

**THE SPECIATION OF SULFUR IN AN OCEAN ON EUROPA.** 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:** The interpretation of images and magnetic measurements obtained with the *Galileo* spacecraft indirectly indicate the existence of a global electrolytic water ocean beneath the icy shell on Europa [1,2]. Although the oceanic composition is unknown, observational data, theoretical models and cosmochemical speculations show that sulfur species could be among the major aqueous solutes. Ultraviolet spectra of the Europa's surface show the presence of sulfur compounds that are, at least in part, of endogenic origin [3,4]. The close association of sulfur-bearing non-water ice material with surface disrupted zones strongly indicates an endogenic origin of the sulfur compounds [5,6]. *Galileo* near-infrared spectra of the non-icy surface material are consistent with the presence of the sulfate functional group ( $\text{SO}_4^{2-}$ ) in hydrated salts [6], frozen brines [7], and/or sulfuric acid hydrate [8]. Sulfate salts and frozen brines could have originated from the ocean [5-7] but sulfuric acid hydrate may be a product of radiolysis of endogenic sulfate at the surface [8]. Brownish coloration of the non-icy material could be caused by elemental sulfur formed through radiolysis of other sulfur species [8-10] or even supplied with oceanic water [11]. Cosmochemical considerations [5, 11-13] and experimental modeling [14] show that sulfur should be a major element extracted from a carbonaceous-chondritic type material, which may represent a primordial euroman mantle. Both aqueous leaching from carbonaceous chondrite-type material and aqueous oxidation of chondritic sulfides during differentiation of Europa could have led to the formation of a sulfate-rich ocean [11-16].

In addition to sulfate, which could be the major sulfur species in the oceanic water, other sulfur-bearing ions, neutral solutes, and solid compounds could be present in the ocean and chemical sediments. Stabilities and abundances of sulfur species are affected by temperature, pressure, bulk concentration of sulfur, concentrations of non-sulfur species, and the ionic strength of oceanic water. Here we use thermodynamic calculations to analyze the speciation of aqueous and solid sulfur species in the present Europa's ocean. In particular, we evaluate conditions at which elemental sulfur and iron sulfides can exist at the oceanic environment.

**Thermodynamic calculations:** As the first step, we assumed that aqueous and solid sulfur species in oceanic water and chemical sediments are in equilibrium with each other. Although this might not be the case for all compounds, this assumption allows us to explore the speciation of sulfur by considering individual chemical equilibria. Activity diagrams were generated with equilibrium constants calculated with the program SUPCRT92 [17] using data from [18,19]. The lines between fields represent equal activities of those species. The activity diagrams were calculated in coordinates of pH ( $-\log a\text{H}^+$ ), fugacity of hydrogen ( $f\text{H}_2$ ), which expresses reduction-oxidation conditions, and activities of ions. The calculations were done for  $0^\circ\text{C}$  and 1375 bar, which may represent ocean floor conditions at the depth of  $\sim 100$  km below the satellite's surface.

**Results and discussion:** At  $0^\circ\text{C}$  and 1375 bar, stable forms of sulfur in the S- $\text{H}_2\text{O}$  system are solid elemental sulfur ( $\text{S}^0$ ), aqueous (aq)  $\text{H}_2\text{S}$ , and the ionic species  $\text{HS}^-$ ,  $\text{SO}_4^{2-}$ , and  $\text{HSO}_4^-$ . Both pH and the oxidation state ( $f\text{H}_2$ ) control the speciation of the system, as shown in Fig. 1. If sulfate dominates over  $\text{H}_2\text{S}$  and  $\text{HS}^-$  in Europa's water, the equilibrium oceanic  $\log f\text{H}_2$  value is less than  $-6$  at pH = 12 and less than  $-10$  at pH = 2. At pH = 7.18, which corresponds to neutrality at  $0^\circ\text{C}$  and 1375 bar, the equilibrium  $f\text{H}_2 < 10^{-7.15}$ . Inside the field where sulfate dominates, the  $[\text{SO}_4^{2-}]/[\text{HS}^- + \text{H}_2\text{S}(\text{aq})]$  activity ratio changes with  $f\text{H}_2$  and pH, as shown in Fig. 2. At a fixed  $f\text{H}_2$  value, higher pH corresponds to higher sulfate/sulfide ratios.

Solid elemental sulfur is stable at acidic pH and moderate  $f\text{H}_2$  values (see Fig. 1). In addition, the stability of elemental sulfur depends on the total amount of sulfur in the system. Higher amounts of total sulfur enlarge the stability field of elemental sulfur. Fig. 3 shows the maximum pH and the total concentration of sulfur compounds ( $\sum \text{S}$ ) that favor the stability of native sulfur at  $0^\circ\text{C}$  and 1375 bar. At pH  $> 0$ , native sulfur is stable if  $\sum \text{S} > 10^{-5.31}$ . Can we expect elemental sulfur in oceanic sediments on Europa? Formation of the sulfate-rich Europa' ocean through aqueous alteration of the silicate mantle may have required non-acidic conditions [16]. Hydrothermal alteration of basic and ultrabasic rocks also leads to non-acidic fluids. It follows that if the ocean represents these cooled fluids, neutral or alkaline conditions are possible. However at higher pH, the stability of native sulfur requires a significant bulk abundance of sulfur in the  $\text{H}_2\text{O}$ -S system. The bulk abundance of sulfur could be limited by precipitation of Ca sulfates (e.g., gypsum) [13] and/or pyrite, as we show below. It follows that native sulfur can be unstable at low-temperature conditions at the oceanic floor. This, however, does not exclude formation of elemental sulfur in hydrothermal systems, if they exist on Europa. But we do not think that sulfur particles, which are denser than water, reach the upper parts of the ocean and contribute to the surface coloration.

In [15] we show that the oxidation state of sulfate-rich oceanic water permits the stability of goethite, which could be present in chemical sediments at the oceanic floor. Here we consider stabilities of minerals in the Fe-S-O system. Fig. 4 shows stability fields of goethite, magnetite, and Fe sulfides at neutral pH. The contour lines represent log activity of sulfate inferred from the net equilibrium  $\text{SO}_4^{2-} + \text{H}^+ + 4\text{H}_2 = \text{HS}^- + 4\text{H}_2\text{O}$  at pH = 7.18. It can be seen that the  $f\text{H}_2$  values that favor the stability of sulfate also support the stable existence of goethite or/and pyrite, depending on  $a\text{HS}^-$ . At pH = 7.18, activities of  $\text{HS}^-$  and  $\text{H}_2\text{S}(\text{aq})$  are similar ( $a\text{HS}^- = 1.3 \times a\text{H}_2\text{S}$ ). If goethite and pyrite coexist stably in chemical sediments, the activity of sulfate of about unity ( $\log a\text{SO}_4^{2-} \sim 0$ ) constrains the equilibrium oxidation state ( $\log f\text{H}_2 \sim -10$ ) and equilibrium activity of sulfide ( $\log a\text{HS}^- \cong \log a\text{H}_2\text{S}(\text{aq}) \sim -11$ ) for neutral oceanic water. The filled ellipse in Fig. 4 represents these conditions. Gypsum could be stable and can

exist in the bottom sediments, as well [13].

Pyrrhotite and magnetite are unstable in contact with sulfate-rich oceanic water (see Fig. 4). If fresh igneous rocks are exposed at the oceanic floor, magnetite could be oxidized to goethite or other Fe<sup>3+</sup> hydroxides, and pyrrhotite could be oxidized to pyrite or sulfate. Redox disequilibrium between ferrous minerals (pyrrhotite, magnetite) and oceanic water provides chemical energy that may be sufficient to support microbial life, which should accelerate those oxidation-reduction reactions. Over time, several factors could have prevented a tremendous mass of oceanic sulfate from reduction. These are: low volcanic activity, easy degassing and escape of H<sub>2</sub>, CO and CH<sub>4</sub> from oceanic water [15], low rates of sulfate reduction at low temperatures, and lack or low efficiency of microbial sulfate reduction.

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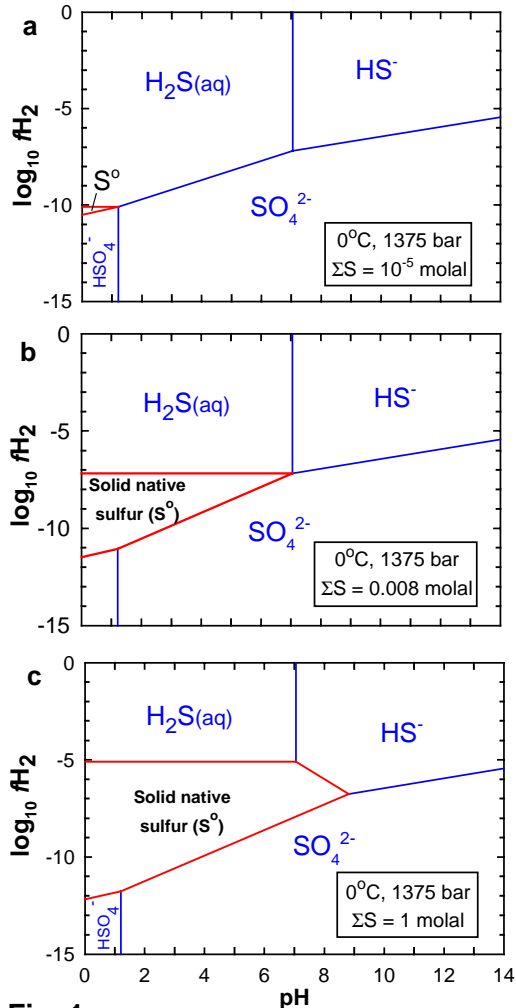


Fig. 1

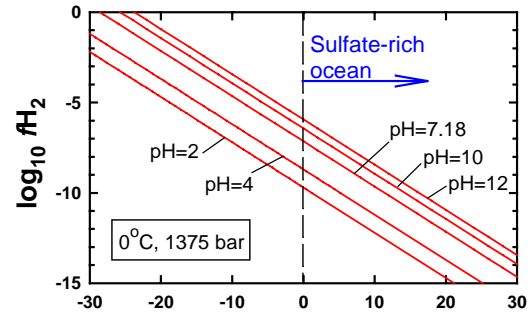


Fig. 2.  $\log_{10} [a\text{SO}_4^{2-} / (a\text{HS}^- + a\text{H}_2\text{S}(\text{aq}))]$

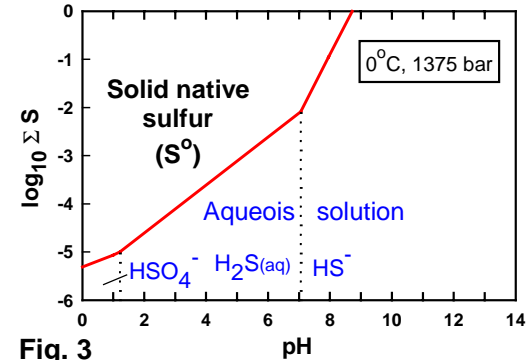


Fig. 3

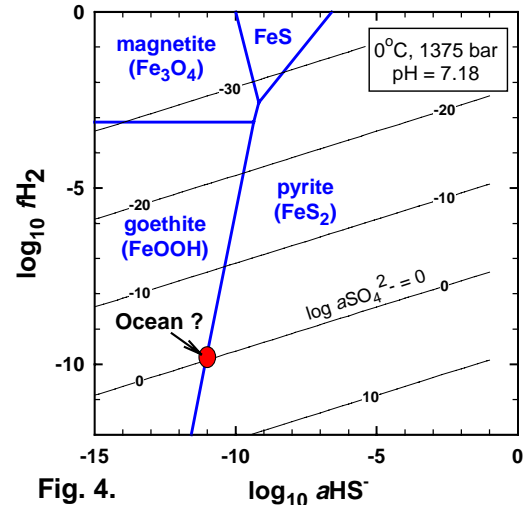


Fig. 4.