

OCEANIC COMPOSITION ON EUROPA: CONSTRAINTS FROM MINERAL SOLUBILITIES. M. Yu. Zolotov, School of Earth and Space Exploration, Arizona State University, Tempe, Arizona 85287-1404. E-mail: zolotov@asu.edu.

Introduction: Although geological observations of the Europa's surface [1] and Galileo magnetometer data [2] are consistent with a water ocean beneath the ice shell, the oceanic composition remains to be evaluated. The detection of sulfate (in Na-Mg salts and/or sulfuric acid hydrate [3-5]) in disrupted surface areas implies endogenic origin of sulfate. In fact, formation of abundant surface sulfate through radiolysis of oceanic sulfides (HS^- and H_2S) is unlikely because sulfides cannot be rich in oceanic water that contacts with Fe-bearing rocks [6]. Recent detection of CO_2 in sulfate-bearing disrupted areas indicates an endogenic (oceanic?) source of carbon [7]. The CO_2 could have been trapped through degassing of oceanic water during disruptions of the ice shell and/or produced via radiolysis of endogenic organic species. Na and K in the Europa's atmosphere could originate from endogenic surface salts and reflect oceanic composition [8-10], as well as represent iogenic plasma and neutral atom torii [11].

Accumulation of alkalis, C and sulfate species in the ocean is consistent with the formation of oceanic composition through interaction of water with accreted rocks and organic matter. Shortly after ice melting in the interior, halogens (Cl, Br, I) and some alkalis could have been accumulated in a primordial ocean. Formation of CO_2 , soluble O-bearing organic compounds (acids, alcohols), and many other organic species needed high-temperature (T) processing of accreted organic polymers. Anoxic oxidation of sulfides to sulfates also required hydrothermal conditions and H_2 escape [6,12]. Carbon and sulfate species could have been delivered into the ocean early in history, and surface observations may not reflect current hydrothermal activity. Here, mass balance constraints and water-rock type chemical equilibria are invoked to evaluate oceanic composition on today's Europa.

Major factors affecting oceanic composition: The composition of present-day ocean would reflect early accumulations of Na, K, Cl, Br, I, S and C species, as well as subsequent water-rock interactions, gas losses, and freezing, thawing and disruptions of the ice shell. Concentrations of Na and especially K could have been affected by ion exchange with clay minerals and depend on the amount of clays in contact with oceanic water. Abundances of Cl, Br and I could be the same as in a primordial ocean. Saturation with respect to alkali chlorides requires significant freezing and may not characterize present-day ocean. Throughout history, abundances of inorganic C species could have been influenced by CO_2 escape through openings in the ice shell and precipitation of carbonates. Sulfate content was affected by precipitation of low-soluble (Ca, Ba) sulfates. Oceanic abundances of Ca, Mg, Fe, Ni, Mn, Cr, Ti, P, etc. could be controlled by aqueous-solid equilibria in permeable rocks and/or chemical sediments. However, saturation with respect to

low-soluble Mg/Na sulfates may not be consistent with a 100 km thick ocean.

Modeling approach: It was assumed that (1) the majority of Cl was extracted from accreted rocks and/or HCl hydrates and remains in the ocean; (2) concentrations of other elements and oceanic pH are controlled by solid-aqueous equilibria in suboceanic rocks/sediments. Water-rock type equilibria were calculated in the O-H-C-S-Cl-Na-K-Mg-Fe-Ca-Si-Al system. Calculations were performed with the GEOCHEQ code [13] that includes properties of one-component solids and non-ideal solid, gas and aqueous solutions. The bulk H_2O -free composition of the Orgueil CI carbonaceous chondrite and basalt were used to exemplify rocks. Formation of CH_4 was suppressed because of low- T inhibition of its formation. Water/rock mass ratio (W/R) and fugacities (f) of H_2 and CO_2 were free parameters. $f\text{H}_2$ represented the redox state of the ocean-rock system and $f\text{CO}_2$ was used to signify bulk C content.

Chemistry of a sulfate-rich ocean: Equilibrium calculations demonstrate that a sulfate ocean could also be

Table 1. Activities of major species in a sulfate-rich Europa's ocean equilibrated with a chondritic rock*.

H_2O	0.96	MgCl^+	6.5E-3
MgSO_4	0.65	Ca^{+2}	5.1E-3
Na^+	0.14	NaCl	1.7E-3
Cl^-	0.12	CaCl^+	2.0E-4
SO_4^{-2}	8.6E-2	MgCO_3	5.6E-5
Mg^{+2}	8.1E-2	HCO_3^-	4.3E-5
CaSO_4	3.0E-2	MgHCO_3^+	3.3E-5
NaSO_4^-	2.0E-2	CaCl_2	1.3E-5

* The rock is presented by the H_2O -free Orgueil CI chondrite, $W/R = 1$, 10% of rock's C reacted, $\log f\text{H}_2$ is set to -9; $T = 0^\circ\text{C}$ and $P = 1375$ bar. Calculated pH is 8.4 and the mineral assemblage consists of Mg-Na-Ca-K-saponite, goethite, dolomite, gypsum, pyrite and chrysotile.

rich in Mg solutes (Table 1, Figs. 1 and 2). Oceanic water rich in Mg sulfate requires at least moderately oxidized conditions ($\log f\text{H}_2 < \sim -9$). These $f\text{H}_2$ values imply significant H_2 escape from a primordial reduced Na-Cl [14] ocean. Na and Cl solutes are the next most abundant species. Although concentrations of sulfate, Na and Cl solutes are not strongly affected by mineral solubility, some effects are related to reactions with clays (saponite, montmorillonite) and gypsum. Oceanic abundance of Mg species is affected by solubility of Mg-phyllsilicates (serpentine, saponite, montmorillonite, sepiolite) that changes with the sulfate content. Concentrations of Ca, Fe, K, Si, inorganic C solutes and aqueous sulfides (HS^- , H_2S) are controlled by solubilities of some of the following secondary minerals: serpentine, saponite, montmorillonite, silica, goethite, pyrite, gypsum and carbonates.

High concentrations of sulfate and Mg in the ocean imply a large amount of altered chondrite-type rocks ($W/R < \sim 1$). At least several tens of km of rocks could have been involved to account for a 100 km thick sulfate ocean. For S-depleted basalts, much larger rock thickness is needed.

In an ocean-rock system rich in inorganic C, serpentine, saponite, goethite, and gypsum could be absent from suboceanic assemblages, while Mg, Ca, and Fe carbonates, silica and montmorillonite are abundant (Fig. 2). Formation of magnesite in a C-rich ocean could be a factor that decreases concentrations of Mg and sulfate species (Fig. 2). A high content of inorganic C (and high fCO_2) may not be consistent with sulfate-rich ocean, and a high sulfate content may indicate some CO_2 escape (in addition to H_2 escape). Note that an amount of inorganic C is limited by separation of CO_2 gas at the ice-ocean boundary (Fig. 2). Thinning or disruptions of the ice shell decrease the fCO_2 value at which degassing may occur.

Calculated pH of a sulfate ocean varies from slightly alkaline to moderately acid (neutral pH is ~ 7.2). Lower pH corresponds to higher fCO_2 and lower fH_2 values.

A sulfate-less ocean is a NaCl solution in which carbonate species (HCO_3^- , CO_3^{2-}) could also be abundant (Figs. 1, 2, [14]). Reduced S species are not abundant owing to low solubility of Fe sulfides. Low concentrations of Mg solutes are accounted for by low-soluble serpentine in rocks. A NaCl type ocean may not be consistent with observations of surface sulfates.

Summary: Mg, Na and Cl solutes could be major constituents in a sulfate-rich ocean on Europa. Such an ocean implies hydrothermal activity earlier in the history and a significant escape of H_2 and, possibly, C gases. Goethite, pyrite, phyllosilicates, silica phases, gypsum and carbonates could be present in permeable suboceanic rocks/sediments.

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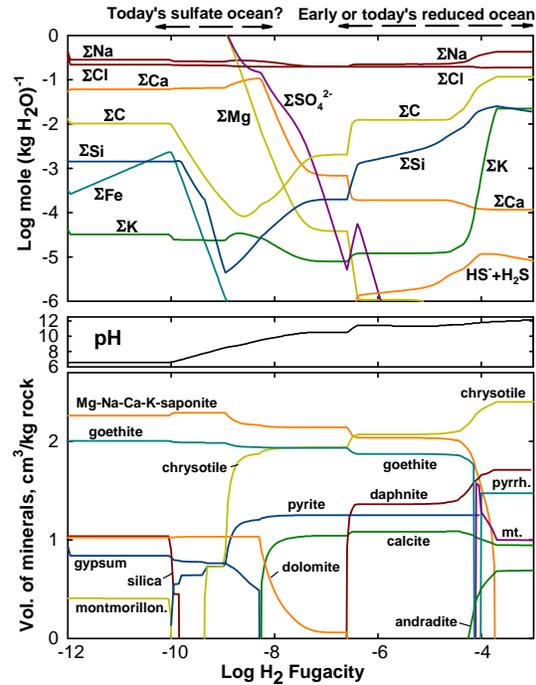


Fig. 1. Modeled Europa's oceanic composition, pH, and secondary rock mineralogy as functions of fH_2 at $0^\circ C$, 1375 bar, $W/R = 1$ and 10% of reacted C in the carbonaceous chondrite type rock. Mt., magnetite; pyrrh., pyrrhotite.

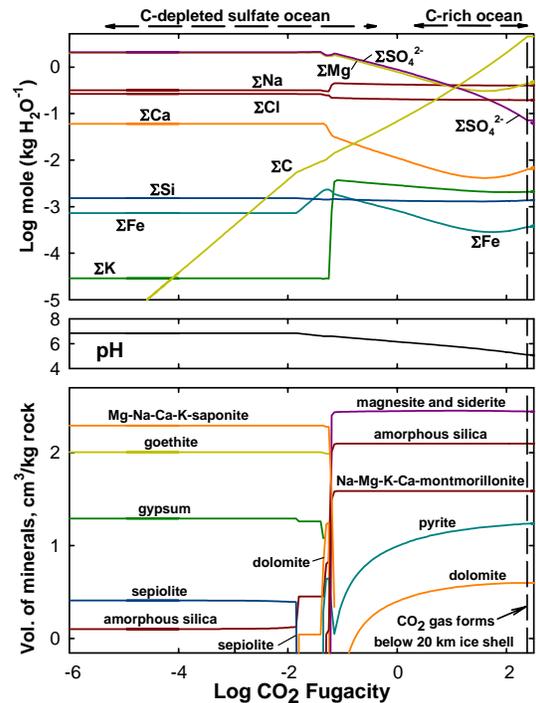


Fig. 2. Modeled composition of a sulfate-rich Europa's ocean, pH, and suboceanic rock mineralogy as functions of fCO_2 at $0^\circ C$, 1375 bar, $\log fH_2 = -10$ and $W/R = 1$.