

## Energy for biologic sulfate reduction in a hydrothermally formed ocean on Europa

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[1] Formation of a sulfate-bearing ocean on Jupiter's satellite Europa by quenched hydrothermal fluids provides a source of metabolic energy for low-temperature sulfate-reducing organisms that use dissolved H<sub>2</sub> as an electron donor. Inhibition of thermodynamically favorable sulfate reduction in cooled hydrothermal fluids creates the potential for biologic reduction. Both high temperature and reduced conditions of ocean-forming hydrothermal solutions favor sulfate reduction in quenched fluids. The maximum amount of energy available to support autotrophic sulfate reduction is on the order of a few kilojoules per kilogram of water and is limited by the low abundances of either H<sub>2</sub> or sulfate in ocean-forming fluids. Although this irreplaceable energy source might have supported early life on Europa, maintenance of biologic sulfate reduction throughout the ocean's history would require a supply of organic compounds from endogenic sources or from the satellite's surface. **INDEX TERMS:** 6218 Planetology: Solar System Objects: Jovian satellites; 1060 Geochemistry: Planetary geochemistry (5405, 5410, 5704, 5709, 6005, 6008); **KEYWORDS:** Europa, ocean, life, sulfate reduction

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### 1. Introduction

[2] Evaluating whether a water ocean beneath the icy shell on Europa is capable of supporting life requires assessments of available metabolic energy. Since the icy shell prevents penetration of light, chemical energy is suggested as a more likely source for oceanic life [Jakosky and Shock, 1998; McCollom, 1999; Kargel *et al.*, 2000]. Several chemical disequilibria between oxidized (SO<sub>4</sub><sup>2-</sup>, CO<sub>2</sub>, O<sub>2</sub>) and reduced species (H<sub>2</sub>, organic compounds, H<sub>2</sub>S(aq), HS<sup>-</sup>, Fe<sup>2+</sup>) have been considered as potential sources of chemical energy in the ocean [e.g., McCollom, 1999; Kargel *et al.*, 2000; Chyba and Phillips, 2001; Schulze-Makuch and Irwin, 2002]. The predominance of sulfate (SO<sub>4</sub><sup>2-</sup>) in the ocean suggested from Galileo near-infrared spectroscopy of Europa's surface [McCord *et al.*, 1999, 2002; Fanale *et al.*, 2000] implies that energy for sulfate-reducing organisms might be available in anoxic (O<sub>2</sub>-free) oceanic water. On Earth, sulfate-reducing microorganisms live in anoxic environments and gain metabolic energy from reduction of sulfate either with organic compounds and methane [D'Hondt *et al.*, 2002] or dissolved H<sub>2</sub> (e.g., in seafloor hydrothermal fluids mixed with oceanic water [Amend and Shock, 2001]). By analogy with the Earth, the presence of organic compounds in Europa's oceanic water and/or in oceanic deposits and hydrothermal

activity that supplies H<sub>2</sub>(aq) into the ocean would provide energy for biotic sulfate reduction on Europa, as discussed by McCollom [1999] and Kargel *et al.* [2000].

[3] The present-day sulfate-bearing ocean may have formed as a result of aqueous oxidation of meteoritic sulfides driven by escape of hydrogen into space [Zolotov and Shock, 2001a]. Such an origin is consistent with the parent-body aqueous origin of sulfates in CI and CM carbonaceous chondrites, as well as the deficiency of strong oxidizing agents (like O<sub>2</sub>) in the satellite's interior. In addition, thermodynamic analysis of the S-H<sub>2</sub>O(l) system shows that high temperatures, low hydrogen fugacity (*f*H<sub>2</sub>), and alkaline conditions that could result from hydrothermal alteration of ultramafic rocks favor the stability of sulfate relative to reduced sulfur species (HS<sup>-</sup> and H<sub>2</sub>S(aq)) [Zolotov and Shock, 2001b]. It follows that the sulfate-bearing ocean may be derived from cooled hydrothermal fluids that formed through aqueous alteration of a previously oxidized silicate mantle. Here we evaluate the potential for sulfate reduction in the ocean formed as a quenched hydrothermal fluid.

### 2. Concept and Model

[4] High-temperature hydrothermal fluids released at the upper boundary of the silicate mantle during Europa's differentiation and subsequent igneous processes are plausible sources for the satellite's ocean. In particular, ocean-forming fluids may have formed from dehydration of early-formed mantle alteration products (e.g., serpentine). High fluid temperatures caused by magmatic activity, together with

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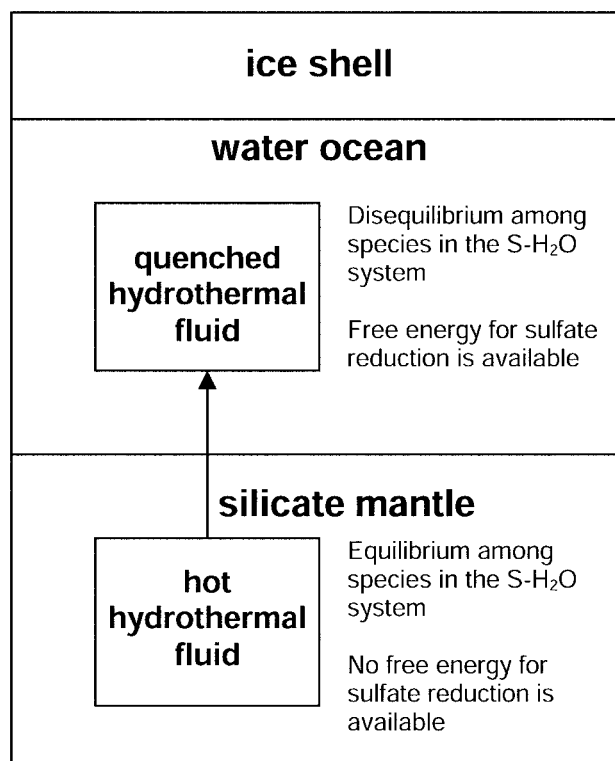
mineral catalysis, would have favored equilibration of H-, O-, and S-bearing aqueous (aq) species in the ocean-forming hydrothermal solutions. If so, despite being relatively oxidized, hot sulfate-bearing fluids would have contained dissolved  $H_2$ . Rapid cooling of these fluids to oceanic temperatures ( $\sim 0^\circ C$ ) would have prevented reequilibration of  $SO_4^{2-}$  and  $H_2(aq)$  owing to inhibition of oxidation-reduction reactions. In other words, concentrations of  $SO_4^{2-}$  and  $H_2(aq)$  will remain unchanged during rapid cooling of hydrothermal fluids released into a cold ocean, as illustrated in Figure 1. The disequilibrium coexistence of sulfate with  $H_2(aq)$  in quenched fluids creates a source of free chemical energy that could be used by autotrophic sulfate-reducing organisms for their metabolism. Sulfate-reducing organisms could facilitate conversion of sulfate to  $HS^-$  and/or  $H_2S$  via net reactions (1) and (2) (see Table 1), which might eventually lead to equilibration of H-, O-, and S-bearing aqueous species in cold oceanic water. The purpose of this paper is to quantify the amount of chemical energy potentially available from sulfate reduction as a function of temperature, pH, the oxidation state, and composition (S abundance) of ocean-forming hydrothermal fluids.

### 2.1. The pH and Oxidation States of Europa's Hydrothermal Fluids

[5] The likely chondrite-like character of the nonicy material from which Europa accreted implies an ultramafic and reduced composition of rocks, which would affect the composition of the satellite's hydrothermal fluids. Although unknown, concentrations of  $H^+$  and  $H_2(aq)$  in Europa's hydrothermal fluids can be constrained from observations of altered ultramafic rocks (serpentinites), the chemistry and mineralogy of aqueously altered chondrites, laboratory experiments and theoretical models of water-rock interactions.

[6] Aqueous alteration of ultramafic igneous rocks usually leads to formation of alkaline fluids, as observed in terrestrial field measurements on continents [e.g., *Barnes and O'Neil*, 1969] and on the seafloor [*Kelley et al.*, 2001], consistent with fluid-speciation and mass-transfer models [*Jove*, 1992; *Ryzenko et al.*, 2000; *Wetzel and Shock*, 2000; *Rosenberg et al.*, 2001]. The presence of secondary Ca carbonates and brucite ( $Mg(OH)_2$ ) in aqueously altered ultramafic rocks (serpentinites) is also consistent with alkaline fluids [e.g., *Schroeder et al.*, 2002]. Some exceptions from this pattern occur at very high ( $>5$ ) water-to-rock mass ratios and at very early stages of hydrothermal alteration when slightly acidic fluids form, as inferred from laboratory experiments [*Janecky and Seyfried*, 1986] and reaction-path models [*Wetzel and Shock*, 2000]. Since Europa's bulk water to silicate ratio is relatively low ( $\sim 0.1$ , see *Anderson et al.* [1998]), and aqueous alteration of chondritic-type ultramafic material was unavoidable during late stages of accretion and differentiation of a homogeneously accreted chondrite-ice mixture, an alkaline nature for Europa's hydrothermal fluids seems likely. Ocean-forming fluids derived through dehydration of a serpentinized mantle driven by radiogenic and tidal heating later in Europa's history should also be alkaline.

[7] Despite the reduced composition of the original chondritic-type material and primary aqueous solutions, separa-



**Figure 1.** The scheme for formation of Europa's ocean by quenching of sulfate-rich hydrothermal fluids. Formation of high-temperature hydrothermal fluids in the silicate mantle is driven by the release of radiogenic, accretional, and tidal heat. Aqueous species in the S-H<sub>2</sub>O(l) system are likely to reach chemical equilibrium in those fluids. Fast cooling of ocean-forming hydrothermal fluids to about 0°C leads to quenched compositions owing to low-temperature inhibition of redox reequilibration. Chemical disequilibrium among  $H_2(aq)$  and  $SO_4^{2-}$  in quenched fluids provides the potential for biologic sulfate reduction in the ocean.

tion of  $H_2$  gas formed through interaction of  $H_2O$  with Fe metal and ferrous minerals, followed by  $H_2$  escape to space, would have driven sequential oxidation of mantle materials and hydrothermal fluids [see also *Zolotov and Shock*, 2001a]. An oxidizing tendency that correlates with an increasing degree of aqueous alteration is observed in the mineralogy of carbonaceous chondrites [e.g., *Brearley and Jones*, 1998], which could be considered as analogs for Europa's altered mantle. Although oxidation processes in carbonaceous chondrites eventually lead to formation of sulfates and carbonates, the overall mineralogy of these meteorites indicates that the oxidation state of the fluid did not exceed that of the hematite-magnetite (HM) buffer. Indeed, magnetite rather than hematite is the major Fe-bearing mineral even in the most oxidized CI-type carbonaceous chondrites. It may be that further oxidation was limited by restricted separation of  $H_2(g)$  from oxidized fluids. By analogy with carbonaceous chondrites, the HM buffer can be considered as an upper limit for the oxidation state of Europa's hydrothermal fluids. Lack of strong oxidizing agents such as  $O_2$  during primordial aqueous alteration of Europa's mantle, as well as suppressed separation of

**Table 1.** Equilibrium Constants for Sulfate Reduction Reactions and Mineral  $f_{\text{H}_2}$  Buffers

	Reaction	Log Equilibrium Constant at 1375 bar <sup>a</sup>
(1)	$\text{SO}_4^{2-} + \text{H}^+ + 4\text{H}_2(\text{aq}) \Rightarrow \text{HS}^- + 4\text{H}_2\text{O}(\text{l})$	$\log_{10}K_1 = 13.22 - 8720T^{-1} + 6.54 \times 10^6T^{-2} - 6.77 \times 10^8T^{-3}$
(2)	$\text{SO}_4^{2-} + 2\text{H}^+ + 4\text{H}_2(\text{aq}) \Rightarrow \text{H}_2\text{S}(\text{aq}) + 4\text{H}_2\text{O}(\text{l})$	$\log_{10}K_2 = 34.36 - 24174T^{-1} + 1.17 \times 10^7T^{-2} - 1.21 \times 10^9T^{-3}$
(3) HM buffer	$2\text{Fe}_3\text{O}_4 + \text{H}_2\text{O}(\text{l}) = 3\text{Fe}_2\text{O}_3 + \text{H}_2(\text{g})$	$\log_{10}K_3 = \log_{10}f_{\text{H}_2}(\text{HM}) = 0.054 - 917T^{-1} - 176600T^{-2}$
(4) QFM buffer	$1.5\text{Fe}_2\text{SiO}_4 + \text{H}_2\text{O}(\text{l}) = \text{Fe}_3\text{O}_4 + 1.5\text{SiO}_2 + \text{H}_2(\text{g})$	$\log_{10}K_4 = \log_{10}f_{\text{H}_2}(\text{QFM}) = 1.88 - 907T^{-1} - 40840T^{-2}$

<sup>a</sup>Note that  $T$  stands for the absolute temperature.

$\text{H}_2(\text{g})$  from oxidizing solutions, could have limited oxidation of the mantle beyond the HM buffer. Note that terrestrial hematite-rich hydrothermal and sedimentary deposits form with the participation of  $\text{O}_2$  from the atmosphere.

## 2.2. Drive for Sulfate Reduction in Cooling Fluids

[8] We start by illustrating that fast, nonequilibrium cooling of hydrothermal fluids creates the potential for reduction of sulfate and bisulfate ( $\text{HSO}_4^-$ ). Note that conversion of sulfate to bisulfate depends only on pH and is not kinetically limited. Comparison of activity diagrams for the S- $\text{H}_2\text{O}(\text{l})$  system at  $500^\circ\text{C}$  and  $0^\circ\text{C}$  depicted in Figure 2 reveals that decreasing temperatures can make sulfate and bisulfate less stable with respect to  $\text{HS}^-$  and  $\text{H}_2\text{S}(\text{aq})$ . As an example, quenching a high-temperature ( $500^\circ\text{C}$ ), alkaline, sulfate-rich fluid that is in equilibrium with the hematite-magnetite assemblage (see equation (3) in Table 1) to the oceanic temperature ( $0^\circ\text{C}$ ) without changing the fugacity of  $\text{H}_2$  results in a potential for reduction of  $\text{SO}_4^{2-}$  to  $\text{HS}^-$ , as illustrated in Figure 2. Likewise, cooling at conditions where the hematite-magnetite assemblage buffers  $f_{\text{H}_2}$  also leads to favorable conditions for sulfate reduction, despite the lower value of  $f_{\text{H}_2}$  at the lower temperature. At neutral or alkaline pH, which likely represents Europa's hydrothermal fluids, sulfate could be reduced to  $\text{HS}^-$  via reaction (1). Cooling of less likely acidic fluids also creates the potential for sulfate reduction to  $\text{H}_2\text{S}(\text{aq})$  via reaction (2). Note that redox conditions more reducing than HM require alkaline pH for sulfate-rich fluids, while in more oxidizing fluids (in the hematite stability field) the pH of sulfate- and/or bisulfate-rich fluids could be either alkaline or acidic, as shown in Figure 2.

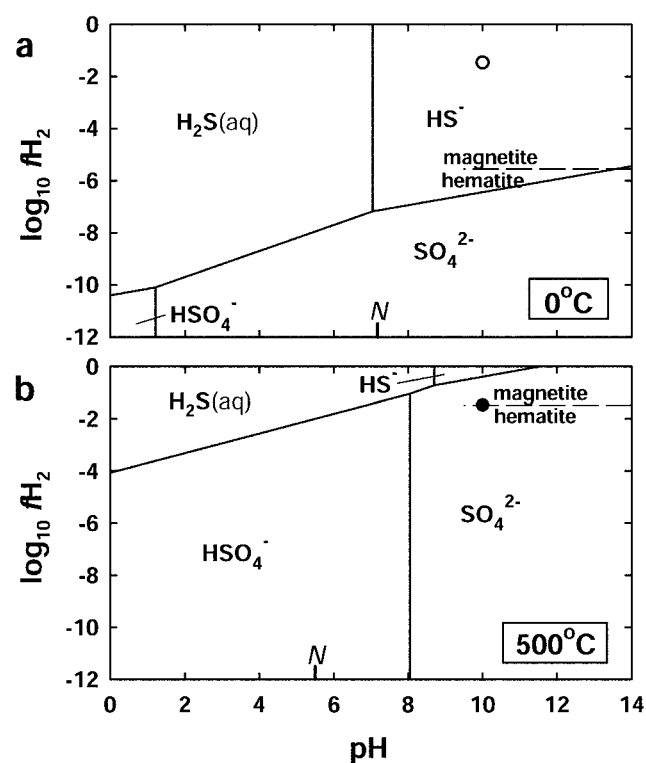
[9] The potential for  $\text{SO}_4^{2-}$  reduction to  $\text{HS}^-$  in cooled alkaline fluids is depicted in Figure 3, where stability fields of sulfate and bisulfide are shown as functions of  $f_{\text{H}_2}$  and temperature at pH 10. The arrowed cooling path of a sulfate-rich fluid, which retains its initial amount of dissolved  $\text{H}_2$ , originates in the field where sulfate prevails and heads to the field where  $\text{HS}^-$  is the dominant sulfur species.

## 2.3. Constraints for Sulfate Reduction

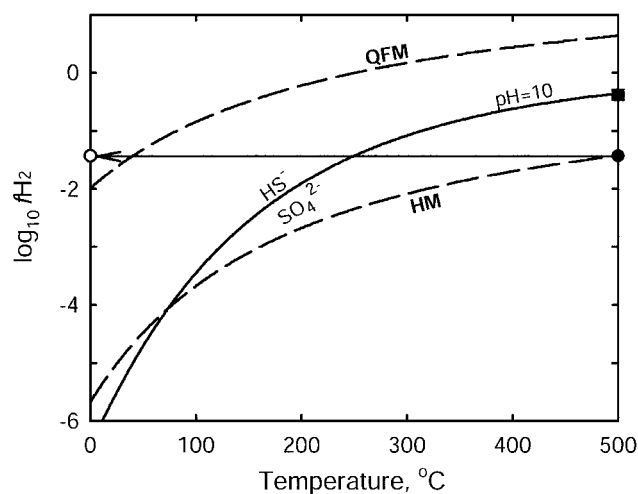
[10] Despite the strong drive for sulfate reduction in cooled fluids, low-temperature conversion of sulfate to  $\text{HS}^-$  and/or  $\text{H}_2\text{S}(\text{aq})$  could be limited by both kinetic and mass balance constraints. It is known from kinetic experiments [Ohmoto and Lasaga, 1982] and terrestrial geochemistry that many abiotic oxidation-reduction reactions among S-O-H aqueous species are extremely slow at room temperatures. For example, in highly anoxic basins like the Black Sea, high concentrations of  $\text{H}_2\text{S}(\text{aq})$  and  $\text{HS}^-$  coexist metastably with  $\text{SO}_4^{2-}$ . In terrestrial anoxic basins and in organic-rich oceanic sediments, thermodynamically favored sulfate reduction occurs only through biologic activity [e.g., D'Hondt et al., 2002]. Without life, sulfate can coexist at

low temperatures with aqueous sulfides at time scales approaching the geologic [Ohmoto and Lasaga, 1982].

[11] As for mass balance constraints, sulfate reduction in quenched fluids is strongly limited by the amount of  $\text{H}_2(\text{aq})$  available in the original sulfate-rich hydrothermal solutions (see equations (1) and (2)). Even in a hypothetical case where kinetics permit abiotic sulfate reduction in cooling fluids, only a tiny amount of the original  $\text{SO}_4^{2-}$  can be



**Figure 2.** Activity diagrams for the S- $\text{H}_2\text{O}(\text{l})$  system at  $0^\circ\text{C}$  (a) and  $500^\circ\text{C}$  (b), at the assumed pressure of Europa's oceanic floor (1375 bar). Fields separated by solid lines represent predominant aqueous sulfur species. The stability field of native sulfur depends on bulk S abundance and is not shown. The location of neutral pH (N) is indicated in each diagram. Dashed lines show conditions of the hematite-magnetite (HM) redox buffer (see equation (3) in Table 1). At lower pH, ends of the HM lines depend on bulk Fe abundance and are uncertain. The filled circle in Figure 2b represents a sulfate-rich hydrothermal fluid at HM, pH 10, and  $500^\circ\text{C}$ . In Figure 2a, the circle signifies a fluid quenched from  $500^\circ\text{C}$  to  $0^\circ\text{C}$  that retains the pH and  $f_{\text{H}_2}$  of the original high-temperature solution. Note that the circle in Figure 2a lies in the field of  $\text{HS}^-$  predominance. The difference in positions of circles in Figures 2a and 2b engenders the possibility for sulfate reduction in quenched hydrothermal fluids.



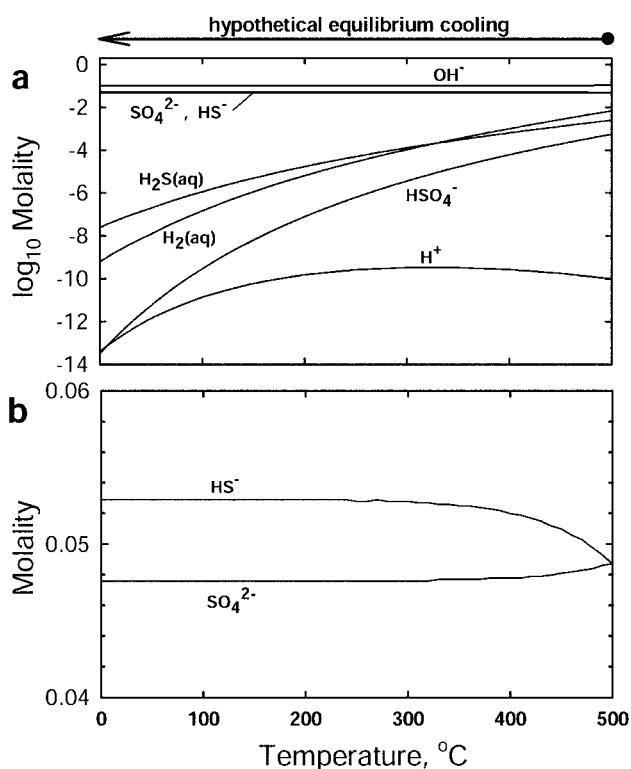
**Figure 3.** Stabilities of sulfate and bisulfide as functions of temperature and  $fH_2$  at 1375 bar. The solid curve represents equal activities of  $SO_4^{2-}$  and  $HS^-$  at pH 10 and corresponds to equilibrium conditions with respect to equation (1). The dashed curves show  $fH_2$  values set by the HM and QFM buffers as functions of temperature (see Table 1). The arrow illustrates a path of nonequilibrium quenching of the 500°C hydrothermal fluid depicted in Figure 2. Note that the path represents a hypothetical situation when  $fH_2$  remains unchanged during cooling.

converted to  $HS^-$  and/or  $H_2S(aq)$ . This can be illustrated by calculating the equilibrium speciation of H-O-S aqueous species as a function of temperature, as shown in Figure 4, which depicts the calculated speciation during a hypothetical equilibrium cooling of a solution that originally contained  $6.8 \times 10^{-3} \text{ mol kg}^{-1}$  of dissolved  $H_2$ , equal concentrations of  $SO_4^{2-}$  and  $HS^-$  of  $0.049 \text{ mol kg}^{-1}$ , and pH 10. During cooling from 500°C to 0°C, the equilibrium concentration of  $H_2(aq)$  decreases by 7 orders of magnitude, which is mainly attributable to the conversion of  $SO_4^{2-}$  to  $HS^-$  via reaction (1). Indeed, the overall decrease in  $SO_4^{2-}$  concentration by  $1.2 \times 10^{-3} \text{ mole kg}^{-1}$  corresponds to a decrease in the concentration of  $H_2(aq)$  by  $6.8 \times 10^{-3} \text{ mole kg}^{-1}$ . The small inconsistency of these values with respect to the stoichiometry of reaction (1) results from the additional consumption of  $H_2(aq)$  through reduction of  $5 \times 10^{-4} \text{ mole kg}^{-1} HSO_4^-$ . The overall increase of  $HS^-$  content by  $4.2 \times 10^{-3} \text{ mole kg}^{-1}$  results from the reduction of  $SO_4^{2-}$  and  $HSO_4^-$ , as well as the deprotonation of  $2.5 \times 10^{-3} \text{ mole kg}^{-1}$  of  $H_2S(aq)$ . The conversion of  $H_2S(aq)$  to  $HS^-$  provides the protons required for sulfate reduction via equation (1). Note that equilibrium cooling leads to an overall increase in pH. Once again, changes of equilibrium speciation with cooling shown in Figure 4 represent potential chemical transformations that are actually inhibited in low-temperature abiotic systems (except protonization and deprotonization reactions). In reality, rapid cooling of Europa's hydrothermal fluids should prevent reequilibration of  $SO_4^{2-}$ ,  $HS^-$  and  $H_2$ , unless effective catalysts like sulfate-reducing organisms are involved. Disequilibrium coexistence of sulfate with  $H_2(aq)$  in cooled solutions provides chemical energy (or affinity) for biologic sulfate reduction,

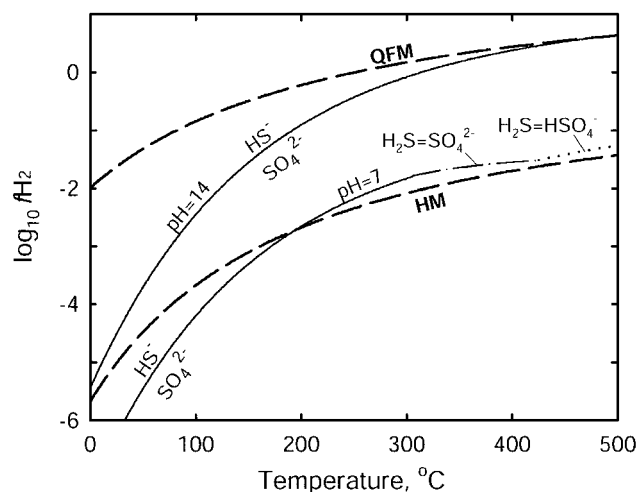
which can be evaluated from the temperature and abundances of  $H_2(aq)$  and  $H^+$  in the original hydrothermal fluids.

[12] Concentrations of  $H_2(aq)$  in hydrothermal fluids and therefore the affinities for sulfate reduction are limited by conditions that allow formation of sulfate-rich solutions in Europa's mantle. Extremely alkaline conditions set upper limits for  $fH_2$  in sulfate-rich hydrothermal solutions (see the curve that represents equal activities of  $SO_4^{2-}$  and  $HS^-$  at pH 14 in Figure 5). The conditions of the HM buffer, which may represent the most oxidized hydrothermal fluids in Europa's mantle, determine lower  $fH_2$  limits. In addition, HM sets a lower limit for the pH of sulfate-rich fluids, as can be seen in Figure 5. In fact at HM and more reduced conditions, sulfate-rich fluids do not form at acidic conditions (see also Figure 2). Although sulfate and/or bisulfate could be stable in acid fluids within the stability field of hematite, these extremely oxidizing conditions may be irrelevant to Europa's hydrothermal fluids. In addition to the typically high pH that results from aqueous alteration of ultramafic rocks, this is another reason why we have evaluated the affinity for sulfate reduction in quenched alkaline rather than acidic fluids.

[13] At 500°C, 1375 bar, and pH 12, conditions where sulfate predominates ( $aSO_4^{2-} \geq aHS^-$ ) set upper limits for



**Figure 4.** Equilibrium speciation of a model sulfate-rich hydrothermal fluid throughout cooling in a closed system from 500°C to 0°C at 1375 bar. Figure 4b gives concentrations in an enlarged format. At 500°C, the fluid is characterized by equal concentrations of  $SO_4^{2-}$  and  $HS^-$ , pH = 10, and  $\log_{10} fH_2 = -0.38$  (1.05  $\log fH_2$  units above the HM buffer), corresponding to the filled box on the right Y axis in Figure 3. The calculation refers to the ideal S-Mg- $H_2O(l)$  system with bulk concentrations of S and Mg of 0.1 and  $0.126 \text{ mol kg}^{-1}$ , respectively.



**Figure 5.** Temperature, oxidation state, and pH of hydrothermal fluids that favor formation of sulfate-rich solutions in the uppermost layer of Europa's silicate mantle (1375 bar). The solid curves represent equal activities of  $\text{SO}_4^{2-}$  and  $\text{HS}^-$  at pH 14 and 7. The dotted-dashed line signifies equal activities of  $\text{SO}_4^{2-}$  and  $\text{H}_2\text{S}(\text{aq})$  at pH 7 and corresponds to equation (2). The dotted line shows equal activities of  $\text{HSO}_4^-$  and  $\text{H}_2\text{S}(\text{aq})$  at pH 7. The area below the curve marked pH = 14 and above the line marked HM characterizes conditions of hydrothermal fluids that could have developed a sulfate-rich ocean on Europa. At moderately alkaline conditions, which represent hydrothermal fluids in ultramafic igneous rocks, formation of sulfate-rich fluids requires relatively high temperatures (>50–100°C) and  $f\text{H}_2$  less than 1–2 log units above HM.

$f\text{H}_2$  and  $x\text{H}_2$  of 1.3 bar and 0.02 mol  $\text{kg}^{-1}$ , respectively. Although unknown, the concentration of  $\text{SO}_4^{2-}$  in Europa's ocean-forming fluids could exceed this upper limit for dissolved hydrogen. A predominance of sulfate abundance over 1/4 of  $\text{H}_2(\text{aq})$  concentration in Europa's hydrothermal fluids implies that the amount of energy for sulfate reduction is restricted by the amount of dissolved  $\text{H}_2$ , as can be inferred from the stoichiometries of the reactions in equations (1) and (2). However, in the case of reduced ocean-forming fluids the potential for sulfate reduction may be limited by the concentration of sulfate rather than that of  $\text{H}_2(\text{aq})$ .

#### 2.4. Evaluation of Affinities for Sulfate Reduction in Quenched Hydrothermal Fluids

[14] The amount of chemical energy for biologic sulfate reduction stored in quenched hydrothermal fluids can be determined by comparing equilibrium speciation modeling of high-temperature fluids with their hypothetical reequilibration at the oceanic temperature. Calculations of this type were performed for the ideal S-Mg- $\text{H}_2\text{O}(\text{l})$  system in three steps. First, the speciation of a sulfate-bearing hydrothermal fluid is modeled at the desired temperature, oxidation state ( $f\text{H}_2$ ), and pH. These parameters were constrained to generate sulfate-rich solutions ( $x\text{SO}_4^{2-} \geq x\text{HS}^-$ ) at HM and/or more reduced conditions (see Figures 2b, 3, and 5). The oxidation state of the high-temperature fluids was set by opening the system with respect to  $\text{H}_2$  gas. The pH was set by varying the  $\text{Mg}^{2+}$  concentration, and the bulk

concentration of sulfur was varied from 0.01 to 1 mol  $\text{kg}^{-1}$ . Second, to model the potential reequilibration of quenched hydrothermal fluids, the equilibrium speciation was calculated for each fluid at 0°C for closed systems in which the bulk compositions remained unchanged compared with the high-temperature counterparts. Third, the amount of chemical energy potentially released in cooled fluids through reaction (1) was evaluated by the expression

$$A = -\Delta G_{1,0^\circ\text{C}} \times 0.25 \times (x_{\text{H}_2,T} - x_{\text{H}_2,0^\circ\text{C}})$$

where  $A$  designates the affinity for sulfate reduction at 0°C in a solution containing 1 kg of  $\text{H}_2\text{O}$ ,  $\Delta G_{1,0^\circ\text{C}}$  represents the standard state Gibbs free energy for reaction (1) at 0°C and 1375 bar ( $-2.63 \times 10^5 \text{ J mol}^{-1}$ ), and  $x_{\text{H}_2,T}$  and  $x_{\text{H}_2,0^\circ\text{C}}$  stand for molal (mol  $\text{kg}^{-1} \text{ H}_2\text{O}$ ) concentrations of  $\text{H}_2(\text{aq})$  in the hydrothermal solution and in the fluid reequilibrated at 0°C, respectively. Note that the term  $0.25 \times (x_{\text{H}_2,T} - x_{\text{H}_2,0^\circ\text{C}})$  represents the number of moles of sulfate that can be reduced via reaction (1) in a solution containing 1 kg of water. The value of  $A$  represents energy that could potentially support the metabolism of sulfate reducing organisms. Multiplication of the affinity and the oceanic mass ( $3 \times 10^{21} \text{ kg}$  for a 100 km thick water layer) leads to the amount of energy that could be supplied by sulfate reduction in the ocean, which may itself have formed through cooling of sulfate-bearing hydrothermal fluids.

[15] The speciation calculations were performed at 1375 bar corresponding to the pressure at the bottom of a 100 km thick ocean on Europa. Note that pressure variations from 500 to 2000 bar have only minor effects on the calculated affinities. The speciation calculations were carried out with the EQCHEM code (written by Mikhail Mironenko, Vernadsky Institute of Russian Academy of Sciences) using thermodynamic data for aqueous species from Shock *et al.* [1989, 1997]. Equilibrium constants for sulfate reduction reactions and mineral  $f\text{H}_2$  buffers can be calculated with expressions given in Table 1.

### 3. Results

[16] The affinity for sulfate reduction in cooled sulfate-rich hydrothermal solutions is evaluated as functions of temperature, oxidation state, pH, and the  $\text{SO}_4^{2-}/\text{HS}^-$  mole ratio of original fluids. The results presented in Figure 6 for equal concentrations of  $\text{SO}_4^{2-}$  and  $\text{HS}^-$  in the original high-temperature solutions demonstrate that the affinity is greatest in quenched, high-temperature, reduced, alkaline fluids. The amount of energy for sulfate reduction increases with increasing  $\text{H}_2(\text{aq})$  concentration in the original hydrothermal fluids. In turn, high temperatures favor higher concentrations of dissolved hydrogen in those fluids. Because alkaline conditions support the formation of sulfate-rich fluids at higher  $f\text{H}_2$  (see Figures 2, 3, and 5), the affinity for sulfate reduction is greater in cooled solutions that originally had higher pH. Quenching models for sulfate-rich fluids where  $x\text{SO}_4^{2-} \geq x\text{HS}^-$  show that affinity values are independent of bulk sulfur abundance in the chosen range.

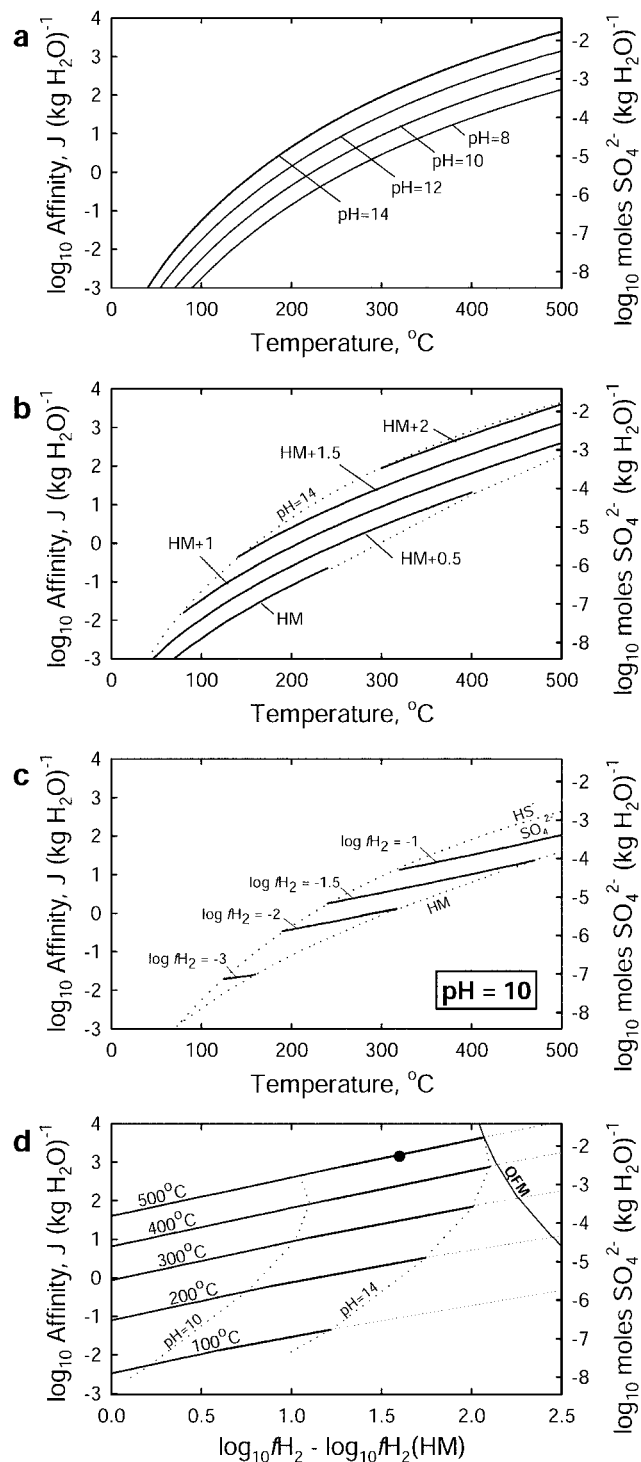
[17] Constraints on temperature- $f\text{H}_2$ -pH conditions that allow formation of sulfate-rich fluids limit the affinity for sulfate reduction to a value of about 1 kJ per kilogram of

H<sub>2</sub>O. In our model, the maximum affinity value ( $\sim 1400$  J kg<sup>-1</sup>) corresponds to a quenched fluid that was originally equilibrated at 500°C, 1.6 log  $f$ H<sub>2</sub> units above HM, and pH 12, and had nearly equal concentrations of SO<sub>4</sub><sup>2-</sup> and HS<sup>-</sup>, which corresponds to the potential reduction of 0.005 moles of sulfate per kilogram of H<sub>2</sub>O (see Figure 6d). Reduction of sulfate is limited by the much lower concentrations of H<sub>2</sub>(aq) in this hydrothermal fluid.

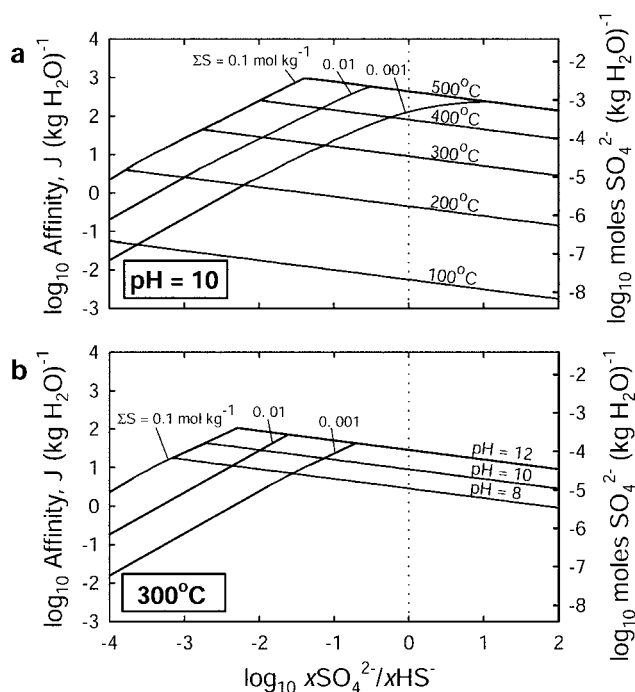
[18] More detailed calculations shown in Figure 7 demonstrate that quenching of moderately reduced fluids, in

which the SO<sub>4</sub><sup>2-</sup> concentration is a few orders of magnitude lower than that of HS<sup>-</sup>, could provide higher affinity for low-temperature sulfate reduction compared with sulfate-rich fluids. The affinity is greater because the reduced fluids have higher H<sub>2</sub> contents but still contain sulfate molecules that can be converted to HS<sup>-</sup> upon quenching. The maximum affinity for sulfate reduction is available in quenched fluids that originally contained a H<sub>2</sub>/SO<sub>4</sub><sup>2-</sup> activity ratio of 4, consistent with the stoichiometry of reaction (1). These affinity values do not exceed a few kilojoules per kilogram of H<sub>2</sub>O. Higher bulk sulfur content in original hydrothermal solutions provides higher affinities in quenched HS<sup>-</sup>-rich, sulfate-bearing fluids. Nevertheless, even in fluids with high sulfur content, sulfate reduction in quenched reduced solutions is limited by low SO<sub>4</sub><sup>2-</sup> abundances, as can be seen in Figure 7.

[19] Although the concentration of sulfate in Europa's ocean is unknown, these results demonstrate that the potentially reducible fraction of sulfate is far from negligible. Cooling of sulfate-rich hydrothermal fluids equilibrated at 200°C–300°C leads to affinities of 0.1–100 J (kg H<sub>2</sub>O)<sup>-1</sup>, respectively. These values are comparable with affinities for sulfate reduction ( $< 42$  J (kg vent fluid)<sup>-1</sup>) available in terrestrial hydrothermal vents during mixing with seawater in oceanic ridges [McCollom and Shock, 1997]. Quenching of low-temperature ( $< 100^\circ\text{C}$ ) fluids leads to values less than 0.1–0.01 J (kg H<sub>2</sub>O)<sup>-1</sup>. Thus depending on the temperature and oxidation state of the original hydrothermal fluids, the affinity for sulfate reduction is likely to be between  $\sim 10^{-2}$



**Figure 6.** (opposite) Affinity for sulfate reduction in aqueous solutions cooled to 0°C as a function of temperature, oxidation state, and pH of original hydrothermal fluids at Europa-like conditions. Also shown on right Y axes are the number of moles of sulfate that could potentially be reduced per kg of H<sub>2</sub>O. The results refer to the S-Mg-H<sub>2</sub>O system with bulk concentration of S of 0.1 mol kg<sup>-1</sup> at 1375 bar. In Figures 6a, 6b, and 6d the original hydrothermal solutions have equal concentrations of SO<sub>4</sub><sup>2-</sup> and HS<sup>-</sup>. Figure 6a represents affinities as functions of pH and temperatures of original fluids. In Figure 6b the lines marked HM +  $n$  represent oxidation states of original fluids, where  $n$  stands for the log  $f$ H<sub>2</sub> units above HM. The upper limit for affinities shown by the dotted line is set by pH 14 in the original hydrothermal fluids. The lower limit for affinity at each temperature of the original fluids is limited by pH about 7. Figure 6c represents affinities in quenched fluids originally at pH 10 and various oxidation states ( $f$ H<sub>2</sub>). The amount of energy for sulfate reduction is bounded by the stability field of sulfate at pH 10 (the upper dotted line) and conditions of the HM buffer (lower dotted line). In Figure 6d the affinity for sulfate reduction is shown as a function of  $f$ H<sub>2</sub> of the original fluids normalized to HM. At each temperature, the affinity is limited by pH = 14 of the original fluid. The curve marked QFM represents affinities for a hypothetical fluid quenched at the  $f$ H<sub>2</sub> governed by the QFM buffer at extremely alkaline conditions (pH > 14). The filled circle represents the affinity that corresponds to an original fluid at 500°C and pH 12. Since pH 14 may be unreasonably high for natural systems, then the corresponding affinity ( $\sim 1400$  J kg<sup>-1</sup>) can be considered to be an upper limit for sulfate-rich fluids on Europa.



**Figure 7.** Affinity for sulfate reduction in aqueous solutions cooled to 0°C as a function of the  $\text{SO}_4^{2-}/\text{HS}^-$  mole ratio, the bulk sulfur abundance, temperature, and pH of original hydrothermal fluids at Europa-like conditions. Figure 7a represents the affinity for various temperatures of original fluids at pH 10, and Figure 7b corresponds to affinities at various pH and 300°C. The dotted lines correspond to equal molal concentrations of  $\text{SO}_4^{2-}$  and  $\text{HS}^-$  in the original fluids. As the  $\text{SO}_4^{2-}/\text{HS}^-$  ratio decreases, the affinity increases and then decreases. The turning points, in which the affinities reach maximum values, represent cases where all  $\text{SO}_4^{2-}$  ions and all  $\text{H}_2(\text{aq})$  molecules could react via equation (1). At these points, molal concentrations of  $\text{SO}_4^{2-}$  are equal to 1/4 of that of  $\text{H}_2(\text{aq})$ . Higher bulk S abundances ( $\Sigma\text{S}$ ) correspond to higher affinities at the turning points. To the right from a turning point, the affinity is limited by the amount of  $\text{H}_2(\text{aq})$  in the original fluid. The increase of affinity is caused by the increasing  $\text{H}_2(\text{aq})$  content as the  $\text{SO}_4^{2-}/\text{HS}^-$  ratio decreases. To the left from a turning point, the affinity is limited by the amount of  $\text{SO}_4^{2-}$ , which decreases. The figure illustrates that energy for biologic sulfate reduction in quenched sulfate-bearing fluids is higher in reduced solutions with low  $\text{SO}_4^{2-}$  content than in  $\text{SO}_4^{2-}$ -rich solutions.

and  $\sim 10^3 \text{ J (kg H}_2\text{O)}^{-1}$ . It follows that for a 100 km thick ocean that contains  $3 \times 10^{21} \text{ kg H}_2\text{O}$ , the affinity could be  $< \sim 3 \times 10^{24} \text{ J}$ . Taking into account the Gibbs free energy for reaction (1), those affinities correspond to potential conversion of  $< \sim 10^{19}$  moles of Europa's oceanic  $\text{SO}_4^{2-}$ , which could be a small portion of the oceanic sulfate inventory. For comparison, reduction of all terrestrial oceanic  $\text{SO}_4^{2-}$  ( $4 \times 10^{19}$  moles) to  $\text{HS}^-$  would yield about  $10^{25} \text{ J}$ .

#### 4. Discussion

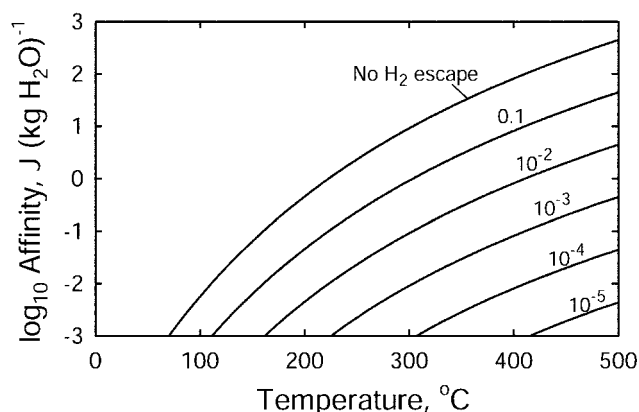
[20] Our modeling demonstrates that some portion of Europa's oceanic sulfate could potentially be reduced by

dissolved hydrogen left in cooled hydrothermal fluids. Low-temperature inhibition of abiotic sulfate- $\text{H}_2$  interaction provides conditions that could support organisms that use sulfate reduction as a source of metabolic energy. Any involvement of life would accelerate sulfate reduction and could even lead to equilibration between  $\text{SO}_4^{2-}$ ,  $\text{HS}^-$ , and  $\text{H}_2(\text{aq})$ . In particular, completion of sulfate reduction would have decreased the  $\text{H}_2(\text{aq})$  content by several orders of magnitude compared to concentrations in quenched hydrothermal fluids. If detected, equilibrium low-temperature relations among these species in Europa's oceanic water would be highly suggestive of the involvement of ancient life.

[21] Although the amount of energy for sulfate reduction in quenched hydrothermal fluids is limited by low concentrations of  $\text{H}_2$  in sulfate-rich solutions, the possibility exists that cooling of alkaline fluids from temperatures higher than 500°C increases this amount. Existence of such fluids seems to be unavoidable during magmatic processes responsible for separation of Europa's metallic core and from its silicate mantle or during subsequent mantle dehydration. Note that our model requires neither present-day hydrothermal activity at the oceanic floor nor organic compounds that provide electron donors for sulfate reduction. The proposed origin of Europa's ocean from cooled hydrothermal fluids [Zolotov and Shock, 2001b] implies that energy for sulfate reduction may have been available since the appearance of sulfates in the ocean-forming fluids.

[22] The proposed model and affinity estimates can also be applied to Ganymede. The differentiated structure and the high water to rock mass ratio ( $\sim 0.47$ ) in the satellite's interior [Anderson *et al.*, 1996] imply intensive high-temperature aqueous alteration on early Ganymede. By analogy with Europa and other solar system bodies [Zolotov and Shock, 2001a], the high-temperature water-rock alteration followed by production and escape of  $\text{H}_2$  could be responsible for the oxidation of the satellite's silicate mantle and ocean. In fact, recent detection of sulfates on Ganymede's surface [McCord *et al.*, 2001] is consistent with a Europa-like high-temperature origin of an ocean, the existence of which is consistent with Galileo magnetometer data [Kiverson *et al.*, 2002].

[23] There are several factors that severely constrain the potential for biologic sulfate reduction in the proposed model. First, the amount of energy for sulfate reduction is irreplaceable since the formation of the sulfate-bearing ocean. Consumption of  $\text{H}_2(\text{aq})$  to an equilibrium level would have led to extinction of sulfate-reducing organisms, unless other electron donors are present. Second, only a small portion of the potentially available energy is usually used for metabolism. It might be that quenched low-temperature solutions cannot support biotic sulfate reduction because of an energy deficiency. Third, molecules of  $\text{H}_2(\text{aq})$  are diluted throughout the volume of oceanic water leading to "diluted" metabolic energy. In contrast, metabolic energy for heterotrophic sulfate-reducing organisms that consume organic compounds could be associated either with organic compounds in oceanic floor sediments/rocks or with an "oil" fraction produced from high-temperature alteration of primordial organic compounds, extracted by hydrothermal fluids and floating beneath the ice shell. Fourth, even low concentrations of  $\text{H}_2(\text{aq})$  available in



**Figure 8.** Affinity for sulfate reduction in aqueous solutions cooled to 0°C as a function of the temperature of the original fluid and the amount of H<sub>2</sub>(aq) left in the ocean after escape into space. The lines are marked by numbers that represent the fraction of H<sub>2</sub>(aq) left in the ocean. The original hydrothermal fluid has pH 10 and equal concentrations of SO<sub>4</sub><sup>2-</sup> and HS<sup>-</sup>.

sulfate-rich hydrothermal fluids could have escaped into space through periodic openings in the icy shell. Such an escape lowers the affinity for sulfate reduction, as illustrated in Figure 8. Finally, H<sub>2</sub> could have been consumed in other reduction processes, for example, methanogenesis.

[24] Nevertheless, the existence of sulfate reducing organisms throughout the satellite's history may have been maintained by periodic volcanic and hydrothermal activity at the oceanic floor and/or by the supply of organic compounds from abiotic and biogenic sources. Abiotic sources could include penetration of cometary/meteoritic organic compounds from Europa's surface, catalytic synthesis in rapidly cooling hydrothermal fluids [Shock and Schulte, 1998], and/or volcanic gases released into the ocean from the mantle [Zolotov and Shock, 2000]. Biogenic sources of organic compounds might involve metabolic products and dead cells. In particular, methane and other organic compounds produced by methanogens either in hot hydrothermal fluids mixed with oceanic water [McCollom, 1999] or in cold oceanic floor rocks/sediments could be consumed by heterotrophic sulfate reducing organisms, which require organic compounds as electron donors. Note also that low-temperature instability of magnetite with respect to sulfate (see Figures 2 and 3) creates a potential for biologic sulfate reduction coupled with magnetite oxidation at the oceanic floor.

[25] Our work shows that a low-temperature ocean formed from cooled hydrothermal solutions is likely to be even more alkaline than ocean-forming fluids (see Figure 4). The alkaline Europa's early ocean proposed by Rosenberg *et al.* [2001] and Kempe and Kazmierczak [2002] could be a promising site for biogenesis.

## 5. Summary

[26] Formation of Europa's ocean from quenched sulfate-bearing hydrothermal fluids provides energy for reduction of sulfate by dissolved hydrogen retained in the ocean. The amount of chemical energy that can support metabolism of

sulfate-reducing organisms in quenched hydrothermal fluids increases with the temperature,  $f_{H_2}$ , and pH of ocean-forming solutions. Energy for sulfate reduction does not exceed several kilojoules per kilogram of fluid and is limited either by the amount of dissolved H<sub>2</sub> in sulfate-rich oxidized fluids or by the amount of sulfate in reduced fluids. Quenching of moderately reduced fluids with sulfate content up to several orders of magnitude lower than that of aqueous sulfides provides even greater amounts of chemical energy compared to sulfate-rich solutions. This energy might have supported an early autotrophic sulfate-reducing metabolism but is likely to have decreased with time owing to consumption of dissolved H<sub>2</sub> through sulfate reduction, cessation of igneous and hydrothermal activity, and H<sub>2</sub> escape. Although the amount of energy could be insufficient to allow sulfate-reducing organisms to persist throughout the ocean's history, periodic supply of abiotic organic compounds into the ocean and/or primary production of biologic materials by methanogens could maintain heterotrophic sulfate-reducing organisms.

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