

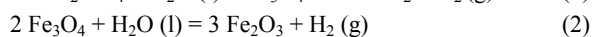
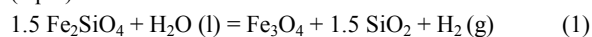
A HYDROTHERMAL ORIGIN FOR THE SULFATE-RICH OCEAN OF EUROPA. M. Yu. Zolotov and E. L. Shock, Department of Earth and Planetary Sciences, Washington University, St. Louis, MO 63130-4899. E-mails: zolotov@zonvark.wustl.edu, shock@zonvark.wustl.edu.

Introduction: *Galileo* near infrared reflectance spectroscopy of Europa's surface indicates the presence of the sulfate functional group (SO_4^{2-}) in hydrated salts [1], frozen sulfate brines [2], or sulfuric acid hydrate [3]. Sulfuric acid hydrate is probably exogenous in origin, being a product of substitution of protons for Na in sodium sulfate [3]. The close association of sulfate-bearing non-icy material with disrupted areas on the surface of Europa seems to indicate an indigenous origin of sulfates [1,4,5]. An oceanic origin for sulfates is plausible [1-5] based on recent interpretations of *Galileo* morphological data [6] and magnetic measurements [7,8]. Several cosmochemical models are consistent with the presence of sulfate in a sulfur-rich European ocean [9-13, 5]. Here we show why a hydrothermal origin for sulfate may be required.

Theoretical models indicate that sulfates did not condense in the solar nebula [e.g., 14] and, likewise, they should not have condensed in the Jovian subnebula [15]. Sulfates are present in meteorites, but they are absent in chondrites that were not altered in parent bodies (asteroids) [16]. It follows that oceanic sulfates on Europa could not have been extracted from original sulfate-bearing chondritic material. Studies of carbonaceous chondrites [e.g., 17] show that meteoritic sulfates formed from primary sulfides during aqueous alteration of asteroids. In analogy with parent bodies of carbonaceous chondrites, we propose that the presence of sulfate in the ocean on Europa is also a result of interaction of water with sulfide-bearing chondritic material. Can the oxidation of sulfide proceed at low temperatures analogous to weathering reactions that generate sulfate on the Earth, or are higher temperature hydrothermal alteration processes required? The differentiation of Europa must have required high-temperature processes [18] that caused melting of accreted ice followed by hydrothermal alteration. Here we present thermodynamic calculations that constrain temperature and pH of hydrothermal processes that could lead to the formation of sulfate-rich solutions on Europa.

Model: The chemistry and mineralogy of carbonaceous chondrites imply that sulfate-rich solutions were formed through aqueous oxidation of reduced sulfur compounds. By analogy with parent bodies of carbonaceous chondrites, we propose that sulfates on Europa were formed during the latest, more oxidizing stages of aqueous alteration. As we have shown [19,20] high water-rock ratios, low gravity, low water solubility of H_2 and CO and other factors should have favored profound oxidation of the silicate part of Europa. We have also suggested that hydrothermal fluids on Europa could have attained oxidation states as high as that set by the hematite-magnetite (HM) assemblage. In the present model, we assume that the oxidation states of the aqueous phase during intermediate and final stages of aqueous alteration on Europa were near to values consistent with the quartz-fayalite-magnetite (QFM) and hematite-magnetite assemblages, respectively. Fugacities (f) of H_2 that represent these oxidation states were calculated for QFM (eq. 1) and HM

(eq. 2) via net reactions:



To explore the stability of sulfate (SO_4^{2-}) in hydrothermal processes on Europa, we generated activity diagrams for aqueous sulfur compounds at temperatures from 0°C to 500°C using equilibrium constants calculated with the SUPCRT92 program [21] and data from [22,23]. The stability of elemental sulfur depends on an unknown total concentration of sulfur and, therefore, was not considered. All the calculations were done for 1375 bar, which represents total pressure beneath a water layer of ~ 100 km thick on Europa. The major purpose of our modeling is to evaluate temperature and pH that would favor the stability of sulfate-rich solutions at oxidation states set by the HM and QFM assemblages.

Results: The stability of sulfate in aqueous solutions depends on the oxidation state, temperature, and the pH. Oxidizing conditions (low f_{H_2}) and high pH favor the stability of sulfate. Increasing temperature makes sulfate more stable at reducing conditions, but raises the lower pH limit, as illustrated in Figs. 1-3.

At 0°C , which could represent current conditions in the vicinity of the oceanic floor, sulfate is not stable if the oxidation state is governed by either QFM or HM (Figs. 1-3). In other words, pore solutions equilibrated even with oxidized igneous rocks at the oceanic floor should not be rich in sulfate. In contrast, aqueous H_2S and/or HS^- are the stable forms of sulfur in these fluids. These results indicate that a sulfate-rich ocean on Europa can not form by low-temperature weathering. The calculations for 0°C also show that sulfate in oceanic water should be out of chemical equilibrium even with oxidized igneous rocks that contain the hematite-magnetite assemblage [see also 19,20].

Sulfate is stable in high-temperature alkaline hydrothermal solutions where the oxidation state is governed by the HM buffer, as shown in Figs. 1-3. Increasing temperature and pH increase the sulfate/sulfide ratio in the aqueous phase (Fig. 3). At the HM buffer and pH 10 to 7, which would represent aqueous alteration of ultrabasic rocks and basalts, sulfate-rich solutions form at temperatures higher than 65°C – 200°C , respectively. The oxidation states governed by QFM do not allow the formation of sulfate-rich solutions within the ranges of temperature and pH we considered.

Summary: 1) It is unlikely that a sulfate-rich ocean on Europa formed through leaching of sulfates from carbonaceous chondrite type material. In contrast, the ocean is probably a result of aqueous oxidation of sulfides, which were present in the material accreted on Europa. 2) Thermodynamic calculations show that the sulfate-rich ocean is not likely to have formed through low-temperature ($< \sim 50^\circ\text{C}$) aqueous alteration of sulfide in the silicate part of Europa. 3) Oxidation states at or below QFM are inconsistent with the formation of sulfate-rich hydrothermal solutions. 4) Oxidation states at or near the HM buffer would favor the stability

of sulfate in hydrothermal solutions, especially at higher temperatures and higher pH. The present sulfate-rich ocean on Europa could have formed through hydrothermal alteration of Fe-sulfides in the silicate mantle at oxidation states at or near those controlled by the HM buffer, but only if the temperature was higher than $\sim 50^\circ\text{C}$. This process is more effective as temperature increases. 4) The formation of a sulfate-rich ocean through hydrothermal processes implies that primordial mantle material has been oxidized significantly. In fact, hematite may be present in the upper

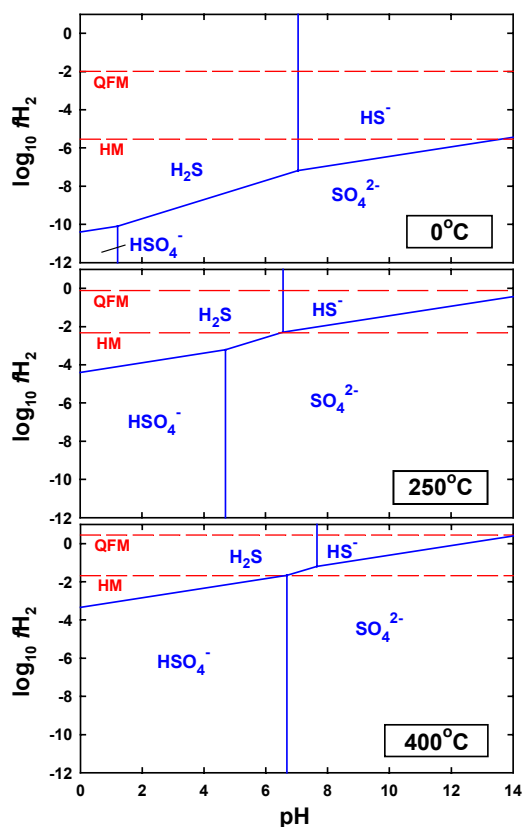


Fig. 1. The stability of aqueous sulfur species in the vicinity of the oceanic floor on Europa at 1375 bar including elevated temperatures of hydrothermal systems. The dashed lines show f_{H_2} governed by the HM and QFM buffers.

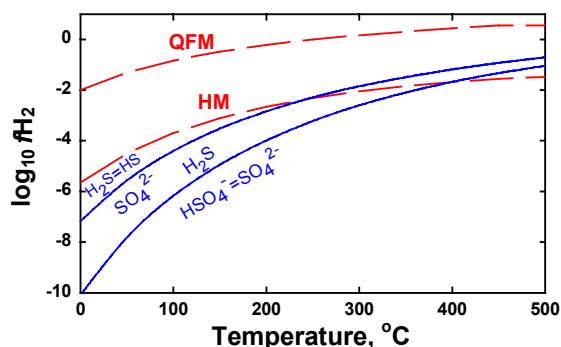


Fig. 2. Stability fields of sulfate and sulfides as function of temperature at 1375 bar. The solid lines represent equal activities of sulfides and sulfate and correspond to the traces of the invariant points in Fig. 1. Sulfate is stable at higher T and lower f_{H_2} .

part of the european mantle. 5) Oceanic sulfate is out of chemical equilibrium with cold ($\sim 0^\circ\text{C}$) unaltered igneous rocks at the ocean floor. 6) It follows that the ice and ocean on Europa should be thought of as a cooled hydrothermal fluid.

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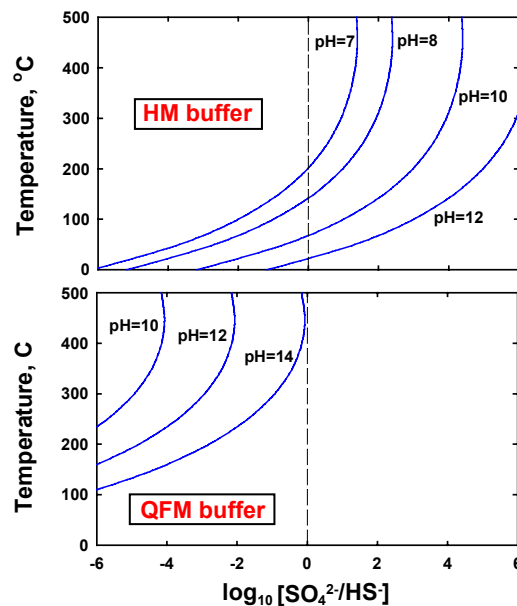


Fig. 3. The equilibrium sulfate/sulfide ratios in european hydrothermal fluids as functions of temperature and pH at 1375 bar. Note that oxidizing conditions, elevated temperatures and alkaline pH all favor higher ratios.