



doi:10.1016/j.gca.2003.06.001

## Thiols in hydrothermal solution: standard partial molal properties and their role in the organic geochemistry of hydrothermal environments

MITCHELL D. SCHULTE<sup>1,\*</sup> and KARYN L. ROGERS<sup>2</sup><sup>1</sup>NASA Ames Research Center, Exobiology Branch, Mail Stop 239-4, Moffett Field, CA 94035, USA<sup>2</sup>Washington University, Department of Earth & Planetary Sciences, Campus Box 1169, One Brookings Drive, St. Louis, MO 63130, USA

(Received October 18, 2001; accepted in revised form June 23, 2003)

**Abstract**—In order to assess the potential role of organic sulfur compounds in hydrothermal systems, we use recent advances in theoretical geochemistry to estimate the standard partial molal thermodynamic properties and parameters for the revised Helgeson-Kirkham-Flowers equation of state for aqueous straight-chain alkyl thiols. Thermodynamic properties are used to determine the potential for thiol formation in both modern and Archean hydrothermal systems. We conclude that organic sulfur compounds may hold the key to the organic chemistry that led to the origin of life in hydrothermal settings. These results may also explain the presence of sulfur in a number of biomolecules present in ancient thermophilic microorganisms. Copyright © 2004 Elsevier Ltd

### 1. INTRODUCTION

Sulfur-bearing compounds have been suggested to play a key role in abiotic organic synthesis in modern hydrothermal environments and also may have been critical in “prebiotic” systems and the origin of life (Wächtershäuser, 1990a,b; de Duve, 1991; Blöchl et al., 1992; Huber and Wächtershäuser, 1997, 1998; Russell and Hall, 1997; Russell et al., 1998). Sulfur itself is ubiquitous in hydrothermal systems as a component of volcanic gases (e.g., SO<sub>2</sub>), in entrained seawater (as SO<sub>4</sub><sup>2-</sup>) and most commonly in sulfur-bearing minerals (e.g., pyrite, pyrrhotite and even S<sup>0</sup> in shallow submarine and terrestrial hydrothermal systems). In fact, sulfur-bearing mineral assemblages are so prevalent in hydrothermal chemistry that they are often used in hydrothermal experiments either as redox buffers, surface catalysts or both (Seewald, 1994, 1997; McCollom et al., 2001). Recent experiments that simulate hydrothermal conditions using H<sub>2</sub>S or sulfur-bearing mineral assemblages suggest that organic sulfur compounds are an inevitable and perhaps essential part of hydrothermal chemistry (Blöchl et al., 1992; Heinen and Lauwers, 1996; Huber and Wächtershäuser, 1997, 1998; Cody et al., 2000). The role that these compounds might have played in the origin of life on Earth remains undetermined; however, the presence of sulfur in a number of key biologic molecules (such as the amino acids methionine and cysteine, and its dimer cystine, and coenzymes M and acetyl CoA) and primitive metabolic processes (S oxidation and reduction in chemolithoautotrophs) lends credence to the idea that organic sulfur compounds were central in the origin and early evolution of life.

Due to the large number of oxidation states of sulfur, it has quite a diverse chemistry, including a near-infinite number of sulfur-bearing organic compounds. The simplest of the sulfur-bearing organic compounds are the thiols (organic compounds containing the –SH functional group), which are specifically known to be common in biochemical processes: coenzyme M is itself a thiol, and thiols are responsible for the distinctive odors of garlic (2-propene-1-thiol), onions (propanethiol) and skunks

(3-methyl-1-butanethiol). To determine the role of thiols in hydrothermal systems and potentially how sulfur became involved in biochemistry, we have developed a correlation scheme to estimate the standard partial molal thermodynamic properties of these compounds.

The role that aqueous organic sulfur compounds play in hydrothermal chemistry is largely unknown owing to a paucity of measurements of these compounds in hydrothermal systems and a lack of thermodynamic data for aqueous organic sulfur compounds that could be used to predict the stability of these compounds under hydrothermal conditions. In an effort to correct the latter of the two issues we have been predicting thermodynamic properties of the aqueous organic sulfur compounds at elevated temperatures and pressures. Here we present data for the simplest of the organic sulfur species, the aqueous 1-alkyl thiols.

To determine the thermodynamic properties of the aqueous alkyl thiols, we have culled the literature to obtain the experimentally-determined properties of organic sulfur compounds. We were able to calculate a number of essential properties, such as free energies of formation, from solubility data available in the literature together with standard properties of organic sulfur gases. However, a number of the properties of aqueous organic sulfur compounds have not been experimentally determined. Furthermore, most of thermodynamic data are available only for 25°C and 1 bar. To determine reaction properties at the temperatures and pressures of the hydrothermal systems, we use equations of state developed by Helgeson and coworkers (Tanger and Helgeson, 1988; Shock et al., 1992). A key piece of information needed to extrapolate thermodynamic properties to elevated temperatures is the partial molal heat capacity, for which experimental data are unavailable for nearly all aqueous organic sulfur compounds, even at standard state conditions (25°C and 1 bar).<sup>1</sup>

<sup>1</sup> In this study, the standard state for H<sub>2</sub>O calls for unit activity of the pure solvent at any pressure and temperature, and the standard state for gases is unit fugacity of the ideal gas at any temperature and 1 bar. The standard state convention for aqueous species is one of unit activity in a hypothetical 1 molal solution referenced to infinite dilution at any pressure and temperature.

\* Author to whom correspondence should be addressed (mschulte@mail.arc.nasa.gov).

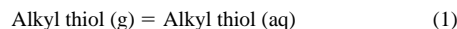
We have used correlation methods to estimate the partial molal heat capacities and volumes of aqueous thiols. These estimates allow us to assess the role of organic sulfur compounds during the reduction of carbon in hydrothermal settings.

## 2. ESTIMATION METHODS

Despite the ubiquity of sulfur in many biomolecules, biochemical processes and metabolisms, there are no published thermodynamic data for aqueous alkyl thiols. In the absence of experimentally determined thermodynamic data for organic sulfur compounds, provisional data can be obtained using established correlations among other groups of aqueous organic compounds. Methods have been developed by Helgeson and coworkers (Shock and Helgeson, 1988, 1990; Shock et al., 1989, 1992, 1997; Sverjensky et al., 1997; Schulte et al., 2001) to estimate the standard partial molal thermodynamic properties of aqueous species. These methods have been extended to include organic compounds, taking advantage of the systematic nature of thermodynamic properties as a function of carbon number within a family of aqueous organic compounds (Shock and Helgeson, 1990; Schulte and Shock, 1993; Shock, 1995; Dale et al., 1997; Schulte, 1997). Recent high temperature experimental measurements of the partial molal volumes and heat capacities of a selected group of compounds (Criss and Wood, 1996; Schulte et al., 1999) have led to improvements in these methods (Schulte, 1997). Described below are the methods by which the standard partial molal thermodynamic properties of the aqueous alkyl thiols were calculated or estimated in this study. The standard partial molal free energy of formation, enthalpy of formation and entropy for short chain aqueous alkyl thiols are calculated using experimentally determined properties of the gas solubility reactions. These are extended to longer-chained thiols using previous correlations that are applicable to aqueous organic compounds. The standard partial molal heat capacity and volume of propanethiol are estimated based on group contribution theory and extended to longer-chain thiols using similar correlations for other families of aqueous organic compounds.

### 2.1. $\Delta\bar{G}_f^\circ$ , $\Delta\bar{H}_f^\circ$ , and $\bar{S}^\circ$

Values of the standard partial molal Gibbs free energy of formation  $\Delta\bar{G}_f^\circ$  for  $C_1$  (methanethiol) through  $C_5$  (pentanethiol) alkyl thiols and enthalpy of formation  $\Delta\bar{H}_f^\circ$  for  $C_1$  through  $C_4$  (butanethiol) alkyl thiols were calculated using the standard Gibbs free energy or standard enthalpy of formation of the gaseous species ( $\Delta\bar{G}_{f,g}^\circ$  or  $\Delta\bar{H}_{f,g}^\circ$ ) along with the experimentally determined Gibbs free energy or enthalpy of the hydration reaction ( $\Delta G_{r,h}$  or  $\Delta H_{r,h}$ ). This can be illustrated with the general reaction



for which the Gibbs free energy of reaction ( $\Delta G_{r,h}$ ) is

$$\Delta G_{r,h} = \Delta\bar{G}_{f,aq}^\circ - \Delta\bar{G}_{f,g}^\circ \quad (2)$$

and the enthalpy of reaction is

$$\Delta H_{r,h} = \Delta\bar{H}_{f,aq}^\circ - \Delta\bar{H}_{f,g}^\circ \quad (3)$$

Using data for the standard property of the gas and hydration reaction, the standard partial molal Gibbs free energy and standard partial molal enthalpy of the aqueous species can be calculated with Eqns. 2 and 3. Values of the standard partial molal Gibbs free energy of formation and standard partial molal enthalpy for the aqueous alkyl thiols from methanethiol to butanethiol were calculated using the properties of the gaseous species from Alberty et al. (1987) and experimentally-determined free energies and enthalpies of the hydration reactions from Abraham et al. (1990). In addition, the standard partial molal Gibbs free energy of formation for aqueous pentanethiol was calculated using data from Alberty et al. (1987) and Amoores and Buttery (1978). There are no corresponding enthalpy data for pentanethiol. Values of the standard partial molal entropy ( $\bar{S}^\circ$ ) of aqueous methanethiol to butanethiol were calculated using the values of  $\Delta\bar{G}_f^\circ$  and  $\Delta\bar{H}_f^\circ$  and values of  $\bar{S}^\circ$  for the elements from Cox et al. (1989). The  $\Delta\bar{G}_f^\circ$  of methanethiol to pentane-

Table 1. Summary of standard partial molal thermodynamic properties of aqueous alkyl thiols at 25°C and 1 bar, calculated with data taken from the literature.

Thiol	$\Delta\bar{G}_f^\circ$ <sup>a</sup>	$\Delta\bar{H}_f^\circ$ <sup>a</sup>	$\bar{S}^\circ$ <sup>b</sup>
Methanethiol	-1840 <sup>c</sup>	-11650 <sup>d</sup>	38.60 <sup>e</sup>
Ethanethiol	-1100 <sup>c</sup>	-17820 <sup>d</sup>	45.50 <sup>e</sup>
Propanethiol	1380 <sup>c</sup>	-23320 <sup>d</sup>	53.90 <sup>e</sup>
Butanethiol	3560 <sup>c</sup>	-28630 <sup>d</sup>	61.30 <sup>e</sup>
Pentanethiol	6150 <sup>f</sup>		

<sup>a</sup> cal mol<sup>-1</sup>. <sup>b</sup> cal mol<sup>-1</sup> K<sup>-1</sup>. <sup>c</sup> Calculated from  $\Delta\bar{G}_f^\circ$ (g) from Alberty et al. (1987) and  $\Delta\bar{G}_f^\circ$ (g $\leftrightarrow$ aq) from Abraham et al. (1990). <sup>d</sup> Calculated from  $\Delta\bar{H}_f^\circ$ (g) from Stull et al. (1969) and  $\Delta\bar{H}_f^\circ$ (g $\leftrightarrow$ aq) from Abraham et al. (1990). <sup>e</sup> Calculated from  $\Delta\bar{H}_f^\circ$  and  $\Delta\bar{G}_f^\circ$  in the table, together with  $\bar{S}^\circ$  of the elements from Cox et al. (1989). <sup>f</sup> Calculated from  $\Delta\bar{G}_f^\circ$ (g) from Alberty et al. (1987) and  $\Delta\bar{G}_f^\circ$ (g $\leftrightarrow$ aq) from Amoores and Buttery (1978).

thiol and  $\Delta\bar{H}_f^\circ$  and  $\bar{S}^\circ$  of methanethiol to butanethiol are listed in Table 1.

Figures 1 to 3 show the resulting values of the standard partial molal Gibbs free energy of formation, standard partial molal enthalpy of formation and standard partial molal entropy, respectively, for the aqueous thiols as a function of the number of carbons in the alkyl chain ( $\bar{n}$ ). As is evident in each figure, the standard partial molal thermodynamic properties of the alkyl thiols, like for all organic compound families, display systematic behavior as alkyl chain length increases. This behavior results from the addition of the  $-\text{CH}_2-$  group in increasing the chain length. The addition of this group increases the standard partial molal Gibbs free energy of formation of aqueous organic species by 2050 cal mol<sup>-1</sup> and decreases the standard partial molal enthalpy by 5670 cal mol<sup>-1</sup> (Shock and Helgeson, 1990). The standard partial molal entropy increases by 6.7 cal mol<sup>-1</sup> K<sup>-1</sup> with each additional  $-\text{CH}_2-$  group (Shock and Helgeson, 1990). These values are applicable to all families of organic compounds (Shock and Helgeson, 1990) and are adopted here for the 1-alkyl thiols. The best line fits to the calculated data using these slopes are shown in Figures 1 to 3. The intercepts of the lines are -4370 cal mol<sup>-1</sup> for  $\Delta\bar{G}_f^\circ$ , -6180 cal mol<sup>-1</sup> for  $\Delta\bar{H}_f^\circ$  and 33.1 cal mol<sup>-1</sup> K<sup>-1</sup> for  $\bar{S}^\circ$ . We use these values to calculate these properties for longer, straight-chained aqueous thiols for which experimental data are not available. The equations used to make these estimates are

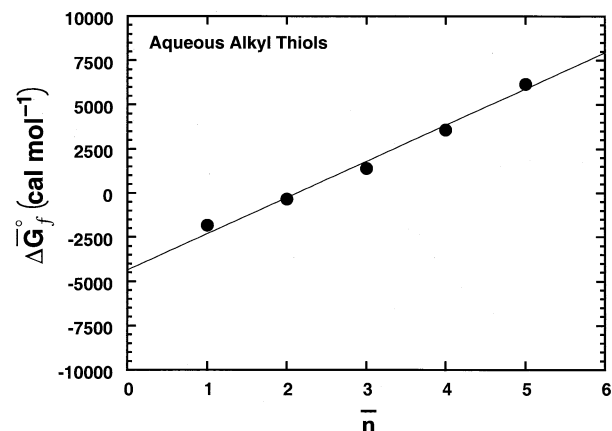


Fig. 1. Standard partial molal Gibbs free energy of formation of aqueous alkyl thiols as a function of the number of carbons in the alkyl chain. The free energy values for the aqueous species were calculated from the standard Gibbs free energies of formation of the gas (Alberty et al., 1987) and the free energy of solubility reactions (Abraham et al., 1990); see text and Table 1 for details.

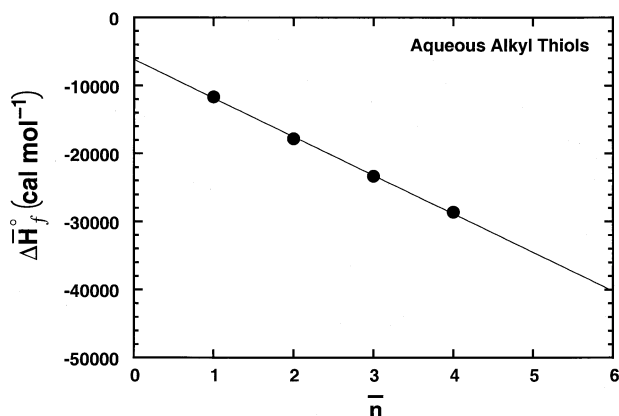


Fig. 2. Standard partial molal enthalpy of formation of aqueous alkyl thiols as a function of the number of carbons in the alkyl chain. The enthalpy values for the aqueous species were calculated from the standard enthalpies of formation of the gas (Alberty et al., 1987) and the free energy of solubility reactions (Abraham et al., 1990); see text and Table 1 for details.

$$\Delta \bar{G}_f^\circ (\text{cal mol}^{-1}) = -4370 + 2050\bar{n}, \quad (4)$$

$$\Delta \bar{H}_f^\circ (\text{cal mol}^{-1}) = -6180 + 5670\bar{n} \quad (5)$$

$$\bar{S}^\circ (\text{cal mol}^{-1} \text{K}^{-1}) = -33.1 + 6.7\bar{n} \quad (6)$$

where  $\bar{n}$  represents the number of carbons in the alkyl chain. Values of  $\Delta \bar{G}_f^\circ$ ,  $\Delta \bar{H}_f^\circ$  and  $\bar{S}^\circ$  at 25°C and 1 bar for methanethiol ( $C_1$ ) through dodecanethiol ( $C_{12}$ ) are in Table 2.

## 2.2. $\bar{C}_p^\circ$ and $\bar{V}^\circ$

At the present time, there are no experimental data for the standard partial molal volumes and heat capacities of aqueous thiols, even at the standard conditions of 25°C and 1 bar. Therefore, we have estimated these properties for the aqueous thiols using a form of group contribution methods. To estimate the heat capacities, we compared the standard partial molal heat capacity of the aqueous amino acid serine to that of the aqueous amino acid cysteine, the only appropriate set of compounds for which data are available. These two amino acids are identical in structure, except for the functional group at the terminal end of the alkyl chain, which is a hydroxyl, (-OH), in serine and a thiol,

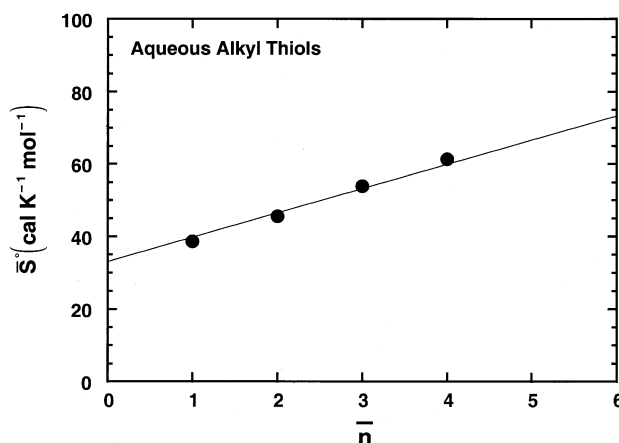


Fig. 3. Standard partial molal entropy of aqueous alkyl thiols as a function of the number of carbons in the alkyl chain. See text and Table 1 for details.

(-SH), in cysteine (Fig. 4). The experimentally determined value of the standard partial molal heat capacity of serine is 28.1 cal mol<sup>-1</sup> K<sup>-1</sup> (Jolicœur and Boileau, 1978), while the standard partial molal heat capacity of cysteine is 44.9 cal mol<sup>-1</sup> K<sup>-1</sup> (Jolicœur et al., 1986). The difference, 16.8 cal mol<sup>-1</sup> K<sup>-1</sup>, can be attributed to the difference in standard partial molal heat capacity between a molecule containing a thiol group relative to that containing a hydroxyl group. Because the amino acids that were compared each contain three carbons in their alkyl chains, we have chosen to add the difference in standard partial molal heat capacity, 16.8 cal mol<sup>-1</sup> K<sup>-1</sup>, to that of propanol (taken from Shock and Helgeson, 1990) to obtain the heat capacity of propanethiol (see Fig. 4 for structure comparison). The resulting value of the standard partial molal heat capacity of aqueous propanethiol is 101.1 cal mol<sup>-1</sup> K<sup>-1</sup>. Values of  $\bar{C}_p^\circ$  for the other aqueous thiols at 25°C and 1 bar were then estimated by adding or subtracting multiples of 21.2 cal mol<sup>-1</sup> K<sup>-1</sup> from this value according to alkyl chain length, following the arguments of Shock and Helgeson (1990) on the systematic behavior of partial molal heat capacities of aqueous organic compound families.

Values of the standard partial molal volume for the aqueous alkyl thiols were estimated in a manner similar to that used for the heat capacities. The difference in standard partial molal volumes between serine ( $\bar{V}^\circ = 60.57 \text{ cm}^3 \text{ mol}^{-1}$ ; Cabani et al., 1981) and cysteine ( $\bar{V}^\circ = 73.44 \text{ cm}^3 \text{ mol}^{-1}$ ; Millero et al., 1978) is 12.87 cm<sup>3</sup> mol<sup>-1</sup>. This value was added to the partial molal volume of propanol (taken from Shock and Helgeson, 1990) to estimate the partial molal volume of propanethiol, resulting in a value of 83.57 cm<sup>3</sup> mol<sup>-1</sup>. The partial molal volumes of aqueous organic compounds also vary systematically with carbon number (Shock and Helgeson, 1990), and multiples of 15.8 cm<sup>3</sup> mol<sup>-1</sup> were added or subtracted from the partial molal volume of propanethiol to estimate the standard partial molal volumes of other aqueous thiols at 25°C and 1 bar.  $\bar{C}_p^\circ$  and  $\bar{V}^\circ$  at 25°C and 1 bar for methanethiol through dodecanethiol are in Table 2 and shown in Figure 5.

## 2.3. Revised Helgeson-Kirkham-Flowers Equation of State Parameters

The standard state thermodynamic properties described above can be used to calculate thermodynamic properties of aqueous alkyl thiols at elevated temperature and pressure using the revised Helgeson-Kirkham-Flowers (HKF) equations of state. The calculated or estimated standard state thermodynamic properties for aqueous alkyl thiols at 25°C and 1 bar listed in Table 2 were used to obtain parameters for the revised Helgeson-Kirkham-Flowers equations of state (Tanger and Helgeson, 1988; Shock et al., 1992) using correlation algorithms for aqueous nonelectrolytes (including neutral organic species) presented by Shock and Helgeson (1990), Schulte (1997) and Schulte and Shock (personal communication). The resulting parameters are also listed in Table 2. These data and parameters can be used with the revised HKF equations of state to calculate standard state properties of aqueous alkyl thiols at elevated temperatures and pressures. The SUPCRT92 computer program (Johnson et al., 1992), which is available free of charge from Prof. Harold Helgeson at the University of California, Berkeley, facilitates such calculations.

## 3. FORMATION OF AQUEOUS THIOLS IN HYDROTHERMAL ENVIRONMENTS

While aqueous thiols have never been observed in hydrothermal systems, the ubiquity of sulfur in hydrothermal environments, key biomolecules and primitive metabolisms, as well as the reported presence of thiols in various hydrothermal experiments, indicates that thiols are central to hydrothermal geochemistry. In the absence of direct measurements, the role of thiols in hydrothermal chemistry can be explored by using the thermodynamic properties presented above to evaluate the potential for thiol synthesis. These calculations account for the thermodynamic properties of thiols as well as the range of temperature, pressure and geochemical conditions found in

Table 2. Summary of standard partial molal thermodynamic properties of aqueous alkyl thiols at 25°C and 1 bar, together with parameters for the revised HKF equations of state (see Shock and Helgeson, 1990; Schulte, 1997) used to calculate the same properties at high temperatures and pressures.

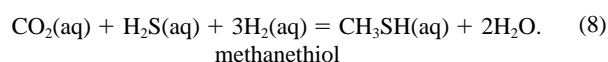
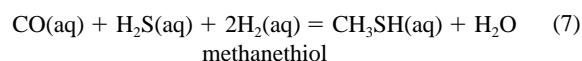
Thiol	$\Delta\bar{G}_f^{\circ a}$	$\Delta\bar{H}_f^{\circ a}$	$\bar{S}^{\circ b}$	$\bar{C}_p^{\circ b}$	$\bar{V}^{\circ c}$	$a_1^d \times 10$	$a_2^a \times 10^{-2}$	$a_3^e$	$a_4^f \times 10^{-4}$	$c_1^b$	$c_2^f \times 10^{-4}$	$\omega_c^a \times 10^{-5}$
Methanethiol	-1840. <sup>g</sup>	-11650. <sup>h</sup>	38.60 <sup>i</sup>	58.70 <sup>j</sup>	52.97 <sup>k</sup>	8.5523	23.5100	-25.8188	-3.7509	62.0673	-5.5753	-0.8704
Ethanethiol	-1100. <sup>g</sup>	-17820. <sup>h</sup>	45.50 <sup>i</sup>	79.90 <sup>j</sup>	67.77 <sup>k</sup>	10.7143	28.3927	-26.8467	-3.9528	80.0173	-3.8792	-0.8543
Propanethiol	1380. <sup>g</sup>	-23320. <sup>h</sup>	53.90 <sup>i</sup>	101.10 <sup>j</sup>	83.57 <sup>k</sup>	12.8901	33.3639	-28.1086	-4.1583	97.9674	-2.2323	-0.8382
Butanethiol	3560. <sup>g</sup>	-28630. <sup>h</sup>	61.30 <sup>i</sup>	122.30 <sup>m</sup>	99.37 <sup>n</sup>	15.0522	38.2464	-29.1770	-4.3601	115.9174	0.5357	-0.8220
Pentanethiol	6150. <sup>o</sup>	-34530. <sup>p</sup>	66.60 <sup>f</sup>	143.50 <sup>m</sup>	115.17 <sup>n</sup>	17.2279	43.1557	-30.2409	-4.5631	133.8675	1.1112	-0.8059
Hexanethiol	7930. <sup>q</sup>	-40200. <sup>p</sup>	73.30 <sup>f</sup>	164.70 <sup>m</sup>	130.97 <sup>n</sup>	19.3900	48.1004	-31.4671	-4.7675	151.8175	2.8073	-0.7898
Heptanethiol	9980. <sup>q</sup>	-45870. <sup>p</sup>	80.00 <sup>f</sup>	185.90 <sup>m</sup>	146.77 <sup>n</sup>	21.5657	53.0097	-32.5313	-4.9704	169.7675	4.4542	-0.7737
Octanethiol	12030. <sup>q</sup>	-51540. <sup>p</sup>	86.70 <sup>f</sup>	207.10 <sup>m</sup>	162.57 <sup>n</sup>	23.7278	57.8922	-33.5994	-5.1723	187.7176	6.1503	-0.7576
Nonanethiol	14080. <sup>q</sup>	-57210. <sup>p</sup>	93.40 <sup>f</sup>	228.30 <sup>m</sup>	178.37 <sup>n</sup>	25.8899	62.8369	-34.8256	-5.3767	205.6676	7.7972	-0.7415
Decanethiol	16130. <sup>q</sup>	-62880. <sup>p</sup>	100.10 <sup>f</sup>	249.50 <sup>m</sup>	194.17 <sup>n</sup>	28.0656	67.7462	-35.8899	-5.5796	223.6177	9.4938	-0.7253
Undecanethiol	18180. <sup>q</sup>	-68550. <sup>p</sup>	106.80 <sup>f</sup>	270.70 <sup>m</sup>	209.97 <sup>n</sup>	30.2277	72.6287	-36.9579	-5.7815	241.5677	11.1407	-0.7092
Dodecanethiol	20230. <sup>q</sup>	-74220. <sup>p</sup>	113.50 <sup>f</sup>	291.90 <sup>m</sup>	225.77 <sup>n</sup>	32.4035	77.5999	-38.1798	-5.9870	259.5177	12.8368	-0.6931

<sup>a</sup> cal mol<sup>-1</sup>, <sup>b</sup> cal mol<sup>-1</sup> K<sup>-1</sup>, <sup>c</sup> cm<sup>3</sup> mol<sup>-1</sup>, <sup>d</sup> cal mol<sup>-1</sup> bar<sup>-1</sup>, <sup>e</sup> cal K mol<sup>-1</sup> bar<sup>-1</sup>, <sup>f</sup> cal K mol<sup>-1</sup>, <sup>g</sup> Calculated from  $\Delta\bar{G}_f^{\circ}(g)$  from Alberty et al. (1987) and  $\Delta\bar{G}_f^{\circ}(g \leftrightarrow aq)$  from Abraham et al. (1990). <sup>h</sup> Calculated from  $\Delta\bar{H}_f^{\circ}(g)$  from Stull et al. (1969) and  $\Delta\bar{H}_f^{\circ}(g \leftrightarrow aq)$  from Abraham et al. (1990). <sup>i</sup> Calculated from  $\Delta\bar{H}_f^{\circ}$  and  $\Delta\bar{G}_f^{\circ}$  in the table, together with  $S^{\circ}$  of the elements from Cox et al. (1989). <sup>j</sup> Estimated by subtracting multiples of 21.2 cal mol<sup>-1</sup> K<sup>-1</sup> (after Shock and Helgeson, 1990) from estimated  $\bar{C}_p^{\circ}$  of propanethiol as discussed in text. <sup>k</sup> Estimated by subtracting multiples of 15.8 cm<sup>3</sup> mol<sup>-1</sup> (after Shock and Helgeson, 1990) from estimated  $\bar{V}^{\circ}$  of propanethiol as discussed in text. <sup>l</sup> Estimated as described in text. <sup>m</sup> Estimated by adding multiples of 21.2 cal mol<sup>-1</sup> K<sup>-1</sup> (after Shock and Helgeson, 1990) to estimated  $\bar{C}_p^{\circ}$  of propanethiol. <sup>n</sup> Estimated by adding multiples of 15.8 cm<sup>3</sup> mol<sup>-1</sup> (after Shock and Helgeson, 1990) to estimated  $\bar{V}^{\circ}$  of propanethiol. <sup>o</sup> Calculated from  $\Delta\bar{G}_f^{\circ}(g)$  from Alberty et al. (1987) and  $\Delta\bar{G}_f^{\circ}(g \leftrightarrow aq)$  from Amore and Buttery (1978). <sup>p</sup> Estimated using Eqn. 5. <sup>q</sup> Estimated using Eqn. 4. <sup>r</sup> Estimated using Eqn. 6.

hydrothermal systems. The first step in determining the potential for thiol synthesis is to identify the most geologically-relevant thiol formation reactions and to evaluate the properties of these reactions at elevated temperature and pressure.

When considering the synthesis of simple organic compounds from abiotic precursors in hydrothermal environments, CO<sub>2</sub> and CO are the most likely starting materials. Most of the carbon emanating from volcanic gases is in the form of CO<sub>2</sub> and CO. Additionally, there is abundant evidence (Von Damm, 1990, 1995; Lilley et al., 1991) that CO<sub>2</sub> is a dominant component of hydrothermal vent fluids and thus a likely candidate for a precursor to thiol formation. In contrast, there are no reliable measurements of CO in seafloor hydrothermal fluids and the role of CO in abiotic organic synthesis in hydrothermal environments remains unconfirmed. However, recent experiments indicate that CO<sub>2</sub> and CO equilibrate in hydrothermal environments as low as 150°C (Foustoukos et al., 2001; Zolotov et al., 2001; see details below). With the abundance of CO<sub>2</sub> in hydrothermal vent fluids, it is reasonable to assume that the equilibrium activity of CO in the reducing conditions of

hydrothermal systems could be a significant source of carbon during abiotic organic synthesis. Thus we consider both CO<sub>2</sub> and CO as carbon sources during synthesis of thiols in hydrothermal systems. Finally, reactions among sulfur-bearing mineral assemblages (e.g., pyrite and pyrrhotite) can produce H<sub>2</sub>S, a source of sulfur, and H<sub>2</sub>, which acts as a reductant, in the formation of thiols from CO and CO<sub>2</sub>. Using these four precursors, the following reactions describe the formation of aqueous methanethiol (CH<sub>3</sub>SH) from CO (Eqn. 7) and CO<sub>2</sub> (Eqn. 8),



Similar reactions can be written to form longer-chained thiols.

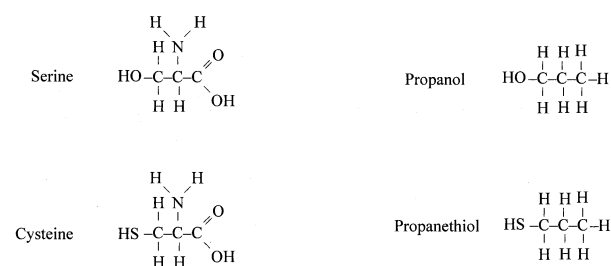


Fig. 4. Structural formulae of serine (an -OH bearing amino acid), cysteine (an -SH bearing amino acid), propanol (an alcohol) and propanethiol (a thiol). Note that the only difference in structure between serine and cysteine is the left-hand terminal functional group. The same is true for propanol and propanethiol.

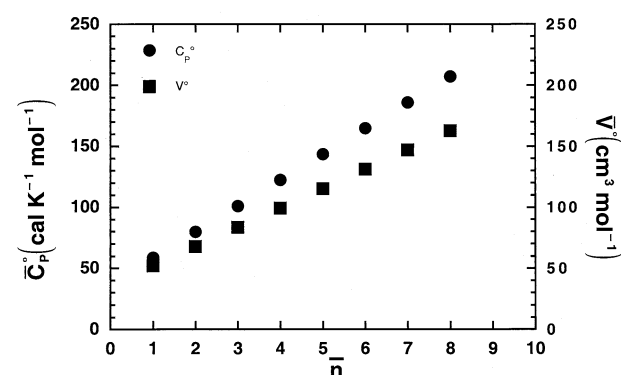


Fig. 5. Estimated values of the standard partial molal heat capacity (left-hand y-axis; filled circles) and volume (right-hand y-axis; filled squares) of aqueous alkyl thiols as a function of the number of carbons in the alkyl chain.

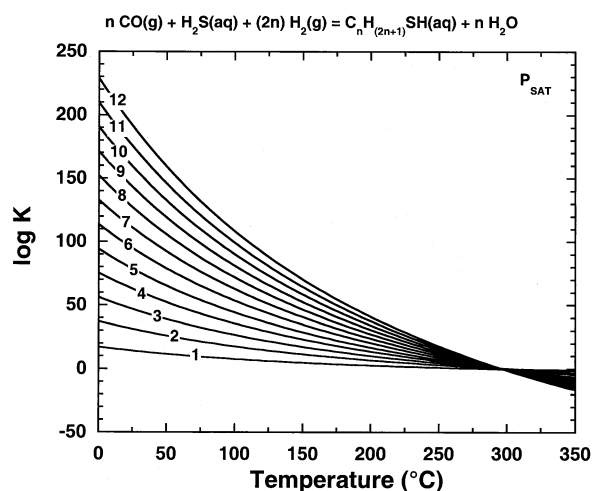


Fig. 6. Logarithm of the equilibrium constants for reactions to form aqueous alkyl thiols from CO, H<sub>2</sub>S and H<sub>2</sub> as a function of temperature (at saturation pressure). The general reaction is shown for reference. The letter “n” in the reaction and the number on each of the curves refers to the number of carbons in the alkyl chain and determines the stoichiometric reaction coefficients for various species in the reactions (e.g., 1 refers to methanethiol, 2 to ethanethiol, etc.).

The equilibrium constant (K) of these reactions at elevated temperature and pressures is obtained using the relation

$$\log K = \frac{\Delta \bar{G}_r^\circ}{-2.303RT} \quad (9)$$

where  $\Delta \bar{G}_r^\circ$  is the standard Gibbs free energy of the reaction at elevated temperature and pressure, R is the gas constant and T is the temperature in Kelvin.  $\Delta \bar{G}_r^\circ$  at elevated temperature and pressure is calculated using the thermodynamic properties of the reactants and products and the revised HKF equations of state (Johnson et al., 1992). Figure 6 shows the logarithms of the equilibrium constants as a function of temperature at saturation pressure for thiol formation of methanethiol (C<sub>1</sub>) to dodecanethiol (C<sub>12</sub>) from CO. The general reaction for formation of a thiol with chain length  $\bar{n}$  is given in the figure. Figure 7 shows the logarithms of the equilibrium constants for thiol formation from CO<sub>2</sub>. Values of the equilibrium constant refer only to the standard state and do not reflect the geochemical conditions found in hydrothermal environments. Thus, determining values of log K at elevated temperature and pressure is the first step in evaluating the potential for thiol synthesis.

The law of mass action is used to determine the thiol activity in equilibrium with the volatile species under hydrothermal conditions. For example, for reaction 7, the equilibrium constant, K<sub>7</sub>, is defined by

$$K_7 = \frac{(a_{\text{CH}_3\text{SH}})(a_{\text{H}_2\text{O}})}{(a_{\text{CO}})(a_{\text{H}_2\text{S}})(a_{\text{H}_2})^2} \quad (10)$$

where  $a_i$  refers to the activity of each chemical species (i) involved in the reaction, raised to the stoichiometric reaction coefficient. Values of log K<sub>7</sub> are shown as a function of temperature in Figure 6. Taking the logarithm and rearranging

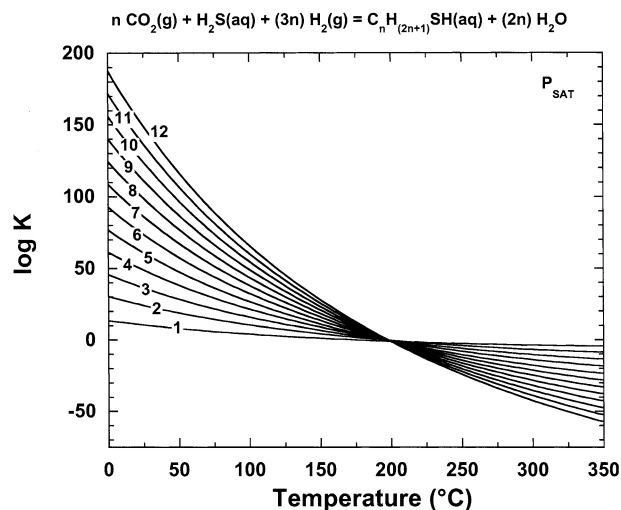


Fig. 7. Logarithm of the equilibrium constants for reactions to form aqueous alkyl thiols from CO<sub>2</sub>, H<sub>2</sub>S and H<sub>2</sub> as a function of temperature (at saturation pressure). The general reaction is shown for reference. The letter “n” in the reaction and the number on each of the curves refers to the number of carbons in the alkyl chain and determines the stoichiometric reaction coefficients for various species in the reactions (e.g., 1 refers to methanethiol, 2 to ethanethiol, etc.).

the law of mass action of reaction 7 while assuming an H<sub>2</sub>O activity of unity gives

$$\log a_{\text{CH}_3\text{SH}} = \log K_7 + \log a_{\text{CO}} + \log a_{\text{H}_2\text{S}} + 2 \log a_{\text{H}_2}, \quad (11)$$

allowing us to assess the activity of aqueous methanethiol given the activities of H<sub>2</sub>, H<sub>2</sub>S and CO. For methanethiol formation from CO<sub>2</sub>, as illustrated by reaction 8, the corresponding law of mass action reduces to

$$\log a_{\text{CH}_3\text{SH}} = \log K_8 + \log a_{\text{CO}_2} + \log a_{\text{H}_2\text{S}} + 3 \log a_{\text{H}_2}. \quad (12)$$

The logarithm of the aqueous methanethiol activity in equilibrium with CO<sub>2</sub> can be calculated using Eqn. 12 and appropriate geochemical constraints. Similar equations can be written for thiols of any chain length, using the general formation reactions given in Figures 6 and 7, and equilibrium thiol activities can be calculated for various sets of temperature, pressure and geochemical conditions. Below we discuss the geochemical constraints imposed by hydrothermal environments, specifically the in situ activities of the starting materials CO, CO<sub>2</sub>, H<sub>2</sub> and H<sub>2</sub>S. We consider a range of activities for the starting materials and combine these with values of log K to evaluate the potential for thiol synthesis in modern and ancient hydrothermal systems.

### 3.1. Geochemical Constraints

The potential for thiol formation in hydrothermal systems is a function of the reaction thermodynamics as described above and the geochemical constraints imposed by the system, including temperature, pressure and the in situ activities of the starting materials. These parameters vary widely in modern hydrothermal systems and the estimated compositions of ancient hydrothermal systems are equally non-unique. Our model calculations incorporate this variability to explore the effect of

system composition on thiol formation. The range in temperature (0°-350°C) and the total pressure (250 bars) used in our calculations are consistent with a 2.5 km deep sea floor hydrothermal system. Shallow hydrothermal systems as well as those deeper in the Earth's crust can be modeled with these data by varying these parameters. The in situ activities of the starting materials, H<sub>2</sub>, H<sub>2</sub>S, CO<sub>2</sub> and CO, are less well constrained in both modern and ancient hydrothermal systems and warrant further discussion.

Mineral assemblages commonly buffer redox potential in hydrothermal systems (Shock, 1990) and are often used in hydrothermal experiments to maintain constant concentrations of H<sub>2</sub> and H<sub>2</sub>S (Seewald, 1994, 1997; McCollom et al., 2001). We use three mineral assemblages to represent the range of possible H<sub>2</sub> and H<sub>2</sub>S activities in modern and ancient hydrothermal systems. In modern vent systems, measurements of the aqueous hydrogen concentrations of vent fluids are consistent with fluid buffering by the pyrite-pyrrhotite-magnetite (PPM) mineral assemblage (Shock et al., 1995). In early Earth hydrothermal systems, the mineral assemblages controlling the composition of the vent fluids may have been more reducing than modern midocean ridge basalts (MORBs), resulting in more hydrogen production during alteration of the crust. These conditions are approximated by the fayalite-magnetite-quartz (FMQ) and iron-wüstite (IW) mineral assemblages. Below ~150°C wüstite is unstable relative to magnetite, so at these temperatures the equilibrium H<sub>2</sub> activity is buffered by the iron-magnetite (IM) assemblage in the model calculations. Furthermore, the FMQ, IW and IM assemblages only constrain the values of H<sub>2</sub>. Activities of H<sub>2</sub>S are constrained by including pyrrhotite. Thus, pyrrhotite-magnetite (PM), pyrrhotite-magnetite-iron (PMI) and pyrrhotite-wüstite (PW) are used in addition to FMQ and IW/IM. These mineral assemblages not only represent modern and ancient hydrothermal systems, but also account for variations in redox conditions that are likely to exist in the crust (Chamberlain et al., 1965; Ashley, 1975; Frost, 1985; Abrajano et al., 1990; Righter and Drake, 1997). The reactions that buffer H<sub>2</sub> and H<sub>2</sub>S activity for each of these assemblages are shown in Table 3. The equilibrium constants for these reactions were evaluated at various temperatures and 250 bars and used to calculate equilibrium activities of H<sub>2</sub> and H<sub>2</sub>S.<sup>2</sup>

Figure 8 shows the calculated logarithm of the activities of H<sub>2</sub> and H<sub>2</sub>S for the mineral assemblages in Table 3 as a function of temperature at 250 bars. As the buffered hydrogen activity increases for each mineral assemblage (PPM < FMQ < IW/IM) the buffered H<sub>2</sub>S activity decreases. Thus our first geochemical constraint on fluid composition is not only the activities of H<sub>2</sub> and H<sub>2</sub>S, but also the coupling of these compounds through various mineral assemblages. We consider all three mineral assemblages in our calculations to evaluate the effects of variable chemical conditions on organic sulfur hydrothermal chemistry.

The activities of CO<sub>2</sub> and CO in modern and ancient hydrothermal systems are the next major geochemical constraint

Table 3. Reactions describing mineral assemblages that can buffer the activities of chemical species in hydrothermal environments.

<b>PPM</b> <b>(Pyrrhotite-Pyrite-Magnetite)</b>		
1.5 FeS + H <sub>2</sub> O = 0.75 FeS <sub>2</sub> + 0.25 Fe <sub>3</sub> O <sub>4</sub> + H <sub>2</sub>	pyrrhotite	pyrite magnetite
0.25 FeS <sub>2</sub> + 0.5 FeS + H <sub>2</sub> O = 0.25 Fe <sub>3</sub> O <sub>4</sub> + H <sub>2</sub> S	pyrite pyrrhotite	magnetite
<b>FMQ</b> <b>(Fayalite-Magnetite-Quartz)</b>		
1.5 Fe <sub>2</sub> SiO <sub>4</sub> + H <sub>2</sub> O = Fe <sub>3</sub> O <sub>4</sub> + 1.5 SiO <sub>2</sub> + H <sub>2</sub>	fayalite	magnetite quartz
<b>PM</b> <b>(Pyrrhotite-Magnetite)</b>		
3 FeS + 4 H <sub>2</sub> O = Fe <sub>3</sub> O <sub>4</sub> + 3 H <sub>2</sub> S + H <sub>2</sub>	pyrrhotite	magnetite
<b>IW</b> <b>(Iron-Wüstite)</b>		
Fe + H <sub>2</sub> O = FeO + H <sub>2</sub>	iron	wüstite
<b>IM</b> <b>(Iron-Magnetite)</b>		
0.75 Fe + H <sub>2</sub> O = 0.25 Fe <sub>3</sub> O <sub>4</sub> + H <sub>2</sub>	iron	magnetite
<b>PMI</b> <b>(Pyrrhotite-Iron-Magnetite)</b>		
0.25 Fe + 0.25 Fe <sub>3</sub> O <sub>4</sub> + H <sub>2</sub> S = FeS + H <sub>2</sub> O	iron magnetite	pyrrhotite
<b>PW</b> <b>(Pyrrhotite-Wüstite)</b>		
FeO + H <sub>2</sub> S = FeS + H <sub>2</sub> O	wüstite	pyrrhotite

placed on thiol formation. Unfortunately, these values are less tractable than H<sub>2</sub> and H<sub>2</sub>S activities. There is no evidence that mineral assemblages buffer the activities of these compounds in hydrothermal systems and reliable measurements of these compounds in modern systems are limited to CO<sub>2</sub> (e.g., Von Damm, 1990, 1995). Thus, we have decided to use a range of values for each of the carbon inorganic precursors based on measurements (where available), early Earth climate models and hydrothermal experiments of volatile composition. We have considered CO<sub>2</sub> activities between 10<sup>-6</sup> and 10<sup>1</sup>, encompassing the range of measurements in modern hydrothermal systems and early Earth climate models, which attribute increased partial pressures of both CO and CO<sub>2</sub> to increased amounts of these volatiles outgassing from the Earth's interior (Kasting et al., 1993; Kasting and Brown, 1998). Thus, ancient hydrothermal systems are represented by the higher end of this range.

The possible range of CO activities is even less well-constrained as there are no reliable measurements of CO concentration in modern hydrothermal vent systems. We have chosen to assume that CO activities range from 10<sup>-9</sup> to 10<sup>-2</sup>. In the case of modern hydrothermal systems, this is consistent with the lower abundance of CO (relative to CO<sub>2</sub>) in modern volcanic volatiles. Recent hydrothermal experiments suggest that the ratio of CO to CO<sub>2</sub> may be controlled by equilibration of the water-gas shift reaction (reaction 13) to temperatures as low

<sup>2</sup> In all of the model calculations, the activities of H<sub>2</sub>O and pure minerals at all temperatures and pressures are taken to be unity, a good approximation for most geological environments (Helgeson et al., 1993; Shock et al., 1995).

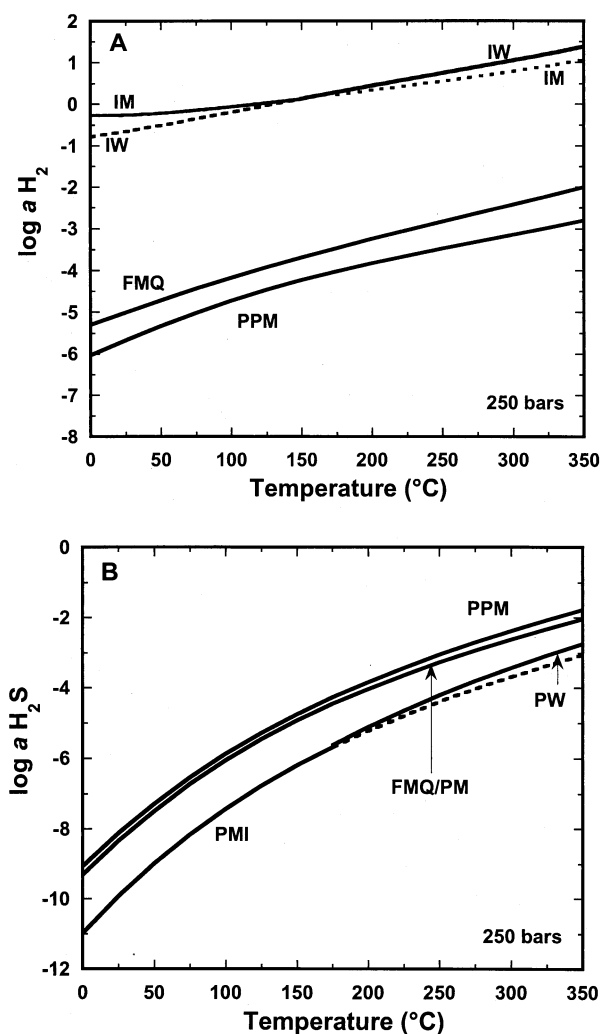
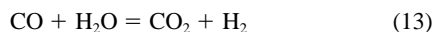


Fig. 8. Logarithm of the activity of (A)  $H_2$  and (B)  $H_2S$  as a function of temperature at 250 bars pressure. The curves correspond to calculated values resulting from equilibration with the mineral assemblages in Table 3. The solid lines indicate the value of the  $\log a_{H_2}$  used to account for the geochemical constraints for modern and early Earth hydrothermal systems. The dashed lines are the continuation of the IM buffer  $> \sim 150^\circ C$  and the IW buffer  $< \sim 150^\circ C$  and are included for completeness.

as  $150^\circ C$  in hydrothermal environments in which mineral assemblages buffer the hydrogen activity (Foustoukos et al., 2001; Zolotov et al., 2001).



The logarithm of the activity ratio of  $CO_2$  to  $CO$  can be calculated using the equilibrium constant for reaction 13 for each of the redox mineral buffers in Table 3. The results are shown as a function of temperature at 250 bars in Figure 9. For each mineral buffer the logarithm of the activity ratio decreases with increasing temperature and as the mineral buffers foster more reducing conditions. Only for the IW buffer at temperatures greater than  $350^\circ C$  is the logarithm of the activity ratio less than zero. The implication is that equilibration of reaction 13 results in the activity of  $CO_2$  always exceeding that of  $CO$

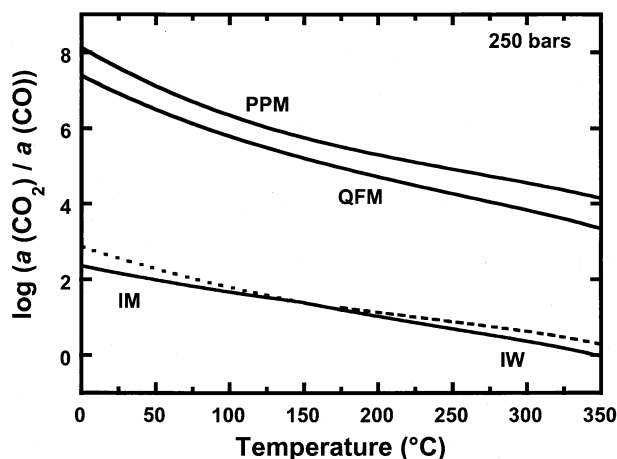


Fig. 9. Logarithm of the activity ratio of  $CO_2$  to  $CO$  as a function of temperature at 250 bars pressure resulting from equilibration of the water-gas shift reaction (see text for details). The curves correspond to ratios calculated for various mineral assemblages buffering the  $H_2$  activity. The dashed lines are the continuation of the IM buffer  $> \sim 150^\circ C$  and the IW buffer  $< \sim 150^\circ C$  and are included for completeness.

in hydrothermal systems at temperatures less than  $350^\circ C$  in which the hydrogen activity is at or below equilibrium with IW. However, it is possible that the water-gas shift reaction did not equilibrate on the early Earth, and the abundance of  $CO$  relative to  $CO_2$  in early Earth hydrothermal systems is unknown.

### 3.2. Application to Modern Systems

The geochemical constraints described above can be combined with thermodynamic data to determine the potential for thiol synthesis in hydrothermal systems. (While these data can be applied to any of the thiols in Table 2, we have chosen to limit our discussion of thiol formation to methanethiol because it is usually the most prevalent thiol observed or used in hydrothermal experiments (Heinen and Lauwers, 1996; Huber and Wächtershäuser, 1997, 1998). For example, the average  $CO_2$  concentration in  $\sim 350^\circ C$  vent fluids from the East Pacific Rise is 13.8 mmolal ( $a = 10^{-1.86}$ ). Along with the value of  $K_8$  at  $350^\circ C$  and 250 bars, and the  $H_2$  and  $H_2S$  activities determined by the PPM mineral assemblage, we calculate that the equilibrium methanethiol activity is  $10^{-8.40}$ . To account for the variability in modern vent fluids, we have applied Eqns. 11 and 12 to a range of temperatures and  $CO_2$  and  $CO$  activities to explore the potential for methanethiol synthesis throughout modern hydrothermal systems. Figure 10A shows the equilibrium activity of methanethiol at PPM as a function of temperature and is contoured for  $CO_2$  activities ranging from  $10^{-6}$  to  $10^1$ . Similarly, Figure 10B shows the equilibrium  $CH_3SH$  activity calculated with Eqn. 12 as a function of temperature for  $CO$  activity ranging from  $10^{-9}$  to  $10^{-2}$ . Examination of Figure 10 reveals that at equal activities of  $CO_2$  and  $CO$ , more methanethiol could potentially be formed from  $CO$  than  $CO_2$ . The values in Figure 10 represent the maximum  $CH_3SH$  activity that can be attained by reactions 7 and 8, for any temperature, or  $CO_2$  or  $CO$  activity of interest at PPM. It can be seen in Figure 10B that at temperatures below  $\sim 175^\circ C$ , calculated

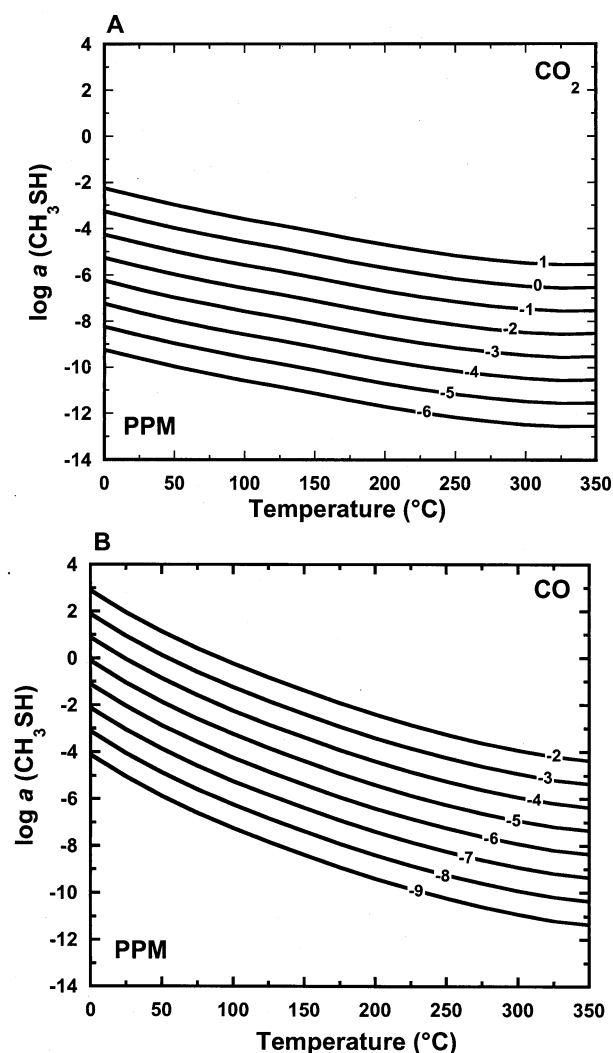


Fig. 10. Logarithm of equilibrium methanethiol activity as a function of temperatures at 250 bars pressure, contoured for the logarithm of the  $\text{CO}_2$  or CO activity, with the activities of  $\text{H}_2$  and  $\text{H}_2\text{S}$  set by the PPM mineral assemblage and. (A) Results for formation of methanethiol from  $\text{CO}_2$  using Eqn. 12; (B) Results for formation of methanethiol from CO using Eqn. 11. The numbers on each curve refer to the initial log  $\text{CO}_2$  or CO activity.

equilibrium methanethiol activities exceed those of CO. We note that if the amount of CO represents the total carbon available, these high activities of methanethiol would not be reached. However, the activity ratio of methanethiol to CO at equilibrium is independent of the carbon abundance.

The calculations described above consider methanethiol formation from  $\text{CO}_2$  and CO separately, even though these species likely coexist in vent systems. In fact, if the water-gas shift reaction equilibrates in modern vent systems, then the equilibrium methanethiol activities calculated from reactions 11 or 12 are equal and there is a single maximum  $\text{CH}_3\text{SH}$  activity possible from either  $\text{CO}_2$  or CO. Despite the greater potential for  $\text{CH}_3\text{SH}$  synthesis from CO, equilibration of the water-gas shift reaction limits methanethiol formation. It is important to note that if one assumes that  $\text{CO}_2$  and CO do not equilibrate,

maximum  $\text{CH}_3\text{SH}$  activity could be attained from the formation from CO.

### 3.3. Extrapolation to Archean Systems

Hydrothermal systems were likely to be present on the early Earth, and may have been more prevalent than in the modern day. The rocks controlling the vent fluid composition were likely to have been more reducing, resulting in more hydrogen production during alteration of the crust (see Fig. 8), and increasing the potential for organic synthesis (Schulte and Shock, 1995; Shock and Schulte, 1998). To evaluate the potential for thiol formation in these environments, we have performed calculations similar to those for modern systems assuming that FMQ and IW buffer the redox potential. Figure 11 shows equilibrium methanethiol activities as functions of temperature for formation from  $\text{CO}_2$  and CO, respectively, in which the  $\text{H}_2$  and  $\text{H}_2\text{S}$  activities are determined by FMQ/PM. Figure 12 shows the equilibrium methanethiol activities as functions of temperature for the IW/PWI buffer. Note the substantial increase in the potential for methanethiol formation with increasing activity of  $\text{H}_2$ , even at comparable values of CO or  $\text{CO}_2$ . For example, at  $200^\circ\text{C}$  and a  $\text{CO}_2$  activity of  $10^{-2}$ , the logarithm of the equilibrium thiol activity is  $-6.68$  at PPM (from Fig. 10A),  $-5.13$  at FMQ (Fig. 11A) and  $4.79$  at IW (Fig. 12A).

In addition, the amounts of  $\text{CO}_2$  and CO in the Archean atmosphere and degassing from the Earth's interior are proposed to be much higher than modern values (Kasting et al., 1993). The implication is that there would have been even greater amounts of carbon available in hydrothermal environments for organic synthesis. In Figures 11 and 12 the same ranges for  $\text{CO}_2$  and CO that were presented for modern vent systems are used; however, it is likely that the activities of both  $\text{CO}_2$  and CO were higher in Archean hydrothermal systems than in modern ones. Thus, the potential for thiol formation would have been greater in Archean systems due to both the increased reduction potential and the increased carbon availability.

Again, it is useful to compare  $\text{CO}_2$  and CO as precursors for thiol formation. While  $\text{CO}_2$  is still the dominant inorganic carbon species, the ratio of  $\text{CO}_2$  to CO resulting from reaction 10 decreases as the conditions become more reducing (Fig. 9), and the relative increase in CO leads to greater potential for thiol formation. As mentioned above, the CO activity only exceeds that of  $\text{CO}_2$  at temperatures greater than  $350^\circ\text{C}$  and conditions more reducing than IW. Additionally, if the water-gas shift reaction does not equilibrate, the potential for thiol synthesis from CO significantly exceeds that possible from  $\text{CO}_2$ . In fact, models of the Earth's early atmosphere suggest that the ratio of CO to  $\text{CO}_2$  could have been 1 to 10 (Kasting, 1993) or even as high as 3 to 1 (Kasting and Brown, 1998). If this composition was also reflected in vent fluids, much higher methanethiol activities could be reached from formation from CO.

The calculations presented above represent the maximum amount of methanethiol that could form from reactions 7 and 8 in early Earth hydrothermal environments. Whether or not they would proceed to equilibrium at the lowest temperatures would depend on the reaction kinetics relative to vent activity; how-



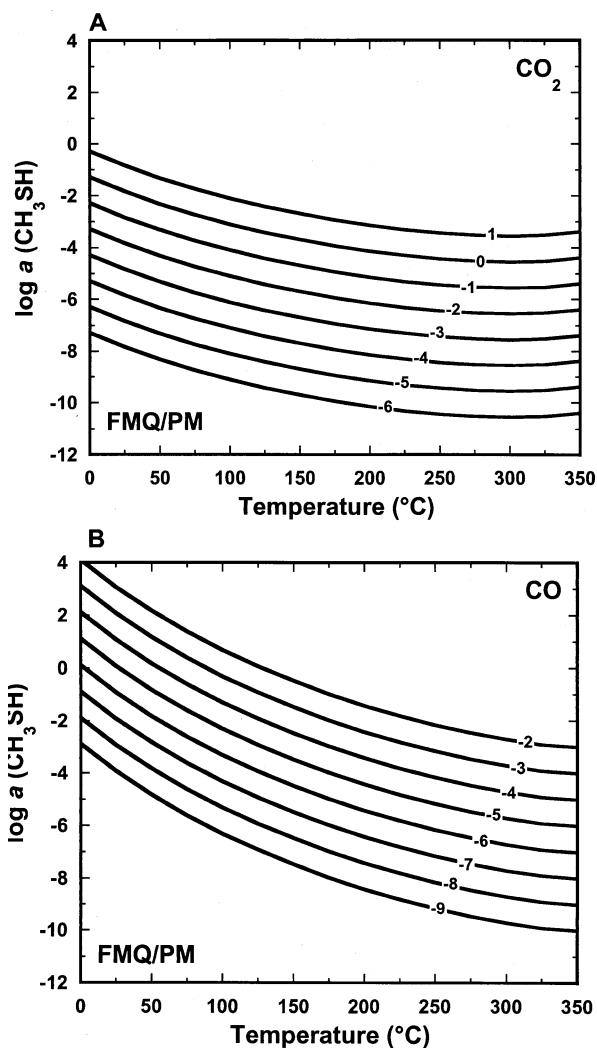


Fig. 11. Logarithm of equilibrium methanethiol activity as a function of temperature at 250 bars pressure, contoured for the logarithm of the CO<sub>2</sub> or CO activity, with the activities of H<sub>2</sub> and H<sub>2</sub>S set by the FMQ and PM mineral assemblages, respectively. (A) Results for formation of methanethiol from CO<sub>2</sub> using Eqn. 12; (B) Results for formation of methanethiol from CO using Eqn. 11. The numbers on each curve refer to the initial log CO<sub>2</sub> or CO activity.

ever, sluggish reaction kinetics may be overcome by the availability of suitable catalytic surfaces, such as sulfide minerals or partially oxidized dissolved inorganic sulfur compounds (Seewald, 1997; Russell et al., 1998; McCollom et al., 2001). Thiol formation may also have been limited by the availability of reactants. Therefore, the high concentrations of methanethiol described here might not have been reached. Nonetheless, even at concentrations below equilibrium, Archean hydrothermal systems could have been environments of significant thiol formation and aqueous alkyl thiols may have been involved in the sulfur and carbon chemistry of these systems.

#### 4. CONCLUDING REMARKS

Using previously developed methods, as well as some new correlations and techniques, we have estimated standard partial

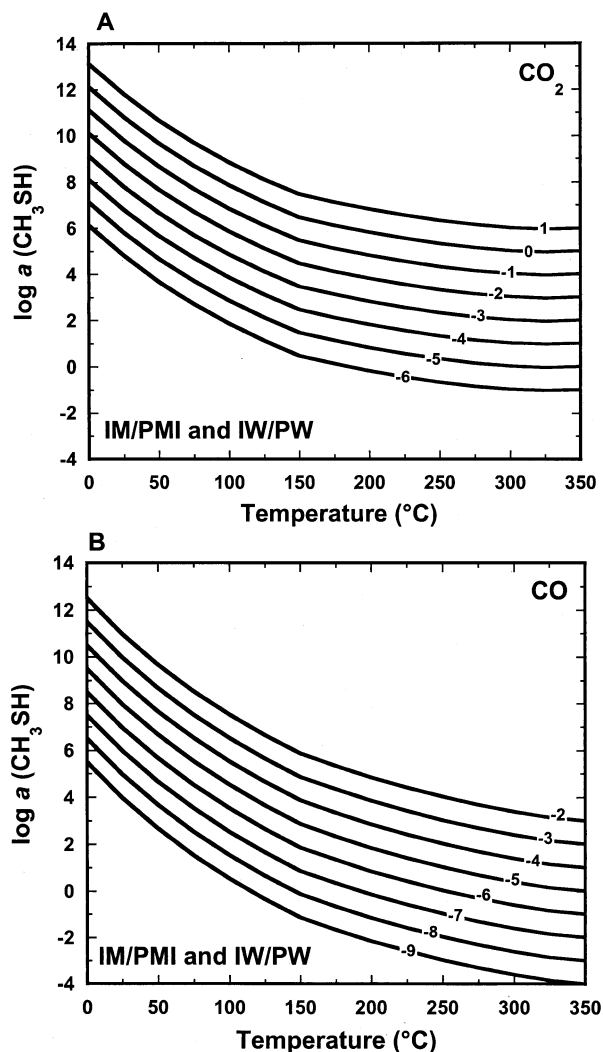


Fig. 12. Logarithm of equilibrium methanethiol activity as a function of temperatures at 250 bars pressure, contoured for the logarithm of the CO<sub>2</sub> or CO activity, with the activities of H<sub>2</sub> and H<sub>2</sub>S set by the IW and PW mineral assemblages, respectively. (A) Results for formation of methanethiol from CO<sub>2</sub> using Eqn. 12; (B) Results for formation of methanethiol from CO using Eqn. 11. The numbers on each curve refer to the initial log CO<sub>2</sub> or CO activity.

molal thermodynamic properties of aqueous alkyl thiols. These estimates also allow calculation of reaction properties involving aqueous thiols at elevated temperatures and pressures using the revised HKF equations of state. We are now capable of incorporating these compounds into organic geochemical models of hydrothermal systems. These data represent the first organic sulfur compounds for which such modeling is possible and as such provide a significant step forward in understanding the organic geochemistry of hydrothermal environments.

The results shown here imply that aqueous thiols may play a key role in the organic geochemistry of hydrothermal systems. We have calculated the equilibrium activity of methanethiol that could be generated in modern and early Earth hydrothermal systems based on constraints provided by the geochemistry of these environments. Thus, not only is the carbon source a major factor in determining the equilibrium thiol activity, but

the composition of the inorganic components of the system plays a role in the distribution of organic compounds as well. Our results indicate that significant amounts of methanethiol could be generated, and that the potential for thiol formation increases with the increased reducing conditions theoretically possible earlier in Earth's history. The formation of organic compounds from thiols would create a positive feedback, in which the consumption of thiols during organic compound synthesis would drop the thiol activity below equilibrium values, further driving thiol synthesis and allowing thiols to persist in hydrothermal environments. We would encourage researchers making measurements of fluid samples from these systems to include these and other kinds of organic sulfur compounds in their analyses. We would also encourage researchers who are performing experiments that simulate organic compound formation under hydrothermal conditions to explore the possibility of thiol formation.

The elevated potential of thiol synthesis in early Earth hydrothermal systems places thiols in a potentially significant role in abiotic organic chemistry. Organic compound synthesis from thiols may have led to the first 'geochemical metabolic cycles' from which modern metabolisms are derived. The presence of sulfur in many essential biomolecules, including coenzyme-M, which is itself a thiol, supports this notion. If life started in a hydrothermal environment, organic reactions may have taken place on sulfur-bearing mineral surfaces, which acted not only as catalysts, but also as a source for the sulfur that drove the first primitive metabolic cycles.

*Acknowledgments*—This work was funded in part by the National Research Council and the Exobiology Branch at NASA Ames Research Center (MDS). KLR was supported by an NSF Graduate Research Fellowship and a Stanford Graduate Fellowship while at Stanford University, and is currently supported by a Mr. and Mrs. Spencer T. Olin Fellowship for Women in Graduate Study at Washington University. We would like to thank the RIDGE program for providing funding to help defray the costs of attending and for organizing the 5th RIDGE Theoretical Institute on the Subsurface Biosphere at Mid-Ocean Ridges, where this work was first presented. We would like to thank Everett Shock, Jan Amend, Sherwood Chang and Hal Helgeson for encouragement and many helpful discussions. Tom McCollom, Mike Russell and an anonymous reviewer greatly improved the quality of this manuscript with very thoughtful, insightful and thorough reviews. We also very much appreciate the patience and guidance of Eric Oelkers.

*Associate editor:* E. H. Oelkers

## REFERENCES

- Abraham M. H., Whiting G. S., Fuchs R., and Chambers E. J. (1990) Thermodynamics of solute transfer from water to hexadecane. *J. Chem. Soc. Perkins Trans.* **2**, 291–300.
- Abrajano T. A., Sturchio N. C., Kennedy B. M., Lyon G. L., Muehlenbachs K., and Böhlke J. K. (1990) Geochemistry of reduced gas related to serpentinization of the Zambales ophiolite, Philippines. *Appl. Geochem.* **5**, 625–630.
- Alberty R. A., Burmenko E., Kang T. H., and Chung M. B. (1987) Standard chemical thermodynamic properties of alkanethiol isomer groups. *J. Phys. Chem. Ref. Data* **16**, 193–208.
- Amore J. E. and Buttery R. G. (1978) Partition coefficients and comparative olfactometry. *Chem. Senses Flavour* **3**, 57–71.
- Ashley P. M. (1975) Opaque mineral assemblages formed during serpentinization in the Coolac ultramafic belt, New South Wales. *J. Geol. Soc. Austr.* **22**, 91–102.
- Blöchl E., Keller M., Wächtershäuser G., and Stetter K. O. (1992) Reactions depending on iron sulfide and linking geochemistry with biochemistry. *Proc. Natl. Acad. Sci. USA* **89**, 8117–8120.
- Cabani S., Gianni P., Mollica V., and Lepori L. (1981) Group contributions to the thermodynamic properties of non-ionic organic solutes in dilute aqueous solution. *J. Solution Chem.* **10**, 563–595.
- Chamberlain J. A., McLeod C. R., Traill R. J., and Lachance G. R. (1965) Native metals in the Muskox intrusion. *Can. J. Earth. Sci.* **2**, 188–215.
- Cody G. D., Boctor N. Z., Filley T. R., Hazen R. M., Scott J. H., Sharma A., and Yoder H. S., Jr. (2000) Primordial carbonylated iron-sulfur compounds and the synthesis of pyruvate. *Science* **289**, 1337–1340.
- Cox J. D., Wagman D. D., and Medvedev V. A. (eds.) (1989) *CODATA Key Values for Thermodynamics*, Hemisphere.
- Criss C. M. and Wood R. H. (1996) Apparent molar volumes of aqueous solutions of some organic solutes at the pressure 28 MPa and temperatures to 598K. *J. Chem. Thermodynam.* **28**, 723–741.
- Dale J. D., Shock E. L., MacLeod G., Aplin A. C., and Larter S. R. (1997) Standard partial molal properties of aqueous alkylphenols at high pressures and temperatures. *Geochim. Cosmochim. Acta* **61**, 4017–4024.
- de Duve C. (1991) *Blueprint for a Cell: The Nature and Origin of Life*. Neil Patterson Publishers.
- Foustoukos D. I., Allen D. E., Fu Q., and Seyfried W. E., Jr. (2001) Experimental study of CO<sub>2</sub>(aq)/CO(aq) redox equilibria at elevated temperatures and pressures: The effect of pH on reaction relations. Eleventh Ann. V. M. Goldschmidt Conference, abstract 3855.
- Frost B. R. (1985) On the stability of sulfides, oxides, and native metals in serpentinite. *J. Petrol.* **26**, 31–63.
- Heinen W. and Lauwers A. M. (1996) Organic sulfur compounds resulting from the interaction of iron sulfide, hydrogen sulfide and carbon dioxide in an anaerobic aqueous environment. *Orig. Life Evol. Biosphere* **26**, 131–150.
- Helgeson H. C., Knox A. M., Owens C. E., and Shock E. L. (1993) Petroleum, oil field brines and authigenic mineral assemblages: Are they in metastable equilibrium? *Geochim. Cosmochim. Acta* **57**, 3295–3340.
- Huber C. and Wächtershäuser G. (1997) Activated acetic acid by carbon fixation on (Fe,Ni)S under primordial conditions. *Science* **276**, 245–247.
- Huber C. and Wächtershäuser G. (1998) Peptides by activation of amino acids with CO on (Ni, Fe) surfaces: Implications for the origin of life. *Science* **281**, 670–672.
- Johnson J. W., Oelkers E. H. and Helgeson H. C. (1992) SUPCRT92: A software package for calculating the standard molal thermodynamic properties of minerals, gases, aqueous species, and reactions from 1 to 5000 bar and 0 to 1000°C. *Comp. Geosci.* **18**, 899–947.
- Jolicoeur C. and Boileau J. (1978) Apparent molal volumes and heat capacities of low molecular weight peptides in water at 25°C. *Can. J. Chem.* **56**, 2707–2713.
- Jolicoeur C., Reidl B., Desrochers D., Lemelin L. L., Zamojska R., and Enea O. (1986) Solvation of amino acid residues in water and urea-water mixtures: Volumes and heat capacities of 20 amino acids in water and in 8 molar urea at 25°C. *J. Solution Chem.* **15**, 109–128.
- Kasting J. F. (1993) Earth's early atmosphere. *Science* **259**, 920–926.
- Kasting J. F., Egglar D. H., and Raeburn S. P. (1993) Mantle redox evolution and the oxidation state of the Archean atmosphere. *J. Geol.* **101**, 245–257.
- Kasting J. F. and Brown L. L. (1998) The early atmosphere as a source of biogenic compounds. In *The Molecular Origins of Life—Assembling Pieces of the Puzzle* (A. Brack, ed.). Cambridge University Press, New York 35–56.
- Lilley M. D., Olson E. J., McLaughlin E., and Von Damm K. L. (1991) Methane, hydrogen and carbon dioxide in vent fluids from the 9°N hydrothermal system. *EOS Trans. Am. Geophys. Union* **72(Suppl)**, 481.
- McCollom T. M., Seewald J. S., and Simoneit B. R. T. (2001) Reactivity of monocyclic aromatic compounds under hydrothermal conditions. *Geochim. Cosmochim. Acta* **65**, 455–468.
- Millero F. J., Lo Surdo A., and Shin C. (1978) The apparent molal volumes and adiabatic compressibilities of aqueous amino acids at 25°C. *J. Phys. Chem.* **82**, 784–792.

- Richter K. and Drake M. J. (1997) Metal-silicate equilibrium in a homogeneously accreting Earth: New results for Re. *Earth Planet. Sci. Lett.* **146**, 541–553.
- Russell M. J. and Hall A. J. (1997) The emergence of life from iron monosulphide bubbles at a submarine hydrothermal redox and pH front. *J. Geol. Soc. Lond.* **154**, 377–402.
- Russell M. J., Daia D. E., and Hall A. J. (1998) The emergence of life from FeS bubbles at alkaline hot springs in an acid ocean. In *Thermophiles: The Keys to Molecular Evolution and the Origin of Life?* (J. Wiegel and MWW Adams, eds.), pp. 77–126. Taylor & Francis.
- Schulte M. D. (1997) Synthesis and processing of aqueous organic compounds during water/rock reactions. Ph.D. thesis. Washington University.
- Schulte M. D. and Shock E. L. (1993) Aldehydes in hydrothermal solution: Standard partial molal thermodynamic properties and relative stabilities at high temperatures and pressures. *Geochim. Cosmochim. Acta* **57**, 3835–3846.
- Schulte M. D. and Shock E. L. (1995) Thermodynamics of Strecker synthesis in hydrothermal systems. *Orig. Life Evol. Biosphere* **25**, 161–173.
- Schulte M. D., Shock E. L., Obsil M., and Majer V. (1999) Volumes of aqueous alcohols, ethers, and ketones at  $T = 523$  K and  $p = 28$  MPa. *J. Chem. Thermodynam.* **31**, 1195–1229.
- Schulte M. D., Shock E. L., and Wood R. H. (2001) The temperature dependence of the standard state thermodynamic properties of aqueous nonelectrolytes. *Geochim. Cosmochim. Acta* **65**, 3919–3930.
- Seewald J. S. (1994) Evidence for metastable equilibrium between hydrocarbons under hydrothermal conditions. *Nature* **370**, 285–287.
- Seewald J. S. (1997) Mineral redox buffers and the stability of organic compounds under hydrothermal conditions. *Mat. Res. Soc. Symp. Proc.* **432**, 317–331.
- Shock E. L., Helgeson H. C., and Sverjensky D. A. (1989) Calculation of the thermodynamic and transport properties of aqueous species at high pressures and temperatures: Standard partial molal properties of inorganic neutral species. *Geochim. Cosmochim. Acta* **53**, 2157–2183.
- Shock E. L. (1990) Geochemical constraints on the origin of organic compounds in hydrothermal systems. *Orig. Life Evol. Biosphere* **20**, 331–367.
- Shock E. L. (1995) Organic acids in hydrothermal solutions: Standard molal thermodynamic properties of carboxylic acids and estimates of dissociation constants at high temperatures and pressures. *Am. J. Sci.* **295**, 496–580.
- Shock E. L. and Helgeson H. C. (1988) Calculation of the thermodynamic and transport properties of aqueous species at high pressures and temperatures: Correlation algorithms for ionic species and equation of state predictions to 5 kb and 1000°C. *Geochim. Cosmochim. Acta* **52**, 2009–2036.
- Shock E. L. and Helgeson H. C. (1990) Calculation of the thermodynamic and transport properties of aqueous species at high pressures and temperatures: Standard partial molal properties of organic species. *Geochim. Cosmochim. Acta* **54**, 915–945.
- Shock E. L., Oelkers E. H., Johnson J. W., Sverjensky D. A., and Helgeson H. C. (1992) Calculation of the thermodynamic properties of aqueous species at high pressures and temperatures: Effective electrostatic radii, dissociation constants and standard partial molal properties to 1000°C and 5 kbar. *J. Chem. Soc. Faraday Trans.* **88**, 803–826.
- Shock E. L., McCollom T., and Schulte M. D. (1995) Geochemical constraints on chemolithoautotrophic reactions in hydrothermal systems. *Orig. Life Evol. Biosphere* **25**, 141–159.
- Shock E. L., Sassani D. C., Willis M., and Sverjensky D. A. (1997) Inorganic species in geologic fluids: Correlations among standard molal thermodynamic properties of aqueous ions and hydroxide complexes. *Geochim. Cosmochim. Acta* **61**, 907–950.
- Shock E. L. and Schulte M. D. (1998) Organic synthesis during fluid mixing in hydrothermal systems. *J. Geophys. Res.* **103**, 28513–28527.
- Stull D. R., Westrum E. F., Jr., and Sinke G. C. (1969) *The Chemical Thermodynamics of Organic Compounds*. Wiley.
- Sverjensky D. A., Shock E. L., and Helgeson H. C. (1997) Prediction of the thermodynamic properties of aqueous complexes to 1000°C and 5 kb. *Geochim. Cosmochim. Acta* **61**, 1359–1412.
- Tanger J. C. and Helgeson H. C. (1988) Calculation of the thermodynamic and transport properties of aqueous species at high pressures and temperatures: Revised equations of state for the standard partial molal properties of ions and electrolytes. *Am. J. Sci.* **288**, 19–98.
- Von Damm K. L. (1990) Seafloor hydrothermal activity: Black smoker chemistry and chimneys. *Ann. Rev. Earth Planet. Sci.* **18**, 173–204.
- Von Damm K. L. (1995) Controls on the chemistry and temporal variability of seafloor hydrothermal fluids. In *Seafloor Hydrothermal Systems: Physical, Chemical, Biological, and Geological Interactions* (eds. SE Humphris, RA Zierenberg, S Mullineaux, and RE Thomson), pp. 222–247. American Geophysical Union Geophysical Monograph 91.
- Wächtershäuser G. (1990a) The case for the chemoautotrophic origin of life in an iron-sulfur world. *Orig. Life Evol. Biosphere* **20**, 173–176.
- Wächtershäuser G. (1990b) Evolution of the first metabolic cycles. *Proc. Natl. Acad. Sci. USA* **87**, 200–204.
- Zolotov M. Yu., Seewald J. S., and McCollom T. M. (2001) Experimental investigation of aqueous carbon monoxide reactivity under hydrothermal conditions. Eleventh Annual V. M. Goldschmidt Conference, abstract 3809.