

GEOCHEMICAL CONSTRAINTS ON CHEMOLITHOAUTOTROPHIC REACTIONS IN HYDROTHERMAL SYSTEMS

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Abstract. Thermodynamic calculations provide the means to quantify the chemical disequilibrium inherent in the mixing of reduced hydrothermal fluids with seawater. The chemical energy available for metabolic processes in these environments can be evaluated by taking into account the pressure and temperature dependence of the apparent standard Gibbs free energies of reactions in the S-H₂-H₂O system together with geochemical constraints on pH, activities of aqueous sulfur species and fugacities of H₂ and/or O₂. Using present-day mixing of hydrothermal fluids and seawater as a starting point, it is shown that each mole of H₂S entering seawater from hydrothermal fluids represents about 200,000 calories of chemical energy for metabolic systems able to catalyze H₂S oxidation. Extrapolating to the early Earth, which was likely to have had an atmosphere more reduced than at present, shows that this chemical energy may have been a factor of two or so less. Nevertheless, mixing of hydrothermal fluids with seawater would have been an abundant source of chemical energy, and an inevitable consequence of the presence of an ocean on an initially hot Earth. The amount of energy available was more than enough for organic synthesis from CO₂ or CO, and/or polymer formation, indicating that the vicinity of hydrothermal systems at the sea floor was an ideal location for the emergence of the first chemolithoautotrophic metabolic systems.

1. Energy Sources for the Earliest Metabolic Systems

The early atmosphere of the Earth was probably not reducing (Levine, 1982, 1985; Levine *et al.*, 1982; Kasting *et al.*, 1983; Stevenson, 1983; Fegley *et al.*, 1986; Kasting, 1993). In the absence of a reduced atmosphere, Miller-Urey synthesis of organic compounds from CH₄ and NH₃ would have been impossible, and the direction of the earliest chemosynthetic reactions was more likely to have been the conversion of CO₂ and/or CO to organic compounds. Inhospitable surface environments, bombarded by UV radiation and cosmic debris, seem less likely to have nurtured the emergence of life than UV-shielded environments such as submarine hydrothermal systems (Maher and Stevenson, 1988; Sleep *et al.*, 1989). These systems provide the combination of elevated temperatures and reducing conditions necessary for fixation of CO or CO₂ (French, 1964; Shock, 1990a, 1992a, b; Wächtershäuser, 1988, 1992; Hennem *et al.*, 1992; Holm, 1992; Cairns-Smith *et al.*, 1992; MacLeod *et al.*, 1994; Russell *et al.*, 1994), and the convergence of thermodynamic, kinetic and geochemical constraints maximizes the potential for reductive organic synthesis at 100–250 °C in submarine hydrothermal systems (Shock, 1990a, 1992a). Submarine hydrothermal systems are an inevitable geophysical and geochemical consequence of a water rich planet cooling from its violent birth. Extrapolation of evidence from modern systems to the earliest systems on the Earth suggests that an unavoidable feature would have been the introduction of reduced, H₂S-rich fluids

into less-reduced seawater likely to contain sulfate (Ohmoto *et al.*, 1993). Mixing of these two solutions in present-day systems provides a source of disequilibrium, and therefore the chemical energy for chemosynthesis, which is the foundation of the food-web of hydrothermal vent communities (Tunnicliffe, 1991; Childress and Fisher, 1992). We propose that the same source of disequilibrium could have enabled the emergence of life on the early Earth.

The catalytic properties of certain RNA molecules has fueled a vision of an early 'RNA world' (Sharp, 1985; Lewin, 1986; Gilbert, 1986; Orgel, 1986; Joyce, 1989), in which single organic polymers could have shared the tasks of holding genetic information and actively interacting with the surrounding environment. Advocates of the RNA world seldom muddy its attractive image by raising the problem of making polymers like RNA from monomers, which requires energy. If the earliest energy source was solar, it was abandoned by the hyperthermophilic organisms that are the closest-known living relatives of a common ancestor of all life on Earth (Woese, 1987; Woese *et al.*, 1990). If the source was chemical energy, it may have been provided by normal geochemical processes, and perhaps conditions still exist on the present-day Earth analogous to those in which the first replicating/catalyzing molecules emerged. Regardless of whether an RNA world ever appeared on the early Earth, polymerization of monomers, even if only to form a membrane, is likely to have been an energy-consumptive process faced by the earliest metabolic systems on the Earth. Modern organisms, endowed with complex information storage and retrieval systems, insure proper information transfer by conducting polymer formation with an excess of chemical energy in the form of ATP (Thauer *et al.*, 1977). Therefore, following arguments set forth in part by Russell *et al.* (1993) and Wächtershäuser (1988, 1990a, b, 1992), we suggest that an early metabolic system would have been chemolithoautotrophic, i.e., able to 'live' off abundant, easily available, inorganic chemical energy. The purpose of this paper is to quantify the chemical energy available as a consequence of the mixing of hydrothermal fluids and seawater in modern systems, and to test several possible reactions involving common, sulfur-bearing geochemical species in a hypothetical Archean ocean/hydrothermal fluid system.

Standard State Free Energies and Geochemical Constraints

Are conditions in hydrothermal environments conducive to supplying sufficient chemical energy for an early metabolic system? The answer to this question has two parts that reflect the two terms on the right side of the familiar expression for the Gibbs free energy (ΔG_r) of a reaction given by

$$\Delta G_r = \Delta G_r^0 + RT \ln Q_r. \quad (1)$$

One part of the answer lies in determining the standard Gibbs free energy of the reaction (ΔG_r^0) at the temperature and pressure of interest, and the other lies in

evaluating the activity product (Q_r) that is governed by geochemical constraints on compositions of minerals, gases, and aqueous solutions. This seems like an elementary point that hardly needs to be made, but the wealth of arguments in the geochemical, biochemical, and bioenergetic literature based solely on *standard* Gibbs free energies belies this necessity. The same is true of the modified standard Gibbs free energy ($\Delta G_r^{\circ'}$), tied to pH = 7 and 25 °C, used in many bioenergetic calculations (see below). A chemolithoautotrophic is fundamentally no different from any other organism; it gets its energy from reactions that have negative values of ΔG_r but are kinetically inhibited. On the other hand, such organisms are likely to be highly sensitive to changes in concentrations of reactants and products. In hydrothermal environments, these changes are dictated by fluid/rock reactions. As shown below, geochemical constraints can overwhelm large, positive values of ΔG_r° and generate large, negative values of ΔG_r . These constraints control whether a reaction actually represents a potential source of chemical energy for a chemolithoautotrophic organism. It is the geochemistry of hydrothermal systems which provides the 'food'.

STANDARD STATE CALCULATIONS

Evaluating the effects of changes in geochemical constraints on the availability of energy from chemical reactions requires a frame of reference. This is provided by the selection of standard states for the chemical species involved in geochemical processes. Selecting a standard state is much like selecting a zero point for a temperature scale; it provides a reference point from which to measure changes in the system, but the standard state 'zero point' has no real inherent meaning in itself since any reference state can be selected as long as the entire system is treated consistently. Standard states commonly selected are unit activity for pure minerals at any pressure and temperature, unit activity for ideal gases at 1 bar and any temperature, unit activity for the pure solvent, H₂O, at any pressure and temperature, and unit activity of a hypothetical one molal solution of an aqueous chemical species referenced to infinite dilution at any pressure and temperature. The choice of these standard states allows calculation of the thermodynamic properties of chemolithoautotrophic reactions at the elevated temperatures and pressures at which such organisms live, including the environments of submarine hydrothermal systems. Note that since the value of the standard free energy, ΔG_r° , is entirely dependent on the standard states chosen, ΔG_r° alone cannot be used to evaluate whether energy is available from a reaction to drive metabolic processes (although this is frequently done in the literature).

Changes in standard Gibbs free energies of chemical species at elevated temperatures and pressures are often evaluated in terms of the apparent standard partial molal Gibbs free energy of formation (Helgeson *et al.*, 1981; Shock *et al.*, 1992) given by

$$\Delta G_{P,T}^{\circ} = \Delta G_{f,P_r,T_r}^{\circ} - S_{P_r,T_r}^{\circ}(T - T_r) + \int_{T_r}^T C_P^{\circ} dT - T \int_{T_r}^T C_P^{\circ} d \ln T + \int_{P_r}^P V_T^{\circ} dP \quad (2)$$

where S° , C_p° , and V° refer to the standard molal entropy, heat capacity and volume, respectively, the subscripts P and T stand for the pressure and temperature of interest, and the subscripts P_r and T_r designate the reference pressure and temperature of 25 °C and 1 bar.

The greatest latitude in applying thermodynamic calculations to geochemical processes is attained by calculating values of the apparent standard partial molal Gibbs free energy of formation for all of the chemical species of interest. The approach taken in this study for aqueous chemical species is to use the revised Helgeson-Kirkham-Flowers (HKF) equation of state (Helgeson *et al.*, 1981; Tanger and Helgeson, 1988; Shock *et al.*, 1992). In its fully integrated form, the revised-HKF expression corresponding to Equation (2) is given by

$$\begin{aligned} \Delta G_{P,T}^{\circ} = & \Delta G_{f,P_r,T_r}^{\circ} - S_{P_r,T_r}^{\circ}(T - T_r) - c_1 \left(T \ln \left(\frac{T}{T_r} \right) - T + T_r \right) \\ & - c_2 \left[\left[\left(\frac{1}{T - \theta} \right) - \left(\frac{1}{T_r - \theta} \right) \right] \left(\frac{\theta + T}{\theta} \right) - \frac{T}{\theta^2} \ln \left(\frac{T_r(T - \theta)}{T(T_r - \theta)} \right) \right] \\ & + a_1(P - P_r) - a_2 \ln \left(\frac{\Psi + P}{\Psi + P_r} \right) \\ & + \left(\frac{1}{T - \theta} \right) \left[a_3(P - P_r) + a_4 \ln \left(\frac{\Psi + P}{\Psi + P_r} \right) \right] \\ & + \omega \left(\frac{1}{\varepsilon} - 1 \right) - \omega_{P_r,T_r} \left(\frac{1}{\varepsilon_{P_r,T_r}} - 1 \right) - \omega_{P_r,T_r} Y_{P_r,T_r}(T - T_r). \end{aligned} \quad (3)$$

where a_1 , a_2 , a_3 , a_4 , c_1 , c_2 and ω stand for species-dependent parameters, θ and Ψ refer to solvent-dependent parameters, ε designates the dielectric constant of H₂O, and Y represents the Born function corresponding to the logarithmic pressure derivative of the Born equation.

Numerous studies provide values of the various revised-HKF parameters for aqueous chemical species (Shock and Helgeson, 1988, 1990; Shock *et al.*, 1989; Shock 1992c, 1993; Schulte and Shock, 1993; Shock and Koretsky, 1993; Shock and McKinnon, 1993; Sverjensky *et al.*, in prep.; Shock, 1994a), which are obtained through regression of experimental data and with estimation methods developed using correlation algorithms (Shock and Helgeson, 1988, 1990; Sassani and Shock, 1992; Shock, 1994a, b; Sverjensky *et al.*, in prep.). The close agreement between

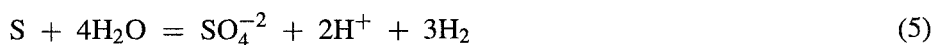
calculated and experimental data at elevated temperatures and pressures for hundreds of aqueous species documented in these papers demonstrates the accuracy of calculations conducted with the revised-HKF equations of state.

An example is shown in Figure 1 of predicted values of the apparent standard partial molal Gibbs free energy of formation for aqueous glycine as a function of temperature at P_{sat} (the vapor-liquid saturation pressure of H_2O). Note that there is a steady, monotonic change of ΔG°_f to more negative values with increasing temperature. Comparisons of the relative magnitudes of changes in ΔG°_f among several aqueous organic compounds can be made with the plot in Figure 2, where the differences at P_{sat} between ΔG°_f at the temperature of interest and that at 25°C are plotted. It can be seen in this figure that shifts of several kilocalories in apparent standard partial molal Gibbs free energies of formation for aqueous organic compounds are common at elevated temperatures, even over the range of temperatures from 0 to 150°C where chemolithoautotrophic organisms are known or expected to thrive. The data shown in Figure 2 help to emphasize that ΔG°_f is a relatively strong function of temperature for many aqueous compounds.

The results depicted in Figures 1 and 2 help to illustrate the need for adopting a frame of reference which is considerably more broad than that often selected for bioenergetic calculations. Although several authors insist on the usefulness of performing bioenergetic calculations at 25°C and $\text{pH} = 7$ (e.g. Alberty, 1992), such calculations are actually highly restrictive, and only apply to macrobiological systems like mammals. Thermophiles, halophiles, acidophiles, and other microorganisms infiltrate widely variable environments, and many of these organisms are hard pressed to survive 25°C , dilute solutions, and/or neutral pH . By adopting the standard states commonly used in geochemistry, which allow any temperature or pressure, we can avoid the traps inherent in the strongly anthropocentric selections of most bioenergetic calculations which are tied to 25°C and 1 bar. As a result, considerable insight can be gained into the geobiochemical energetics which support life in modern submarine hydrothermal systems.

THE EFFECT OF GEOCHEMICAL CONSTRAINTS ON ΔG_r

Current speculation by microbiologists suggests that life may thrive to temperatures as high as 150°C (Daniel, 1992; Seeger *et al.*, 1993). Many of the known hyperthermophilic organisms (living at temperatures $>80^{\circ}\text{C}$) are found in hydrothermal systems in which pH , oxidation states and concentrations of dissolved chemical species are controlled, or strongly influenced, by high-temperature fluid/rock reactions. Several species of modern hyperthermophiles which thrive at hydrothermal conditions pursue chemosynthetic strategies tied to the oxidation of sulfur or H_2S . Reactions which represent the *overall* chemolithotrophic oxidation processes are given by



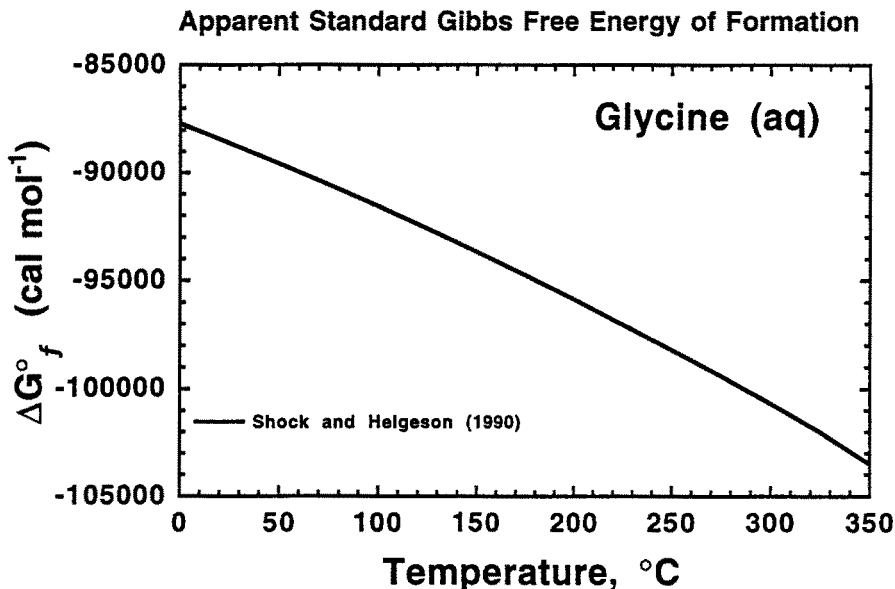


Fig. 1. Values of the apparent standard Gibbs free energy of formation of aqueous glycine as a function of temperature at P_{sat} , calculated with the revised HKF equation of state using data and parameters from Shock and Helgeson (1990). Note the nearly 16000. cal mol^{-1} decrease in ΔG_f° from 0 to 350°C.

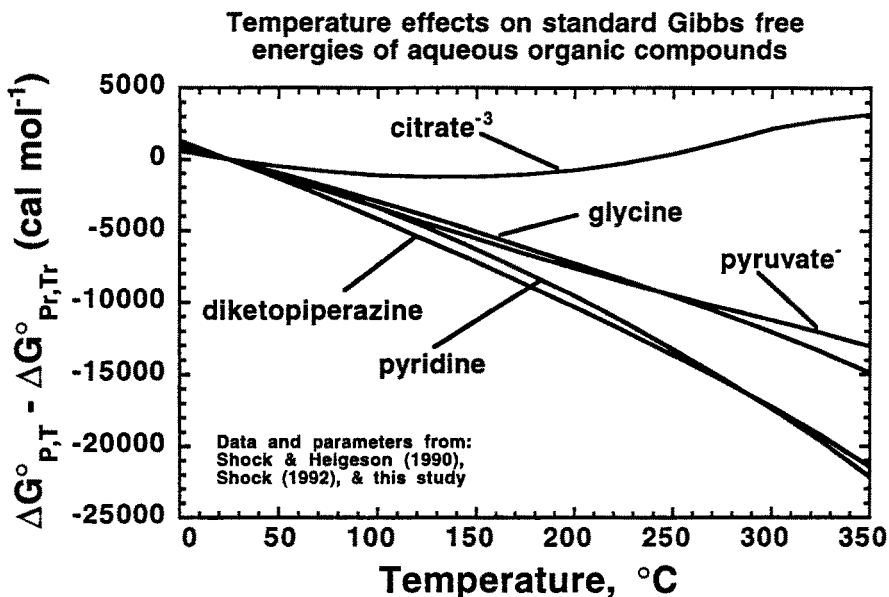
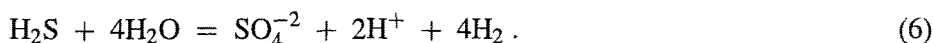


Fig. 2. Values of the difference in the apparent standard Gibbs free energies of formation at various temperatures and P_{sat} and that at 25°C and 1 bar for several aqueous organic compounds, calculated with the revised HKF equation of state using data from Shock and Helgeson (1990), Shock (1992), and ongoing research from this lab.

and



Reactions (4) and (5) correspond to a two-step oxidation process in which H_2S is first oxidized to native S followed by oxidation of S to sulfate, and reaction (6) represents the direct oxidation of H_2S to sulfate. Values of ΔG_r° for reactions (5) and (6) are discussed below.

Activity products, Q_r for these three reactions are given by

$$Q_4 = f_{\text{H}_2}/a_{\text{H}_2\text{S}} \quad (7)$$

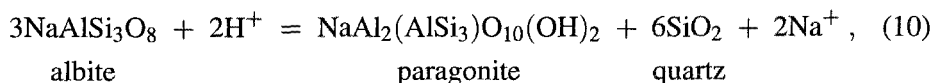
$$Q_5 = (a_{\text{SO}_4^{-2}})(a_{\text{H}^+})^2(f_{\text{H}_2})^3 \quad (8)$$

and

$$Q_6 = (a_{\text{SO}_4^{-2}})(a_{\text{H}^+})^2(f_{\text{H}_2})^4/(a_{\text{H}_2\text{S}}), \quad (9)$$

where f and a represent fugacity (gases) and activity (aqueous species), respectively. Note that these activity products are written with the assumption that native S can be represented by the standard state (pure mineral) so that its activity is unity, and that the activity of H_2O is also unity, an assumption which introduces minimal uncertainty in thermodynamic calculations for many geologic fluids (Helgeson, 1979, 1985). Equations (7–9) indicate that activities of dissolved constituents, pH and the fugacity of H_2 dictate Q_r , which can have a large influence on ΔG_r . Geochemical processes control the activities and fugacities of species involved in geochemical reactions, and in many cases reactions between aqueous fluids and natural assemblages of minerals provide buffers for pH, f_{H_2} and solute activities. Examples of these buffers are presented here, and the impact of geochemically controlled values of Q_r are demonstrated by the examples in the next section.

How is pH controlled in hydrothermal fluids? This is a question of considerable interest to geochemists studying the consequences of fluid/rock reactions. Many reactions have been proposed to meet the criteria imposed by various geologic settings. An example of a fluid/rock reaction which can be used as a pH indicator and serves as a pH buffer is given by



which involves quartz, a feldspar (albite) and a mica (paragonite). Assuming pure phases, the logarithmic activity product for reaction (10) reduces to

$$1/2 \log Q_{10} = \log(a_{\text{Na}^+}/a_{\text{H}^+}). \quad (11)$$

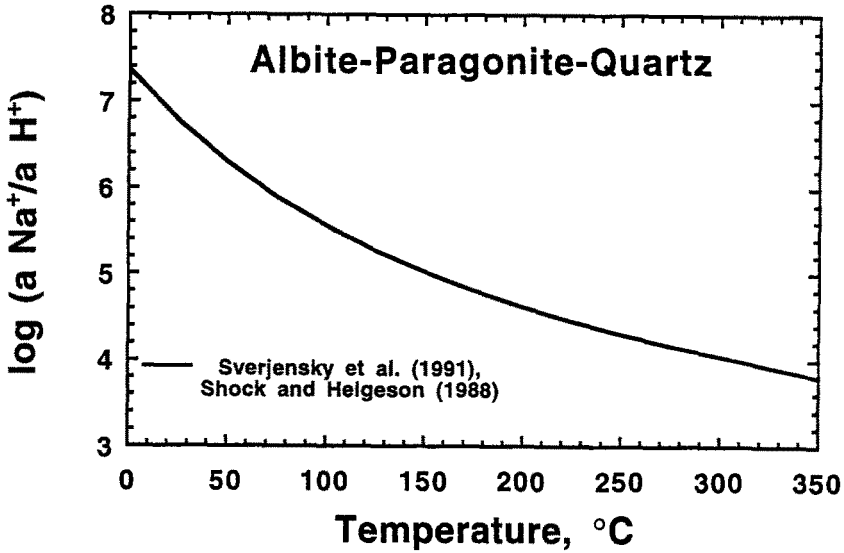


Fig. 3a.

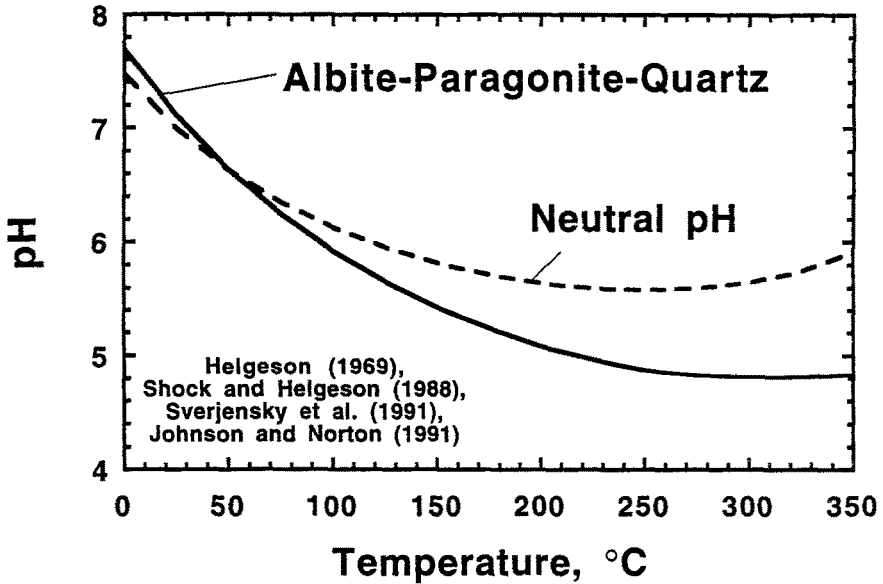


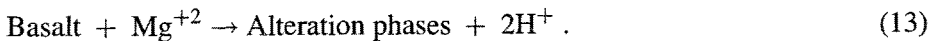
Fig. 3b.

Figs. 3(a)–(b). Calculated values of the ratio of the activity of Na^+ to that of H^+ for an aqueous solution in equilibrium with the albite-paragonite-quartz assemblage. Data and parameters for the minerals are consistent with Sverjensky *et al.* (1991) and those for aqueous ions and the revised HKF equation of state from Shock and Helgeson (1988). (b) Evaluated pH from the activity ratio in Figure 3a (solid curve) using activity coefficients for Na^+ from Helgeson (1969), and pH values of neutrality for pure H_2O (dashed curve) calculated with data and parameters for the ions from Shock and Helgeson (1988) and for H_2O from Johnson and Norton (1991).

At equilibrium, $\Delta G_{10} = 0$ and Q_{10} equals the equilibrium constant K_{10} which can be calculated from ΔG°_{10} and the relation

$$\Delta G^{\circ}_r = -2.303RT \log K_r. \quad (12)$$

Evaluation of ΔG°_{10} allows calculation of the equilibrium Na^+ to H^+ activity ratio (Equation 11), which allows calculation of pH from the activity of Na^+ . Equilibrium values of $\log (a \text{Na}^+ / a \text{H}^+)$ appropriate for reaction (10) are shown in Figure 3a. Combining these values with appropriate activity coefficients for Na^+ (γNa^+) taken from Helgeson (1969), together with the relation $a = m\gamma$, allows calculation of pH for a given molality (m) of Na^+ . An example for a 1 molal NaCl solution is shown by the solid curve in Figure 3b. At low temperatures, these values of pH are slightly alkaline relative to the neutral pH of pure H_2O , which is depicted in Figure 3b as a dashed curve. At higher temperatures, and especially in the range of hydrothermal systems, pH values buffered by the albite-paragonite-quartz assemblage are somewhat acidic. Reaction (10) has been used extensively in hydrothermal experiments to control pH (see Sverjensky *et al.*, 1991), and is one of many examples of fluid/rock equilibria which buffer pH in hydrothermal fluids. In submarine hydrothermal systems, reactions involving basaltic minerals and seawater lead to an increase in pH of the fluid and addition of Mg^{+2} from seawater to the rock. This process is illustrated by



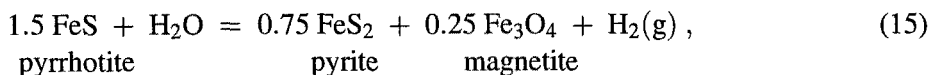
Calculations for submarine hydrothermal vent fluids indicate that pH lies between 3.5 and 4.7 at 350°C (Janecky and Seyfried, 1984; Bowers *et al.*, 1985, 1988; Bowers and Taylor, 1985). We have employed albite-paragonite-quartz equilibria in the following calculations to facilitate experimental tests of our results.

What controls the oxidation state in hydrothermal fluids? This is another question of considerable interest to geochemists because trace element speciation, organic compound stability and solubilities of sulfides, iron oxides, iron silicates and many other minerals all depend on the redox conditions. Again, reactions between fluids and mineral assemblages can produce redox buffers. Various methods of tracking the oxidation state of hydrothermal fluids and mineral assemblages are used in the geochemical literature, including Eh, pe and the fugacities of oxygen and hydrogen. In this study we have chosen to represent the oxidation state in terms of the hydrogen fugacity ($f\text{H}_2$), because it is easiest to couple redox reactions between minerals and aqueous organic compounds through H_2 . It should be kept in mind, however, that corresponding values of oxygen fugacity ($f\text{O}_2$) can be calculated from values of $f\text{H}_2$ by taking account of the equilibrium constant for the reaction



which is known to be rapid in hydrothermal solutions (Chou, 1987), through the relation $f\text{O}_2 = 2(\log K_{13} - \log f\text{H}_2)$ and the assumption that $a\text{H}_2\text{O} = 1$.

Fluid/rock buffering of $f\text{H}_2$ is illustrated by the reaction between H_2O and the PPM (pyrrhotite-pyrite-magnetite) assemblage



one of many mineral assemblages which can buffer $f\text{H}_2$. At equilibrium, the logarithmic expression for the equilibrium constant of reaction (15) reduces to

$$\log K_{15} = \log f\text{H}_2, \quad (16)$$

and allows the calculation of $f\text{H}_2$. Numerous experimental results demonstrate that mineral assemblages effectively buffer $f\text{H}_2$ at temperatures and pressures of hydrothermal systems (Seyfried *et al.*, 1987; Seewald, 1994). Values consistent with the PPM assemblage provide a good approximation of the $f\text{H}_2$ of submarine hydrothermal fluids that vent at sulfide mounds at ridge crests (Haymon and Kastner, 1981; Janecky and Seyfried, 1984). Other assemblages can buffer the $f\text{H}_2$ to higher (more reduced) or lower (more oxidized) values as fluids circulate through the oceanic crust, which influences the potential for organic synthesis and/or destruction in hydrothermal systems (Shock, 1990a, 1992a).

These examples of pH and $f\text{H}_2$ buffering by fluid/rock reactions illustrate the fact that there is considerably more to hydrothermal fluids than hot water. The fugacity of H_2 and activity of H_2S corresponding to the PPM assemblage can be evaluated with the help of the phase diagram for the Fe-O-S-H system shown in Figure 4. The solid lines in this figure show the phase relations at 100°C and the dotted lines correspond to 350°C . Note that a stability field for FeO exists at 350°C , but this phase is not stable at 100°C . It can be seen that at the invariant point corresponding to PPM, the activity of H_2S is much more sensitive to changes in temperature than is the fugacity of H_2 . The $f\text{H}_2$ of submarine hydrothermal vent fluids (350°C) is close to PPM, and reference to Figure 4 explains why the activity of H_2S is 10^{-2} in these fluids (Von Damm, 1990). At lower temperature, the activity of H_2S would drop considerably if the PPM assemblage continued to buffer the $f\text{H}_2$ of the system. The activity of H_2S would drop further if the system became more oxidized and hematite (Fe_2O_3) replaced magnetite. In fact, the assemblage of iron sulfides and oxides which allows the greatest equilibrium activity of H_2S is PPM at temperatures up to at least 350°C .

If naturally occurring mineral assemblages in the Fe-O-S-H system do not include iron oxides, then invariant points in Figure 4 are avoided and higher activities of H_2S are possible. However, it is difficult to construct scenarios which avoid the presence of iron oxide minerals during alteration of basalt in hydrothermal systems in the Earth's crust. An inadequate understanding of the nature of fluid/rock reactions has led many chemists to conduct poorly constrained experiments that

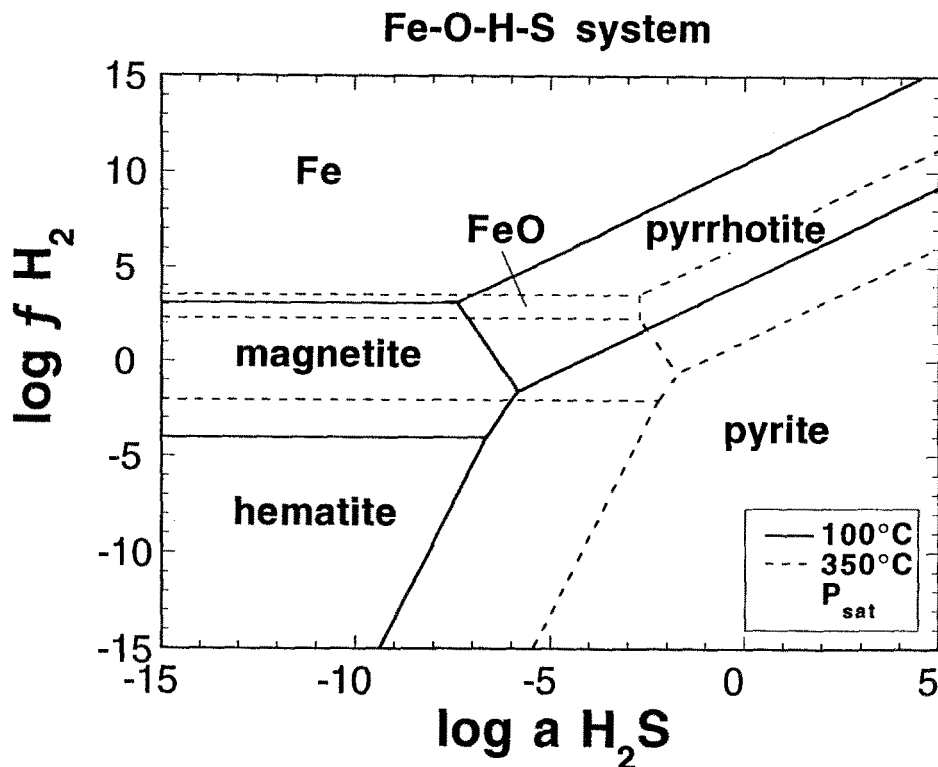


Fig. 4. Phase diagram for the Fe-O-S-H system showing mineral stabilities as functions of fugacity of H_2 and activity of aqueous H_2S . The solid lines indicate phase relations at 100°C and the dashed lines refer to 350°C. Both sets of phase boundaries are constructed at the liquid-vapor saturation pressure for H_2O . There are three invariant points at 100°C corresponding to the assemblages Fe-magnetite-pyrrhotite, pyrite-pyrrhotite-magnetite and magnetite-hematite-pyrite. At 350°C, the latter two invariant points are also present, together with two others corresponding to Fe-FeO-pyrrhotite and FeO-magnetite-pyrrhotite. At either temperature, and all intermediate temperatures, the pyrite-pyrrhotite-magnetite invariant point corresponds to the highest activity of aqueous H_2S of any of the invariant points in the system.

are asserted to represent hydrothermal conditions (see critiques in: Shock, 1990a, 1992b). As an example, an experiment conducted by Drobner *et al.* (1990), in which pyrrhotite was reacted with H_2S at 100°C to form pyrite through the reaction



could plot at any point along the univariant line separating pyrite and pyrrhotite in Figure 4. Drobner *et al.* (1990) used a concentration of H_2S of 10^{-2} m and showed H_2 production during pyrite formation, and argued that reaction (17) could provide enormous reduction potential in hydrothermal fluids. As discussed above, fH_2 is commonly buffered by mineral assemblages which include iron oxides, so it is not an independent variable. By the same token, if fH_2 is set by the PPM assemblage, then the activity of H_2S is also set by equilibrium between reactions (15) and

(17). As a consequence, Drobner *et al.* (1990) employed an activity of H_2S which exceeds by ~ 4 orders of magnitude that which is set by PPM equilibrium at 100°C . Indeed, the equilibrium $f\text{H}_2$ at the conditions employed by Drobner *et al.* (1990) corresponds to a partial pressure of H_2 in excess of 100 bars. On the other hand, the results presented by Drobner *et al.* (1990) could apply to a scenario in which 350°C vent fluids were cooled to 100°C without mixing with seawater or other fluids and then allowed to react with pyrrhotite but no other iron oxides or sulfides. This elaborate scheme seems implausible for a natural system, and illustrates that a limited understanding of natural systems, coupled with confusing the laboratory for nature, can lead to misconceptions of the potential of those systems.

Chemosynthesis in Present-Day Hydrothermal Environments

One of the sources of energy for the thriving biological communities at submarine hydrothermal vents is the introduction of H_2S into seawater at concentrations extremely far from equilibrium. In many of these systems native S precipitates as reduced hydrothermal fluids cool and mix with much more oxidized seawater, and in most of these systems barite (BaSO_4) and/or anhydrite (CaSO_4) precipitate from seawater as it is heated in the vent-chimney environment. Because sulfur should be present as sulfate at equilibrium in present-day seawater, the introduction of reduced forms of sulfur (H_2S and S) into seawater serves as a source of disequilibrium and therefore a source of chemical energy. This energy can be tapped by microorganisms because the oxidation of H_2S and S to sulfate is sluggish during mixing of hydrothermal fluids with low-temperature bottom-water in the ocean (2 to 3°C) (Zhang and Millero, 1993). This kinetic barrier provides an opportunity for metabolic systems, which act as catalysts, to extract energy from the disequilibrium provided by the mixing of reduced and oxidized fluids. The energy available to organisms in the present-day systems is enormous.

The energy available to chemolithoautotrophs in present-day hydrothermal systems can be calculated by combining standard Gibbs free energies for the appropriate reactions with geochemical constraints. Calculated standard Gibbs free energies for the sulfur oxidation reaction (reaction 5) are shown in Figure 5, where it can be seen that ΔG_r° is about 49 kcal mol^{-1} at 0°C , minimizes around 100°C and increases to $>66 \text{ kcal mol}^{-1}$ at 350°C and Psat. At all temperatures considered, ΔG_r° for sulfur oxidation is a large positive number. In contrast, ΔG_r for sulfur oxidation can be negative once geochemical constraints are imposed. For example, the calculated value of the standard partial molal Gibbs free energy for reaction (5) is $48820. \text{ cal mol}^{-1}$ at 25°C . Outside of a geochemical reference frame, it might be argued that the positive value for ΔG_r° would prohibit this from being a useful chemolithoautotrophic reaction. However, geochemical constraints imposed by present-day seawater ($\text{pH} = 8.22$, $\log a \text{ SO}_4^{-2} = -2.6$, and $\text{Eh} = 0.5\text{v}$) lead to $2.303RT \log Q_5 = -162290 \text{ cal mol}^{-1}$. As a result, ΔG_r for the sulfur oxidation reaction at 25°C in seawater is $-113470. \text{ cal mol}^{-1}$, and therefore any sulfur precip-

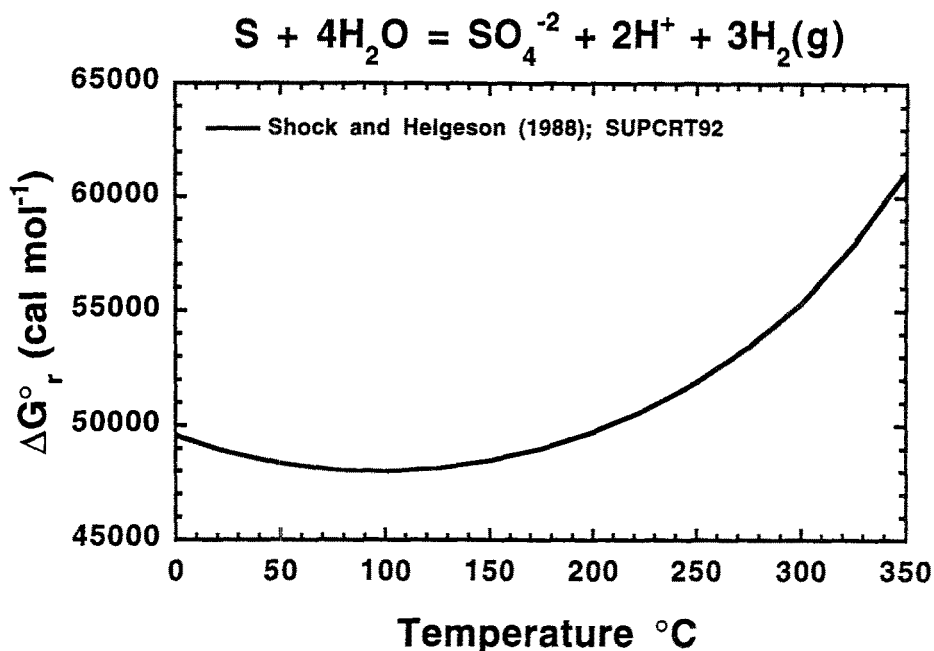


Fig. 5. Standard Gibbs free energies of reaction (5) as a function of temperature at P_{sat} calculated with the SUPCRT92 computer program using data and parameters for the aqueous ions from Shock and Helgeson (1988).

itating from cooling hydrothermal fluids becomes food (i.e. a source of metabolic energy) when it enters present-day seawater. This example demonstrates how geochemical constraints allow organisms to obtain energy through sulfur oxidation even at anaerobic conditions. *Note that the oxygen used to form sulfate can be derived from H_2O and free O_2 is not required. Isotopic labelling experiments have shown that some anaerobic organisms use H_2O as a source of oxygen* (Vogel and Grbic-Galic, 1986; Pereira *et al.*, 1988).

The sulfur oxidation reaction can also provide energy at higher temperatures in the zone of mixing between hydrothermal fluids and seawater. This is shown schematically in Figure 6, where ΔG_r for reaction (5) is plotted against temperature. Three contours of ΔG_r are shown in this plot for $f\text{H}_2$ values corresponding to that set by the PPM assemblage, 2 log $f\text{H}_2$ units more oxidized (PPM-2) and 4 log $f\text{H}_2$ units more oxidized (PPM-4). All of the calculations shown in this figure were conducted at pH values set by the albite-paragonite-quartz assemblage (see Figure 3). The arrow in Figure 6 indicates a likely trajectory of decreasing temperature and increasing oxidation state which would occur as hydrothermal fluids mix with seawater, in which $f\text{H}_2$ is more than 30 log units more oxidized than PPM. Note that this trajectory leads to a set of conditions where ΔG_r becomes negative. Hyperthermophilic archaea which thrive at around 100°C have been

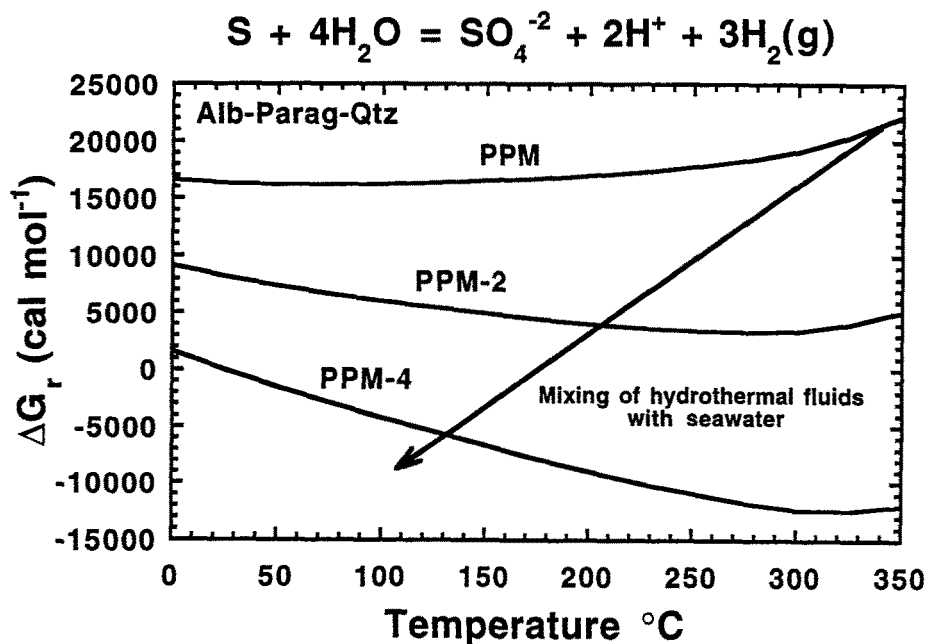


Fig. 6. Values of the Gibbs free energy of reaction (5) as a function of temperature at P_{sat} at conditions corresponding to pH buffering by albite-paragonite-quartz and a 1 molal NaCl solution, and $f\text{H}_2$ buffering by the PPM assemblage (upper curve). Also shown are two contours for this reaction representing the values of ΔG_r resulting from mixing of the more oxidized seawater with hydrothermal fluids. Contours are labelled in terms of the shift in $f\text{H}_2$ due to mixing.

cultured from these systems, and the calculations depicted in Figure 6 show that sulfur oxidation could be a viable lifestyle for some of these organisms.

Oxidation of H_2S to sulfate (reaction 6) is another lifestyle pursued by thermophilic archaea (e.g. *Sulfolobus*). The plot shown in Figure 7 indicates that ΔG_r° for this reaction, as in the case of the sulfur oxidation reaction, is positive throughout the temperature range considered. Geochemical constraints on the fugacity of H_2 and activities of aqueous species involved in this reaction must allow ΔG_r to be negative so that H_2S oxidation will provide energy and therefore will represent food to a microorganism. That this is the case can be demonstrated by comparing the activity ratio of H_2S to sulfate in hydrothermal fluids with that of present-day seawater. If we constrain the pH and the $f\text{H}_2$ we can calculate equilibrium values of $(a\text{SO}_4^{-2}/a\text{H}_2\text{S})$ from the equilibrium constant for reaction (6) (see Equation (9)). Using the albite-paragonite-quartz assemblage to set pH and the PPM assemblage to set $f\text{H}_2$ leads to the values of $(a\text{SO}_4^{-2}/a\text{H}_2\text{S})$ shown in Figure 8. The choice of albite-paragonite-quartz yields a conservative pH which may be slightly higher than that of submarine hydrothermal vent fluids, but provides a reference frame for the following calculations which can be tested experimentally with relative ease. It can be seen in Figure 8 that H_2S predominates by several orders-of-magnitude over

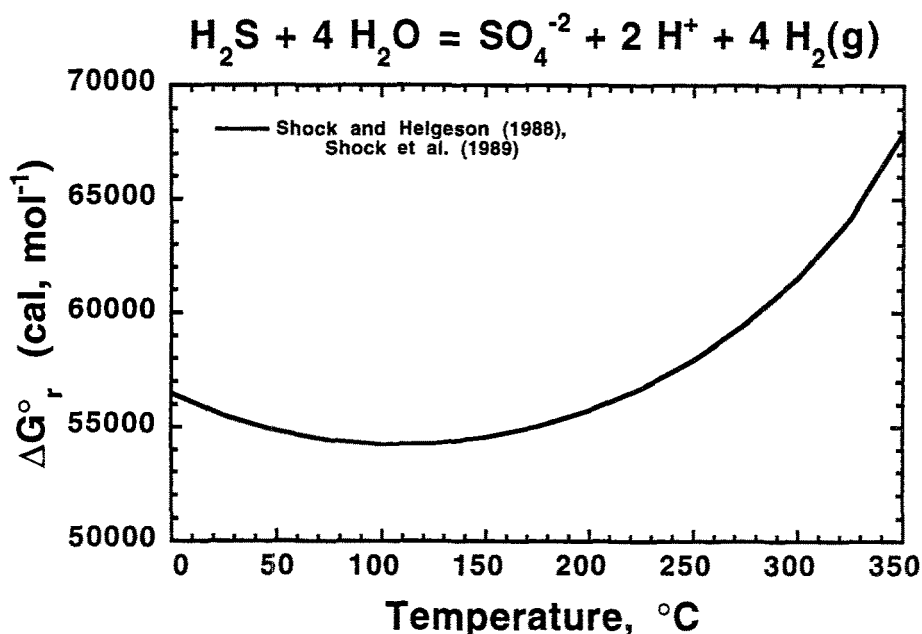


Fig. 7. Values of the standard Gibbs free energy of reaction (6) as a function of temperature at P_{sat} calculated with the SUPCRT92 program using data and parameters for the ions from Shock and Helgeson (1988) and for aqueous H_2S from Shock *et al.* (1989).

SO_4^{-2} at all temperatures considered. Similarly, sulfur in submarine hydrothermal fluids in which $f\text{H}_2$ is buffered by PPM will be detectable only as H_2S , which is consistent with geochemical observations (Von Damm, 1990). In contrast, present-day seawater is relatively oxidized and sulfate predominates over H_2S . Using an estimate of the oxidation state of seawater from Baas-Becking *et al.* (1960) ($E_h=0.5$ V) yields equilibrium fugacities of H_2 and O_2 of $10^{-33.3}$ and $10^{-16.4}$, respectively. If the sulfur system was able to reach equilibrium in seawater, $\log(a\text{SO}_4^{-2}/a\text{H}_2\text{S})$ would equal 109.2 at these conditions! Therefore, there is a potential difference of ~ 120 orders of magnitude in the sulfate to sulfide ratio as hydrothermal fluids mix with seawater in present-day systems. At 100°C , disequilibrium between the two fluids corresponds to more than 200 000 calories of chemical energy per mole of H_2S which would be oxidized. The direct result of the constant supply of H_2S is that life is prolific around hydrothermal vents and probably has been since the first thermophilic organisms appeared.

Extrapolation to the Early Earth

The calculations described above are appropriate to the present-day situation in the oceans. Conditions on the early Earth were likely to be different than at present, most notably the oxidation state of the early atmosphere. A number of models

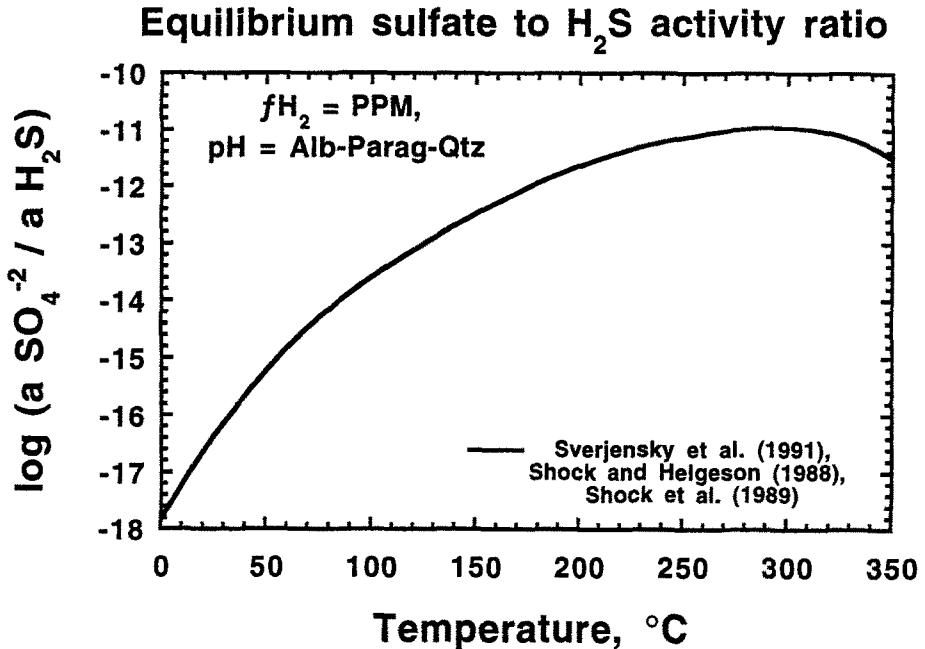


Fig. 8. Calculated ratios of the activity of SO_4^{-2} to that of H_2S as a function of temperature at P_{sat} and conditions consistent with pH buffering by the albite-paragonite-quartz assemblage and $f\text{H}_2$ buffering by the PPM assemblage. Note that at the high temperatures of hydrothermal systems H_2S will predominate over SO_4^{-2} by many orders of magnitude, consistent with the inability of available techniques to find SO_4^{-2} in hydrothermal fluids.

for the composition of the early atmosphere have been proposed which take into account (to varying extents) the effects of photochemistry, impacts, greenhouse gases, reduced solar luminosity, enhanced solar UV, outgassing of the mantle, atmosphere/hydrosphere/crust reactions, contributions from comets and meteorites, and hydrothermal fluxes. Although these models differ in detail, one general consensus is that the generation and/or preservation of a reduced atmosphere was unlikely (Levine, 1982, 1985; Levine *et al.*, 1982; Kasting *et al.*, 1983; Stevenson, 1983; Kasting, 1993). In the early 1980's, Walker argued that the early atmosphere would have been N_2 dominated like the present atmosphere, but would differ in a much lower partial pressure of O_2 , and possibly by a much greater partial pressure of CO_2 (Walker, 1983). Levine (1982) calculated partial pressures of O_2 in such an atmosphere and obtained values approximately 10^{-15} of the present atmospheric level. If we assume that this ~ 15 order-of-magnitude decrease would be reflected by a ~ 15 order-of-magnitude decrease in the $f\text{O}_2$ of seawater, the corresponding Eh (0.28 V) remains well within the predominance range of sulfate. Several investigators have argued that there could have been significant CO in the early atmosphere, introduced from volcanic gases, cometary material or shock-heating during impacts (Fegley *et al.*, 1986; Kasting, 1990, 1993). Thus the atmosphere

may have been more reduced than the N_2 - CO_2 - H_2O mixture proposed by Kasting *et al.* (1983) and Kasting (1993). Indeed, Kasting *et al.* (1983) propose an Archaean atmosphere with equal concentrations of CO and CO_2 . However, none of these models produces an atmosphere for the early Earth which would drive seawater out of the predominance range of sulfate. At 25°C, equal activities of H_2S and sulfate in seawater requires the fO_2 to be 10^{-71} which is lower than any of the recent models predict.

Although we are not certain what the fO_2 of the early atmosphere/ocean system was, we can make some *conservative* choices to evaluate the effect on the availability of chemical energy from H_2S oxidation during mixing of hydrothermal fluids with seawater. If we assume that the partial pressure of O_2 was 30 orders of magnitude lower than that of the present atmosphere, the corresponding Eh of seawater would still be in the predominance range of sulfate. The calculated value of $\log(aSO_4^{-2}/aH_2S)$ at equilibrium would be 50. Assuming that Archean hydrothermal fluids are well-represented by modern fluids, there would be approximately 60 orders-of-magnitude difference in this ratio between hydrothermal fluids and seawater, corresponding at 100 °C to more than 100 000 calories per mole of H_2S . Present-day hydrothermal fluids often contain about 10^{-2} molal H_2S , and have flow rates of at least 1 L sec^{-1} . Therefore, the chemical power of a single hydrothermal vent on the floor of an Archean ocean would have been 4000 W. Either in terms of energy or as power, the consequences for chemical reactions are enormous. Individual ridge crest systems have lifetimes on the order of hundreds of years (Haymon *et al.*, 1981) and heat flow anomalies exist in oceanic crust for about 65 million years at plate boundaries (Mottl and Wheat, 1994). The long duration of hydrothermal systems, the large degrees of chemical disequilibrium coupled with kinetically sluggish reactions, and the extremely tight localization of chemical energy sources make the mixing zones around hydrothermal vents ideal locations for organic synthesis and/or the emergence of an early metabolic system.

Concluding Remarks

The emergence of a metabolic system requires a source of energy. In present-day hydrothermal systems, chemical energy resulting from the disequilibrium between hydrothermal fluids and seawater is tapped by chemolithoautotrophic organisms. Calculations presented above help to quantify the available energy at present-day conditions and at those hypothesized to exist on the early Earth. We believe that the energy available as fluids mix on the seafloor may have been sufficient to allow the emergence of a metabolic system. A similar conclusion is reached by Russell *et al.* (1993), although the details are different.

The type of calculations described above can be used with thermodynamic data for CO_2 , CO and aqueous organic compounds to test the thermodynamic feasibility of organic synthesis reactions and early metabolic processes at hydrothermal conditions. These calculations can also be used to construct 'menus' of appropriate

aqueous compounds which present-day archaea require at the wide range of temperature, pressure, pH, oxidation state and salinity at which they thrive in actual natural systems. This type of approach could lead to breakthroughs in the success of culturing archaea and other microorganisms from hydrothermal systems.

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