

**CHEMISTRY OF A PRIMORDIAL OCEAN ON EUROPA.** M. Yu. Zolotov<sup>1</sup>, M. L. Krieg<sup>1</sup>, E. L. Shock<sup>1,2</sup>, and W. B. McKinnon<sup>3</sup>, <sup>1</sup>Department of Geological Sciences, <sup>2</sup>Department of Chemistry and Biochemistry, Arizona State University, Tempe, Arizona 85287, <sup>3</sup>Department of Earth and Planetary Sciences, Washington University, St. Louis, MO 63130. E-mails: zolotov@asu.edu, michelle.krieg@asu.edu, eshock@asu.edu, mckinnon@wustl.edu.

**Introduction:** Jupiter's moon Europa is a differentiated body that consists of a Fe-rich core, a silicate mantle, and a water shell, which could contain an ocean [1]. The presence of sulfate-bearing compounds on the moon's icy surface has been interpreted in terms of frozen oceanic water [2]. However, evaluations of oceanic chemistry from surface observations are limited because of radiolysis [3] and the implantation of chemical species from Io and interplanetary sources. Although the oceanic composition remains unknown, attempts have been made to consider the origin and evolution of oceanic chemistry [4-7]. In the framework of this strategy, we develop physical-chemistry models for fluids that could have formed a primordial ocean.

**Bulk composition of Europa:** According to "gas-starved" accretion models, the Galilean satellites formed from a mixture of water ice and a rocky component that accumulated from the surrounding solar accretion disc [8]. The bulk composition of the rocks delivered from the Sun's side was likely to be solar and can be represented by CI/CM carbonaceous chondrites [9,6]. In fact, visible and near-infrared reflectance spectra of these meteorites are somewhat similar to spectra of P and D classes of asteroids that are abundant in the outer asteroid belt and Trojan groups. The material accreted from the outer part of the solar system would not have been processed in the solar nebula and could consist of presolar mineral grains and abundant organic matter. Although the bulk composition of that material is unknown, it could also be solar. Accretion of solids as dust, small particles and small planetesimals implies that minerals would not necessarily have been aqueously altered, unlike larger bodies (asteroids). Therefore, Europa could have accreted from reduced and anhydrous minerals (Fe-Ni metal, FeS, Mg-, and Ca-silicates, feldspars, Ca-Al-oxides, presolar grains), abundant organic compounds, and water ice.

**Formation of a primordial ocean:** 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 [10]. Subsequent warming of the ice-rock mixture in the moon's interior driven by radioactive decay resulted in melting of ice and outward migration of water. Although relative contributions of these two ocean-forming processes are not known [6], the primordial ocean would have a composition consistent with its being formed through low-temperature aqueous alteration of rocks, often in the presence of partially melted water ice. Dissolution of minerals and organic species, release and synthesis of gases, and precipitation of secondary minerals all affected solution chemistry. Competitive hydration and oxidation could have led to formation of serpentine, saponite, magnetite, chromite, tochilinite, phosphates and other phases that typically form during aqueous alteration of parent bodies of chondrites (asteroids) [11]. Degassing and escape of H<sub>2</sub>, which forms through oxidation by water, caused oxidation of rocks and fluids [12,7]. Interaction of water with presolar aromatic polymer with aliphatic and S-, N-, O-bearing groups led to partial oxidation and

release of O-, N-bearing compounds (e.g., carbonate species, methanol, formic and other carboxylic acids, amino acids) into upward moving solutions.

The upward migration of solutions caused their sequential interaction with surrounding rock fragments. It follows that fluid-rock interaction in the uppermost rock layers determined the composition of ocean-forming fluids. These rocks would be the most altered because all upwelling fluids should have passed through them. If a primordial ocean formed during upward migration of fluids, the water/rock mass ratio (*W/R*) for a 10-km thick layer can be estimated as  $Europa\ H_2O\ mass/Mass\ of\ rocks = (2.5-4.4) \times 10^{21} kg / 8 \times 10^{20} kg = 3.0 - 5.4$ . In reality, the *W/R* rock ratio could differ from this estimation. On the one hand, intensive ice melting during rapid accretion and water consumption through oxidation and hydration deeper in the interior would have led to lower *W/R* ratios in the upper rock horizons. On the other hand, incomplete alteration of large mineral grains and rock fragments would correspond to larger local *W/R* ratios. In addition, the upper rock horizons would be affected by interaction with oceanic water. Some interaction with oceanic water can occur while rocks remain permeable at pressures up to ~3 kbar [13] corresponding to 40-80 km below the ocean floor.

**Modeling aqueous chemistry:** The effects of alteration of sub-oceanic rocks on the composition of ocean-forming fluids were evaluated with chemical equilibrium models in the O-H-Mg-Fe-Ca-Si-Al-C-P-S-Cr-Na-K-Cl-Mn-Co-Ni system. The bulk-water-free chemistry of the Orgueil CI carbonaceous chondrite [14] was selected to exemplify Europa's nominal rock composition. For comparison, several other chondritic compositions were also considered. In particular, the composition of the Semarkona meteorite [14] was used to represent LL type ordinary chondrites proposed for Europa's rocks in [15]. The calculations were performed for 0 °C, pressures from 0.2 to 5 kbar, and *W/R* ratios of 1-10. We used the GEOCHEQ code [16] that includes thermodynamic properties of 123 one-component solids, 23 solid solutions, a non-ideal gas solution and a non-ideal aqueous solution (98 species). Formation of CH<sub>4</sub> and other light hydrocarbons was suppressed because of inhibition of their formation at low temperatures.

**Results and discussion:** We evaluated concentrations and activities of organic and inorganic aqueous species, fugacities and concentrations of H<sub>2</sub>, H<sub>2</sub>O, H<sub>2</sub>S, CO<sub>2</sub>, and CO in the gas phase, and amounts and volumes of minerals that coexisted with ocean-forming fluids. The fluids are extremely reduced, non-saline and alkaline with pH of 12.5-13.5. The major solutes are H<sub>2</sub>, Na<sup>+</sup>, OH<sup>-</sup>, Cl<sup>-</sup>, and K<sup>+</sup>, as shown by the example in Table 1. Ocean-forming solutions are depleted in Mg which precipitates in Mg phyllosilicates (e.g., serpentine). Sulfur is not abundant and is mostly in HS<sup>-</sup>. Small concentrations of HS<sup>-</sup> are caused by low solubility of troilite. Sulfate ion is not present. The most abundant carbon species is methanol, and concentrations of CO<sub>3</sub><sup>2-</sup> and

formate ( $\text{HCOO}^-$ ) ions are 3-5 orders of magnitude lower. The resulting ocean would not have been saline, unless subjected to severe freezing/evaporation.

**Table 1.** Molal concentrations, mol/(kg  $\text{H}_2\text{O}$ ), of major solutes in ocean-forming fluids at 0 °C, 2 kbar, water/rock mass ratio of 4, and the bulk composition of the  $\text{H}_2\text{O}$ -free Orgueil CI carbonaceous chondrite. The salinity of solution (without dissolved  $\text{H}_2$ ) is 4.5 gram/liter.

$\text{H}_2$	$2.5 \times 10^{-1}$	$\text{CaOH}^+$	$2.8 \times 10^{-5}$
$\text{Na}^+$	$9.0 \times 10^{-2}$	$\text{HS}^-$	$8.6 \times 10^{-6}$
$\text{OH}^-$	$8.6 \times 10^{-2}$	$\text{HMnO}_2^-$	$5.8 \times 10^{-6}$
$\text{Cl}^-$	$7.4 \times 10^{-3}$	$\text{MnO, aq}$	$2.7 \times 10^{-6}$
$\text{K}^+$	$4.7 \times 10^{-3}$	$\text{MnOH}^+$	$1.3 \times 10^{-6}$
$\text{HFeO}_2^-$	$4.1 \times 10^{-3}$	$\text{CaCl}^+$	$9.7 \times 10^{-7}$
$\text{NaOH, aq}$	$1.4 \times 10^{-3}$	$\text{Methanol, aq}$	$4.7 \times 10^{-7}$
$\text{Ca}^{2+}$	$1.0 \times 10^{-3}$	$\text{MnO}_2^{2-}$	$2.9 \times 10^{-7}$
$\text{NaHSiO}_3, \text{aq}$	$1.3 \times 10^{-4}$	$\text{FeO, aq}$	$1.5 \times 10^{-7}$
$\text{NaCl, aq}$	$4.1 \times 10^{-5}$	pH	13.0
$\text{KOH, aq}$	$3.6 \times 10^{-5}$	Ionic strength	0.1

In the range of  $W/R$  ratios of 1-10, the composition of solution is relatively uniform, while fluids are diluted at higher  $W/R$  ratios. At 0.2-5 kbar, the effect of pressure on aqueous chemistry is also modest. With increasing pressure, concentrations and activities of  $\text{H}^+$ ,  $\text{NaHSiO}_3, \text{aq}$ , and Ca and Fe solutes increase, the pH decreases with pressure (0.34 per kbar), and concentrations of  $\text{HS}^-$  and  $\text{H}_2, \text{aq}$  (> 1 kbar) decrease with pressure. Rock composition has only minor effects on solution chemistry because the latter is controlled by formation of secondary minerals, which are similar for different chondritic analogs.

Aqueous oxidation of rocks by  $\text{H}_2\text{O}$  leads to  $\text{H}_2$ -rich solution and gas. In solution, typical concentrations of  $\text{H}_2, \text{aq}$  are 0.03-0.26 mol/(kg  $\text{H}_2\text{O}$ ), and the lower value corresponds to 5 kbar. At 2 kbar, concentration of dissolved  $\text{H}_2$  is ~0.25 mol/(kg  $\text{H}_2\text{O}$ ),  $\log f_{\text{H}_2} = 3.9$  (at the  $\text{H}_2$  fugacity coefficient of 4.0) and  $\log f_{\text{O}_2} = -97$ . The activity ratios of redox pairs are:  $\text{HS}^-/\text{SO}_4^{2-} = 10^{32}-10^{35}$ ,  $\text{Fe}^{2+}(\text{tot.})/\text{Fe}^{3+}(\text{tot.}) = 10^8-10^9$ ,  $\text{H}_2\text{COH}/\text{CO}_3^{2-} = 10^3-10^5$ . In the gas phase, the  $\text{H}_2\text{O}/\text{H}_2$  mole ratio is  $4 \times 10^{-5}$  to  $1.4 \times 10^{-4}$  for 1 kbar and 5 kbar, respectively. Mole ratios of  $\text{H}_2\text{S}$ ,  $\text{CO}_2$  and  $\text{CO}$  are below  $10^{-12}$ . The gas could have accumulated beneath an icy shell from which it could periodically escape. Separation and escape of  $\text{H}_2$ -rich gas would have made the ocean more oxidized than ocean-forming fluids and altered rocks.

Major secondary minerals are hydrated and moderately oxidized phases (serpentine, saponite, chlorite, chromite, whitlockite).  $\text{Fe}^0$ -metal is only partially oxidized and a Fe-Ni alloy remains stable. Magnetite may form at early stages of alteration at elevated  $W/R$  ratios; ferric silicates (e.g., andradite) can be stable otherwise. Iron sulfide (troilite) is stable. Tochilinite can also form, but its stability cannot be evaluated precisely. Sulfates and carbonates do not form. Some precipitation of minimally soluble minerals (e.g., sulfides) can also occur at the oceanic floor where upwelling fluids mix with oceanic water.

Polyaromatic compounds remain mainly unaffected and only a small portion of the original organic matter can be altered to alcohols and carboxylic acids. Water-soluble organic species may be released and/or formed through altera-

tion of S-, O-, N-bearing chains. Although carbonate species may equilibrate with methanol and formate [17], equilibria among organic compounds was unlikely to have been attained.

Freezing and/or evaporation of primordial oceanic water would have led to further degassing and precipitation of minerals at the oceanic floor. Owing to the deficiency of alkalis and Cl in Europa's water shell compared to Earth [5], precipitation of Na and K chlorides can only occur through freezing and/or evaporation.

*Astrobiological applications:* Although escape of  $\text{H}_2$  favored oxidation of solutions and rocks, abiotic redox re-equilibration is unlikely to have occurred at low temperatures. Redox disequilibria may support metabolic oxidation of sulfides, ferrous iron species and organic carbon. The maximum amounts of chemical energy and nutrients would have been available in the lower parts of the ocean where rocks were in contact with  $\text{H}_2$ -depleted water and where upwelling fluids were released. It is possible that amino acids formed through partial oxidation of N-bearing organic compounds (amine groups) and provided building blocks and nutrients for potential life.

**Summary:** The composition of Europa's primordial ocean is likely to have been controlled by low-temperature water-rock reactions at pressures below ~3-5 kbar. Ocean-forming fluids and the ocean were cold, reduced, alkaline, Na-, Cl-rich but not saline, depleted in Mg, sulfides and sulfates, and departed from redox equilibria because of  $\text{H}_2$  gas separation and escape.

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