CHEMICAL EVOLUTION OF AN EARLY OCEAN ON EUROPA: A KINETIC-THERMODYNAMIC MODELING.

M. Yu. Zolotov[1] and M. V. Mironenko[2], [1]School of Earth and Space Exploration, Arizona State University, Tempe, Arizona 85287-1404, e-mail: zolotov@asu.edu. [2]Vernadsky Institute of Geochemistry and Analytical Chemistry, Russian Academy of Sciences, 19 Kosygin Str., Moscow 119991, e-mail: mironenko@geokhi.ru.

Introduction: A release of heat from radioactive decay and tidal dissipation on Jupiter's moon Europa could have maintained an existence of a water ocean throughout history [1]. Although the oceanic composition remains unknown, it could be evaluated by modeling of origin and evolution of water-rock interactions in the satellite's interior [3-6]. Here, we evaluated the timing of water-mineral chemical reactions that drove an early evolution of a primordial ocean.

Formation of chemical composition of an early ocean (the concept): Europa was accreted as a mixture of water ice, a polycyclic aromatic polymer, and a reduced anhydrous material of solar composition. Melting of ice in the outer part of the satellite could have occurred at late stages of accretion [7]. Inside the body, release of radioactive heat also caused melting of ice and accumulation of liquid water in an ocean. The ocean was likely to be covered by an icy shell, which was often disrupted by impacts. The composition of oceanic water was controlled by dissolution and precipitation of minerals in a layer of permeable rock beneath the ocean [6,8]. Water-rock reactions led to hydration and oxidation of primary rocks. H_2 production in oxidation reactions was followed by its upward migration, separation into the gas phase, and escape [5,6,8]. An accumulation of H_2 gas beneath the icy shell and its escape drove oxidation beneath the oceanic floor.

Coupled kinetic-thermodynamic models: Aqueous alteration of a rocky suboceanic material was investigated through numerical modeling. The model includes dissolution kinetics of primary and secondary solids, the oxidation rate of Fe-rich metal by H_2O, as well as chemical equilibration among solutes, precipitates, and dissolved gases. In the model, secondary phases form through dissolution of primary minerals, all species in aqueous solution are in equilibrium, and secondary precipitation is controlled by solubilities of minerals. A thermodynamic block of the model is based on the GEOCHEQ code [9], which uses the Gibbs free energy minimization method to calculate equilibria.

Alteration was modeled for 0°C and 2 kbar in the system H-O-Fe-Mg-Ca-Al-Si-Na-K-S-Cl-C that was either closed or open with respect to H_2 gas. Closed system models represent conditions when H_2 is not allowed to leave the system (e.g., alteration beneath impermeable icy shells or rock layers). Open system calculations are used to model H_2 removal. For the open system, fugacity (*f*) of H_2 was 127 bar, which corresponds to the conditions of gas separation at the bottom of ~10 km thick icy shell. The rock composition was assumed to be solar and the original mineralogy was represented by Fe-metal, forsterite, enstatite, diopside, feldspars, and troilite. Pyrene ($C_{16}H_{10}$) was used as a proxy for polyaromatic compounds. In nominal models, primary and secondary mineral grains (1 μm in diameter) were entirely exposed to the solution. The calculations were performed for the water/rock mass ratio of unity, which corresponds to interaction of a 100 km thick ocean with the underling rock layer of ~30-40 km thick. Freshly melted water was represented by 0.044 molal (mol per kg H_2O) HCl solution [c.f. 10]. The solution also contained CO (10^{-5} molal) added to represent water-soluble carbon compounds. Formation of CH_4 and other light hydrocarbons was suppressed because of the inhibition of their formation at low temperatures.

Results and discussion: The closed system modeling shows an increase in fH_2 through oxidation of Fe-metal, which quickly leads to equilibration between metal and magnetite at $\log fH_2 = 3.9$,

$$3Fe^o + 4H_2O(liq.) = Fe_3O_4 + 4H_2(aqueous/gas) \quad (1).$$
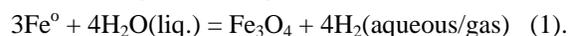
Further oxidation does not occur unless H_2 is allowed to leave the system. Alteration of silicates leads to Mg-rich phyllosilicates. The closed system scenario is not consistent with sulfate-bearing composition of the ocean [11]. In addition, a low thickness of the icy shell in geologic history (3-70 km [1]) should have not prevented H_2 escape.

Open system models demonstrate rapid oxidation of Fe^o metal according to reaction (1). Fe-rich metal, pyroxenes, and feldspars are completely altered during first ~10^3 yr. Forsterite dissolves by ~2×10^4 yr, and abundances of troilite and pyrene do not change much during at least 10^4yr (Fig. 1a). At early stages of alteration, magnetite and greenalite (Fe-serpentine) are major secondary phases (Fig 1b). At later stages, significantly altered rocks consist of Mg-Fe-serpentine, Fe-chlorite, brucite, portlandite, calcite, Ca-K-saponite, magnetite, and mostly unaltered troilite and polyaromatic compound(s). Each time, rock mineralogy consists of secondary minerals equilibrated with solution, previously precipitated unstable phases, and unaltered primary phases. Total volume of solids increases in time, while the amount of solution decreases because of hydration and H_2 removal (Fig. 1c).

Rapid neutralization of the original acidic fluid led to an alkaline solution with pH ~12-13.5. The solution
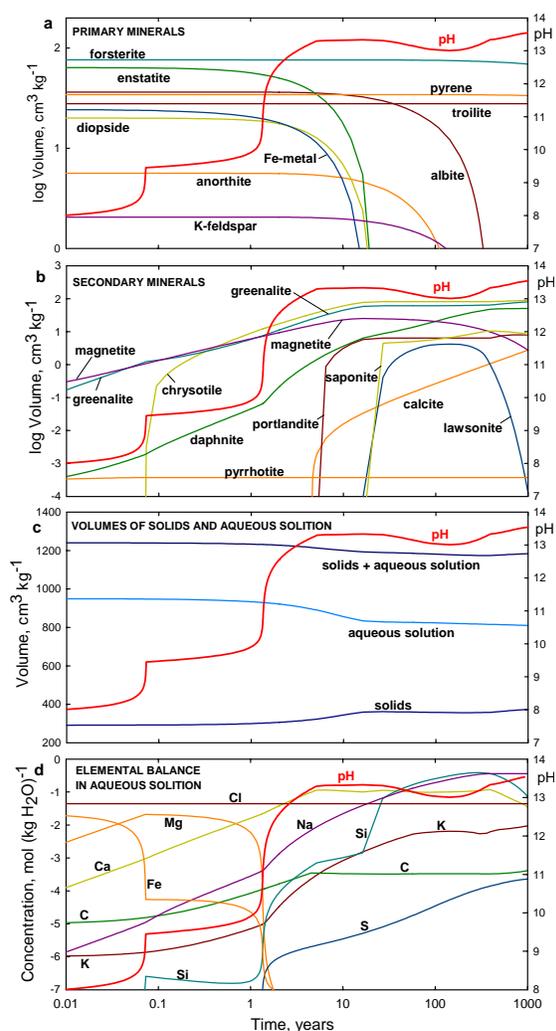
Figure 1. Temporal changes in mineralogy and aqueous chemistry during early evolution of Europa's ocean at 0°C and 2 kbar total pressure. The system is open with respect to H_2 (fH$_2$ = 127 bar). Water-rock mass ratio = 1.

becomes more saline in time and the ionic strength reaches ~0.7 by 10^4 yr. Variations in pH and solution composition were affected by precipitation of secondary phases (Figs. 1b and 1d). At very early low-pH stages, Cl^-, Fe^{2+}, Mg^{2+}, and Ca^{2+} were the dominant solutes. At advanced alkaline stages, Na^+, Ca^{2+}, K^+, Cl^-, OH^-, and H_2 dominate (Table 1). Carbon species are mostly presented by methanol, CO_3^{2-}, and formate. Note that abundance and speciation of aqueous C species are limited by inefficient dissolution of primary organics and by low rates of redox reactions. Sulfur is in sulfide form (HS$^-$ + S^{2-}) and its concentration increases with pH. Sulfate species are not present.

The timescales shown in Fig. 1 represent a fast evolution scenario. Alteration could have occurred several orders of magnitude slower due to large grain sizes and low permeability of rocky materials. Note that the change in rock volume during hydration (Fig. 1c) could have decreased effective surface area and rock permeability.

Summary: The composition of an early ocean on Europa evolved dramatically during the first 10^4-10^5 yr after ice melting. Rapid oxidation of Fe-metal, H_2 escape, and pervasive alteration of micron-size mineral particles led to extremely alkaline oceanic water that slowly approached equilibrium with underlying altered rocks. Note that slow dissolution of troilite and polyaromatic compounds favored their survival among secondary minerals.

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Table 1. Concentrations, mol/(kg H_2O), of major solutes in oceanic water 1000 years after ice melting. 0°C, 2 kbar, water/rock = 1, fH$_2$ = 127 bar.

Na^+	3.4×10^{-1}	Cl^-	5.2×10^{-2}
$NaHSiO_3$,aq	7.2×10^{-2}	$HSiO_3^-$	4.5×10^{-3}
NaOH,aq	1.7×10^{-2}	HS^- + S^{2-}	2.7×10^{-4}
K^+	1.1×10^{-2}	CO_3^{2-}	1.7×10^{-4}
KOH,aq	2.7×10^{-4}	H_2,aq	3.9×10^{-3}
Ca^{2+}	3.5×10^{-2}	Methanol, aq	1.0×10^{-6}
$CaCO_3$,aq	3.3×10^{-4}	Formate	1.5×10^{-7}
$CaOH^+$	2.5×10^{-3}	pH	13.6
OH^-	3.6×10^{-1}	Ionic strength	0.46