5\text{H}_2(\text{aq})$$  \(\text{(28)}\)

$$8\text{Fe}_3\text{O}_4 + \text{SO}_4^{2-} + \text{H}^+ + 12\text{H}_2\text{O} \rightarrow 24\text{FeOOH} + \text{HS}^-$$  \(\text{(29)}\)

$$8\text{Fe}_3\text{O}_4 + \text{HCO}_3^- + \text{H}^+ + 13\text{H}_2\text{O} \rightarrow 24\text{FeOOH} + \text{CH}_4(\text{aq}).$$  \(\text{(30)}\)

Although reactions like (29) and (30) could represent thermodynamically favorable overall pathways in Europa’s ocean, no known organisms gain energy directly from these reactions. However, by analogy with known living species, oxidation of ferrous iron coupled with reduction of sulfate and bicarbonate could proceed in two steps. First, hydrogen is produced through reduction of water coupled with oxidation of ferrous iron (reactions (25) and (26)). Second, $\text{H}_2(\text{aq})$ participates in the reduction of $\text{HCO}_3^-$ and $\text{SO}_4^{2-}$ (reactions (10) and (15)). Reduction of water can occur abiotically, but low-temperature reduction of sulfate and oxidized carbon compounds requires catalysis, which is the role played by life (see section 4). In fact, abiotic reduction of water by ferrous minerals (e.g., olivine) can potentially result in $\text{H}_2$ (aq) concentrations of mmol levels [e.g., Charlot et al., 2002; McCollom and Seewald, 2001] placing pore solutions in the stability fields of $\text{HS}^-$ and $\text{CH}_4(\text{aq})$ (see Figures 1c, 2, and 3). Although extensive oxidation of mantle rocks, which is required to form sulfate-bearing fluids, would limit their capacity to generate $\text{H}_2$ in pore solutions, some amount of $\text{H}_2$ can still be produced through low-temperature weathering of magnetite (see Figure 2 and reaction (28)) and silicates with low activities of ferrous iron. Note, however, that there is no potential for methanogenesis at the rock-ocean interface if $[\text{H}_2]$ in pore fluids is less than $\sim 10^{-5.5}$, and sulfate reduction is only possible if $[\text{H}_2] > \sim 10^{-7}$, depending on the pH (see Figure 3).

### Table 2. Major Anaerobic Metabolic Processes That Can Occur Through Interaction of Europa’s Ocean, Underlying Rocks, and Sediments

<table>
<thead>
<tr>
<th>Pathway</th>
<th>Overall Metabolic Reaction*</th>
<th>Example Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>Coupled $\text{Fe}^{2+}$ oxidation-water reduction</td>
<td>(25), (26)</td>
</tr>
<tr>
<td>b</td>
<td>Coupled $\text{Fe}^{2+}$ oxidation-sulfate reduction</td>
<td>(29)</td>
</tr>
<tr>
<td>c</td>
<td>Coupled $\text{H}_2(\text{aq})$ oxidation-sulfate reduction</td>
<td>(15)</td>
</tr>
<tr>
<td>d</td>
<td>Coupled $\text{Fe}^{2+}$ oxidation-$\text{HCO}_3^-$ reduction (methanogenesis)</td>
<td>(30)</td>
</tr>
<tr>
<td>e</td>
<td>Coupled $\text{H}_2(\text{aq})$ oxidation-$\text{HCO}_3^-$ reduction (methanogenesis)</td>
<td>(10)</td>
</tr>
<tr>
<td>f</td>
<td>Coupled $\text{H}_2(\text{aq})$ oxidation-$\text{HCO}_3^-$ reduction (acetogenesis)</td>
<td>(14)</td>
</tr>
<tr>
<td>g</td>
<td>Coupled oxidation of organic compounds-sulfate reduction</td>
<td>(16)</td>
</tr>
<tr>
<td>h</td>
<td>Coupled $\text{CH}_4$ oxidation-sulfate reduction</td>
<td>(17)</td>
</tr>
<tr>
<td>i</td>
<td>Coupled $\text{CH}_4$ oxidation-water reduction</td>
<td>(18)</td>
</tr>
<tr>
<td>j</td>
<td>Oxidation of $\text{HS}^-$</td>
<td>(31)–(33), (35)</td>
</tr>
<tr>
<td>k</td>
<td>Coupled $\text{Fe}_2\text{O}_3$ oxidation-water reduction</td>
<td>(34)</td>
</tr>
<tr>
<td>l</td>
<td>Coupled $\text{HS}^-$ oxidation-formation of native sulfur</td>
<td>(35), (36)</td>
</tr>
<tr>
<td>m</td>
<td>Coupled native sulfur oxidation-ferric iron reduction</td>
<td>(19)</td>
</tr>
<tr>
<td>n</td>
<td>Coupled native sulfur oxidation-water reduction</td>
<td>(37)</td>
</tr>
<tr>
<td>o</td>
<td>Coupled native sulfur reduction-$\text{H}_2$ oxidation</td>
<td>(20), (38)</td>
</tr>
<tr>
<td>p</td>
<td>Coupled native sulfur reduction-organic C oxidation</td>
<td>(22), (39)</td>
</tr>
<tr>
<td>q</td>
<td>Disproportionation of native sulfur</td>
<td>(23)</td>
</tr>
<tr>
<td>r</td>
<td>Coupled ferric iron reduction-$\text{H}_2$ oxidation</td>
<td>(24)</td>
</tr>
<tr>
<td>s</td>
<td>Coupled ferric iron reduction-$\text{HS}^-$ and $\text{H}_2\text{S}$ oxidation</td>
<td>(32)</td>
</tr>
<tr>
<td>t</td>
<td>Coupled ferric iron reduction-organic C oxidation</td>
<td>–</td>
</tr>
</tbody>
</table>

*Overall anaerobic pathways a, b, d, h, and k are not known to be conducted by specific organisms. Pathways b and d could proceed through combination of the abiotic process a and biomediated reactions c and e. Pathway h can go through sequential biologic processes i and c.

[34] Mixing of oceanic sulfate and bicarbonate with $\text{H}_2$-bearing pore fluids generates conditions conducive for biological catalysis. As a result, $\text{H}_2(\text{aq})$ is consumed by sulfate reducers, methanogens, and acetogens. On Earth, sulfate-reducing organisms that utilize $\text{H}_2$ require organic compounds (acetate) in their metabolic cycles. If Europan counterparts also require organic compounds to utilize $\text{H}_2$, then autotrophic methanogenesis (reactions (10) and (11)) and acetogenesis (reaction (14)) may account for primary biologic productivity in Europa’s ocean.

[35] Instability of organic carbon species with respect to $\text{SO}_4^{2-}$ creates the potential for coupled sulfate reduction and organic carbon oxidation that can occur in the open ocean, in organic-bearing sediments, and in mixing zones of oceanic water and pore solutions. In particular, organic compounds produced by methanogens, acetogens, and sulfate reducers that utilize $\text{H}_2(\text{aq})$, as well as organic species from abiotic sources, could be consumed by heterotrophic sulfate-reducing organisms that produce $\text{HCO}_3^-$ and $\text{HS}^-$ (reaction (16)). Release of $\text{HCO}_3^-$ into oceanic water completes a carbon cycle that starts with methanogenesis.

### 5.2. Oxidation of $\text{HS}^-$ and Conversions of Native Sulfur

[36] Bisulfide that forms in pore fluids through dissolution of sulfides and biologic sulfate reduction becomes unstable when these solutions mix with oceanic water and make contact with ferric minerals. Although abiotic formation of pyrite through the reactions

$$2\text{HS}^- + \text{Fe}^{2+} \rightarrow \text{FeS}_2 + \text{H}_2(\text{aq})$$  \(\text{(31)}\)

$$2\text{FeOOH} + 2\text{HS}^- + 4\text{H}^+ \rightarrow \text{Fe}_2\text{S}_2 + \text{Fe}^{2+} + 4\text{H}_2\text{O}$$  \(\text{(32)}\)

provides likely pathways for $\text{HS}^-$ oxidation [e.g., Rickard, 1997], formation of sulfate is mechanistically complicated. In fact, at Europan conditions, $\text{HS}^-$ cannot be oxidized by
bicarbonate (and CO$_3^{2-}$) (see Figure 3), and the thermodynamically possible oxidations of HS$^-$ and FeS$_2$ through reduction of water,

$$\text{HS}^- + 4\text{H}_2\text{O} \rightarrow \text{SO}_4^{2-} + \text{H}^+ + 4\text{H}_2(\text{aq}) \quad (33)$$

$$\text{FeS}_2 + 8\text{H}_2\text{O} \rightarrow 2\text{SO}_4^{2-} + \text{Fe}^{2+} + 2\text{H}^+ + 7\text{H}_2(\text{aq}), \quad (34)$$

are not known to support metabolism. Solid native sulfur can form as an intermediate product of HS$^-$ and FeS$_2$ oxidation, for example, through the reaction

$$\text{HS}^- + \text{H}^+ \rightarrow \text{S}^0 + \text{H}_2(\text{aq}). \quad (35)$$

At high bulk S abundance and/or low pH, formation of native sulfur could be thermodynamically favorable during mixing of pore fluids with oceanic water via the reaction

$$3\text{HS}^- + \text{SO}_4^{2-} + 5\text{H}^+ \rightarrow 4\text{S}^0 + 4\text{H}_2\text{O}. \quad (36)$$

[37] At moderately oxidized acidic and slightly alkaline conditions, native sulfur can be stable with respect to both pyrite and oceanic sulfate (see Figure 1c). In such cases, no metabolic reactions that consume S$^0$ are expected. However, at pH higher than ~8, which could characterize the ocean, S$^0$ is unstable with respect to both oxidation and reduction. Since low-temperature abiotic oxidation of S$^0$ is inhibited even in O$_2$-bearing fluids, S$^0$ will coexist metastably with alkaline oceanic water. Although such coexistence creates sources of chemical energy, there is no exact terrestrial alkaline oceanic water. Although such coexistence creates sources of chemical energy, there is no exact terrestrial alkaline oceanic water. Therefore, any of these reactions could be biologically mediated.

5.3. Why Not O$_2$ and H$_2$O$_2$ as Energy Sources?

[18] Chyba [2000] and Chyba and Phillips [2001] proposed that the supply of radiolytically formed O$_2$ and H$_2$O$_2$ from the surface can provide chemical energy for metabolism in the ocean. Although this suggestion is a popular notion, several considerations interfere with its application to Europa. As a consequence, this energy resource remains controversial.

[38] First, there seems to be no effective mechanism to deliver surface materials into the ocean in the present epoch. Both the geological sequence of events (formation of plains, bands, ridges, chaos, and then impact craters) and the nearly complete lack of tectonic deformation of impact craters are consistent with rapid decrease of the rate of tectonic resurfacing [Figueroed and Greeley, 2004] in an initial period of the visible geologic history (the last 30–80 Myr [Zahnle et al., 2003]). The lack of remnants of older surfaces may imply that a previously exited icy shell was completely melted. At the time of intensive resurfacing of a thin shell, oxidants would not have had time to accumulate on the surface. Once the shell thickness reached several kilometers, intensive disruptions that affected the whole shell thickness ceased, and since then, exchange of surface material with the ocean probably was inefficient. This scenario is consistent with an increasing ice thickness with time, as evaluated from morphology and sizes of ridges, chaotic terrains, and impact craters [cf. Pappalardo et al., 1999; Figueroed and Greeley, 2004]. Ridge morphologies are consistent with ice thickness <1–2 km [e.g., Greenberg et al., 1998]; some chaotic terrains indicate a thickness of 2–3 km [e.g., Carr et al., 1998; Williams and Greeley, 1998]; and impact craters reveal the thickness to be more than 3–19 km [e.g., Turtle and Pierazzo, 2001; Schenk, 2002], which could represent the present-day conditions. Solid-state convection, if it developed in a thick shell [McKinnon, 1999], does not affect near-surface layers [e.g., Showman and Han, 2004]. Although formation of some elevated chaotic terrains in a thick crust by thermal diapirs [e.g., Figueroed et al., 2002] could bring oceanic material to the surface, it is unclear how surface materials can be delivered to the ocean.

[40] Second, melt-through events, if they take place in a thick shell, and impacts should cause water boiling, degassing, H$_2$O$_2$ decomposition to O$_2$, and escape of oxidants from a thin (~1 m [Johnson et al., 2003]) surface layer. Local heating of the surface layer and/or submergence of ice in warmer zones of the icy shell would result in sequential sublimation of O$_2$ and other oxidants, H$_2$O$_2$, decomposition, and diffusion of gaseous oxidants to the surface. If the icy shell is resurfaced by catastrophic events of unknown nature, supply of oxidants could only occur once in ~10$^7$–10$^8$ years. However, a complete melting of the icy shell during a resurfacing event would drive thorough degassing of the ocean.

[41] Third, irregularly delivered O$_2$ and H$_2$O$_2$ in the ocean could be consumed through rapid abiotic reactions involving reduced chemical species. In fact, low-temperature abiotic oxidation of O$_2$ and H$_2$O$_2$ by H$_2$S(\text{aq}),$\text{HS}^-$, and Fe$^{2+}$ (in non-acidic conditions) occurs spontaneously without life. In the terrestrial ocean the half-life for abiotic oxidation of H$_2$S is ~30 hours [Millero and Hershey, 1989] and for Fe$^{2+}$ is only 1–5 min [Millero et al., 1987]. Evidently, O$_2$ formed through radiolysis of oceanic water driven by the decay of $^{40}$K [Chyba and Hand, 2001] would not survive rapid abiotic reduction. Terrestrial organisms that consume O$_2$ and H$_2$O$_2$ in the ocean or beneath the continental surface require a constant supply of oxidants,
which would not be the case on Europa. In oxic conditions, nonbiologic oxidation of ferrous silicates and glasses and sulfide minerals also occurs rapidly from a geological perspective [White et al., 1985; Kamei and Ohmoto, 2000]. Thus not enough dissolved O\textsubscript{2} would be left to support anaerobic life in the ocean.

[42] Fourth, irregular and/or minute supplies of O\textsubscript{2} and H\textsubscript{2}O\textsubscript{2} into the ocean coupled with their rapid consumption in abiotic reactions would prevent adaptation of organisms to using strong oxidants and would limit life’s opportunity to evolve toward aerobic metabolism. It has been suggested that oxygen respiration on Earth is a result of a prolonged evolution of anaerobic organisms that used ferric iron and sulfur respiration [Vargas et al., 1998; Richardson, 2000]. If Europan organisms have not evolved to consume O\textsubscript{2} and H\textsubscript{2}O\textsubscript{2}, these strong oxidants would be harmful rather than useful. However, some anaerobic organisms could facultatively use traces of O\textsubscript{2}.

6. Biogeochemical Cycles

[43] The potential that S, C, and Fe in various oxidation states can be mixed together in the cold outer shells of Europa means that there is, at least, the potential for interconnected biogeochemical cycles of these elements. In the following discussion we illustrate how these cycles might be linked and describe the major reservoirs, as well as the abiotic and potential biologically mediated pathways.

6.1. Sulfur Cycle

[44] The oceanic sulfur cycle starts with dissolution of sulfate minerals and hydrolysis of sulfides, leading to the supply of SO\textsubscript{4}\textsuperscript{2−} and HS\textsuperscript{−} at the ocean-rock interface (see Figure 6). Once in contact with oceanic water, HS\textsuperscript{−} can be partially converted to pyrite, which can remain stable. Oxidation of HS\textsuperscript{−} to SO\textsubscript{4}\textsuperscript{2−} requires radiolysis at the icy surface and/or biomediation in the ocean. Native sulfur can form as an intermediate product, and its further conversions are kinetically inhibited without catalysis by organisms.

[45] Sinks of SO\textsubscript{4}\textsuperscript{2−} include precipitation of sparingly soluble sulfate minerals (e.g., gypsum) and biological sulfate reduction where H\textsubscript{2}(aq), CH\textsubscript{4}(aq), and organic compounds are electron donors. Again, native sulfur may form as an intermediate product of sulfate reduction. The biologic sulfur cycle can be incomplete because pyrite and native sulfur formed through sulfate reduction may not be easily oxidized back to sulfate unless hydrothermal processes are involved. In fact, water is not known to be an electron acceptor in metabolic versions of those reactions, and oxidized carbon solutes coexist stably with pyrite, native sulfur, and HS\textsuperscript{−} at moderately reduced conditions.

[46] Although pyrite is the likely final product of sulfate reduction, several factors could prevent profound conversion of oceanic sulfate to reduced sulfur minerals on Europa. The reduction could be limited by the abundances of H\textsubscript{2}(aq) [Zolotov and Shock, 2003b], organic compounds, and/or ferrous iron in bottom rocks compared with the mass of oceanic sulfate. (A 100-km thick ocean contains 3 × 10\textsuperscript{18} to 3 × 10\textsuperscript{19} kg of sulfate at SO\textsubscript{4}\textsuperscript{2−} concentration of 0.01–0.1 mol (kg H\textsubscript{2}O)\textsuperscript{−1}.) The likely lack of plate tectonics prevents a sink of FeS\textsubscript{2}-bearing rocks and sediments into the mantle. Hydrogen escape during events that disrupt the icy shell can maintain an elevated oxidation state of the ocean. However, escape of H\textsubscript{2} from the icy surface through radiolysis of water ice [e.g., Johnson et al., 2003] can eventually be followed by escape of O\textsubscript{2} and H\textsubscript{2}O\textsubscript{2} (see section 5.3) and may not affect the oxidation state of the ocean. Sporadic hydrothermal activity in an oxidized upper mantle might supply sulfate-rich fluids throughout the satellite’s history. Hydrothermal activity would also facilitate oxidation of buried pyrite and sulfur and would work toward the completion of the sulfur cycle. Finally, if radi nuclides become exhausted in the satellite’s interior, or if tidal heat is preferentially produced in the icy shell, there would not be a volcanic supply of reduced material from the deep mantle. If life is not involved in sulfur redox reactions, sulfate, bisulfide, native sulfur, and pyrite would coexist metastably. In such a case the only low-temperature processes that can proceed are the oxidation of frozen sulfides.

Figure 6. The biogeochemical cycle of sulfur in Europa’s ocean. Bold arrows represent reactions that can be biologically mediated.
at the surface to $S^0$ and $SO_4^{2-}$ and formation of pyrite by reactions (31)–(32). High-temperature processes would be required to complete an abiotic cycle.

### 6.2. Carbon Cycle

[47] Without life, low-temperature redox reactions of carbon are limited to oxidation of cosmogenic organic material at the surface [Cooper et al., 2001]. If cosmogenic organic material reaches the ocean, it would not be oxidized until dissolved organic compounds are delivered back to the surface with oceanic water or until igneous and hydrothermal processes are involved.

[48] Another abiotic process is dissolution and precipitation of carbonates at the ocean floor. In contrast to the terrestrial ocean, carbonate sediments could buffer the abundances of oxidized carbon species and the pH. Re-equilibration between carbonates in sediments and oceanic water may follow disturbances such as supply of $CO_2$-bearing fluids from the mantle and substantial losses of $CO_2$ through openings in the icy shell. Despite the stability of $CO_2$ hydrates at temperatures and pressures of the ocean, periodic degassing of oceanic water would limit the amount of dissolved $CO_2$ and would not favor formation of clathrate hydrate.

[49] If life is present, oceanic bicarbonate could be consumed through methanogenesis and acetogenesis (see Figure 7). Bicarbonate returns to oceanic water when anaerobic methanotrophs, heterotrophic sulfate reducers, and ferric iron reducers oxidize methane and organic material. The carbon cycle may be complete in the presence of life.

### 6.3. Iron Cycle

[50] The oceanic iron cycle starts with hydrolysis of ferrous silicates and FeS in igneous rocks, followed by supply of $Fe^{2+}$ into pore fluids and the ocean (Figure 8). At the ocean-rock interface, pyrite forms through oxidation of $HS^-$ and FeS and reduction of magnetite. Secondary magnetite can only form in Fe-rich and S-depleted pore fluids isolated from oceanic water. If in contact with oceanic sulfate, magnetite from igneous and altered rocks could be converted to goethite and/or pyrite through biologically mediated reactions. Formation of a pyrite-goethite assemblage at the oceanic floor at the expense of ferrous silicates, magnetite, and FeS indicates net oxidation of iron. Escape of $H_2$ and $CH_4$ and formation of ferric iron through radiolysis at the surface contribute to oxidation.

[51] Goethite in sediments can be affected by upwelling reduced fluids that allow biological reduction to $Fe^{2+}$, which enters oceanic water, and ferrous minerals, as shown in Figure 8. Reduction beneath the seafloor, deposition of radiolytically formed ferric iron, and weathering of igneous rocks all can lead to goethite accumulation in a narrow layer at the ocean-rock (sediment) interface. Somewhat similar mechanisms are responsible for the formation of Fe-Mn nodules on the terrestrial oceanic floor. In reduced sulfur-rich solutions, pyrite rather than magnetite forms at the expense of reducing goethite (reaction (32)). In turn, decreasing bulk sulfur content and $fH_2$ in fluid mixing zones favors pyrite oxidation to goethite. Conversion of goethite to pyrite and vice versa may involve organisms and provides a mechanism that affects abundances of sulfur and ferrous aqueous species and $H_2(aq)$ in oceanic water.

### 7. Concluding Remarks

[52] Galileo near-infrared observations and use of carbonaceous chondrites as analogs can be consistent with a sulfate- and carbonate-bearing ocean on Europa formed in conjunction with high-temperature oxidation of the interior. Although $SO_4^{2-}$ and $CO_2$ could have coexisted with partially oxidized mantle minerals (e.g., magnetite) at high temperatures, at the oceanic floor, there are potentials for further low-temperature oxidation of these minerals coupled with reduction of oceanic water and sulfate and carbonate species. These potentials should have existed for periods of time following the formation of the ocean and episodes of tectonic/volcanic activity at the oceanic floor.

[53] Inhibition of redox reactions at temperatures near $0^\circ C$ implies that oceanic sulfate is out of chemical
equilibrium with ferrous minerals, reduced chemical species in pore fluids, and organic compounds. Likewise, bicarbonate and carbonate ions are far from equilibrium with organic compounds and ferrous silicates. Thermodynamically favorable oxidation processes involving ferrous minerals, bisulfide, native sulfur, and methane and organic compounds could be biologically mediated. Circulation of oceanic water in underlying rocks also creates the potential

Figure 8. The biogeochemical cycle of iron in Europa’s ocean.

Figure 9. The major pathways and reservoirs of coupled cycles of S, C, and Fe in Europa’s ocean. Reservoirs are shown by quadrangles, and potential chemical processes are shown by ovals. The ovals represent chemical processes that can be biologically mediated. Processes that involve nature sulfur are not shown. Although oxidation of ferrous iron by water proceeds abiotically, there is a potential for biological mediation.
for biologic reduction of bicarbonate, sulfates, native sulfur, and ferric iron. Chemotrophic organisms can inhabit the portions of the oceanic floor where oceanic water contacts igneous rocks and mixes with reduced pore fluids, as well as the whole ocean volume where oxidized and reduced species coexist metastably. Biologically mediated oxidation and reduction processes could proceed at the same place owing to disequilibria among the majority of chemical species in the S-C-Fe-H-O system. By analogy with terrestrial ecosystems, diversity of possible metabolic processes could correspond to microbial diversity. Supply of radiolytically formed oxidants from the satellite’s surface is not required to support such organisms and is unnecessary in order to maintain an ecosystem.

Although the majority of metabolic reactions predicted for Europa have known terrestrial analogs, several processes (e.g., oxidation of ferrous iron and bisulfide by water and direct oxidation of ferrous minerals by sulfate and bicarbonate) are not presently associated with any particular organisms. This, of course, does not preclude the existence of such organisms on Earth or elsewhere.

Circulation of oceanic water facilitates cycling of elements in sequential oxidation and reduction processes, as generalized in Figure 9. Biogeochemical cycles of S and C can be coupled through microbial methanogenesis, acetogenesis, and heterotrophic sulfate reduction; Fe and C cycles are connected through involvement of organic species in reduction of ferric iron, and S and Fe cycles are linked through transformations among FeS, pyrite, magnetite, and goethite. Even with participation of life, sulfur and iron cycles could be incomplete because of (1) net formation of pyrite-goethite assemblage out of ferrous silicates, FeS, and magnetite; (2) inefficient reduction of ferric iron species in non-acidic conditions; and (3) low efficiency of oxidation of native sulfur and pyrite in anoxic conditions. Net oxidation of iron could be driven by escape of H2.

The amount of energy available for metabolism of chemotrophic organisms depends on the difference of redox conditions between minerals and oceanic water. Amounts can be quantified for individual reactions if values of fH2 and pH and bulk S, C, and Fe abundances are specified. Note that the amount of energy in environments with chemical disequilibria should exceed an apparent minimal energy requirement. In life as we know it, this amount corresponds to the energy required for ATP synthesis and also varies for different organisms [e.g., Hoehler et al., 2001]. Therefore environments that deviate only slightly from equilibrium may not be able to support life.

Although proposed disequilibria and corresponding metabolic processes are based on the assumption of a sulfate-bearing ocean, a more reduced, sulfide-bearing ocean would also support several metabolic processes. In particular, a HCO3-, HS−-rich ocean can sustain such processes as oxidation of ferrous iron in silicates and FeS; methanogenesis; methanotrophy; and reduction of sulfate, native sulfur, and ferric iron. In turn, if mantle rocks and pore fluids are oxidized as much as the hematite-magnetite buffer (fH2 = 10^{-5.7} at 0°C and 1375 bar), there is no potential for bicarbonate reduction (methanogenesis and acetogenesis). However, methane and organic compounds can be oxidized both in pore fluids and in the ocean. Besides that, there are potentials for reduction of oceanic SO4^{2−} and oxidation of HS− from pore fluids. In other words, several metabolic processes could occur at the ocean-mantle interface unless oceanic water, pore fluids, and minerals are fully equilibrated.

Signs of chemical disequilibria in the ocean, which could be obtained from further observations, would indicate potential sources of chemical energy for metabolism and should not be considered as biosignatures. In contrast, signs of equilibration among species that otherwise do not react at low temperatures would be indicative of ancient life and the lack of energy for life in the present epoch. However, a more careful kinetic analysis is required to establish that some abiotic equilibrations will not occur over billions of years.

Acknowledgments. This work has benefited from thoughtful reviews by Norm H. Sleep and another reviewer. We also thank Melanie Holland, Susanne Neuer, William McKinnon, and Patricio Figueredo for helpful discussions and comments and Yin Ngeou for assistance. This work is supported by NASA Exobiology grant NAG5-7696.

References


Richardson, D. J. (2000), Bacterial respiration: A flexible approach for a changing environment, Microbiology, 146, 551–571.

Richardson, D. J. (2000), Bacterial respiration: A flexible approach for a changing environment, Microbiology, 146, 551–571.


