GEOCHEMICAL CONSTRAINTS ON THE ORIGIN OF ORGANIC COMPOUNDS IN HYDROTHERMAL SYSTEMS

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Abstract. It is proposed that abiotic synthesis of organic compounds occurs in metastable states. These states are permitted by kinetic barriers which inhibit the approach to stable equilibrium in the C-H-O-N system. Evidence for metastable equilibrium among organic compounds in sedimentary basins is reviewed, and further evidence is elucidated from hydrous pyrolysis experiments reported in the literature. This analysis shows that at hydrothermal conditions, organic compounds are formed or destroyed primarily through oxidation/reduction reactions, and that the role of temperature is to lower the kinetic barriers to these reactions. These lines of evidence allow the development of a scenario in which abiotic synthesis can occur at hydrothermal conditions through the reduction of CO_2 and N_2. This scenario can be tested quantitatively with distribution of species calculations as functions of temperature, pressure, hydrogen fugacity (fH_2) and initial composition. One example of such a test is given for an early, sudden outgassing of the Earth, in which CO_2, H_2O, and N_2 are transported from the mantle to the atmosphere by hydrothermal solutions. Activities of metastable aqueous organic species which form as a consequence of this process are evaluated at conditions appropriate for seafloor hydrothermal systems, and are found to maximize at about 200 °C and between the oxidation states set by two mineral assemblages common in the oceanic crust.

1. Introduction

In the C-H-O-N chemical system, stable equilibrium is dominated by CO_2, CO, CH_4, N_2, NH_3, H_2O, H_2, O_2, graphite, and/or diamond depending on temperature, pressure, and bulk composition (French, 1966; Frost, 1979; Holloway, 1981, 1984), and equilibrium activities of organic compounds other than simple hydrocarbons are typically vanishingly low (Suess, 1962; Eck *et al.*, 1966; Dayhoff *et al.* 1967, Thorstenson, 1970). Therefore, the central problem in the abiotic synthesis of organic compounds from inorganic compounds is identifying the circumstances at which stable thermodynamic equilibrium is not reached owing to kinetic constraints. If barriers of this type exist, they will allow the formation of metastable states, and in the case of the C-H-O-N system such states may be dominated by organic compounds.

The basic idea of a metastable state is illustrated in Figure 1. Starting from state A, stable equilibrium calculations would indicate that state C forms in preference to state B. However, as shown in the figure, the parth from A to C passes through a larger kinetic barrier than the path from A to B. Therefore, with sufficient energy to overcome barrier A–B, but not A–C, state B will form from state A in preference to state C. State B is a metastable state and the *only* condition of interest to the abiotic synthesis of organic compounds.

Abiotic synthesis experiments have shown repeatedly that by establishing a
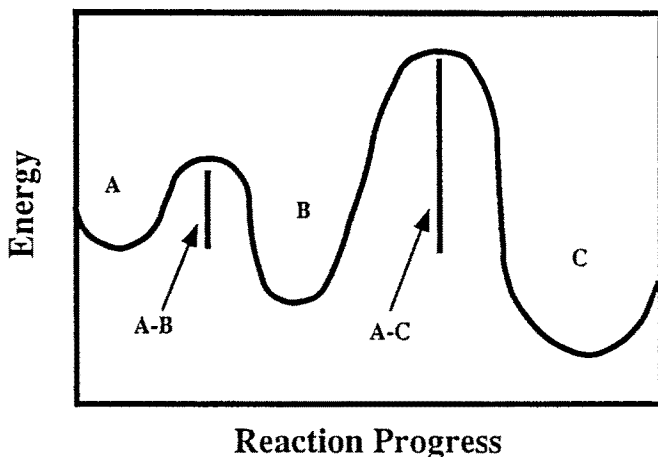
Reaction Progress

Fig. 1. Plot of energy against reaction progress for a hypothetical system in which a metastable state (B) exists between two stable states (A) and (C). A–B and A–C indicate activation energies between states A and B and A and C, respectively.

situation analogous to that in Figure 1, and supplying sufficient energy to overcome a lower set or sets of kinetic barriers, organic compounds can be formed at metastable states in preference to the inorganic compounds which would dominate at stable equilibrium. Much of what Cairns-Smith (1982) calls 'the current doctrine of chemical evolution studies' is based on the relative ease with which mixtures of reduced inorganic compounds can be caused to react and form organic compounds, given sufficient energy. The first, and arguably most important, of these demonstrations was the familiar Miller-Urey synthesis of numerous organic compounds from CH_4, NH_3, H_2, and H_2O with the energy coming from a spark discharge (Miller, 1953, 1955; Abelson, 1956, 1957; Miller and Urey, 1959; Ring et al., 1972; Wolman et al., 1972). Other investigators have shown that heat (Harada and Fox, 1964, 1965; Fox and Windsor, 1970; Hayatsu et al., 1971; Wolman et al., 1971; Lawless and Boynton, 1973; Yanagawa et al., 1981), ultraviolet radiation (Groth and Van Weyssenhoff, 1960; Sagan and Khare, 1971; Bar-Nun and Hartman, 1978; Reiche and Bard, 1979), shock waves (Bar-Nun et al., 1970, 1971), and other forms of energy (Palm and Calvin, 1962; Gilvary and Hochstim, 1963; Scattergood et al. 1989) can be used to overcome the kinetic barriers to the formation of metastable states from reduced starting mixtures. Perhaps owing to the success of these experiments, it is commonly thought that reduced starting materials are required for abiotic synthesis on the early Earth. However, it is important to keep in mind that the carbon and nitrogen in all organic compounds are effectively more oxidized than the carbon and nitrogen in CH_4 and NH_3. Therefore, the requirements for abiotic synthesis from reduced inorganics gases are kinetic barriers which allow oxidation to organic compounds but not to CO_2 and N_2.

Over the past decade, it has become increasingly evident that a reduced mixture of gases in the atmosphere of the early Earth would have been subjected to photo-

chemical oxidation in the presence of water vapor and the young sun's ultraviolet radiation (Levine *et al.*, 1982; Zahnle and Walker, 1982; Canuto *et al.*, 1982, 1983; Kasting *et al.*, 1983; Levine, 1985). Experiments and simulations of prebiotic atmospheres show that at these conditions the half lives of CH_4 and NH_3 are $\sim$ 50 years and $\sim$ 1 week, respectively (Kuhn and Atreya, 1979; Levine *et al.*, 1982). The resulting atmosphere would be dominated by N_2 and CO_2 much like the modern atmosphere of the Earth, but without the present high concentration of O_2 which is a byproduct of photosynthesis (Berkner and Marshall, 1965; Walker, 1976; Kasting *et al.*, 1984; Lewis and Prinn, 1984; Nisbet, 1987). These results are in conflict with the supposition that reduced starting materials are necessary for abiotic synthesis to proceed. This is particularly true if all important abiotic synthesis reactions went on in the atmosphere.

Atmospheric reactions have been the focus of attention ever since Oparin (1924) and Haldane (1929) placed their origin of life scenarios in the ocean-atmosphere system. Spark discharge experiments were conducted in gas mixtures in order to simulate lightning in prebiotic atmospheres (Miller, 1953, 1955). We might ask why the atmosphere has been the favorite location for abiotic synthesis experiments given the wide variety of geologic environments available on the early Earth. The answer might involve the observation that life is found at the surface of the Earth, generally in contact with the atmosphere, or near to it. However, the set of conditions at which life flourishes is not necessarily the same set as that in which organic compounds can form.

Perhaps a geologic analogy will illustrate this point. Granite is found at the surface of the Earth, and we are well aware that it does not form there. Similarly, the great majority of organic carbon on the Earth is found in sedimentary rocks, outweighing all of the organic carbon in the biomass by more than 2000 times (Tissot and Welte, 1984). Although the majority of this organic carbon is apparently fixed at the surface through photosynthesis, the realm of organic compounds is evidently not limited to the surface of the Earth. Indeed, most organic compounds reside within sedimentary basins and at metamorphic conditions where temperature and pressures are generally much greater than those which life can tolerate. Therefore, just as the surficial conditions at an outcrop of granite tell us little about the conditions of its formation, the reference frame provided by life does little to identify the conditions at which most organic compounds occur in the Earth. As we know from the occurrence of organic compounds in carbonaceous chondrites, comets, and interstellar space, the presence of life tells us little about the conditions at which organic compounds can form.

2. The Thermal Stability of Organic Compounds

Organic compounds are found in the Earth over wide ranges of temperature and pressure. Evidence from deep wells in the Gulf of Mexico indicates that petroleum hydrocarbons are found in rocks which are presently at 300 °C or higher, and

at pressures in excess of 7 kilobars (Price *et al.*, 1979, 1981, 1982). Analysis of altered sediments and hydrothermal solutions from the Guaymas basin and other spreading centers shows that hydrocarbons and other organic compounds persist to temperatures in excess of 300 °C even at lower pressures (Simoneit, 1988; among others, see below). In addition to evidence from sedimentary basins, carbonaceous matter found in metamorphic rocks appears to survive high temperatures without being completely converted to graphite. Several lines of evidence indicate that carbonaceous matter in metamorphic rocks, which is often identified as graphite petrographically, is actually a variety of highly-polymerized aromatic hydrocarbons (Buseck and Huang, 1985; Clayton and Bostick, 1986; Robinson *et al.*, 1986).

These data are in conflict with the conventional wisdom of petroleum geochemistry which advocates the destruction of hydrocarbons through disproportionation reactions leading to methane and graphite. These reactions are imagined to go to completion by 200 °C (Hunt, 1979). However, it must be kept in mind that these ideas were established mostly in the absence of experimental data, and before many samples were collected from environments with temperatures in excess of 200 °C. Evidently, despite the fact that most exploited concentrations of petroleum are found at temperatures ≤ 150 °C, hydrocarbons are preserved to much higher temperatures in the Earth's crust. As in the case of a biology-centered view of the stability of organic compounds, one based on the economy of extracting them from the Earth can not replace actual observations of nature.

Organic compounds are also found in hydrothermal systems on the continents as well as in ocean basins. Hot springs at Yellowstone and elsewhere emit petroleum hydrocarbons and other organic compounds along with hot water (Love and Good, 1970; Kvenvolden *et al.*, 1989; Clifton *et al.*, 1990). Fossil evidence linking organic matter to hydrothermal solutions can be found in a variety of ore deposits including sediment-hosted base metal deposits (Macqueen and Powell, 1983; Sverjensky, 1986; Diedel and Püttman, 1988; Pütmann *et al.*, 1989) as well as deposits of mercury (Barnes *et al.*, 1973; White, 1981; Wells and Ghiorso, 1988), uranium and vanadium (Breger and Deul, 1959; Idez *et al.*, 1986; Johnson *et al.*, 1987; Zielinski and Meier, 1988), and gold (Butler *et al.*, 1920; Krauskopf, 1955; Radtke and Scheiner, 1970; Saxby, 1976; Farfel *et al.*, 1984; Ilchik *et al.*, 1986; Gatellier and Disnar, 1989). Considerable research has focused on using the presence of organic compounds in these deposits to identify the oxidation states and/or pH values of aqueous solutions at the time of ore deposition (Garrels and Pommer, 1959; Hausen and Kerr, 1968; Radtke and Scheiner, 1970; Rytuba, 1985; Kettler, 1990).

As compelling as these observations are for demonstrating the compatibility between organic compounds and hydrothermal conditions, they are not as dramatic as those from the submarine hot springs in the Guaymas Basin of the Gulf of California (Simoneit and Lonsdale, 1982; Simoneit, 1983, 1984, 1985; Simoneit *et al.*, 1984, 1990; Somoneit and Kawka, 1987; Kawka and Simoneit, 1987, 1990; Gieskes *et al.*, 1988; Whelan *et al.*, 1988; Didyk and Simoneit, 1989, 1990; Peter *et al.*, 1990; Martens, 1990; Schoell *et al.*, 1990). In this tectonically active setting,

characterized by considerable input of continentally-derived sediment, hydrothermal solutions, driven by the cooling of recently formed oceanic lithosphere, generate and transport petroleum. Direct observations of hydrocarbon transport are common during submersible dives in the area and are best summarized by Simoneit (1983) who wrote 'one vent was discharging a water-oil emulsion'. These observations indicate that organic compounds are not limited to environments within sedimentary and metamorphic rocks, but are transported in hydrothermal solutions within the Earth's crust. Numerous lines of evidence show that the realm of temperatures and pressures where organic compounds are preserved in the Earth extends to at least 500 °C and 10 kilobars.

At first glance, all of this evidence is incompatible with widely held beliefs that organic compounds decompose rapidly at elevated temperatures. These beliefs are often expressed in the literasture on the origin of life (Chang, 1982; Chang et al., 1983; Miller and Bada, 1988; and many others). We might ask how ideas directly in conflict with observations of nature can be so widely held. The answer lies in the study of organic compounds in the laboratory, where what is often meant by the thermal destruction of an organic compound in an experiment is actually its alteration through oxidation, reduction, decarboxylation, hydrolysis, or other reactions.

3. Metastable Equilibria Among Aqueous Organic Species

At crustal conditions, the enormous lengths of time involved in the conversion of organic compounds to the thermodynamically stable assemblages of compounds in the C-H-O-N system allow the preservation of organic matter in a wide variety of forms. Although the majority of the organic matter exists as disseminated particles throughout sedimentary and metamorphic rocks, a small amount is preserved as natural gas, petroleum, coal, oilshale, and compounds in aqueous solution. Therefore, it is evident that a variety of kinetic barriers exists at the conditions of the Earth's crust, and that these barriers allow several distinct assemblages of organic compounds. With this in mind, the first problem is how to characterize these assemblages thermodynamically. We can begin by asking whether the concentrations of organic compounds in a given natural assemblage can be treated as a metastable assemblage. The answer to such questions lies in whether thermodynamic calculations allow us to identify which coexisting species are in metastable equilibrium, and characterize the descriptive variables which control the metastable states found in nature. Calculations of this type are limited by the availability of thermodynamic data, but evidence from the study of organic acids in sedimentary basins suggests that the relative concentrations of these acids are controlled by metastable equilibria.

3.1. EVIDENCE FROM SEDIMENTARY BASINS

It has been shown that acetic and propanoic acids in oil-field brines are present at concentrations consistent with redox equilibria among the acids, and between

the acids and CO_2 (Shock, 1988, 1989). Thermodynamic calculations indicate that methane fugacities in equilibrium with the high concentrations of the organic acids (up to 10 000 ppm) in these fluids exceed the total pressures in sedimentary basins by orders of magnitude, and are therefore physically impossible. On the other hand, it appears that a metastable assemblage prevails which consists of CO_2, acetic acid and propanoic acid, and that the relative concentrations of these compounds are set by metastable redox equilibria. Although a more thorough analysis is given elsewhere (Shock, 1988; 1989), a brief summary is necessary to emphasize the evidence from nature of metastable redox equilibria.

Observations of the relative concentrations of organic acids in sedimentary basin brines is suggestive of homogeneous metastable equilibrium, as shown by the three examples in Figures 2 through 4. Figure 2 contains a plot of the molalities of propanoic and acetic acid from several analyses of natural solutions at ~100 °C reported by Carothers and Kharaka (1978). Similar data from the same source at ~125 °C are shown in Figure 3, and Figure 4 depicts molalities of butanoic and propanoic acids from samples analyzed by Willey *et al.* (1975). In the case of propanoic acid and acetic acid, the distribution of points in Figures 2 and 3 are consistent with the reaction

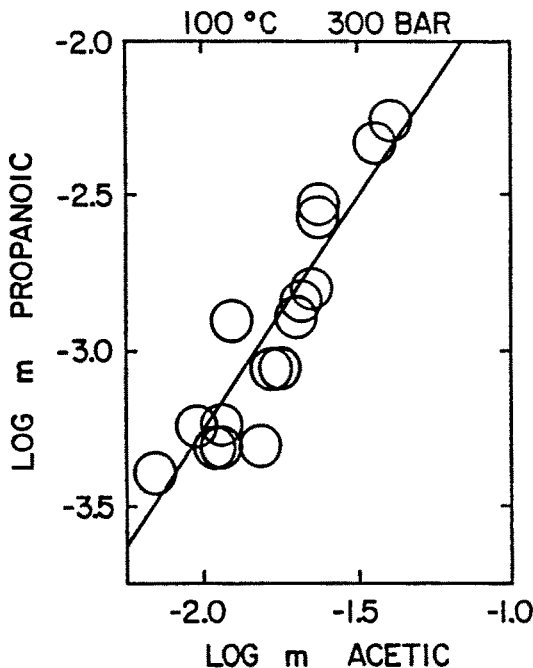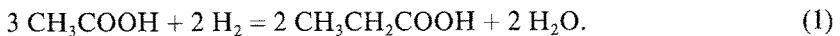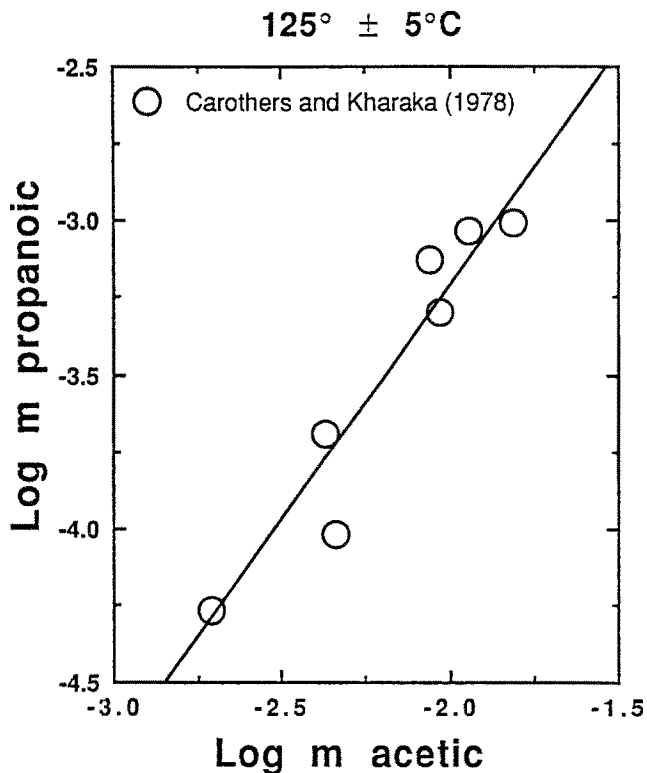$$3 \ CH_3COOH + 2 \ H_2 = 2 \ CH_3CH_2COOH + 2 \ H_2O. \tag{1}$$

Fig. 2. Log molality of propanoic acid plotted against log molality of acetic acid for natural samples of oil-field brines reported by Carothers and Kharaka (1978). Samples shown were collected at temperatures within ±5 °C of 100 °C. The line has a 3/2 slope consistent with Equation (3).

125° ± 5°C

Fig. 3. Log molality of propanoic acid plotted against log molality of acetic acid for natural samples of oil-field brines reported by Carothers and Kharaka (1978). Samples shown were collected at temperatures within ±5 °C of 125 °C. The line has a 3/2 slope consistent with Equation (3).

The distribution of points in Fig. 4 is consistent with the reaction

$$4\ CH_3CH_2COOH + 2\ H_2 = 3\ CH_3CH_2CH_2COOH + 2\ H_2O. \tag{2}$$

Assuming that the activity of H_2O is unity, which is often the case for geologic fluids (Helgeson, 1985), the logarithmic law of mass action expressions for reactions (1) and (2) can be arranged to yield

$$\log a_{propanoic\ acid} = 3/2 \log a_{acetic\ acid} + 1/2\ (\log K_1 - 2 \log f H_2) \tag{3}$$

and

$$\log a_{butanoic\ acid} = 4/3 \log a_{propanoic\ acid} + 1/3\ (\log K_2 - 2 \log f H_2). \tag{4}$$

These expressions correspond to equations of straight lines, and it can be seen that the slopes in these expressions are the same as the slopes of the distribution of points in Figures 2–4 (as indicated by the lines in the figures). In addition, by evaluating K_1 and K_2, the hydrogen fugacities consistent with these natural samples can be determined.

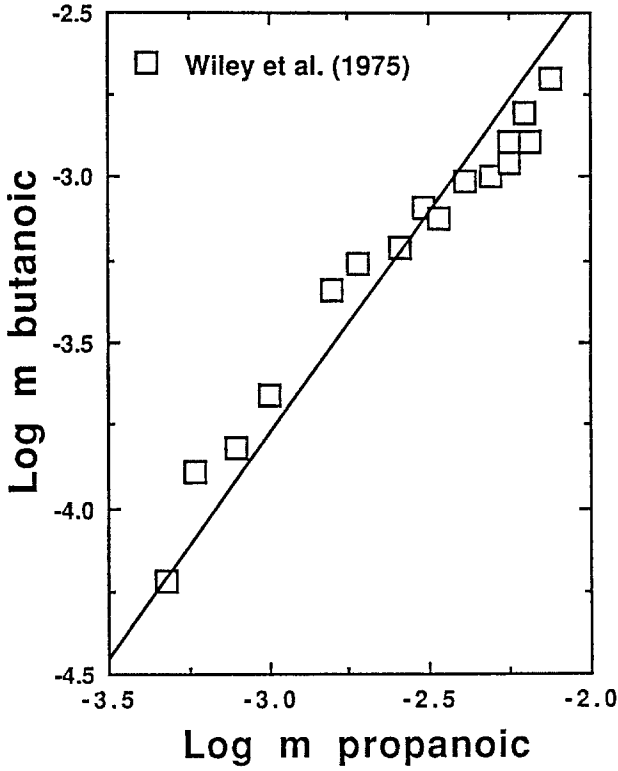Values of $f H_2$ obtained from Equation (3) using the activities of acetic acid and

Fig. 4. Log molality of butanoic acid plotted against log molality of propanoic acid for natural samples of oil-field brines collected by Willey *et al.* (1975). The line has a 4/3 slope consistent with Equation (4).
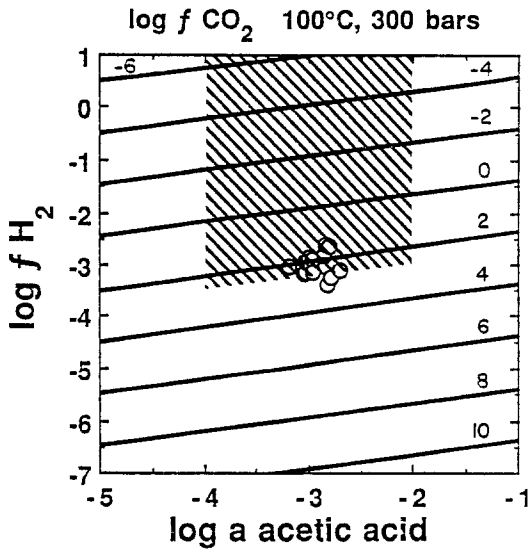

Fig. 5. Log $f\mathrm{H}_2$ – log a acetic acid plot constructed for 100 °C and 300 bars. Solid lines are contours of log $f\mathrm{CO}_2$, shaded area represents the region of diagenetic significance and symbols correspond to values of log $f\mathrm{H}_2$ and log a acetic acid calculated for natural samples shown in Figure 2.

propanoic acid determined from concentrations measured in natural samples, together with $\log K_1$ calculated with data and equations given by Shock and Helgeson (1990), are shown as symbols in Figure 5. The labeled contours in this figure correspond to values of $\log fCO_2$ calculated from

$$2\ CO_2 + 4\ H_2 = CH_3COOH + 2\ H_2O. \tag{5}$$
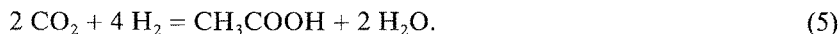
The shaded area of Figure 5 is bounded by the range of reported activities of acetic acid in oil-field brines, and by $\log fCO_2 \leq$ the total pressure, and is therefore the geologically attainable part of the diagram during sediment diagenesis. It can be seen that the majority of the natural samples are consistent with equilibrium with respect to reaction (5). These calculations show that the acids and CO_2 in solution, and therefore the carbonate minerals in the rock, are at metastable equilibrium. This metastable equilibrium assemblage is linked to silicate minerals through pH, and the inorganic composition of the brines. However, this metastable state does not include methane as depicted in Figure 6 where it can be seen that the natural samples fall outside the geologically attainable region bounded as in Figure 5, but including $\log fCH_4 \leq$ the total pressure. This indicates that metastable equilibrium with respect to the reaction

$$CH_3COOH + 4H_2 = 2\ CH_4 + 2\ H_2O \tag{6}$$

is kinetically inhibited, at least at the conditions of sediment diagenesis.

Carboxylic acids are only a few of the organic species which may coexist in the metastable states found in petroleum reservoirs. Preliminary calculations
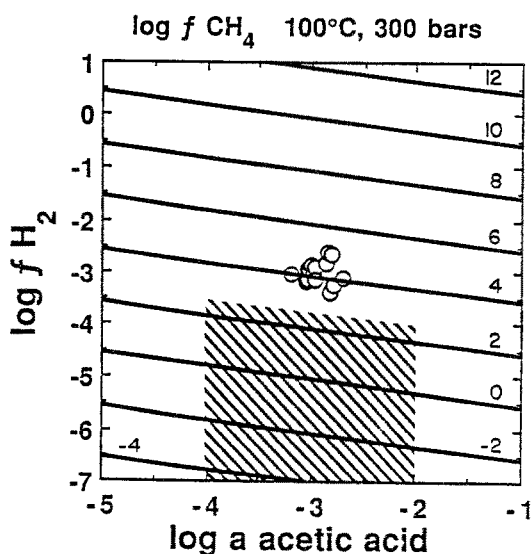

Fig. 6. Log fH_2 – log a acetic acid plot constructed for 100 °C and 300 bars. Solid lines are contours of log fCH_4, shaded area corresponds to the region of diagenetic significance and symbols indicate values of log fH_2 and log a acetic acid calculated for natural samples shown in Figure 2.

(Helgeson and Shock, 1988; Shock, 1990b) show that many of the hydrocarbons in the coexisting petroleum are at relative concentrations consistent with the metastable equilibria observed between the acids and CO_2. The full range of compounds which may be involved is the subject of ongoing research, but these early results provide the means to demonstrate how organic and inorganic constituents of sedimentary basin systems are reacting with one another. As a result of this research it is also becoming evident that organic compounds react with one another within naturally occurring aqueous solutions. Finally, these calculations suggest that acetic acid and propanoic acid react reversibly at values of fH_2 set by a buffer in the petroleum reservoir. The only stable mineral in the Fe-O-C-H system at these conditions is siderite (Shock, 1988), and it is probably the mixture of aliphatic and aromatic hydrocarbons in the coexisting petroleum which buffers the fH_2 (Helgeson and Shock, 1988; Shock, 1990b).

3.2. EVIDENCE FROM HYDROUS PYROLYSIS EXPERIMENTS

It is also possible to deduce the nature of metastable equilibria from hydrous pyrolysis experiments in which aqueous solutions and organic compounds are heated and their reaction products analyzed. Many experiments of this type have been conducted using samples of petroleum source rocks in order to evaluate their production potential, or to correlate the products of the experiments with naturally occurring petroleum (Lewan et al., 1979; Lewan, 1983, 1985, 1987; Winters et al., 1983; Hoering, 1984; Saxby and Riley, 1984). The complicated natures of the samples used in these experiments, together with the limited thermodynamic data on aqueous and non-aqueous hydrocarbons, as well as other organic compounds and their mixtures, hinder a detailed thermodynamic analysis (Sato, 1990). However, several experiments on individual organic compounds, or well characterized groups of compounds, have been conducted. Many such experiments have been conducted for amino acids (Abelson, 1954; Vallentyne, 1964, 1968; Povoledo and Vallentyne, 1964; White, 1984; Bernhardt et al., 1984; Miller and Bada, 1988). In principle, it should be possible to evaluate the results of these experiments in a thermodynamic framework. The main barrier to such an analysis is the lack of thermodynamic data for aqueous amino acids at the experimental conditions (Cabani and Gianni, 1986). Predictions for a subset of the amino acids are possible with the equations, data, and parameters presented by Shock and Helgeson (1990). Data predicted with these methods together with experimental data reported by Miller and Bada (1988) allow an investigation of metastable redox equilibria among amino acids at elevated temperatures and pressures.

Miller and Bada (1988) report the results of an experiment in which a hydrothermal cell was loaded with an aqueous solution of leucine, aspartic acid, alanine, and serine, each at a concentration of 10^{-3} mol L^{-1}, and heated to 250 °C at 265 atm for a 6 hr period. Although they tried to use an organic pH buffer, they made no attempt to constrain the fugacities of H_2, O_2, CO_2, NH_3, or any other potential reaction product or descriptive variable of the system. Their motivation for this
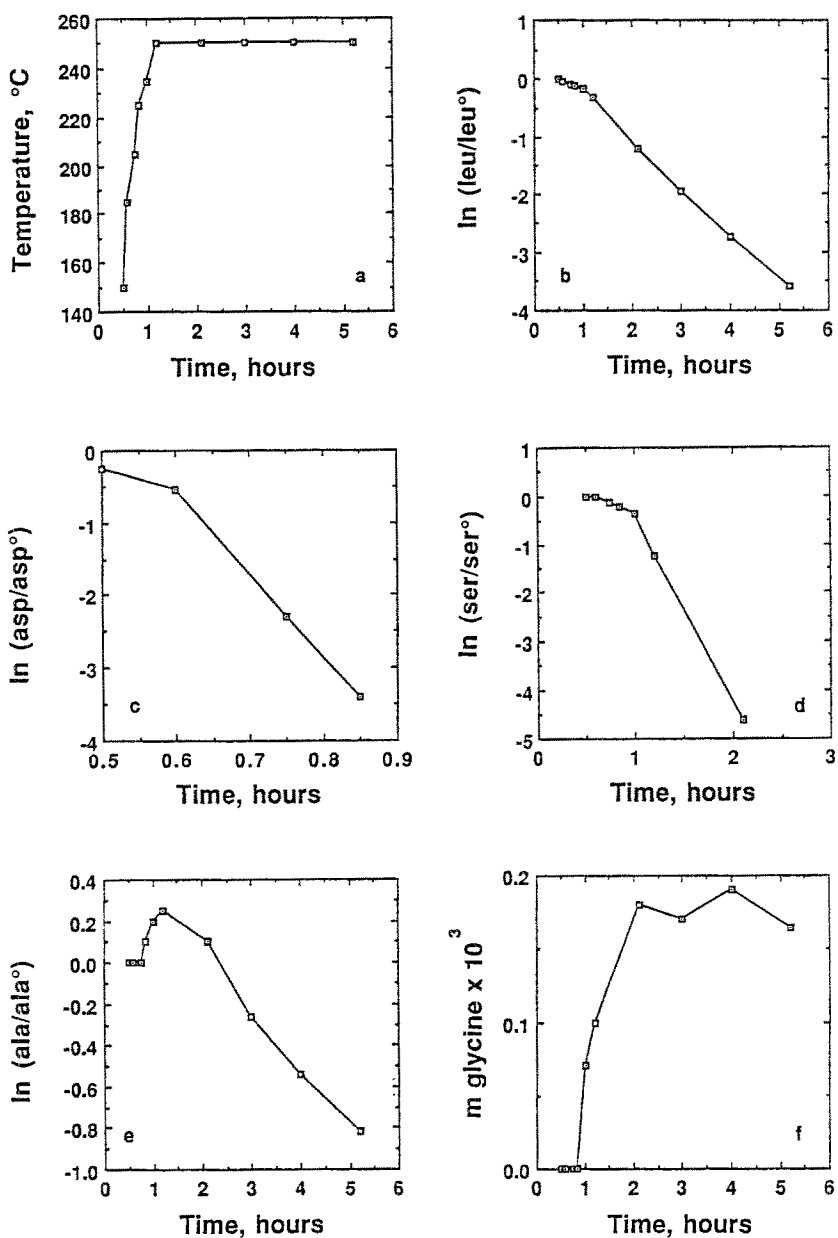
Fig. 7. Experimental results for hydrous pyrolysis of a mixed solution of amino acids at 250 °C and 265 atm reported in a figure by Miller and Bada (1988) (see Table I): (a) temperature as a function of time, (b) the logarithm of the concentration of leucine relative to its initial concentration as a function of time, (c) the logarithm of the concentration of aspartic acid relative to its initial concentration as a function of time, (d) the logarithm of the concentration of serine relative to its initial concentration as a function of time, (e) the logarithm of the concentration of alanine relative to its initial concentration as a function of time, (f) the molality of glycine as a function of time.

TABLE I

Data read from figures presented by Miller and Bada (1988) and used in the present study to evaluate metastable amino acid relations

Sample number	Time (hr)	Temp. (°C)	$\ln(leu/leu_0)$	$\ln(asp/leu)$	$\ln(ser/leu)$	$\ln(gly/leu)$	$\ln(ala/leu)$	$m\ leu \times 10^3$	$m\ asp \times 10^3$	$m\ ser \times 10^3$	$m\ gly \times 10^3$	$m\ ala \times 10^3$
1	0.5	150	0.0	-0.25	$(0.0)^a$	–	(0.0)	1.0	0.78	(1.0)	–	(1.0)
2	0.6	185	-0.05	-0.5	(0.0)	–	(0.0)	0.95	0.58	(1.0)	–	(1.0)
3	0.75	205	-0.075	-2.2	-0.05	–	(0.0)	0.93	0.10	0.88	–	(1.0)
4	0.85	225	-0.10	-3.2	-0.1	–	0.2	0.90	0.033	0.81	–	1.10
5	1.0	235	-0.15	–	-0.2	-2.5	0.35	0.86	–	0.70	0.071	1.22
6	1.2	250	-0.30	–	-0.95	-2.0	0.55	0.74	–	0.29	0.10	1.28
7	2.1	250	-1.20	–	-3.4	-0.5	1.3	0.30	–	0.01	0.18	1.10
8	3.0	250	-1.95	–	–	0.2	1.7	0.14	–	–	0.17	0.77
9	4.0	250	-2.75	–	–	1.1	2.2	0.064	–	–	0.19	0.58
10	5.2	250	-3.6	–	–	1.8	2.8	0.027	–	–	0.165	0.44
11	5.8	250	–	–	–	1.8	2.8	–	–	–	–	–

[a] Values in parentheses are estimated.

experiment was to demonstrate 'that biomolecules are very unstable at high temperatures and that their stability is not enhanced by high pressure', and as a consequence they seem to have overlooked their own experimental evidence that the amino acids were approaching relative concentrations consistent with metastable equilibrium. A detailed analysis of the experimental results in terms of metastable equilibrium is given elsewhere (Shock, 1990a), but a brief summary is included here to illustrate the approach.

Data read from figures reported by Miller and Bada (1988) are depicted in Figure 7 and listed in Table I, together with calculated molalities of the individual amino acids. The temperature of the experimental run as a function of time is shown in Figure 7a. In order to extract rate constants, Miller and Bada (1988) chose to depict their data on semi-log plots of concentration ratios vs. time, and their plot for leucine looks much like that shown in Figure 7b. Changing concentrations of other amino acids with respect to time were depicted by Miller and Bada (1988) as ratios relative to the changing concentration of leucine. By examination of Figure 7c–e, it can be seen that changes in the concentrations of the other amino acids relative to their own initial concentrations exhibit straight segments, consistent with first-order kinetics, only after the system reached 250 °C. It should be noted that concentrations of alanine, as depicted in Figure 7e, increased during the first two hours of the experiment. This increase in alanine concentration occurs over the same time interval that the concentration of aspartic acid decreases 97%, that of
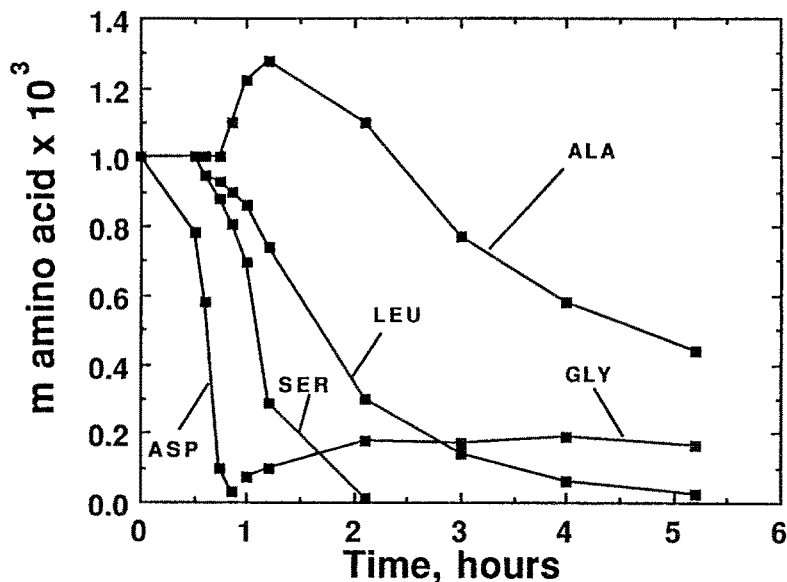

Fig. 8. (after Shock, 1990a) Molalities of amino acids at the times of sampling during the experiment reported by Miller and Bada (1988). Symbols represent the various amino acids as indicated, and correspond to data listed in Table I.

leucine decreases 10%, and that of serine decreases 18%. Glycine, which was not initially present in the solution, was formed during the experiment as shown in Figure 7f. Note that the appearance of glycine corresponds to decreases in the concentrations of leucine, serine and alanine. From this analysis, it is unclear which reactions are responsible for the increase in alanine concentration, and the formation of glycine.

The data listed in the five right-hand columns of Table I are also plotted in Figure 8. It can be seen in Figures 7 and 8 that the concentration of aspartic acid and serine decrease rapidly, attaining concentrations $\ll$ those plotted on the axes of the figure. In contrast, the molal concentrations of leucine and alanine decrease less with increasing time as shown in Figure 8, and appear to be approaching constant limiting values with increasing time. Concentrations which change little with time are suggestive of metastable states. This is also shown in Figure 9 where the total molality of amino acids (m_T) in the experiment is shown as a function of time, and in Figure 10 where the relative percentages of the amino acids are shown as functions of time. Note that at the end of the experiment alanine, glycine and leucine represent the bulk of amino acids in solution and that their relative percentages were beginning to stabilize when the experiment was terminated.

A log $f\mathrm{CO}_2$ – log $f\mathrm{O}_2$ diagram constructed at 250 °C and 265 atm was used to analyze in detail the experimental conditions imposed on the mixture of amino acids, and is described elsewhere (Shock, 1990a). Interpretation of these data with the aid of thermodynamic calculations is given in the same communication, but is summarized here. The equations used to calculate thermodynamic properties
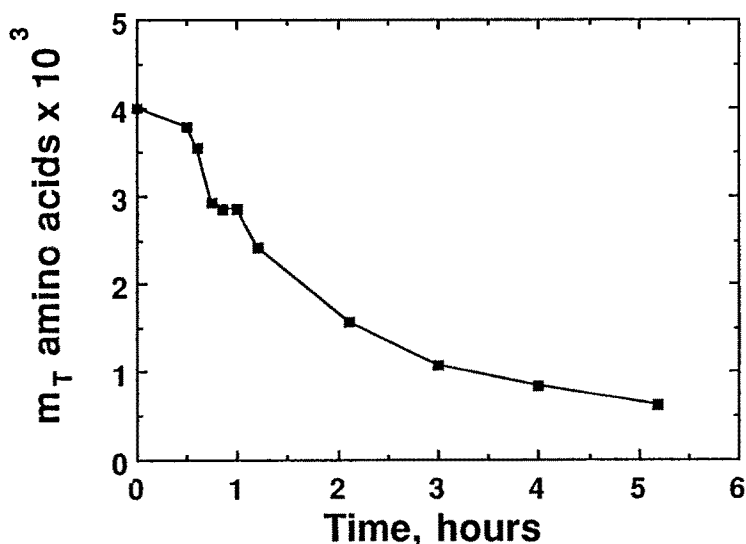
Fig. 9. (after Shock, 1990a) The total molality (m_T) of amino acids in solution at the times of sampling during the experiment reported by Miller and Bada (1988). Symbols represent the sum of molalities in the right-hand five columns of Table I.
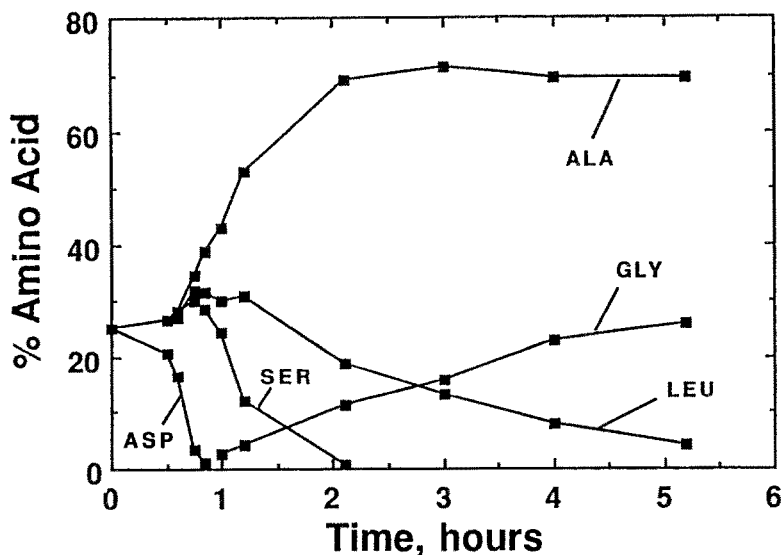
Fig. 10. (after Shock, 1990a) Percent which each amino acid contributes to the total molality of amino acids in solution at each sample time during the experiment reported by Miller and Bada (1988). The symbols correspond to the various amino acids shown. Percentages were calculated from data listed in Table I.

of aqueous organic species, as well as the necessary data and parameters for the calculations, were taken from Shock and Helgeson (1990).

Prompted by observations made with the aid of Figure 10 we can write the following reaction among glycine, alanine, and leucine, in which nitrogen, hydrogen, carbon and oxygen are conserved in the amino acids (see Shock, 1990a),

$$C_6H_{13}NO_2 + 3 \; C_2H_5NO_2 = 4 \; C_3H_7NO_2. \tag{7}$$

leucine   glycine   alanine
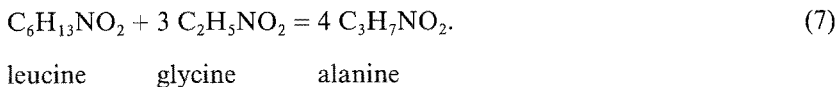
The thermodynamic requirement for equilibrium is obtained when the chemical affinity for the reaction (A_r) equals zero. The chemical affinity is defined by

$$A_r = -\left(\frac{\partial \Delta G_r}{\Delta \xi} \right)_{T,P}, \tag{8}$$

where ΔG°_r stands for the Gibbs free energy of reaction and ξ represents the progress variable for the reaction (DeDonder, 1920; Prigogine and Defay, 1954; Helgeson, 1968). Taking account of Equation (8) and

$$\Delta G_r = \Delta G^{\circ}_r + RT \sum_i \nu_{i,r} \ln a_i, \tag{9}$$

where ΔG°_r stands for the standard molal Gibbs free energy of reaction, a_i represents the thermodynamic activity of the i-th species, and $\nu_{i,r}$ indicates the stoichiometric reaction coefficient of the i-th species in the r-th reaction (positive for products and negative for reactants), R for the gas constant, and T for temperature, it can be shown that

$$A_r = RT \ln(K_r/Q_r), \tag{10}$$

where Q_r represents the activity product and K_r the equilibrium constant for the reaction.

Values of Q_r for reaction (7) can be calculated from data in Table I and

$$Q_7 = \frac{(m_{ala})^4 \, (\gamma_{ala})^4}{(m_{gly})^3 \, (\gamma_{gly})^3 \, (m_{leu}) \, (\gamma_{leu})}, \tag{11}$$

where the γ's represent activity coefficients. Although activity coefficients for aqueous amino acids are not known at the experimental conditions, we can assume that they will be nearly equal for these three amino acids. If this is the case, then the ratio of the product of four activity coefficients in the numerator and four in the denominator of Equation (11) should be nearly unity, and we can assume that Q_7 can be approximated by a molality product. These values of Q_7 were combined with values of K_7 computed with equations and data given by Shock and Helgeson (1990) (see Table II) to calculate chemical affinities of reaction (7), which are plotted as a function of time in Figure 11. It can be seen in Figure 11 that the affinity of reaction (7), which is initially $-\infty$ owing to the absence of glycine in the starting mixture, rapidly approaches zero as the experiment proceeded. Metastable equilibrium appears to have been slightly overstepped, and, as indicated in the figure, the system may have been returning to the metastable state when the experiment
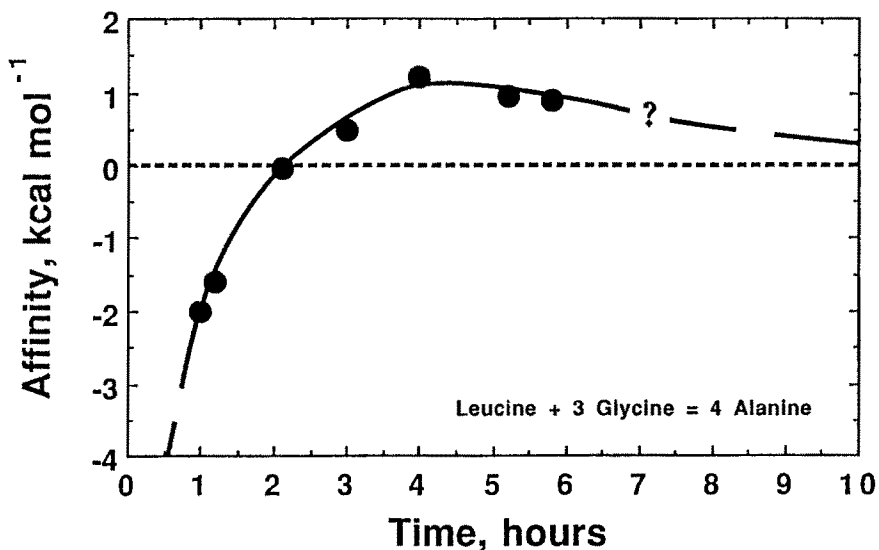

Fig. 11. The chemical affinity of reaction (7) as a function of time computed from Equation (10), using values of log Q_7 evaluated with Equation (11) and data given in Table I and values of log K_7 of 3.0 at 235 °C and 265 atm, and 2.9 at 250 °C and 265 atm calculated with equations and parameters from Shock and Helgeson (1990).

TABLE II

Values of Log K for reaction (7) at various temperatures and 265 bars calculated with equations and parameters from Shock and Helgeson (1990)

T(°C)	25	50	100	150	200	250	300	350
log K	5.4	4.8	4.1	3.6	3.2	2.9	2.7	2.4

was stopped. Uncertainties in calculated apparent standard molal Gibbs free energies of formation (Shock and Helgeson, 1990) may contribute to the offset between the calculated affinities and the metastable state, but not to the trajectory of the curve shown in Figure 11.

It is perhaps remarkable that a system so far from equilibrium can equilibrate as quickly as this system seems to have in these experiments. The equilibration times are certainly shorter than those required for hydrothermal reactions in inorganic mineral systems (Holloway and Wood, 1988). Perhaps this is not surprising because the amino acid reactions occur in a homogenous phase, but the prevailing view of amino acid stability in aqueous solutions at high temperatures and pressures excludes the possibility of such re-equilibration (Vallentyne, 1964; White, 1984; Miller and Bada, 1988). Nevertheless, the results summarized here and elsewhere (Shock, 1990a) indicate that there is a great deal more interaction in high temperature aqueous solutions of organic compounds than is generally appreciated. One implication is that considerable new territory for hydrothermal experimentation has been revealed. In future experiments it will be possible to increase rapidly the understanding of hydrothermal organic reactions by conducting appropriately constrained experiments.

A careful reading of Miller and Bada's (1988) paper indicates that they hold the belief that temperature is the single most important variable in determining the stability of amino acids and, by implication, other organic compounds at hydrothermal conditions. This can only be the case if there is evidence for no net oxidation or reduction of carbon and/or nitrogen in the reactions through which the organic compounds are destroyed. This in turn requires careful monitoring of reaction products in order to prove that temperature alone is the main control of amino acid destruction. The lack of any effort to do this is not unique to the experiments conducted by Miller and Bada (1988), but describes the experiments conducted by Abelson (1954), Vallentyne (1964; 1968), and White (1984), among others. Somehow, in the absence of any quantitative, supporting evidence, the concept of the *thermal* instability of amino acids and other organic compounds has permiated the literatures of organic chemistry, organic geochemistry, and the study of origin of life. As a result, many pyrolysis experiments, with and without aqueous solutions, have been conducted in an affort to study 'thermal stability'. In most cases, as in the results reported by Miller and Bada (1988), temperature dependent rates

for the thermal destruction of organic compounds are evaluated from these experiments by monitoring the destruction of the organic compound of interest, but not by monitoring the reaction products. Even in cases where reaction products are monitored, and it is evident that oxidation and/or reduction has occurred (Vallentyne, 1964; Bernhardt et al., 1984), the results are still characterized in terms of thermal instability, and rates are reported for 'thermal destruction' of organic compounds.

Although hydrous pyrolysis experiments can be subjected to a kinetic analysis, the general lack of concern for how organic compounds are altered at high temperatures and pressures obscures the reactions to which the rates refer. This lack of concern is manifested by the omission of adequate experimental constraints, or any demonstration of mass balance between products and reactants. Since no constraints are placed on fH_2, fO_2, fCO_2, fCH_4, and the other components of the systems under study, the reactions which occur are simply unknown. This is exemplified by the above discussion of possible sources of alanine and glycine in the experiments reported by Miller and Bada (1988). For these reasons, rates from these experiments can not be used to infer anything about reactions involving organic compounds which occur in geochemical processes. In such processes, the composition of the system imposes constraints on all the thermodynamic components including those which make up the organic compounds. The most accurate description of what happens during these experiments is that elevated temperatures and pressures lower kinetic barriers to oxidation, reduction, hydrolysis, decarboxylation, and other reactions among organic compounds. This is not surprising given everyday experience in the kitchen. Until experiments are conducted at buffered oxygen fugacities consistent with those set by mineral assemblages in hydrothermal systems, and until the reaction products are fully characterized so that the actual reactions can be identified, the rates obtained from hydrous pyrolysis experiments will remain bulk properties of unidentified processes which occur at conditions greatly removed from nature.

4. Hydrothermal Systems and Organic Synthesis

The idea that organic compounds may form from inorganic starting materials in hydrothermal systems was first proposed by Ingmanson and Dowler (1977), with numerous elaborations and developments over the years (Ingmanson and Dowler, 1981; Corliss et al. 1981, Berry and Wilde, 1983; Baross and Hoffman, 1985; Nisbet, 1987; Wächtershäuser, 1988a, 1988b; Maher and Stevenson, 1988; Russell et al., 1989). If abiotic synthesis occurs in hydrothermal systems, it is only possible because kinetic barriers block the establishment of stable equilibrium. Therefore, the search for likely conditions can be focussed on those conditions in which CH_4 and NH_3 are incompletely oxidized or CO_2 and N_2 are incompletely reduced. The evidence from sedimentary basins summarized above indicates that at 100 °C organic acids and CO_2 are in a metastable assemblage which excludes methane. Based on this

evidence from nature, and the observations of metastable equilibrium among amino acids in Miller and Bada's (1988) experiments, we can develop an hypothesis of abiotic synthesis in hydrothermal systems.

Let us suppose that the kinetically allowed reaction path for abiotic synthesis at elevated temperatures and pressures is one of reduction from CO_2 and N_2 to organic compounds. The corollary of this assumption is that complete reduction to CH_4 and NH_3 is blocked or inhibited so that stable equilibrium is avoided. To test this hypothesis we need to ask several questions.

(1) What controls the oxidation state imposed on hydrothermal solutions in nature?

(2) Under what conditions are CO_2 and N_2 the dominant compounds at stable equilibrium?

(3) Is there evidence for disequilibrium between CO_2 and CH_4 and/or N_2 and NH_3 in hydrothermal experiments and/or natural systems, and if so, at what temperatures do the kinetic barriers impede the approach to stable equilibrium?
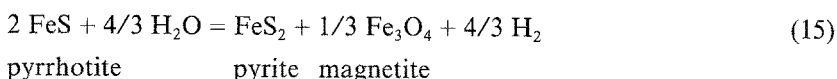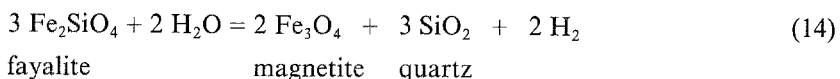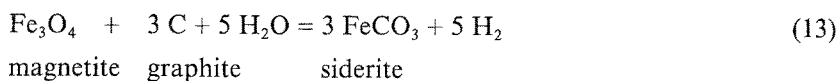
(4) How can CO_2 and N_2 be moved from conditions in which they predominate to those in which they should be reduced to CH_4 and NH_3?

(5) Are there conditions in nature which will allow this transport consistent with any constraints we may identify by answering question 3?
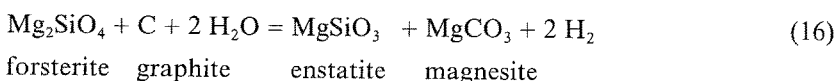
By addressing these questions we can establish a set of geochemical constraints on abiotic synthesis in hydrothermal systems. We can then impose these constraints upon distribution-of-species calculations and test quantitatively the hydrothermal synthesis proposal.

4.1. REDOX STATES IN SUBMARINE HYDROTHERMAL SYSTEMS

Oxidation states in hydrothermal systems are controlled by mineral buffer assemblages. The buffering capacity of these assemblages can be represented by reactions among the minerals, H_2O and H_2, and quantified by thermodynamic calculations. Examples of the assemblages encountered in hydrothermal systems include

$$2 \, Fe_3O_4 + H_2O = 3 \, Fe_2O_3 + H_2 \tag{12}$$
hematite   magnetite

$$Fe_3O_4 \;+\; 3 \, C + 5 \, H_2O = 3 \, FeCO_3 + 5 \, H_2 \tag{13}$$
magnetite   graphite   siderite

$$3 \, Fe_2SiO_4 + 2 \, H_2O = 2 \, Fe_3O_4 \;+\; 3 \, SiO_2 \;+\; 2 \, H_2 \tag{14}$$
fayalite   magnetite   quartz

$$2 \, FeS + 4/3 \, H_2O = FeS_2 + 1/3 \, Fe_3O_4 + 4/3 \, H_2 \tag{15}$$
pyrrhotite   pyrite   magnetite

and

$$Mg_2SiO_4 + C + 2 \, H_2O = MgSiO_3 \;+\; MgCO_3 + 2 \, H_2 \tag{16}$$
forsterite   graphite   enstatite   magnesite

Among these, there are two of primary importance in seawater-basalt systems: the fayalite-magnetite-quartz (FMQ) assemblage and the pyrite-pyrrhotite-magnetite (PPM) assemblage. In submarine hydrothermal systems, sea water circulates deep into oceanic crust (at least 5 km) and a variety of alteration occurs (Humphris and Thompson, 1978; Edmond *et al.* 1979; Von Damm *et al.*, 1985). In the shallow parts of the circulation system, and in the hydrothermal chimneys, sea water sulfate reacts with basalt and yields assemblages dominated by sulfide minerals. In the chimneys (Haymon and Kastner, 1981), and at depths greater than ~300 m in altered basalt (Alt *et al.*, 1986), the PPM assemblage is present and can buffer fH_2. Recent studies of the deepest samples from the oceanic crust show the presence of the PPM assemblage at depths approaching 1.3 km (Alt *et al.*, 1989). Deeper in the circulation systems, below the point where sea water sulfur has been effectively removed from the hydrothermal solution, it is likely that hydrogen fugacities at or near the FMQ buffer values prevail. At the deepest point of the circulation system, where hydrothermal solutions may approach the crystallizing margin of the magma chambers, values of fH_2 could be above those set by the FMQ buffer based on a variety of petrologic evidence (Christie *et al.*, 1986; Mattioli and Wood, 1986, 1988; Wood and Virgo, 1989; Bryndzia *et al.*, 1989). As a result, there is a gradient in hydrogen fugacity throughout a submarine hydrothermal system which can be thought of as a gradient in redox potential.

Temperatures in submarine hydrothermal systems vary from ~ 2 °C at the basalt-seawater interface to at least 600 °C and probably higher depending on the extent to which hydrothermal solutions interact with magma chambers (Lister, 1974; Cann and Strens, 1982). Therefore, quantifying the temperature dependence of possible gradients in redox potential which act upon hydrothermal solutions requires evaluation of the buffered values of fH_2. Values of fH_2 or fO_2 can be calculated from empirical fits of experimental data (Chou, 1987) or from thermodynamic data for water and the minerals of interest (Helgeson *et al.*, 1978; Robie *et al.*, 1979; Berman, 1988). Fugacities of hydrogen set by the FMQ and PPM assemblages were calculated with data and equations from Helgeson *et al.* (1978), and are shown as solid curves in Figure 12. Also shown in Figure 12 is a dotted curve indicating the position of equal fugacities of CO_2 and CH_4 obtained from the law of mass action expression for

$$CO_2 + 4\,H_2 = CH_4 + 2\,H_2O, \tag{17}$$

calculated with data and equations from Helgeson *et al.* (1978), together with the assumption of unit activity for H_2O. It can be seen in Figure 12 that both oceanic crust hydrogen-buffer assemblages are compatible with ratios of CO_2 to CH_4 > 1 at high temperatures, and ratios < 1 at low temperatures. Similar relations are found for the N_2–NH_3 couple. These calculations allow an answer to the second question set out above: CO_2 and N_2 should be the dominant volatile species at high temperatures at hydrogen fugacities buffered by mineral assemblages in the oceanic crust.
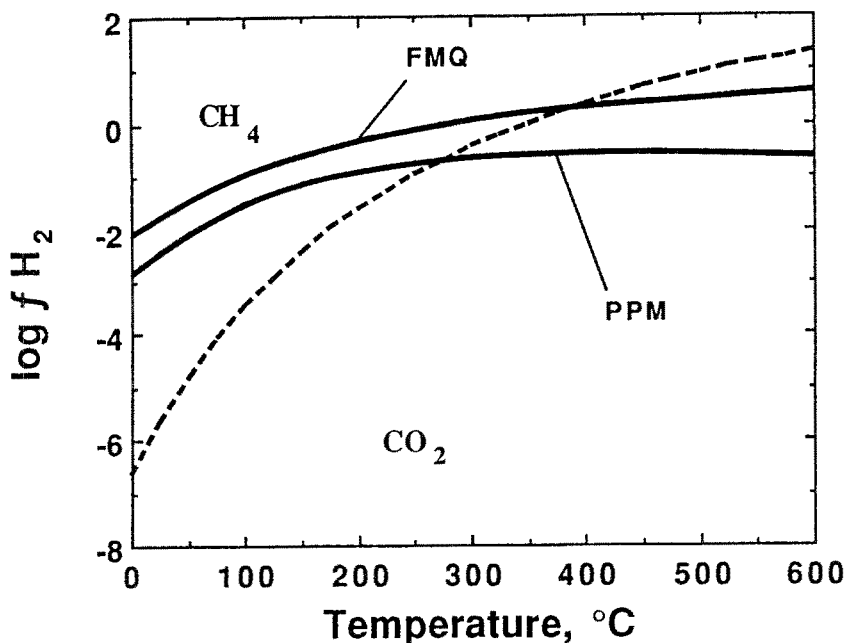
Fig. 12. Plot of $\log f\mathrm{H}_2$ against temperature. Solid curves correspond to the pyrite-pyrrhotite-magnetite (PPM) buffer assemblage (lower curve), and the fayalite-magnetite-quartz (FMQ) buffer assemblage (upper curve). Dotted line indicates equal fugacities of CO_2 and CH_4 in equilibrium with H_2O, and the fields of relative predominance are labeled.

Examination of Figure 12 suggest that as a hydrothermal solution cools from near magma-chamber conditions to ocean-floor conditions, at hydrogen fugacities set by mineral assemblages, it passes from conditions at which CO_2 is dominant to those at which CH_4 predominates at stable equilibrium. Therefore, the first condition for organic synthesis from CO_2 reduction could be met if kinetic barriers inhibit stable equilibrium in the C-H-O-N system. Evidence for the existence of such kinetic barriers at hydrothermal conditions comes from natural samples and from hydrothermal experiments.

4.2. DISEQUILIBRIUM IN HYDROTHERMAL SYSTEMS

Coexisting CO_2 and CH_4 from samples of actively venting submarine hydrothermal fluids have isotopic signatures which indicate that the two gases were last in isotopic equilibrium at 640 to 720 °C (Welhan and Craig, 1983; Evans et al., 1988). Although this implies stable thermodynamic equilibrium at these conditions as well, it does not necessarily set a lower temperature limit for stable equilibrium. Evidence in this regard comes from less dynamic geothermal systems, in which 320 °C appears to be the lowest temperature of isotopic equilibration (Sheppard, 1981). These differences in isotopic equilibration temperature probably reflect the differences in flow rates for these systems (see below).

Experimental determination of the rate of isotopic exchange between CO_2 and

CH$_4$ at 500 to 680 °C obtained by Harting and Maass (1980) were interpreted by Giggenbach (1982) who concluded that chemical equilibrium is about 100 times faster than isotopic equilibrium in this system. Lengths of time required for chemical equilibration between CO$_2$ and CH$_4$ are estimated to be $\sim$ 100 years at 400 °C and $\sim$ 100 000 years at 300 °C (Giggenbach, 1982). Further evidence of slow isotopic and thermodynamic equilibration of CO$_2$ and CH$_4$ comes from studies of fumarolic gas compositions (Giggenbach, 1987). This interpretive study of natural samples shows that of the redox pairs studied (CO$_2$–CO, CO$_2$–CH$_4$, N$_2$–NH$_3$, SO$_2$–H$_2$S), CO$_2$–CH$_4$ equilibration is the slowest and is only attained at the highest temperatures ($>$600 °C). Studies of the N$_2$–NH$_3$ system in natural samples indicate that equilibration in this system is attained at conditions and rates similar to those at which coexisting CO$_2$ and CH$_4$ equilibrate (Giggenbach, 1980; 1987). These studies corroborate practical experience with hydrothermal experiments which indicates that CO$_2$–CH$_4$ equilibration is too slow at temperatures $<$500 °C for mixing of these gases to be a useful method of buffering the fugacity of oxygen on a laboratory time scale (Sackett and Chung, 1979; Barnes, 1987). In summary, several lines of evidence indicate that kinetic barriers inhibit the approach to stable equilibrium in the C-H-O-N system in both natural and experimental hydrothermal solutions. Therefore, if transport of CO$_2$ and N$_2$ occurs from relatively oxidizing to relatively reducing conditions, there may be some combination of temperatures and compositions in which these same barriers allow the formation of metastable states, and these states may be populated by organic compounds.

Hydrothermal solutions resulting from seawater-basalt reactions vent at mid-ocean ridges and off-axis vents on the flanks of the ridges. Temperatures of the venting solutions at ridge crests are often in the vicinity of 350 °C (Corliss *et al.*, 1979; Von Damm *et al.*, 1985; Von Damm and Bischoff, 1988), while those in cooling systems and at off-axis vents generally range from 25 to 200 °C (Edmond *et al.*, 1979; Campbell *et al.*, 1988). In either case, fluids which have reacted with basalt in the deepest regions of these systems are reaching the ocean-seafloor interface. At high temperatures the carbon and nitrogen in these fluids should be predominantly CO$_2$ and N$_2$ as shown in Figure 12. Depending on the mineral assemblage which controls the fH$_2$, these species are transported into relatively reducing conditions at either $\sim$385 °C for the FMQ assemblage, or $\sim$275 °C for the PPM assemblage. Based on the evidence outlined above, stable equilibrium may prevail at the cross-over point at the FMQ buffer, but is likely to not prevail at conditions set by the PPM buffer. The attainment of stable equilibrium depends in part on the rate at which the solutions move through the hydrothermal systems.

The residence times of hydrothermal solutions in submarine systems are not well established, especially for the off-axis systems. Nevertheless, based on a variety of isotopic evidence, the rates of transport of 350 °C solutions at the mid-ocean ridges are extremely rapid. These rates span the range of a maximum of 45 yr based in ^{228}Ra/^{226}Ra ratios in clam shells (Turekian and Cochran, 1986), to less than 3 yr based on ^{210}Pb/Pb and ^{228}Ra/^{226}Ra ratios from venting fluids (Kadko

and Moore, 1988). The more rapid rates are consistent with estimates made from heat-flow and mass-flow measurements (Converse *et al.*, 1984). In addition, geophysical simulations indicate that transport times in the upward flow regime of submarine vent systems are less than one year (MacDonald *et al.*, 1980; Lister, 1982), although rates can be longer in the cooler off-axis systems (Fehn *et al.*, 1983).

These various lines of evidence show that fluids move from high-temperature zones to the hot spring vents on time scales much shorter than those required to establish stable equilibrium. It is expected that similar conclusions will be reached for the off-axis systems which have yet to be studied comprehensively. Therefore, in all cases of seawater-basalt reactions, the fluids containing CO_2 and N_2 are easily transported to lower-temperature, more-reducing conditions. This combination of an oxidizing source, a reducing sink, a temperature decrease, and a rapid transport mechanism makes submarine hydrothermal systems prime candidates for organic compound synthesis in metastable states.

4.3. Metastable equilibria and organic synthesis in submarine hydrothermal systems

Based on the evidence outlined above, a scenario for organic synthesis in hydrothermal systems was developed in the present study with the following characteristics.

(1) Owing to the presence of mineral buffer assemblages, CO_2 and N_2 are the predominant forms of carbon and nitrogen deep in hydrothermal solutions.

(2) These species are moved to lower temperatures by circulation of hydrothermal solutions.

(3) The redox conditions imposed on these solutions as they move are controlled by mineral buffer assemblages.

(4) As hydrothermal solutions cool at buffered valued of fH_2, the solutions move from conditions at which CO_2 and N_2 predominate to those in which CH_4 and NH_3 would predominate at stable equilibrium (see Figure 12).

(5) Kinetic barriers may inhibit the complete reduction of CO_2 to CH_4 and N_2 to NH_3.

(6) As a result, metastable states are established in which CO_2 and N_2 are partially reduced to organic compounds.

Within this framework, it is possible to evaluate the potential of abiotic synthesis in a variety of geologic environments. In the present study, this scenario was applied to submarine hydrothermal systems, but continental hydrothermal systems and metamorphic conditions, as well as lower temperature sedimentary basin conditions could also be evaluated.

One conclusion reached early on in the present study is that the spectacular, high-temperature, mid-ocean ridge hot spring systems characterized by black smoker chimneys are *not* the appropriate environment for abiotic synthesis starting from oxidized gases. The chimneys are composed predominately of sulfides and oxides, and combined petrologic studies and thermodynamic calculations show that hydrogen fugacities set by the PPM assemblage are appropriate for the chimney/

mound environment (Haymon and Kastner, 1981; Bowers *et al.*, 1985). It can be seen in Figure 12 that at 350 °C the PPM buffer is situated well inside the field of relative predominance of CO_2. As a consequence, no reduction of CO_2 and N_2 to organic compounds is expected at these conditions. However, given the appropriate kinetic constraints, oxidation of CH_4 and NH_3 might be possible in black smoker vents, providing a terrestrial environment where something analogous to Miller-Urey synthesis may be possible. At lower temperatures, it appears that conditions amenable to the abiotic synthesis of organic compounds through reduction of CO_2 and N_2 may exist as shown in Figure 12. This can be tested quantitatively by calculating the distribution of aqueous organic compounds as functions of temperature in metastable equilibrium with CO_2 and N_2 at values of $f H_2$ set by the PPM assemblage.

The distribution of species can be established by evaluating a set of mass action expressions for aqueous organic compounds, together with constraints on the initial concentrations of the components. Many calculations of this type have been conducted for the inorganic constituents of hydrothermal systems (Helgeson, 1968; 1969; 1970; 1979; Helgeson *et al.*, 1970; Brimhall, 1980; Brimhall and Ghiorso, 1983; Sverjensky, 1984; 1986; 1987; Janecky and Seyfried, 1984; Bowers *et al.*, 1985; 1988; Bowers and Taylor, 1985), but few calculations have been performed for the coexisting organic compounds (Thorstenson, 1970; Shock and Schulte, 1990). The reactions considered are of the form

$$\nu_1 \, CO_2 + \nu_2 \, N_2 + \nu_3 \, H_2 = \nu_4 \, \text{Organic} + \nu_5 \, H_2O \tag{18}$$
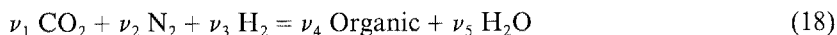
in which the ν's represent the stoichiometric reaction coefficients. The law of mass action given by

$$K_r = \pi \, a_i^{\,\nu_{i,r}}, \tag{19}$$

can be written for reaction (18) as

$$K_{18} = \frac{(a_{\text{Organic}})^{\nu_4} \, (a_{H_2O})^{\nu_5}}{(f_{CO_2})^{\nu_1} \, (f_{N_2})^{\nu_2} \, (f_{H_2})^{\nu_3}}. \tag{20}$$

Constraints placed on components in the following calculations include an assumption of unit activity of H_2O and buffered values of $f H_2$.

Constraints on the fugacities of CO_2 and N_2 are much less easily obtained. Considerable debate has focussed on whether the volatile budget of the Earth originated from gradual or early, sudden outgassing of the planet during or soon after accretion (Rubey, 1955; Fanale, 1971; Hamano and Ozima, 1978; Bernatowicz and Podosek, 1978; Allègre *et al.*, 1987; Schubert *et al.*, 1989), or whether it was obtained through late-stage accretion of comets and other volatile rich bodies (Weisman, 1989; Dreibus and Wänke, 1989). In the present study, the early outgassing scenario was chosen as a starting point, but it should be emphasized that analogous

calculations could be applied to the gradual outgassing, or the late-stage accretion models, including the cycling of cometary material through hydrothermal systems. Similar calculations of the distribution of species during aqueous alteration of polycyclic aromatic hydrocarbons in carbonaceous chondrite parent bodies are presented elsewhere (Shock and Schulte, 1990).

In the outgassing scenario envisioned in the present study, volatile species are transferred from the mantle to the atmosphere through hydrothermal systems in the oceanic crust, much as they are at present. One major difference lies in the fugacities chosen for CO_2 and N_2 which are several orders of magnitude higher than in modern mid-ocean ridge systems. In the calculations described below, the partial pressures of CO_2 and N_2 are set to 400 and 100 bars respectively. These relatively high values are arbitrary, but allow simulation of abiotic synthesis in metastable states during an early major outgassing event which released a majority of the carbon, hydrogen and nitrogen presently found in the atmosphere, oceans, and sediments, as well as the sedimentary and metamorphic rocks of the Earth.

Distribution of species calculations were conducted for 76 aqueous alkanes, alkenes, alkynes, alkylbenzenes, ketones, alcohols, carboxylic acids, amines, and amino acids for which standard molal thermodynamic data can be evaluated at high temperatures and pressures (Shock and Helgeson, 1990). Law of mass action
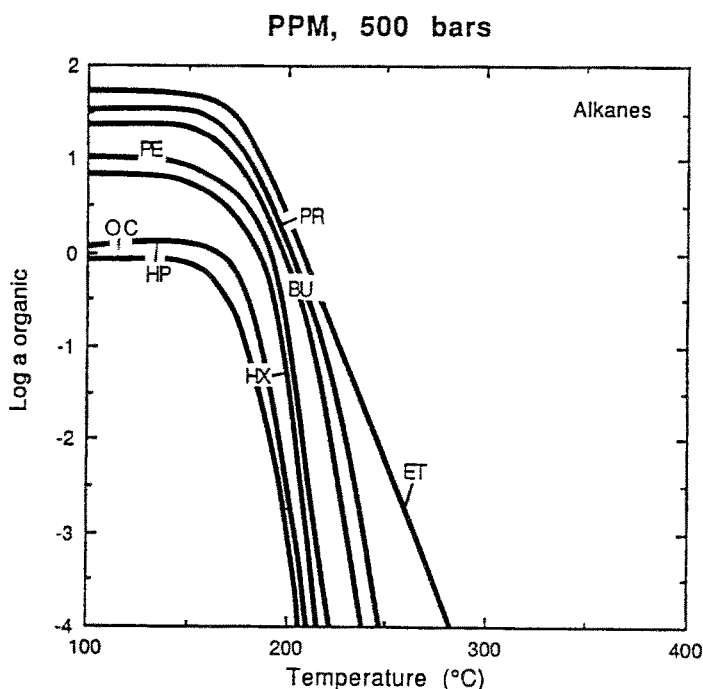

Fig. 13. Plot of the logarithms of the acitivities of aqueous alkanes as functions of temperature at 500 bars, in equilibrium with an initial log $f CO_2$ = 2.6, hydrogen fugacities set by the PPM assemblage, and the aqueous organic species in Figures 14–17.
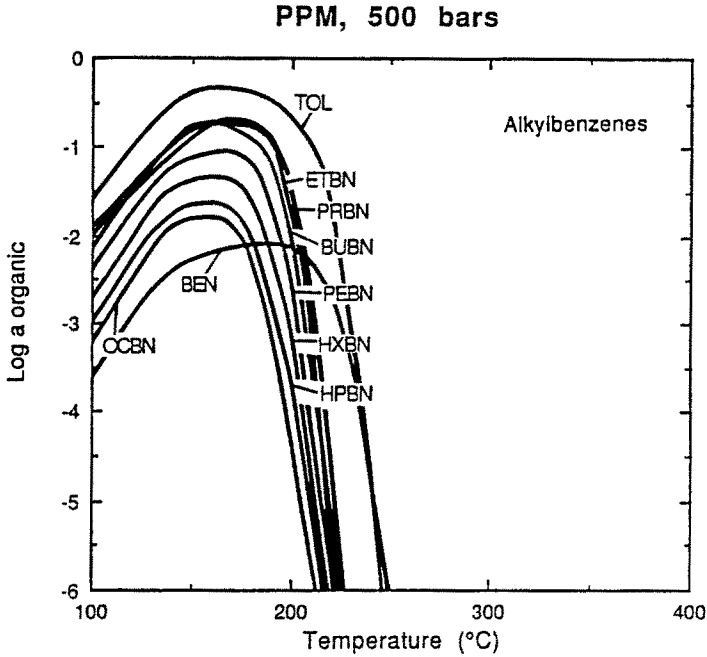
PPM, 500 bars

Fig. 14. Plot of the logarithms of the activities of aqueous alkylbenzenes as functions of temperature at 500 bars, in equilibrium with an initial log fCO$_2$ = 2.6, hydrogen fugacities set by the PPM assemblage, and the aqueous organic species in Figures 13 and 15–17.
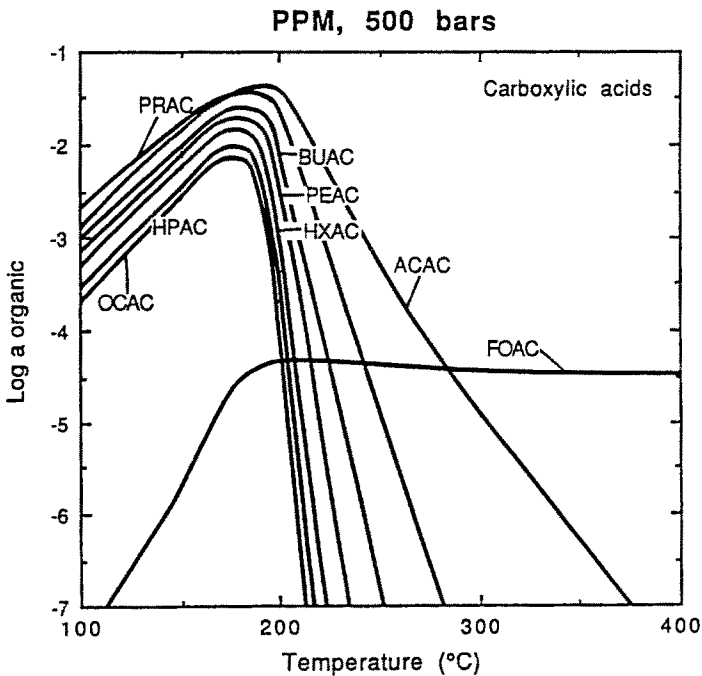
PPM, 500 bars

Fig. 15. Plot of the logarithms of the activities of aqueous carboxylic acids as functions of temperature at 500 bars, in equilibrium with an initial log fCO$_2$ = 2.6, hydrogen fugacities set by the PPM assemblage, and the aqueous organic species in Figures 13, 14, 16 and 17.

expressions analogous to Equation (20) for these 76 compounds, together with constraints on the four components of the system CO_2, N_2, H_2O, and H_2, provide a system of 80 equations which can be solved simultaneously to obtain activities of the various aqueous organic species. The calculations were performed with the MCCMT code written by P. C. Lichtner. A representative sample of these results as functions of temperature at 500 bars, the PPM buffer and initial log fugacities of CO_2 and N_2 of 2.6 and 2.0, respectively, are summarized in Figures 13–17. It is important to note that these five figures contain results from the same set of calculations. Results are shown for different families of organic compounds in this set of figures for clarity of presentation and a key to the abbreviations is given in Table III.

Figure 13 shows the distribution of the seven aqueous normal alkanes for which data can be calculated. It can be seen that the activities of these hydrocarbons increase with decreasing temperature at 500 bars and values of fH_2 set by the PPM assemblage. The slopes of the curves flatten at lower temperatures at the point where all of the CO_2 in the original assemblage has been converted to organic compounds. Results for aqueous alkylbenzenes from the same set of calculations are shown in Figure 14 where it can be seen that the activities of these compounds maximize with decreasing temperature in the range 150 to 175 °C, except that of benzene which maximizes slightly above 200 °C. Note that the calculated activities
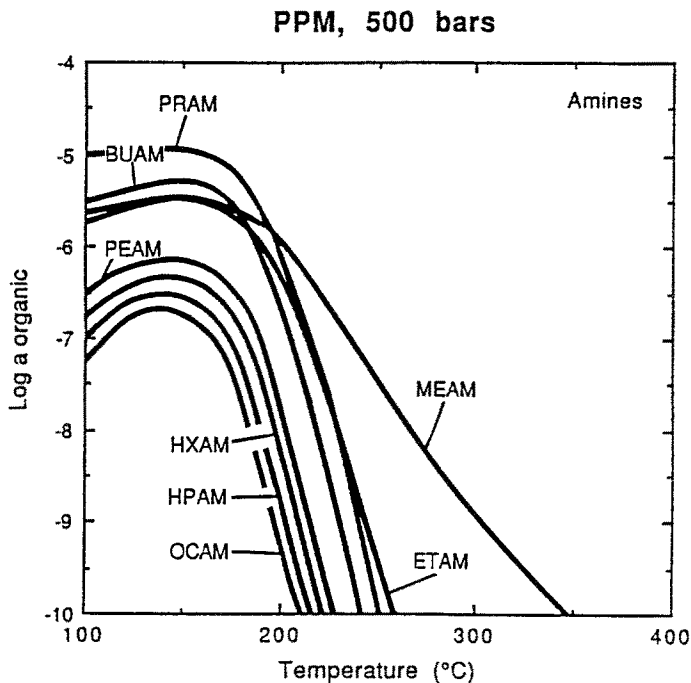

Fig. 16. Plot of the logarithms of the activities of aqueous amines as functions of temperature at 500 bars, in equilibrium with initial log fCO_2 = 2.6, log fN_2 = 2.0, hydrogen fugacities set by the PPM assemblage, and the aqueous organic species in Figures 13–15, and 17.
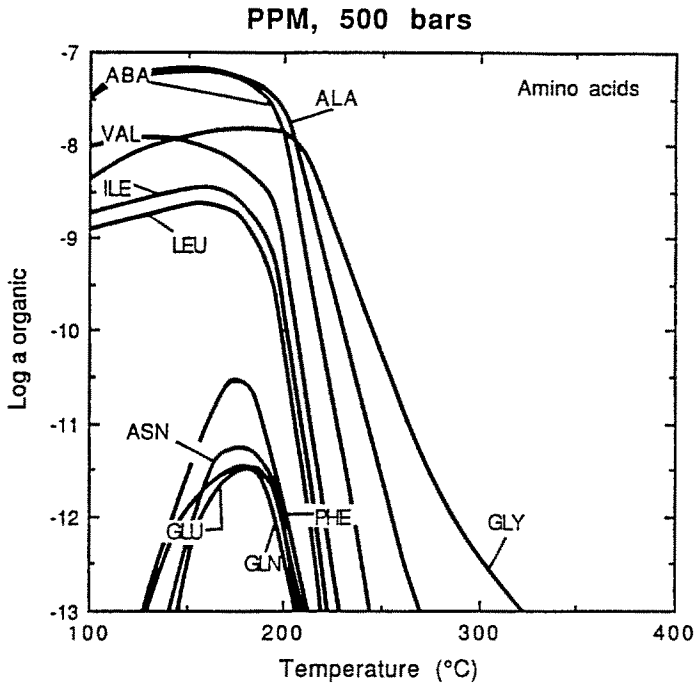
PPM, 500 bars

Fig. 17. Plot of the logarithms of the activities of aqueous amino acids as functions of temperature at 500 bars, in equilibrium with initial log fCO_2 = 2.6, log fN_2 = 2.0, hydrogen fugacities set by the PPM assemblage, and the aqueous organic species in Figures 13–16.

TABLE III

Abbreviations for aqueous organic species shown in Figures 13–19

ET	ethane	HPBN	heptylbenzene	HXAM	hexanamine
PR	propane	OCBN	octylbenzene	HPAM	heptanamine
BU	butane	FOAC	formic acid	OCAM	octanamine
PE	pentane	ACAC	acetic acid	GLY	glycine
HX	hexane	PRAC	propanoic acid	ALA	alanine
HP	heptane	BUAC	butanoic acid	ABA	α-aminobutyric acid
OC	octane	PEAC	pentanoic acid	VAL	valine
BEN	benzene	HXAC	hexanoic acid	LEU	leucine
TOL	toluene	HPAC	heptanoic acid	ILE	isoleucine
ETBN	ethylbenzene	OCAC	octanoic acid	ASN	asparagine
PRBN	propylbenzene	MEAM	methanamine	GLU	glumatic acid
BUBN	butylbenzene	ETAM	ethanamine	GLN	glutamine
PEBN	pentylbenzene	PRAM	propanamine	PHE	phenylalanine
HXBN	hexylbenzene	BUAM	butanamine	ASP	aspartic acid
		PEAM	pentanamine		

of the alkylbenzenes are generally two orders of magnitude lower than those for the alkanes. The other hydrocarbons considered in these calculations, 1-alkenes and 1-alkynes, have activities many orders of magnitude lower than the alkanes and alkylbenzenes, and do not contribute significantly to the resulting mass balance of carbon.

Among the oxygen-bearing organic compounds considered, the carboxylic acids predominate by several orders of magnitude over the ketones and alcohols. As in the case of the 1-alkenes and 1-alkynes, the ketones and alcohols are not considered further, although they may be important intermediates in reaction pathways. Results for carboxylic acids are shown in Figure 15, where it can be seen that acetic acid is the predominant carboxylic acid over the range 175 to 280 °C with formic acid dominating at higher temperatures and propanoic acid dominating at lower temperatures. With the exception of formic acid, the activities of the other carboxylic acids maximize in the range 175 to 200 °C in Figure 15. By comparison to Figures 13 and 14 it is evident that the carboxylic acid activities maximize at temperatures somewhat higher than the alkane and alkylbenzene activities. This suggests that upon cooling the carboxylic acids would be the first compounds to form if kinetic constraints on CO_2 reduction are similar for all the reactions considered. The relative positions of these maxima may also have important implications given the apparently strong temperature dependence of the kinetic barriers acting upon compounds in the C-H-O system. For example, if metastable states can form only at conditions consistent with a narrow range of temperatures around the intersection of the PPM assemblage and CO_2-CH_4 equal fugacity curves depicted in Figure 12, a resulting metastable assemblage might be dominated by carboxylic acids.

Activities of nitrogen bearing organic compounds are shown in Figures 16 and 17. Figure 16 depicts calculated activities of aqueous amines which can be seen to exhibit maxima at temperatures from ~120 to ~160 °C. Note that the activities of aqueous amines are in general about four orders of magnitude lower than the corresponding carboxylic acids shown in Figure 15. Calculated activities for amino acids in the same solution are shown in Figure 17 where it can be seen that they fall into two groups. These groups can be characterized as the amino alkanoic acids (glycine, alanine, α-amino butyric acid, valine, leucine, and isoleucine) and amino acids with additional functional groups (glutamic acid, asparagine, glutamine, and phenylalanine). Note that activities of the first group maximize at temperatures from ~150 to 200 °C at values about 2.5 log units lower than the corresponding amines, while those of the second group exhibit much sharper maxima at ~175 °C and about six log units lower than the amines. Other amino acids considered in these calculations (aspartic acid, threonine, serine, tyrosine, and tryptophan) did not attain log activities greater than −13. As in the case of the carboxylic acids, the maxima in the amino acid curves in Figure 17 occur at temperatures slightly higher than the corresponding curves for amines in Figure 16.

The calculations summarized above indicate that organic compounds, including carboxylic and amino acids which may have been important for the origin of life,
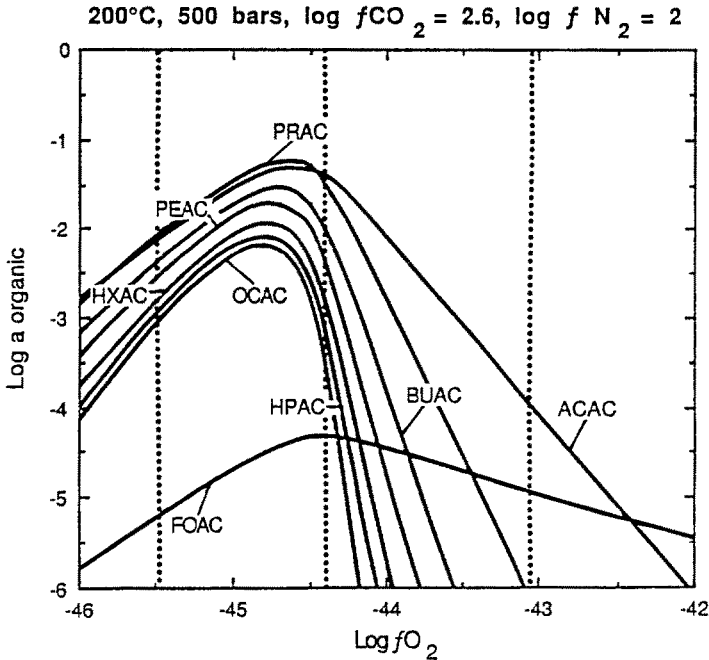
Fig. 18. Plot of the logarithms of the activities of aqueous carboxylic acids as functions of log fO_2 at 200 °C, 500 bars, initial log $fCO2 = 2.6$, log $fN2 = 2.0$, and the other aqueous organic compounds shown in Figures 13, 14, 16 and 17. Dotted lines correspond to oxygen fugacities set by the FMQ (left), PPM (center), and Nickel-Bunsenite (right) assemblages.

are energetically favored products of abiotic synthesis at ~200 °C in hydrothermal systems in which the hydrogen fugacity is buffered by the PPM assemblage. Oxygen fugacities, which are more familiar to most petrologists, can be calculated from hydrogen fugacities for hydrothermal systems by taking account of the equilibrium constant for

$$H_2O = H_2 + 1/2 \, O_2 \tag{21}$$

together with the equilibrium constants for the mineral buffer reactions given above. The effects of variations in redox conditions, expressed as log fO_2, at 200 °C and 500 bars for the same initial fugacities of CO_2 and N_2 as above, are shown in Figures 18 and 19 for the carboxylic and amino acids, respectively. The vertical, dotted lines in these figures indicate the positions of the FMQ and PPM assemblages, as well as the Nickel-Bunsenite assemblage, a reference commonly used for hydrothermal experiments, and given by

$$Ni + 1/2 \, O_2 = NiO. \tag{22}$$

Perhaps the most striking feature of these figures is that the curves for both the carboxylic acids and amino maximize at log fO_2 values intermediate between the two buffers appropriate for oceanic crust as it reacts with seawater.
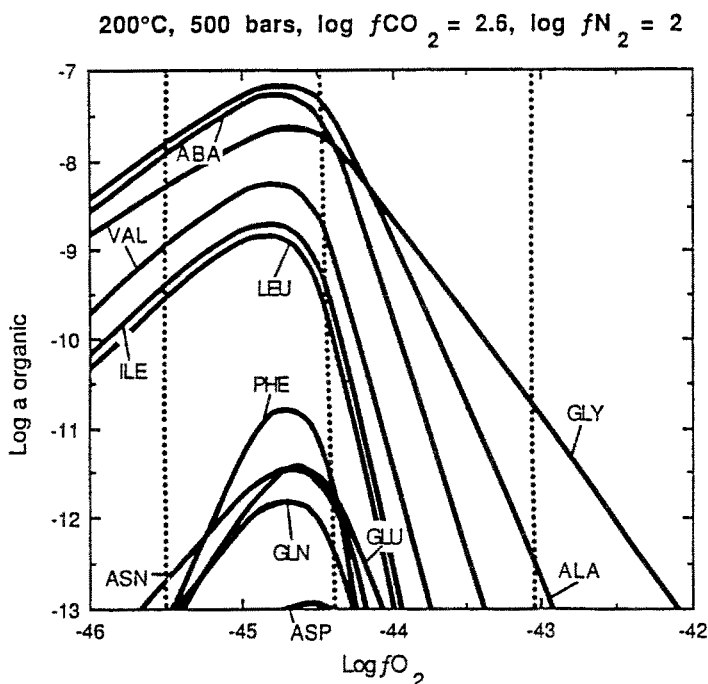
Fig. 19. Plot of the logarithms of the activities of aqueous amino acids as functions of $\log fO_2$ at 200 °C, 500 bars, initial $\log fCO2 = 2.6$, $\log fN2 = 2.0$, and the other aqueous organic compounds shown in Figures 13–16. Dotted lines correspond to oxygen fugacities set by the FMQ (left), PPM (center), and Nickel-Bunsenite (right) assemblages.

The activities of aqueous carboxylic and amino acids in the calculations summarized above are about 10^{-2} and 10^{-8}, respectively, at ~200 °C and appropriate oceanic crust fO_2 or fH_2 values. Evaluation of the potential effectiveness of these activities in the global production of organic compounds in hydrothermal systems requires an estimate of the volume of the oceanic crust which resides at ~200 °C, and the amount of hydrothermal fluid which passes through this zone. Any estimate of this type will be influenced by the range of permiabilities chosen to represent the fracture system in the basalt, as well as estimates of the heat flow (Becker *et al.*, 1982; Karato and Becker, 1983; Becker and Von Herzen, 1983a; 1983b; Fehn *et al.*, 1983; Morton and Sleep, 1985). Regardless of the model chosen, the 200 °C isothermal surface is located at shallow depths (≤ 2 km) to at least 25 km on either side of spreading centers. Oxygen isotope measurements from ophiolites indicate that hydrothermal fluids penetrate to at least 5 km throughout newly formed oceanic crust at high water-to-rock ratios (Gregory and Taylor, 1981; Kimball, 1988; Harper *et al.*, 1988; Schiffman and Smith, 1988). Hydrothermal circulation at lower temperatures persists in the crust as it moves away from spreading centers for several million years (Embley *et al.*, 1983; Orcutt *et al.*, 1988). Therefore, it is appropriate to think of the entire oceanic crust surrounding spreading centers as a zone of high potential for organic synthesis. If abiotic synthesis can proceed

at ~200 °C in the oceanic crust, circulating fluids will move organic compounds up through the overlying altered basalt in which a variety of zeolites, clay minerals, and other alteration products reside. Therefore, adsorption of organic compounds by these minerals could provide the means for their separation, isolation, and concentration within the crust before the fluids reach the sea floor and disperse their constituents into the overlying ocean.

5. Concluding Remarks

The calculations summarized above indicate that interactions of hydrothermal solutions with oceanic crust at ~200 °C are amenable to the metastable reduction of CO_2 and N_2 to aqueous organic compounds. Given kinetic barriers to complete reduction, the formation of a wide variety of organic compounds is energetically favorable. Results presented here are one of many possible evaluations of abiotic synthesis in hydrothermal systems. There are numerous areas in which such calculations can be improved including the evaluation of the fugacities of CO_2 and N_2 during early, sudden outgassing of the mantle, and determining the degree which various groups of organic compounds may be kinetically inhibited from forming. The latter point is especially important for the shorter alkanes which are predominant in the lower-temperature calculations. If kinetic barriers block the formation of any of these compounds, the activities of other organic compounds could be greatly under-represented in the present analysis. Finally, no matter how promising the results presented above appear, only an integrated program of well constrained experiments and theoretical calculations will identify the extent to which hydrothermal systems were involved in the origin of organic compounds and the origin of life.

Acknowledgments

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