

# THERMODYNAMICS OF STRECKER SYNTHESIS IN HYDROTHERMAL SYSTEMS

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**Abstract.** Submarine hydrothermal systems on the early Earth may have been the sites from which life emerged. The potential for Strecker synthesis to produce biomolecules (amino and hydroxy acids) from starting compounds (ketones, aldehydes, HCN and ammonia) in such environments is evaluated quantitatively using thermodynamic data and parameters for the revised Helgeson-Kirkham-Flowers (HKF) equation of state. Although there is an overwhelming thermodynamic drive to form biomolecules by the Strecker synthesis at hydrothermal conditions, the availability and concentration of starting compounds limit the efficiency and productivity of Strecker reactions. Mechanisms for concentrating reactant compounds could help overcome this problem, but other mechanisms for production of biomolecules may have been required to produce the required compounds on the early Earth. Geochemical constraints imposed by hydrothermal systems provide important clues for determining the potential of these and other systems as sites for the emergence of life.

## Life in Hydrothermal Systems

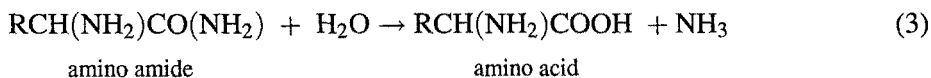
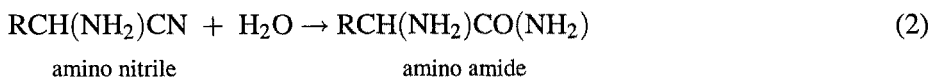
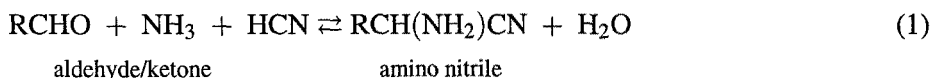
Sequencing of 16S ribosomal RNA indicates that extremely thermophilic archaea and bacteria, which are abundant in hot springs and other hydrothermal environments, are closer to a common ancestor of all life than any other organisms (Woese, 1987). It follows that the common ancestor of archaea, bacteria and eucarya may have also lived at elevated temperatures. Perhaps evolution has allowed organisms to leave the relative comfort of high temperature, hydrothermal environments, where fluid mixing through mineral matrices provides abundant chemical energy (Wächtershäuser, 1988a, b; Russell *et al.*, 1989; Cairns-Smith *et al.*, 1992; Shock *et al.*, 1994), and penetrate a wide variety of lower-temperature, considerably more hostile environments. This paradigm shift in biology has contributed to wider acceptance of submarine hydrothermal systems as possible sites for the emergence of life. Support for this view comes from the discovery of abundant, thriving, seemingly self-sustained ecosystems in hydrothermal systems; the notion that life originating at the seafloor would be more likely to survive impact frustration in the early Archean (Maher and Stevenson, 1988; Sleep *et al.*, 1989); and the inevitability of abundant hydrothermal systems on the early Earth (Holm and Hennes, 1992).

If the emergence of life in submarine hydrothermal systems depended upon the availability of organic compounds (for arguments against this point, see Cairns-Smith *et al.*, 1992), it seems logical to test the capacity of hydrothermal conditions for organic synthesis. Theoretical studies which take explicit account of the metastability of organic compounds, and metastable equilibrium states among organic compounds of the type documented in nature (Shock, 1988, 1989, 1990,

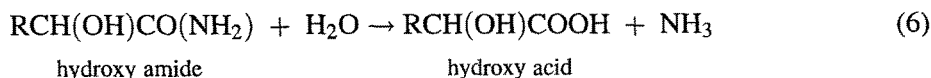
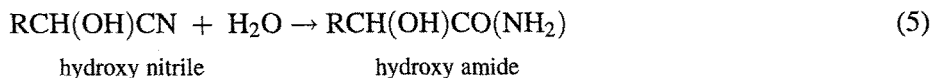
1994a; Helgeson, 1991; Helgeson *et al.*, 1993), have shown that there is considerable potential for organic synthesis in submarine hydrothermal systems (Shock, 1990, 1992). This conclusion is reached through a complete analysis of mass balance, oxidation states, temperatures, pressures and thermodynamic properties of reactions among inorganic gases, minerals and aqueous solutions containing inorganic and organic solutes. Theoretical results are supported by experimental studies which demonstrate that presumed starting materials required for life could be produced in hydrothermal systems (French, 1964; Hennes *et al.*, 1992). These pioneering efforts are likely to be complemented by many more experimental studies. In order to help realize successful experiments, we have begun several theoretical studies in an effort to help identify likely pathways for organic synthesis at hydrothermal conditions. Results appropriate for the popular Strecker synthesis pathway are presented in this paper.

### Strecker Synthesis

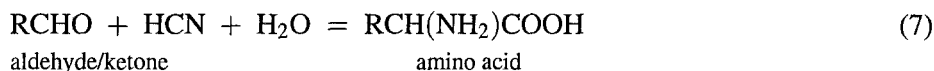
Strecker synthesis, or an analogous reaction scheme, has been postulated as a synthesis mechanism for organic compounds on the early Earth and elsewhere (Miller, 1957; Miller and Van Trump, 1981; Peltzer *et al.*, 1984; Cronin and Chang, 1993; Miller, 1993). The Strecker synthesis pathway for production of amino acids from aldehydes (or ketones) and hydrogen cyanide



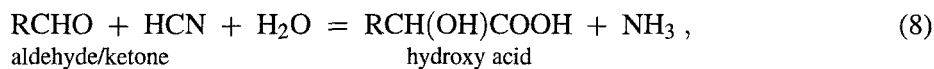
and for hydroxy acids



can be represented by the overall reactions



and



where R represents an alkyl group. Combination of reactions (7) and (8) allows evaluation of the fugacities of  $\text{NH}_3$  required to produce amino acids rather than hydroxy acids. Analogous considerations for aqueous solutions permit calculation of favorable activities of aqueous  $\text{NH}_3$  and/or  $\text{NH}_4^+$  (Shock and Helgeson, 1988; Shock *et al.*, 1989).

Most applications of the Strecker pathway to studies of organic synthesis related to the origin of life have concerned aqueous reactions driven by a flux of reactions formed in a reduced atmosphere from a spark discharge or other source of energy. The assumption of a reduced atmosphere is tenuous given the present understanding of the photochemical destruction of reduced gases (Kuhn and Atreya, 1979; Kasting *et al.*, 1983), volatile cycling through the atmosphere, hydrosphere, crust and mantle of the Earth (DesMarais, 1985; Kasting *et al.*, 1993), and the flux of impactors onto the early Earth revealed by the lunar cratering record (Stevenson, 1983; Sleep *et al.*, 1989; Kasting, 1990; Chyba and Sagan, 1992). Is the Strecker mechanism a plausible pathway for organic synthesis in the absence of an atmospheric source of reactants? Clues to the answer to this question lie in the thermodynamic properties of Strecker reactions and likely geochemical constraints on hydrothermal systems.

In a thermodynamic sense, a reaction is feasible if the Gibbs free energy of the reaction ( $\Delta G_r$ ) is negative. The relation

$$\Delta G_r = \Delta G_r^\circ + (2.303)RT \log Q_r \quad (9)$$

where  $\Delta G_r^\circ$  represents the standard Gibbs free energy of reaction and  $Q_r$  stands for the activity product, helps to illustrate the standard state ( $\Delta G_r^\circ$ ) and geochemical ( $\log Q_r$ ) constraints on  $\Delta G_r$ .

In this study, values of the standard Gibbs free energy of reaction for several Strecker synthesis reactions were evaluated using the revised Helgeson-Kirkham-Flowers (HKF) equations of state (Shock *et al.*, 1992), along with data and parameters for aqueous ions, organic compounds and neutral solutes from Shock *et al.* (1989), Shock and Helgeson (1990), Shock (1994b), Schulte and Shock (1993) and Shock and McKinnon (1993). Geochemical constraints consist of naturally buffered activities and fugacities of the chemical species which occur in these reactions, and can be incorporated with values of  $\Delta G_r^\circ$  to determine the feasibility of Strecker reactions in hydrothermal systems. In the following sections, each of these consideration is addressed.

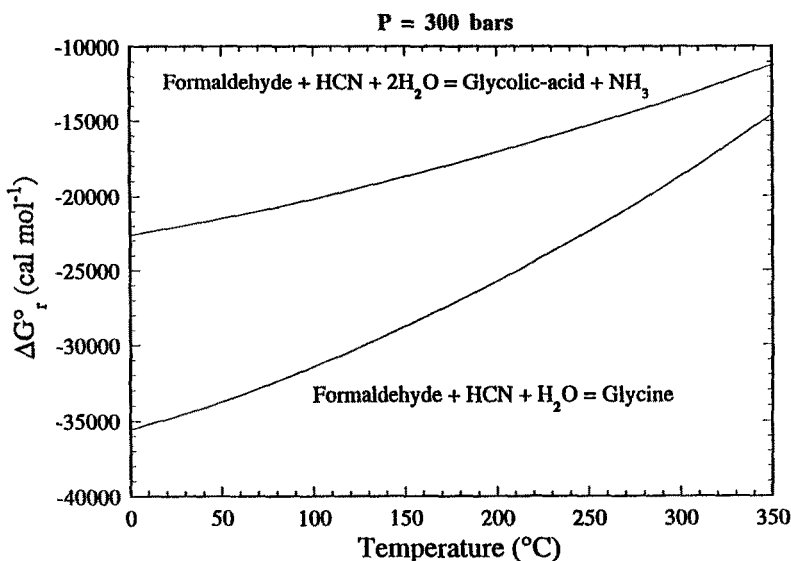


Fig. 1.  $\Delta G_r^0$  as a function of temperature for Strecker synthesis reactions which produce glycine and glycolic acid from formaldehyde and HCN at 300 bars pressure.

### Standard Gibbs Free Energies of Reaction

The standard Gibbs free energies of overall Strecker reactions for the formation of glycine and glycolic acid from formaldehyde and HCN in solution are shown as functions of temperature at 300 bars in Figure 1. Notice that the reaction that yields glycine has a more negative value of  $\Delta G_r^0$  than the reaction to form glycolic acid. Values of  $\Delta G_r^0$  for both reactions become decreasingly negative with increasing temperature. Figure 2 is analogous to Figure 1, but refers to the formation of alanine and lactic acid from acetaldehyde and HCN. Again, the  $\Delta G_r^0$  for the reaction which yields the amino acid is more negative than that for the formation of the corresponding hydroxy acid, and values of  $\Delta G_r^0$  for both reactions become decreasingly negative with increasing temperature. Because Strecker synthesis can proceed with ketones as starting materials (Cronin, 1989), the standard Gibbs free energy of reactions which produce  $\alpha$ -aminobutyric acid and  $\alpha$ -hydroxybutyric acid as functions of temperature from acetone (a ketone) and propanal (an aldehyde) are plotted in Figures 3 and 4, respectively. Comparison of Figures 3 and 4 shows that for equal activities of all reactants, values of the standard Gibbs free energy of formation from the aldehyde are more negative than those for formation from the ketone.

The calculations summarized in Figures 1–4 indicate that if possible reactants for Strecker synthesis are available and abundant in a hydrothermal system, production of amino and hydroxy acids is thermodynamically favored over all ranges of temperatures appropriate for the hydrothermal system. As an example, Figure 5

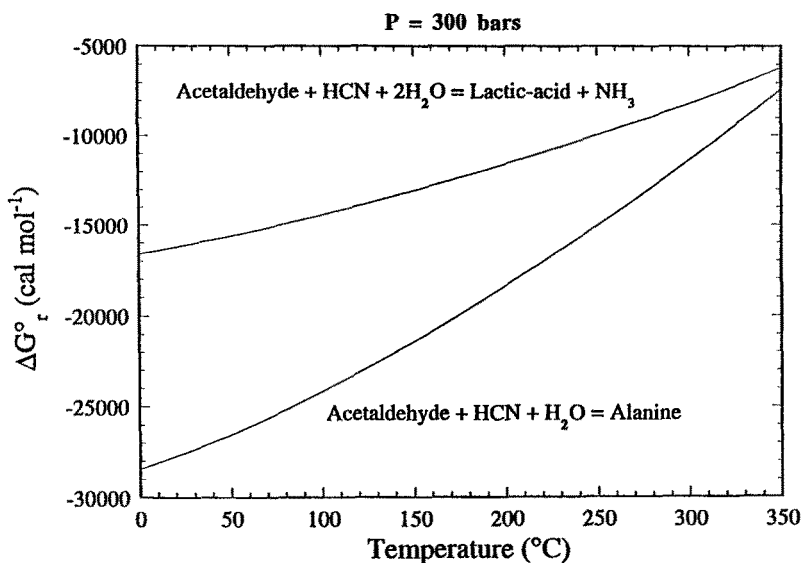


Fig. 2.  $\Delta G_r^0$  as a function of temperature for Strecker synthesis reactions which produce alanine and lactic acid from acetaldehyde and HCN at 300 bars pressure.

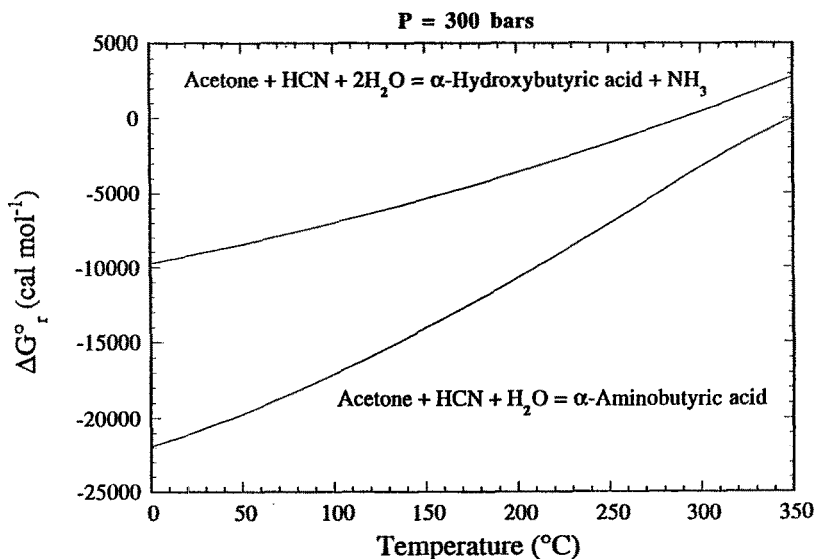


Fig. 3.  $\Delta G_r^0$  as a function of temperature for Strecker synthesis reactions which produce  $\alpha$ -aminobutyric acid from and  $\alpha$ -hydroxybutyric acid from acetone and HCN at 300 bars pressure.

shows contours of the log activity of aqueous glycine at 200 °C and 300 bars which would be in equilibrium with various activities of formaldehyde and HCN, based on the value of  $\log K$  (11.893) for the appropriate analog of reaction (7). It can be

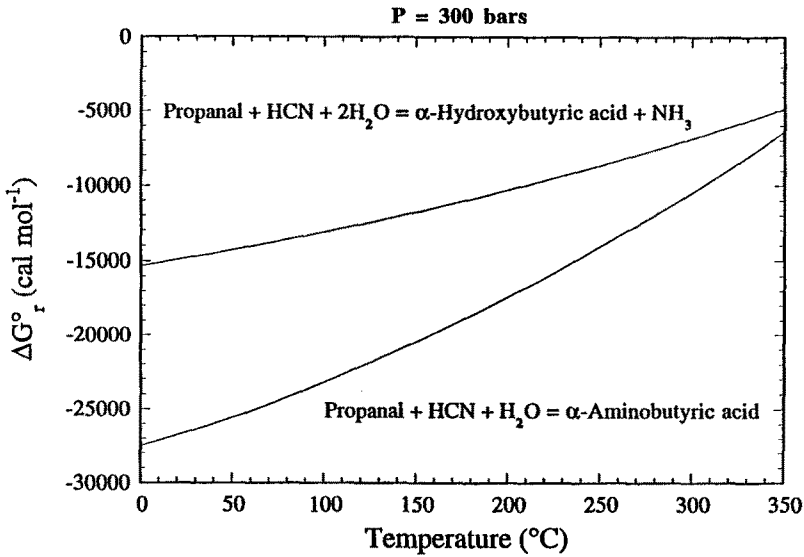


Fig. 4.  $\Delta G_r^0$  as a function of temperature for Strecker synthesis reactions which produce  $\alpha$ -aminobutyric acid and  $\alpha$ -hydroxybutyric acid from acetone and HCN at 300 bars pressure.

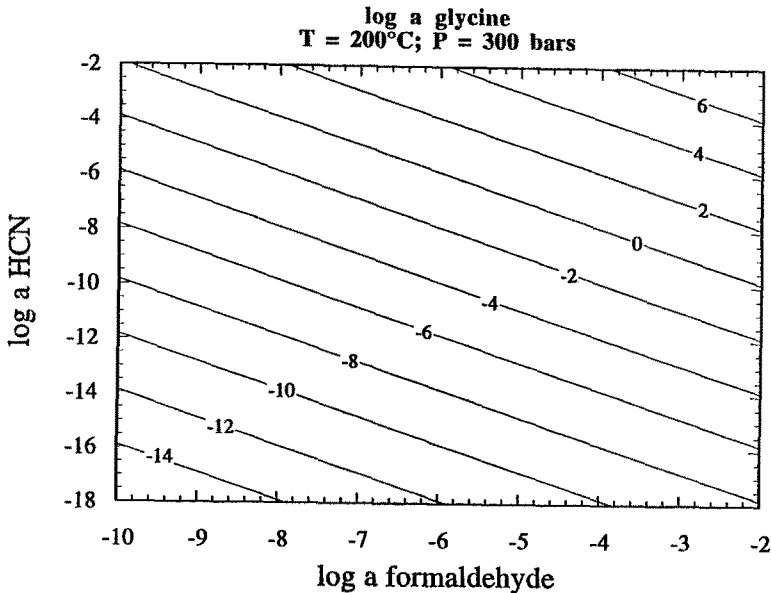


Fig. 5. Contours of log  $a$  glycine plotted as a function of log  $a$  HCN and log  $a$  formaldehyde at 200 °C and 300 bars, calculated with data presented in Figure 1.

seen in Figure 5 that high concentrations of glycine are in equilibrium with low concentrations of HCN and formaldehyde. For example, a solution at equilibrium with  $10^{-6}$  M of both formaldehyde and HCN would have a glycine concentration

TABLE I  
Mineral reactions which can buffer hydrogen fugacity

$\text{Fe} + \text{H}_2\text{O} = \text{FeO} + \text{H}_2$	<b>(FeFeO)</b>
$\text{Fe}_3\text{O}_4 + 3/2\text{SiO}_2 + \text{H}_2 = 3/2\text{Fe}_2\text{SiO}_4 + \text{H}_2\text{O}$	<b>(QFM)</b>
$3/2\text{FeS} + \text{H}_2\text{O} = 3/4\text{FeS}_2 + 1/4\text{Fe}_3\text{O}_4 + \text{H}_2$	<b>(PPM)</b>
$3\text{Fe}_2\text{O}_3 + \text{H}_2 = 2\text{FeS}_3\text{O}_4 + \text{H}_2\text{O}$	<b>(HM)</b>

of nearly 1 M. Calculations such as those shown in Figure 5 do not take account of mass balance. A 1 M glycine solution can not be generated from  $10^{-6}$  M solutions of formaldehyde and HCN. In addition, because hydrothermal systems operate at conditions which differ from those of the standard state, consideration must be given to the constraints placed on the reactions by the natural geochemical system. These constraints include concentrations of reactant compounds, pH, oxidation state, pressure and temperature. In the following section, mass balance and geochemical constraints which are appropriate in the context of submarine hydrothermal systems are described and incorporated with standard state calculations.

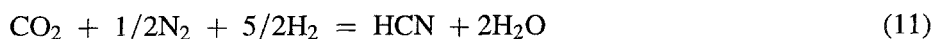
### Geochemical Constraints

In order for Strecker reactions to occur, there must be a source of starting materials, such as formaldehyde and HCN. The potential for production of such starting materials in hydrothermal systems is demonstrated in Figures 6 and 7. For each of the following calculations, total pressure is 300 bars, the  $\text{CO}_2$  fugacity was set to 10 bars and  $\text{N}_2$  fugacity was set to 1 bar (after Kasting, 1993). Mineral assemblages which can buffer  $f\text{H}_2$  (**FeFeO**, iron-iron oxide; **QFM**, quartz-fayalite-magnetite; **PPM**, pyrite-pyrrhotite-magnetite; **HM**, hematite-magnetite; see Table I) have been plotted for reference and can be compared to contours of the equilibrium activities of formaldehyde and HCN.

Figure 6 shows calculated activities of formaldehyde and HCN in equilibrium with  $\text{CO}_2$  and  $\text{N}_2$  at a range of submarine hydrothermal conditions. The reaction for formaldehyde is



and the reaction for HCN is



Rearranging the logarithm of the law of mass action for both of these reactions gives

$$\log f\text{H}_2 = -1/2 \log K - 1/2 \log (a \text{CH}_2\text{O}) - 1/2 \log f\text{CO}_2 \quad (12)$$

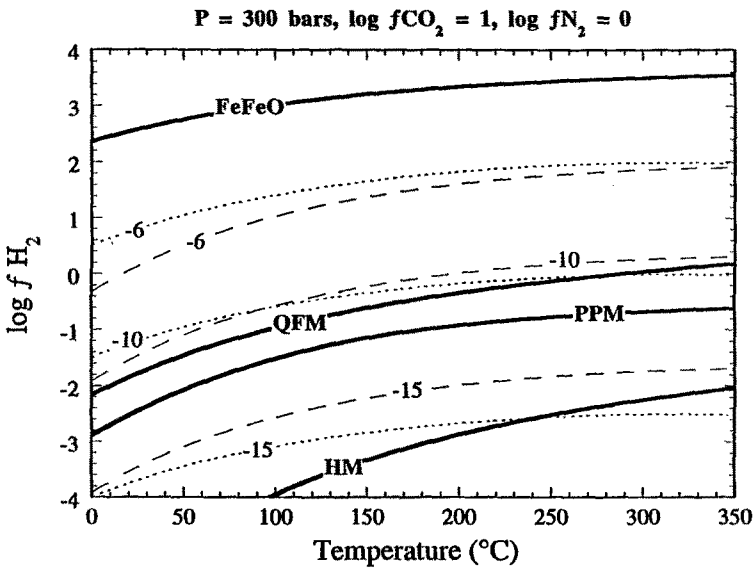


Fig. 6.  $\log f_{\text{H}_2}$  as a function of temperature at 300 bars showing contours of the activities of formaldehyde (dotted lines) and HCN (dashed lines) in equilibrium with 10 bars of  $\text{CO}_2$  ( $\log f_{\text{CO}_2} = 1$ ), 1 bar of  $\text{N}_2$  ( $\log f_{\text{N}_2} = 0$ ) and hydrothermal fluids. Solid curves represent values of  $f_{\text{H}_2}$  buffered by the mineral assemblages listed in Table I.

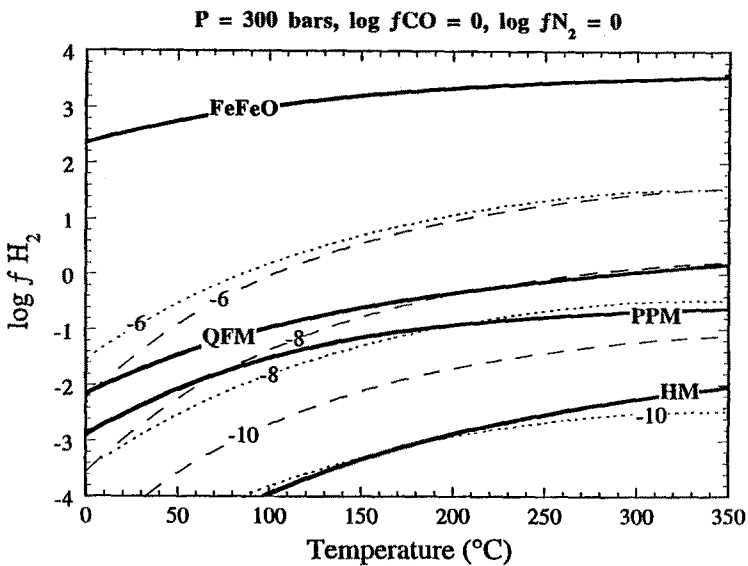


Fig. 7.  $\log f_{\text{H}_2}$  as a function of temperature at 300 bars showing contours of the activities of formaldehyde (dotted lines) and HCN (dashed lines) in equilibrium with 1 bar of  $\text{CO}$  ( $\log f_{\text{CO}} = 0$ ), 1 bar of  $\text{N}_2$  ( $\log f_{\text{N}_2} = 0$ ) and hydrothermal fluids. Solid curves represent values of  $f_{\text{H}_2}$  buffered by the mineral assemblages listed in Table I.



and

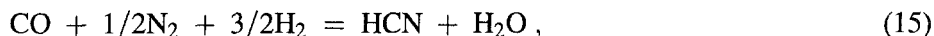
$$\log f\text{H}_2 = 2/5[-\log K + \log (a \text{ HCN}) - 1/2 \log f\text{N}_2 - \log f\text{CO}_2] \quad (13)$$

where  $f$  and  $a$  represent fugacity and activity, respectively. Values of  $\log K$  were combined with fugacities of  $\text{N}_2$  and  $\text{CO}_2$  discussed above to evaluate  $\log (a \text{ CH}_2\text{O})$  and  $\log (a \text{ HCN})$  as functions of  $\log f\text{H}_2$  and temperature, and the results are shown as contours in Figure 6. The contours are plotted as dotted lines (formaldehyde) and dashed lines (HCN).

Figure 7 contains a similar plot for the production of formaldehyde and HCN from CO. The fugacity of CO has been set to an extremely high value of 1 bar in the calculations (after Kasting, 1993). The formation of formaldehyde and HCN from CO is represented by the reactions



and



respectively. Rearranging the logarithms of the laws of mass action for each of these reactions together with the constraints  $f\text{N}_2 = 1$  and  $f\text{CO} = 1$ , gives

$$\log f\text{H}_2 = -\log K + \log (a\text{CH}_2\text{O}) \quad (16)$$

and

$$\log f\text{H}_2 = 2/3[-\log K + \log (a \text{ HCN})] . \quad (17)$$

As in Figure 6, the contours of equilibrium activities of formaldehyde and HCN are plotted as dotted lines (formaldehyde) and dashed lines (HCN).

Comparison of Figures 6 and 7 shows that for temperatures of 100–250 °C and hydrogen fugacities buffered by the **QFM** and/or **PPM** mineral assemblages (conditions appropriate for present-day systems and hypothetical Archean hydrothermal systems), metastable equilibrium constrains  $\log a \text{ CH}_2\text{O}$  and  $\log a \text{ HCN}$  to values from  $-12$  to  $-7$ , and that greater production of these aqueous species could have been derived from CO.

With constraints such as these placed on calculations, the potential for Strecker synthesis of amino acids can then be evaluated. For example,  $\Delta G_r$  for the reaction which produces glycine from formaldehyde and HCN at 150 °C, 300 bars and  $\log f\text{H}_2$  buffered by the **PPM** mineral assemblage can be calculated as follows:  $\Delta G_r^0$  (from Figure 1) =  $-28780. \text{ cal mol}^{-1}$ . The values of  $\log a \text{ CH}_2\text{O}$  and  $\log a \text{ HCN}$  (from Figure 7) are  $-7.85$  and  $-8.56$ , respectively. The value of  $\Delta G_r$  obtained at the point in reaction progress where all of the nitrogen originally present as HCN

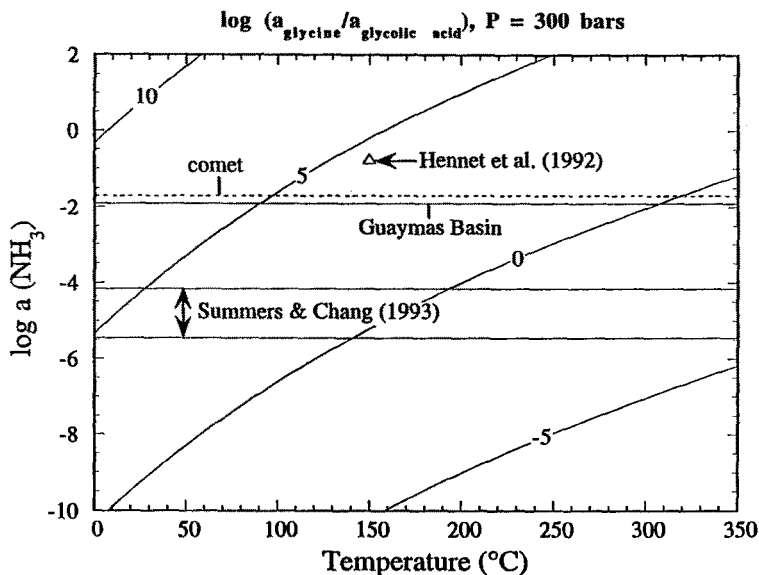


Fig. 8.  $\log a(\text{NH}_3)$  as a function of temperature at 300 bars showing contours of the log of the ratio of equilibrium activities lines of glycine to glycolic acid. Dashed lines and shaded area represent cosmochemical and geochemical constraints on  $a(\text{NH}_3)$  described in the text.

is converted to glycine is  $-13580. \text{ cal mol}^{-1}$ . This demonstrates that the reaction should be spontaneous and that the production of glycine is favored in this environment, but the low activities of reactants will limit the efficiency and productivity of the reaction to a glycine concentration of  $10^{-8.56}$ . In addition, it is not apparent whether such low concentrations of reactants are likely to efficiently combine to form the thermodynamically favored product. Although the thermodynamic properties of reactions to form the reactants needed for Strecker synthesis from  $\text{N}_2$ ,  $\text{CO}_2$  and/or  $\text{CO}$ , as well as the overall Strecker synthesis reactions, are favorable in the hydrothermal environment, a major function in whether Strecker synthesis will proceed efficiently is the extent to which potential reactants can be concentrated. Possible mechanisms for concentrating reactants may include adsorption onto clay or other mineral surfaces, incorporation into proto-membranes possibly forming in the same environment (Russell *et al.*, 1994a, b), or recirculation of reactant-bearing fluids through sediment and/or oceanic crust.

Results of Strecker synthesis are also sensitive to the activity of  $\text{NH}_3$  in the reaction medium. Insufficient  $\text{NH}_3$  results in the synthesis of hydroxy acids in greater quantities than amino acids (Miller and Van Trump, 1981). As shown in Figure 8, these results are completely consistent with the thermodynamic properties of overall Strecker synthesis reactions. Figure 8 shows contours of equilibrium activities of glycine and glycolic acid as functions of ammonia activity and tem-

perature. Total pressure for each of the calculations is 300 bars. These contours are calculated from  $\Delta G_r^\circ$  for the reaction



by rearranging the logarithm of the law of mass action for this reaction to yield

$$\log a \text{NH}_3 = \log K + \log (a \text{glycine}/a \text{glycolic acid}) . \quad (19)$$

Also plotted on this figure are possible activities of ammonia which vary depending on the source of ammonia as described in the references indicated. The numbers given for each of the sources are upper limits on the total ammonia activity. The value from Hennes *et al.* (1992) is calculated assuming that all nitrogen unaccounted for by amino acids from the experiment is in the form of ammonia. The value labelled 'comet' is calculated using the ammonia and water content of comet Halley (Fegley, 1993) assuming that Halley is representative of comets and that the ammonia and H<sub>2</sub>O could survive the incorporation process on the early Earth. The value for the Guaymas Basin, a highly sedimented spreading center, was taken from Von Damm (1990), where the concentration is reported as NH<sub>4</sub><sup>+</sup> for ~300 °C. The values from Summers and Chang (1993) are obtained based on their model of reduction of nitrite in the 'prebiotic' ocean, and refer to differences in the sink for ammonia. It can be seen in this figure that at geochemically and cosmochemically reasonable ammonia activities, glycine predominates over glycolic acid. In one extreme (that for the cometary composition), this holds for temperatures up to ~300 °C. In the other extreme (that for compositions reported by Summers and Chang, 1993), this holds only to ~150 to ~175 °C.

## Conclusions

Many investigators are beginning to realize that submarine hydrothermal systems may be likely environments for the emergence of life. Calculations such as the ones presented here provide thermodynamic tests of the potential for organic compound synthesis within the geochemical constraints provided by hydrothermal environments. Amino and hydroxy acid synthesis via a Strecker mechanism is thermodynamically favored in hydrothermal environments. However, because Strecker synthesis requires aldehydes (or ketones) and HCN, and these are likely to be generated at low concentrations in hydrothermal systems, only dilute solutions of amino acids would form. If Strecker synthesis is the main synthesis pathway, concentration mechanisms involving clay or other mineral surfaces may have been required for further reactions leading to the emergence of life. In any event, it is unlikely that Strecker synthesis is the only pathway available for amino acid production in hydrothermal systems.

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