

GEOCHEMICAL CONSTRAINTS ON THE OXIDATION STATES OF THE EUROPEAN OCEAN AND MANTLE. M. Yu. Zolotov and E. L. Shock, Department of Earth and Planetary Sciences, Washington University, St. Louis, MO 63130-4899. E-mails: zolotov@zonvark.wustl.edu, shock@zonvark.wustl.edu.

Introduction: *Galileo* gravity [1] data indicate that Jupiter's moon Europa is differentiated. Europa could consist of an Fe-rich core, a silicate mantle, and an outermost water shell, which could contain an unfrozen global layer (ocean) beneath the icy crust [1-7]. The oxidation states of the european core, mantle, oceanic sediments, and ocean should be determined by ratios of oxidized and reduced compounds of such abundant elements as Fe, S, and C. Here we use observational, meteoritic, and physical-chemical data to constrain the oxidation states of the silicate and water shells on Europa.

Observational data on the european surface: The surface of Europa is composed of a mixture of compounds of multiple origin. Although both oxidized (H₂O, SO₂, sulfates, CO₂, H₂O₂, and O₂) and reduced (organic compounds, elemental sulfur) compounds are detected at the surface, the endogenic components are oxidized: water ice and the sulfate group (SO₄²⁻). The sulfate group could be present in hydrated salts [6], in frozen brines [7], and/or in sulfuric acid hydrate, which is likely to be produced from sulfate salts at the surface [8]. The endogenic origin of sulfate at the surface indirectly indicates that the ocean could be rich in sulfate [4-7].

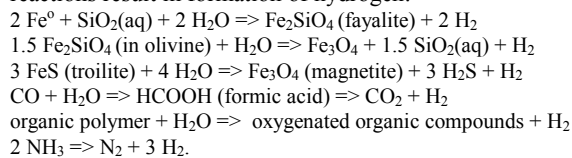
Surface CO₂ [9] could be endogenic or exogenic if it is produced by radiolysis of carbonates and/or organic compounds [10]. Although an endogenic source of elemental sulfur is speculated [4], sulfur could be produced through radiolysis of several S-bearing species [7]. Sulfur dioxide could be implanted from Io or produced by radiolysis of endogenic sulfur compounds [7,11]. The source of organic compounds [9,12] is probably cometary dust rather than the satellite's interior.

Chemistry of jovian subnebula: Thermodynamic modeling of the jovian subnebula [13] shows that iron could have condensed above ~500 K, and lower temperature phases could contain FeS, Fe₃O₄, silicates, water ice, and hydrates of CO, CH₄, and NH₃. All these solid species could have accreted on Europa, and therefore, the undifferentiated satellite could have consisted of a mixture of oxidized and reduced compounds. So far, neither CH₄ nor NH₃ have been positively detected on surfaces of Galilean satellites. This is consistent with oxidation or escape of these reduced compounds during post-accretion evolution of these satellites.

Insights from the oxidation states of Io and other solar system bodies: The predominance of SO₂ in Io's volcanic gases indicates that the mantle of this Jovian moon is oxidized and does not contain Fe-metal [14,15]. Interaction of water with Fe-metal and ferrous compounds followed by H₂ escape is suggested as a major mechanism responsible for oxidation of Io's mantle [14]. Reactions of this type could also have been responsible for oxidation of the martian mantle [16] and Venus's lithosphere [17]. Europa is a water-rich body, and water-rock alteration was unavoidable during differentiation of the satellite. Low surface gravity should have favored hydrogen escape, driving the oxidation of the silicate part of Europa. Data for the Moon, Venus, Mars, and Earth

show that the oxidation states of planetary interiors correlate with increasing amount of accreted water. Extrapolation of this trend to Europa implies that the european mantle could even be more oxidized than the terrestrial mantle. Although rapid separation of a metal core could have prevented oxidation of a significant amount of the original Fe-metal, the rest of the Fe-metal in the mantle should have been oxidized in a water-rich environment. It is even possible that an upper part of the silicate mantle is as oxidized as the hematite-magnetite buffer. In fact, formation of sulfate-rich hydrothermal fluids on Europa requires such an oxidizing environment in silicate rocks, as shown by [18].

Oxidative processes in asteroids: Aqueous alteration on parent bodies of carbonaceous chondrites (low albedo asteroids) could be considered as an analog for oxidative processes on Europa. These parent bodies were probably accreted from reduced material (ferrous silicates and sulfides, Fe-metal, and organic polymer) and cometary-type water ice containing CO and NH₃ hydrates. Subsequent heating by short-living radionuclides (e.g., ²⁶Al) led to melting of ice followed by oxidative water-rock interaction. The oxidative reactions result in formation of hydrogen:



Leaking and escape of H₂ should have led to profound oxidation of the parent bodies. That oxidation has led to formation of magnetite, ferric hydroxides, carbonates, sulfates, and several classes of oxygenated organic compounds (e.g., carboxylic acids). These minerals and compounds are observed in CI chondrites, the most oxidized group among the meteorite classes [19,20,21]. The presence of these oxidized species in CI carbonaceous chondrites implies that they have been deposited from solutions rich in sulfate, carbonate (CO₂, HCO₃⁻, CO₃²⁻), and soluble oxygenated organic species. On Europa, solutions of this type could have infiltrated to the surface and formed a primordial ocean.

Solubility of gases in the ocean: In addition to predominantly oxidized species, solutions that could have formed an early european ocean might have contained some amount of reduced (CO, H₂, CH₄) gases. Periodic disruptions of the icy shell (if any) should have led to degassing of oceanic water because of low surface gravity and the lack of a dense atmosphere. Hydrogen, CO, and CH₄, should have degassed and escaped more easily than CO₂ owing to their lower water solubility (Fig. 1) and lower masses. Preferential loss of these reduced gases from oceanic water could have contributed to the formation and maintenance of a high oxidation state in the ocean. In addition, a high pH of the oceanic water, which is typical for water-mafic rock interaction, should have favored the stability of the non-volatile aqueous forms of oxidized carbon HCO₃⁻ and CO₃²⁻. Therefore, even an early european ocean could have been rich in oxidized

carbon species.

Even if accreted, NH_3 should have been oxidized to N_2 during high-temperature differentiation, followed by N_2 degassing and escape owing to its low water solubility.

The oxidation states of C and Fe in the european ocean: The speciation of C and Fe in the sulfate-rich ocean can be explored with thermodynamic calculations for assumed conditions of the ocean and oceanic floor. Fig. 2 shows that the oxidized carbon (C^{4+}) species CO_2 , HCO_3^- , and CO_3^{2-} are stable in sulfate-rich oceanic water, depending on pH. Reduced species of carbon (methane and organic compounds) are not stable in the sulfate-rich ocean, but could be stable in pore waters of igneous rocks at the oceanic floor, along with H_2S or HS^- .

Analysis of the $f\text{H}_2$ -pH stability diagram for Fe species (Fig. 3) shows that even in a sulfate-rich ocean, aqueous Fe is predominantly present as Fe^{2+} . Solid ferric species (e.g., goethite) can be present in chemical sediments in equilibrium with oceanic Fe^{2+} , as well with sulfate and carbonate ions.

In contrast to ferric oxide(s) in ocean sediments, even hematite-magnetite bearing igneous rocks appear to be more reduced than oceanic sulfate-carbonate water (see Fig. 2). It follows that freshly exposed igneous rocks should be in oxidation-reduction disequilibrium with seawater. If so, Fe^{2+} in silicates and magnetite could be oxidized to ferric hydroxides, and oceanic oxidized species could be reduced to H_2S , HS^- , and CH_4 . However, at low temperature these oxidation-reduction reactions are slow, and the presence of igneous rocks at the cold oceanic floor should not significantly affect the mass of oceanic sulfate, and therefore the oxidation state of the ocean. Nevertheless, disequilibrium between an oxidized sulfate-carbonate oceanic water and igneous rocks provides chemical energy that could support several types of microbial communities in the vicinity of the oceanic floor.

Summary: Observational data on the european surface, insights from Io and carbonaceous chondrites, and physical-chemical constraints suggest that Europa has an oxidized Fe-metal free mantle and an oxidized sulfate-carbonate rich ocean. Sulfate-carbonate oceanic water should be out of equilibrium even with oxidized igneous rocks at the oceanic floor, providing energy sources for anaerobic life.

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Fig. 1. Henry's law constants for gases at pressures representing an ocean on Europa calculated with data from [23,24]. Reduced gases (H_2 , CO , and CH_4) are much less water-soluble than CO_2 .

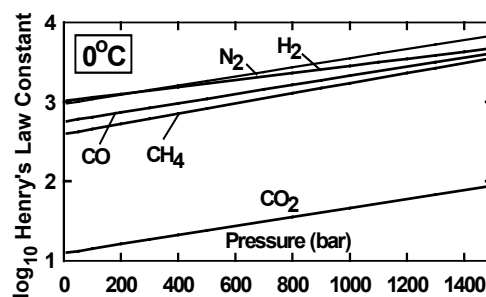


Fig. 2. Speciation of aqueous sulfur (solid lines) and carbon (dashed lines) species in the vicinity of the oceanic floor on Europa (0°C, 1375 bar). The lines denote boundaries where activities of two species are equal.

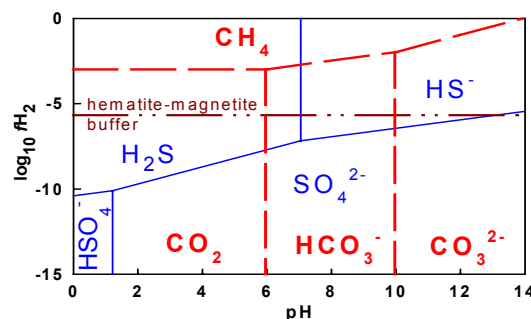


Fig. 3. Stability of goethite ($\alpha\text{-FeOOH}$) in the vicinity of the oceanic floor on Europa (0°C, 1375 bar, $a_{\text{Fe}} = 10^{-3.6}$). The "ocean" box could represent $f\text{H}_2$ -pH conditions at the oceanic floor, if goethite is present in chemical sediments.

