

# EVIDENCE FOR ORGANIC SYNTHESIS IN HIGH TEMPERATURE AQUEOUS MEDIA – FACTS AND PROGNOSIS \*

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**Abstract.** Hydrothermal systems are common along the active tectonic areas of the earth. Potential sites being studied for organic matter alteration and possible organic synthesis are spreading ridges, off-axis systems, back-arc activity, hot spots, volcanism, and subduction. Organic matter alteration, primarily reductive and generally from immature organic detritus, occurs in these high temperature and rapid fluid flow hydrothermal regimes. Hot circulating water (temperature range – warm to  $> 400$  °C) is responsible for these molecular alterations, expulsion and migration. Compounds that are obviously synthesized are minor components because they are generally masked by the pyrolysis products formed from contemporary natural organic precursors. Heterocyclic sulfur compounds have been identified in high temperature zones and hydrothermal petroleum of the Guaymas Basin vent systems. They can be interpreted as being synthesized from formaldehyde and sulfur or  $\text{HS}_e^-$  in the hydrothermal fluids.

Other products from potential synthesis reactions have not yet been found in the natural systems but are expected based on known industrial processes and inferences from experimental simulation data. Various industrial processes have been reviewed and are of relevance to hydrothermal synthesis of organic compounds. The reactivity of organic compounds in hot water (200–350 °C) has been studied in autoclaves, and supercritical water as a medium for chemistry has also been evaluated. This high temperature aqueous organic chemistry and the strong reducing conditions of the natural systems suggest this as an important route to produce organic compounds on the primitive earth. Thus a better understanding of the potential syntheses of organic compounds in hydrothermal systems will require investigations of the chemistry of condensation, autocatalysis, catalysis and hydrolysis reactions in aqueous mineral buffered systems over a range of temperatures from warm to  $> 400$  °C.

## 1. Introduction

Hydrothermal systems are found along the active tectonic areas of the earth and are defined here as fluid flow regimes with thermal gradients at elevated temperatures (Holm and Hennet, 1992). The different types of hydrothermal systems being studied with their fluid temperatures are summarized in Table I and comprise spreading ridges, off-axis systems, backarc activity, hot spots, volcanism and subduction. There are currently about 100 locations with known hydrothermal activity and associated mineralization at various seafloor spreading centers (divergent plate boundaries) (cf. reviews by Rona, 1984, 1988). Those with associated organic matter alteration have been extensively reviewed (e.g., Kennish *et al.*, 1992; Simoneit, 1985, 1992a, 1994; Simoneit *et al.*, 1987, 1990). Both of these compilations are expected to expand as exploration continues. Fossil hydrothermal systems are also

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TABLE I  
Types of hydrothermal systems

Geologic type	Examples studied	Typical discharge temperatures (°C)	References
Marine (recharge sea water):			
Sediment-covered spreading ridge	Guaymas Basin, Escanaba Trough, Middle Valley, Red Sea	warm up to ~400 °C	Bazyliński <i>et al.</i> , 1988; Davis <i>et al.</i> , 1992; Kvenvolden <i>et al.</i> , 1986; 1992; Michaelis <i>et al.</i> , 1990; Simoneit and Lonsdale, 1982; Simoneit, 1985; 1993; Simoneit <i>et al.</i> , 1987
Mid-Ocean ridge (no sediment)	East Pacific Rise, Mid-Atlantic Ridge	warm up ~450 °C	Brault and Simoneit, 1989; Brault <i>et al.</i> , 1985, 1989
Off-axis flanks and basins	—	—	—
Back-arc	Bransfield Strait	no discharge (< 150 °C)	Brault and Simoneit, 1988; Whitticar <i>et al.</i> , 1985
Hot spots	—	—	—
Subduction	Oregon Margin	ambient	Kulm <i>et al.</i> , 1986
Continental (recharge meteoric water):			
Hot spots	Yellowstone National Park	< 96 °C	Clifton <i>et al.</i> , 1990
Rift valleys	Lake Tanganyika	65–80 °C	Tiercelin <i>et al.</i> , 1989
Volcanism	Waiotapu, New Zealand	< 100 °C	Czochanska <i>et al.</i> , 1986

— = Organic matter not yet studied.

preserved in the geologic record (e.g., Scott, 1985; Shaw, 1976; Shepeleva *et al.*, 1990).

The alteration of organic matter, generally strongly reducing from immature organic detritus, occurs in these high temperature and rapid fluid flow hydrothermal regimes. The agent of thermal alteration and mass transfer, hot circulating water (temperature range – warm to > 400 °C), is responsible for molecular alterations (primarily reductive), and product expulsion and migration from the sediment and rock sequences (Didyk and Simoneit, 1989, 1990; Simoneit, 1983). Organic compound alteration to other compounds predominates in these systems over destruction by complete oxidation. These hydrothermal systems generally produce disequilibrium reaction products comprised mostly of reduced but also some oxidized species (e.g. methylcyclopentane vs. benzene, cholestane vs. Diels' hydrocarbon; Kawka and Simoneit, 1987, 1990; Simoneit *et al.*, 1988, 1990, 1992a, b). Organic compounds which are obviously synthesized from inorganic precursors by hydrothermal activity are minor components in the contemporary systems studied to date. Such *de novo* products would predictably be overwhelmed by the excess of the pyrolysis products formed from contemporary natural organic precursors (e.g., hydrocarbons, alkanolic acids, etc.).

Hydrothermal activity is a continuous process which can occur in one region over long geologic time periods (Holm and Hennet, 1992). However, individual vent systems are generally active over briefer periods (decades to millenia, Peter *et al.*, 1991; Simoneit and Kvenvolden, 1994).

This paper combines the experimental and observational evidence on the fate, chemical alterations and possible syntheses of organic compounds under hydrothermal conditions with the known industrial processes and high-temperature chemical reactions for organic transformations. It then proceeds to postulate chemical pathways and experimentation for aqueous organic synthesis and explores their relevance to chemical evolution in hydrothermal environments.

## 2. Chemical and Physical Processes in Hydrothermal Systems

### 2.1. ORGANIC MATTER ALTERATION

The alteration of organic matter in hydrothermal systems proceeds via three recognizable reaction processes – reduction, oxidation and synthesis (Simoneit, 1992a). Reductive reactions are the primary mechanism of organic matter alteration in sedimented systems and generate, for example, aliphatic hydrocarbons (Simoneit, 1985, 1992a). Oxidation occurs at higher temperatures generating, for example, aromatics (i.e., polynuclear aromatic hydrocarbons, PAH) and alkanones. Synthesis of organic species from inorganic precursors is a trace process in sedimented hydrothermal systems and has been proposed for the origin of some of the thioheterocyclic compounds (Kawka and Simoneit, 1987; Simoneit, 1992a). The precursor organic matter in the contemporary systems consists of immature lipids and biogenic detritus which is converted rapidly to more mature products by ini-

tially undergoing accelerated diagenesis followed by catagenesis (Simoneit, 1985, 1992a, b; Tissot and Welte, 1984).

The rapid reductive and oxidative alteration of organic matter is typified by an example from Middle Valley, Northeastern Pacific Ocean (Simoneit, 1994). Typical molecular signatures for the maturation trend of steroid biomarkers are shown in the gas chromatography-mass spectrometry (GC-MS) data in Figure 1. The labile lipid precursors are the C<sub>27</sub> to C<sub>29</sub> sterols (Figure 2), which are rearranged to stan-3-ones and oxidized to 4-sten-3-ones with the same carbon number range as the in situ temperature increases. Subsequent reduction occurs at higher temperature (200–300 °C) to steranes (Figure 2) with primarily the 5 $\alpha$ (H), 14 $\alpha$ (H), 17 $\alpha$ (H), 20R- and lesser 5 $\beta$ (H), 14 $\alpha$ (H), 17 $\alpha$ (H), 20R- configurations (Figure 1, immature geosteranes, Simoneit, 1994). At even higher in situ temperatures (300–350 °C) further isomerization of the steranes occurs to yield the fully mature mixture comprised mainly of diasteranes and 5 $\alpha$ (H), 14 $\beta$ (H), 17 $\beta$ (H), 20S- and R- and 5 $\alpha$ (H), 14 $\alpha$ (H), 17 $\alpha$ (H), 20S and R-steranes (Figures 1 and 2, Simoneit, 1994). Stanols, sterenes (e.g.,  $\Delta^2$ ,  $\Delta^3$ , or  $\Delta^4$ ) and steradienes (e.g.  $\Delta^{2,4}$ ) are not detectable in any sample from Middle Valley. This suggests that products from dehydration reactions of sterols, as were described for sediments from Banskfield Strait, Antarctica (Brault and Simoneit, 1988), are not preserved in this higher temperature hydrothermal system. This maturation trend also parallels the steroid biomarker data for hydrothermal petroleum from the Guaymas Basin and Escanaba Trough systems (Kawka and Simoneit, 1987; Simoneit, 1985; Kvenvolden and Simoneit, 1990).

Oxidative alteration to aromatic steroid residues occurs concurrently and proceeds from various unsaturated and/or oxygenated precursors (Figure 3, Simoneit, 1994; Simoneit *et al.* 1992a). An example of the GC-MS data for the aromatic steroid hydrocarbons of a hydrothermal petroleum can be compared to the same data for laboratory hydrous pyrolysis of cholesterol with Se in Figure 4. The dominant hydrocarbon products from cholesterol are triaromatics without retention of the C-18 and C-19 methyl substituents (peaks in *m/z* 217 only, Figure 4b). The triaromatic steroid hydrocarbons of the hydrothermal petroleum are enriched in Diels' hydrocarbon with significant amounts of compounds that retained the C-18 methyl substituent (peaks in *m/z* 231, Figure 4a). This indicates that oxidative aromatization in the natural system occurs rapidly but probably via multiple pathways (e.g., Figure 3).

Synthesis of organic compounds from inorganic substrates is more difficult to demonstrate in the contemporary sedimented hydrothermal systems because any potential products could also be derived from thermal alteration of organic precursors. One possible exception is the group of heterocyclic polythio compounds (Kawka and Simoneit, 1987) discussed below.

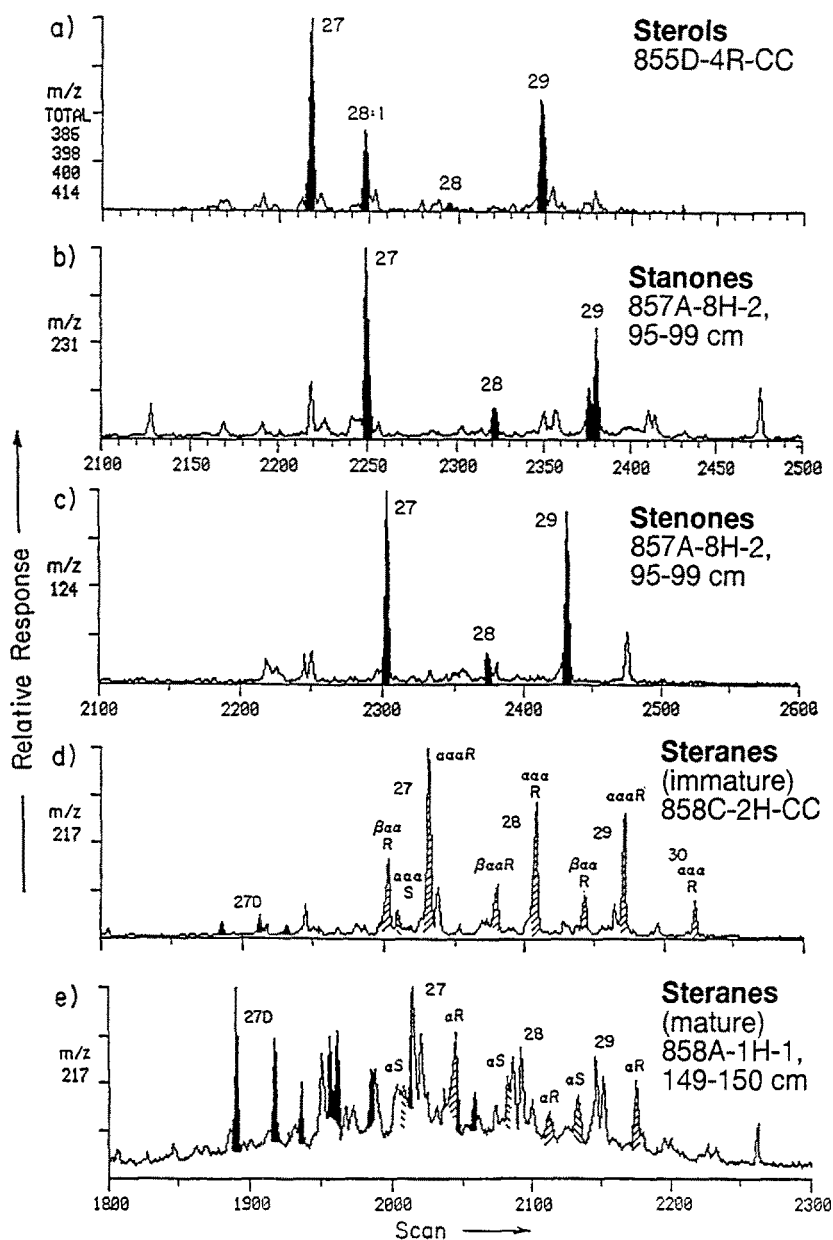


Fig. 1. Salient features of the gas chromatography-mass spectrometric data showing the hydrothermal interconversion of sterol precursors to geo-steranes in total extract bitumen from sediments of Middle Valley (Simoneit, 1994): (a) summed molecular ion fragmentogram for sterols; (b)  $m/z$  231 fragmentogram, key ion for stanones; (c)  $m/z$  124 fragmentogram, key ion for stenones; (d)  $m/z$  217 fragmentogram, key ion for steranes, immature composition; (e)  $m/z$  217 fragmentogram, mature sterane composition (numbers refer to carbon skeleton,  $\alpha$  or  $\alpha\alpha\alpha = 5\alpha(H)$ ,  $14\alpha(H)$ ,  $17\alpha(H)$ -steranes,  $\beta\alpha\alpha\alpha = 5\beta(H)$ ,  $14\alpha(H)$ ,  $17\alpha(H)$ -steranes, D = diasteranes, R and S = configuration at C-20).

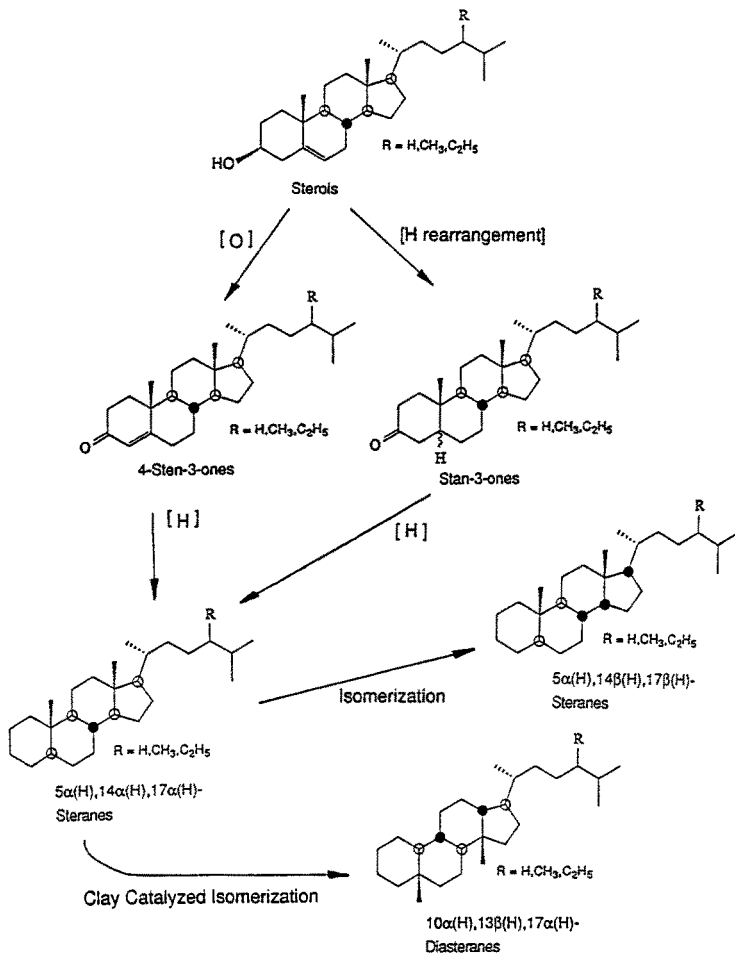


Fig. 2. Reductive alteration scheme for sterols to geo-steranes.

## 2.2. EXPULSION/EXTRACTION/MIGRATION

The formation of hydrothermal petroleum commences under low temperature conditions ( $\sim 60$  °C) and generates products from cleavage of weaker bonds. As the temperature regime rises (up to 400 °C) additional products are derived from more refractory organic matter and are even 'reformed' from smaller fragments (e.g., PAH). These products are continuously removed by fluid flow. Water is the dominant fluid in hydrothermal systems and is at ambient to supercritical temperatures. Water at high temperatures is more capable of dissolving organic compounds (e.g., Connolly, 1966; Price, 1976, 1993). Hydrothermal fluids also contain large concentrations of methane and carbon dioxide (Sakai *et al.*, 1990; Simoneit and Galimov, 1984; Simoneit *et al.*, 1988; Welhan and Lupton, 1987). Both CH<sub>4</sub> and CO<sub>2</sub> as well as many other possible trace components, are supercritical under the

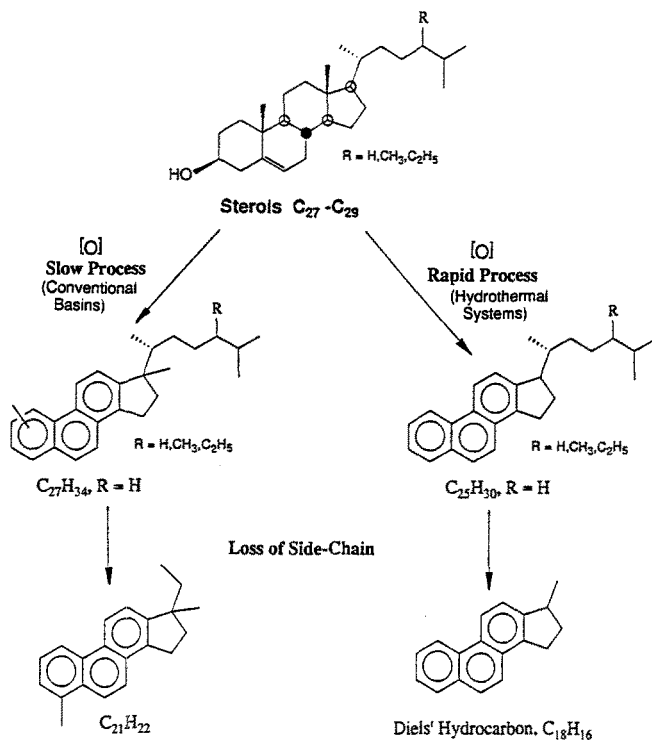


Fig. 3. Oxidative alteration scheme for sterols to aromatic steroid hydrocarbons.

temperature and pressure conditions of typical hydrothermal systems (Simoneit, 1992a). Their effects on the critical point of seawater are not known, although the phase behavior of  $CH_4$  and  $CO_2$  separately in supercritical water have been reported. Carbon dioxide fluid (supercritical) is also an excellent solvent for organic compounds.

The alteration process progresses from reductive to more oxidative reactions of the residual organic matter as the temperature increases. Reduction is strongly mediated by metal sulfides and other catalytic surfaces, with the hydrogen being derived from both water and organic matter (Leif, 1993). Oxidation of organic matter in the system is enhanced by the presence of sulfur and sulfate, yielding hydrogen sulfide (Leif *et al.*, 1992). At very high temperatures, organic matter is only partly destroyed, probably because the thermogenic products are soluble in the ambient fluid (Connolly, 1966; Price, 1976; Sanders, 1986) which rapidly moves away from the hot zone by convection. This product extraction and subsequent migration by bulk phase movement and by the fluids is extremely efficient and thus provides a mechanism for product transport along a decreasing temperature gradient. The migration of hydrothermal petroleum has been observed to occur as bulk phase, emulsion, and solution, with deposition of the less soluble and less volatile products in the cooler zones of the system and venting of the more volatile

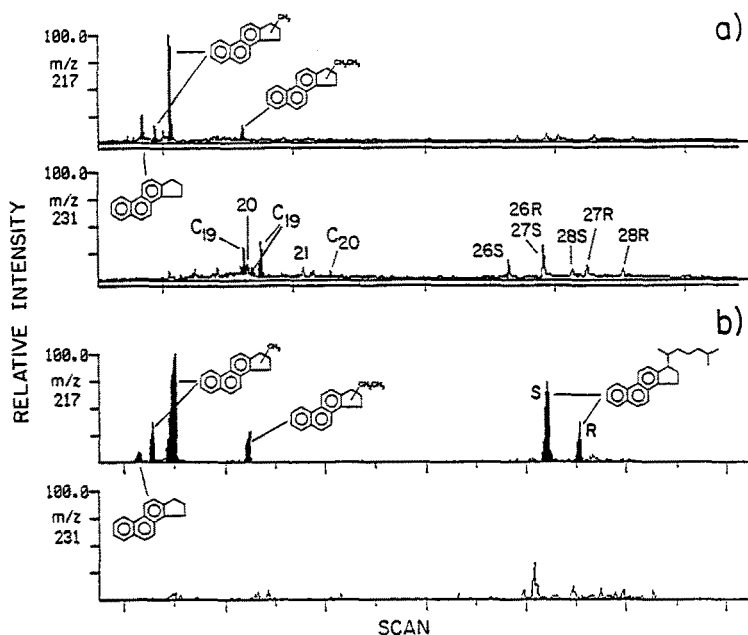


Fig. 4. Salient features of the GC-MS data for triaromatic steroid hydrocarbons in: (a) a hydrothermal petroleum from Guaymas Basin, Gulf of California (sample 1172-4), and (b) thermal alteration of cholesterol with Se (Simoneit *et al.*, 1992a) (numbers refer to carbon skeleton).

and more soluble products in the fluids (e.g., Didyk and Simoneit, 1990; Kawka and Simoneit, 1987; Simoneit, 1985, 1992a).

### 2.3. LABORATORY SIMULATION

Hydrous pyrolyses of sediments and model compounds have been carried out by many laboratories to simulate geological effects on organic matter (e.g., Moldowan *et al.*, 1992; Smith *et al.*, 1989; Eglinton and Douglas, 1988; Comet *et al.*, 1986; Lewan, 1985 and references therein). Laboratory studies of hydrothermal petroleum generation have been carried out using sediments with immature organic matter as starting substrate (Leif, 1993; Leif *et al.*, 1991, 1992; Simoneit, 1992b). Although these hydrous pyrolysis experiments have been conducted in sealed bombs, the products resemble those from the natural systems in that they are primarily aliphatic from reductive reactions. Furthermore, the laboratory simulations correlate well with the natural systems because hydrothermal alteration of organic matter is such a rapid geological process (Peter *et al.*, 1991; Simoneit and Kvenvolden, 1994). Typical experiments are conducted at 330 to 350 °C for 3 days, the optimal conditions for maximum yield of aliphatic pyrolysate (e.g., Comet *et al.*, 1986; Leif, 1993; Leif *et al.*, 1992; Lewan, 1985; Simoneit *et al.*, 1981). Unsaturated and aromatic products can be minimized by control of the system pH



and content of mineral buffers (Leif, 1993; Leif *et al.*, 1992). The rates of compound isomerizations, i.e. ionic processes, are much more rapid than reductions, i.e. radical processes, because hydrogenation is surface catalyzed and thus diffusion controlled (Leif, 1993).

### 3. Hydrothermal Chemical Reactions

#### 3.1. HIGH TEMPERATURE AQUEOUS ORGANIC CHEMISTRY

The reactivity of organic compounds in hot water (200–350 °C) has been studied to model the geochemical and technological implications of this chemistry (see review by Siskin and Katritzky, 1991) and the potential of supercritical water as a medium for chemistry has also been reviewed (Shaw *et al.*, 1991; Postorino *et al.*, 1993). The extensive study of the hydrothermal alteration of some simple organic compounds has been published by Katritzky *et al.* (1990, 1991) and Siskin *et al.* (1990, 1991) as cited and summarized in the overview by Simoneit (1992a). A series of pure organic compounds was subjected to reactions in water at 250 or 343 °C and all alteration products were determined semi-quantitatively. Four reaction categories were defined: condensation, bond cleavage, hydrolysis and autocatalysis reactions. Dimer formation from aliphatic and aromatic aldehydes and alkan-2-ones was observed by aldol condensation and polymerization resulted from experiments with styrene, phenol plus benzaldehyde, and mandelic acid. All other organic compounds tested either did not react or degraded to smaller molecular species (Katritzky *et al.*, 1990, 1991 and Siskin *et al.*, 1990, 1991 as cited in Simoneit, 1992a). These authors are now extending the study to conduct the same experiments in supercritical water at 460 °C (Katritzky *et al.*, 1994a, b). They submitted a selection of benzenoid hydrocarbons, and oxygen- and sulfur-containing derivatives to thermolytic reactions in water and in aqueous solutions of formic acid or sodium formate. Most substrates showed significant change within one hour in the supercritical medium. The onset of reduction was observed for example for phenanthrene to 9,10-dihydrophenanthrene (Katritzky *et al.*, 1994a).

Supercritical fluid technology has been successfully applied in the processing industry in three major areas: (1) extraction, (2) coal liquefaction (hydrogenation), and (3) waste oxidation (Josephson, 1982). Some of the basic chemistry has implications for hydrothermal systems and thus these chemical engineering research areas are mentioned here. The numerous symposium volumes, reports, and reviews summarizing the state of the art in supercritical fluid technology are cited by Simoneit (1992a). Additional information has been discussed by Ferris (1992). Reductive reactions with supercritical water have been applied primarily for upgrading shale oil and liquefying waste, biomass and coals, and oxidative reactions with supercritical water are utilized primarily for waste disposal (Simoneit, 1992a).

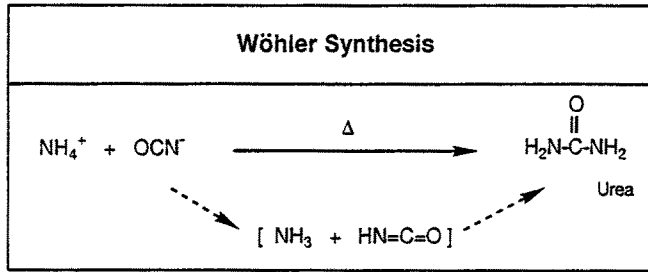


Fig. 5. The Wöhler Synthesis of urea.

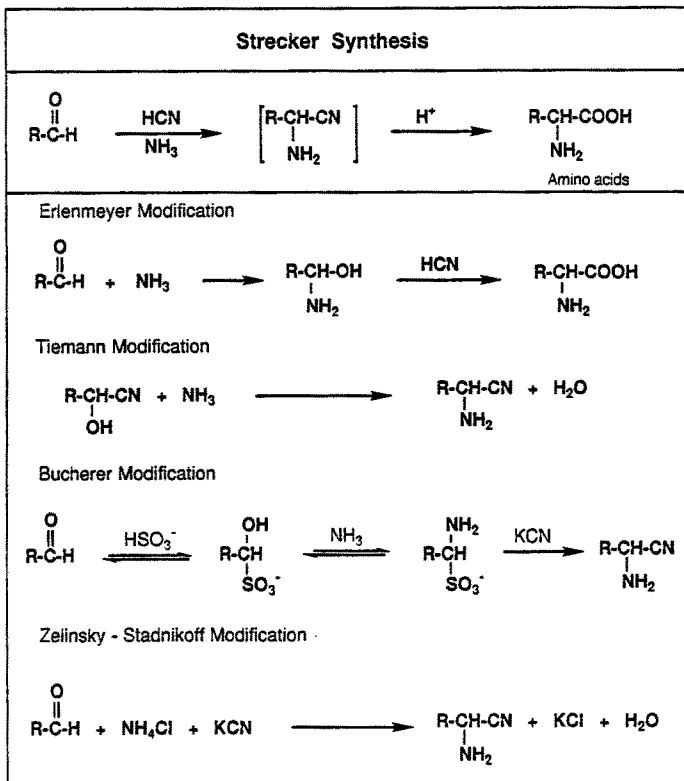


Fig. 6. The Strecker Synthesis with the various modifications.

### 3.2. INDUSTRIAL PROCESSES

Organic synthesis processes used by the chemical industry which start with inorganic species or low molecular weight organic compounds as feed stocks are summarized in Table III. These types of reactions are generally carried out in the gas phase over catalysts at elevated temperatures.

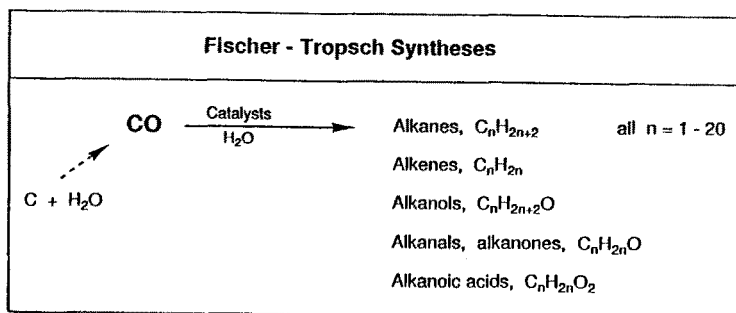


Fig. 7. The Fischer-Tropsch Syntheses of aliphatic compound series.

The classical Wöhler Synthesis consists of heating an aqueous solution of ammonium cyanate to yield urea as indicated in Figure 5 (Wöhler, 1828). Simple evaporation of an ammonium cyanate solution to dryness by heating yields urea, probably by the isocyanic acid and ammonia intermediate (Figure 5; Kauffman and Chooljian, 1979). The Wöhler Synthesis has been extended to the preparation of other urea derivatives (e.g., Jannelli, 1958; Kauffman and Chooljian, 1979).

The Strecker Synthesis for amino acids has had many modifications (Figure 6) as reviewed by Mowry (1948). The original synthesis consisted of reacting an aliphatic aldehyde with HCN,  $NH_4OH$ , and HCl in aqueous solution at elevated temperature, followed by acidic hydrolysis (e.g., Strecker, 1850, 1854). The Erlenmeyer modification conducts the synthesis in two steps (Erlenmeyer and Passavant, 1880) and the Tiemann modification starts with a hydroxynitrile and alcoholic ammonia (e.g., Tiemann, 1880; Tiemann and Friedländer, 1881). The Zelinsky-Stadnikoff modification replaces the volatile HCN and  $NH_3$  of the original Strecker procedure with a mixture of the corresponding salts (Figure 6; e.g., Zelinsky and Stadnikoff, 1906; Stadnikoff, 1907). The Bucherer modification of the Strecker procedures uses bisulfite adducts of the aldehydes (Figure 6; Bucherer and Steiner, 1934). It is more economical and is currently used for large scale production of  $\alpha$ -amino acids (Greenstein and Winitz, 1961; Shafran *et al.*, 1989).

A set of Strecker-type synthesis experiments has been carried out under hydrothermal conditions (Hennet *et al.*, 1992). The general autoclave procedure consisted of heating the acidified aqueous phase with dissolved formaldehyde,  $NH_4Cl$  and KCN (each  $\sim 0.2$  M) over mineral buffers under a gas phase of  $CO_2$  and  $H_2$  (3:1, resultant pressure 10 bars) to  $150^\circ C$  for varying periods of time. The major amino acids generated were glycine, dl-alanine, dl-aspartic acid and dl-glutamic acid.

Many variants of the Fischer-Tropsch Synthesis, also called oxo synthesis or Synthol Process, have been explored since its inception (Figure 7; Fischer and Tropsch, 1923). It is currently used to synthesize hydrocarbons (synthetic fuels), and aliphatic alcohols, aldehydes and ketones by catalytic hydrogenation of carbon monoxide (Storch *et al.*, 1951; Anderson, 1984). The reaction mechanisms, supercritical phase behavior of the reagent CO, and catalysis have been reviewed

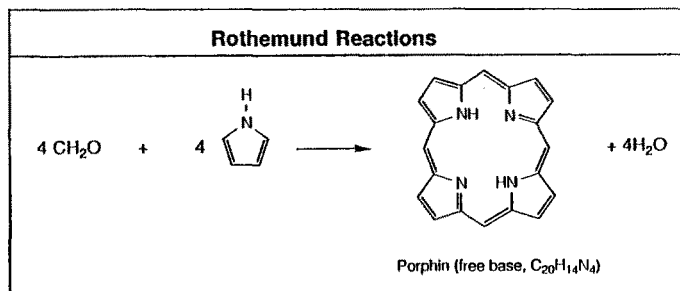
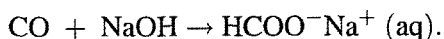


Fig. 8. An example of a Rothemund Reaction, the synthesis of porphyrin.

(Rofer-De Poorter, 1981; Yokota and Fujimoto, 1989; Herrmann, 1982) and provide an insight into the complexity of this process. Aliphatic hydrocarbons, mainly normal and 2- to 7-methyl branched isomers, were produced in a classical open flow (gas phase) Fischer-Tropsch process using meteoritic iron as catalyst (Gelpi *et al.*, 1970). The product distributions closely resembled the composition of synthetic fuels (Pichler *et al.*, 1968; Bruner, 1949). Fatty acids up to  $\sim C_{20}$  have been synthesized by a closed system Fischer-Tropsch process (Nooner and Oró, 1979). Meteoritic iron was used as catalyst with various alkali carbonates as promoters as react hydrogen and CO in a pressure vessel at 400 °C for typically 1–2 days. The alkanolic acids were interpreted to be derived from oxidation of catalyst-bound oxygenated intermediates. Reduced carbonaceous matter has been reported to form in basalt on cracked surfaces of olivine by reaction of C-O-H species possibly by Fischer-Tropsch-like processes (Tringle and Hochella, 1993).

The Goldschmidt Reaction is the hydration of carbon monoxide at 6–10 bar and 120–200 °C. Under these conditions CO is absorbed by strong alkaline solutions almost as fast as CO<sub>2</sub> at normal temperature. The reaction is carried out industrially to produce formic acid (Shreve, 1956):



At temperatures above 400 °C, alkali formates liberate hydrogen forming a radical-type intermediate which dimerizes immediately to alkali oxalate (Shreve, 1956):



The reduction of carbon dioxide to organic substances has long been a goal for synthetic chemists, but remained difficult. Homogeneous catalytic hydrogenation of carbon dioxide in the supercritical state has now been reported (Jessop *et al.*, 1994; Reetz *et al.*, 1993). The supercritical CO<sub>2</sub> is an excellent solvent for the H<sub>2</sub>, catalysts and formic acid product, thus greatly enhancing contact and reduction efficiency.

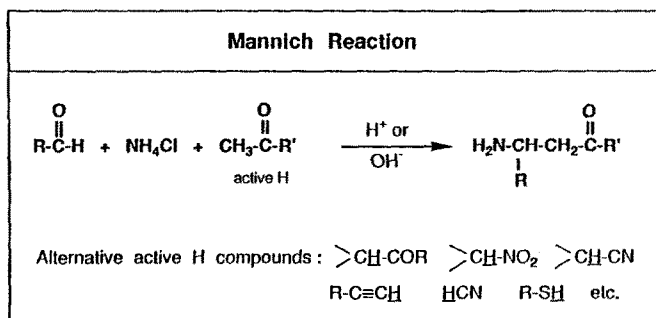


Fig. 9. The Mannich Reaction for aminomethylations.

The Rothemund reaction is used for the preparation of *meso*-tetra substituted porphyrins by condensation of pyrrole with an aldehyde (Rothemund, 1935, 1936, 1939). The original reaction of formaldehyde with pyrrole to yield porphin is illustrated in Figure 8. This process has found wide application (e.g., Little, 1981) and it may be a mechanism for pigment synthesis under hydrothermal conditions.

The Mannich Reaction is a condensation of formaldehyde (or other aldehydes) with ammonia, in the form of its salt, and a compound containing an active hydrogen as shown in Figure 9 (e.g., Mannich and Heilner, 1922; Mannich and Ganz, 1922; Reichert, 1959; Tramontini and Angiolini, 1990). This can formally be considered to give  $\text{H}_2\text{NCH}_2\text{OH}$  which undergoes nucleophilic substitution. Many active hydrogen compounds give the reaction as for example: aldehydes, ketones, esters, nitro compounds, nitriles, phenols, alkylazo compounds, acetylenes, thiols, alkanols, HCN, etc. The Mannich Reaction is now an important biosynthetic route to natural products and many alkaloids and intermediates have been synthesized (e.g., Gevorgyan *et al.*, 1984; Robinson, 1917).

All these reactions need to be attempted under hydrothermal conditions to correlate with nature. The Fischer-Tropsch type syntheses should first be demonstrated in the laboratory, because in the hydrothermal systems such products are masked by the overwhelming pyrolysates from in situ organic matter alteration. Similarly, the Strecker Synthesis of amino acids is masked in hydrothermal systems by the extensive pyrolysis of proteinaceous residues from contemporary biota. It should be noted that hyperthermophilic archaeobacteria have been found to thrive in deep petroleum reservoirs at temperatures up to 102 °C (Stetter *et al.*, 1993), as well as in hydrothermal vent fluids (e.g., Huber *et al.*, 1989, 1990; Deming and Baross, 1993). Gold (1993) even hypothesized about the possible existence of a deep high temperature biosphere. Hydrothermal synthesis of the extensive list of prebiotic organic compounds reviewed by Ferris (1992) should also be carried out.

TABLE II

Chemistry relevant for organic synthesis observed in hydrothermal systems

Competing Chemistry Documented for Hydrothermal Systems	
1. Radical vs. Carbonium Ion Reactions	
2. Polymerization vs. Depolymerization (also cracking)	
3. Reduction vs. Oxidation Processes	
4. Synthesis by Condensation	
Controlling Physical Conditions	
1. Temperature vs. Time of Reactions:	High (> 250 °C) – hours-days Lower (50–250 °C) – weeks
2. Pressure and High Temperature	Maintain Fluid State Aid Solvent Efficiency of Fluid and Migration of Products
3. Mineralogy:	Catalysis and Hydrogen Fugacity

#### 4. Synthesis

The implications of chemical processes in hydrothermal systems for chemical evolution of relevance to the origin of life are beginning to be evaluated. Organic syntheses need to be demonstrated and distinguished from organic matter alteration both in laboratory and in the field. Organic synthesis under hydrothermal conditions is theoretically possible (Shock, 1990). Various established industrial processes are commonly used to synthesize organic compounds with the aid of catalysis from inorganic substrates, and they set the precedent as described above.

The chemistry of relevance for organic synthesis in hydrothermal systems is summarized in Table II. The competing chemical reactions which have been observed in hydrothermal systems are listed and have been described in detail elsewhere (Brault and Simoneit, 1988; Kawka and Simoneit, 1987, 1990; Leif, 1993; Leif *et al.*, 1992; Simoneit, 1985, 1992a, b, 1993). The physical conditions which control the organic chemistry are also listed and have been discussed previously (e.g., Kawka and Simoneit, 1987; Leif, 1993; Leif *et al.*, 1992; Simoneit, 1985, 1992a,b, 1993). Thus brief contact time at high temperatures is the hydrothermal process, longer contact times at intermediate temperatures occur in intrusive systems, and geologically long contact times at low temperatures (< 150 °C) are found in conventional basins. High pressure (> 150 bar) is required to maintain the fluid state at high temperatures, which aids both the solvation capacity for organic compounds and migration of the products (Price, 1976, 1993; Price and Wenger, 1992; Simoneit, 1983, 1985, 1992a, b, 1993). The mineralogical composition controls the buffering capacity, i.e. hydrogen fugacity, and aids catalysis (Leif, 1993; Leif *et al.*, 1992; Shock, 1990).

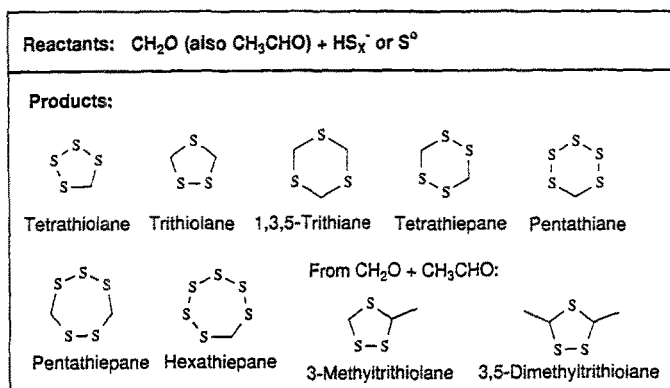


Fig. 10. Structures of the polythio heterocyclic compounds identified in hydrothermal petroleum and laboratory simulation products.

Preliminary evidence for the synthesis of heterocyclic sulfur compounds in the Guaymas Basin hydrothermal system, as for example tetrathiolane ( $\text{CH}_2\text{S}_4$ , Figure 10), pentathiane ( $\text{CH}_2\text{S}_5$ ), pentathiepane ( $\text{C}_2\text{H}_4\text{S}_5$ ) and hexathiepane ( $\text{CH}_2\text{S}_6$ ), has been reported (Kawka and Simoneit, 1987). All the compounds in Figure 10 were detected in the bitumen (petroleum) from hydrous pyrolysis of Guaymas Basin sediment (Simoneit, 1992b and unpublished results). Because these compounds are significant components in the Guaymas Basin samples and are not known marine natural products, they can be interpreted as being derived via synthesis from formaldehyde (also acetaldehyde, Figure 10) and sulfur or  $\text{HS}_x^-$  in the hydrothermal fluids. Condensation of formaldehyde with  $\text{H}_2\text{S}$  was proposed for a similar suite thio compounds formed in an attempted synthesis experiment of amino acids (Cole *et al.*, 1994). Other products from potential synthesis reactions have not been defined in the natural systems but will be determined based on inferences from experimental results. A confined-pyrolysis apparatus has been successfully evaluated for hydrothermal synthesis experimentation (Leif and Simoneit, 1994). Key indicator compounds will then be sought in the natural hydrothermal systems, and whether truly synthetic processes leading to organic compounds occur there, especially in the off axis areas, remains as a longer term goal.

## 5. Prognosis

As aptly pointed out by J. P. Ferris during the discussion of this paper the opposing groups of scientists are at extreme ends of the origin of life spectrum. The experimentalists studying chemical evolution by spark discharge ('Arcists') and allied experiments are on one side, and the theorists (called 'Ventists' by the Arcists) claiming organic synthesis occurs under hydrothermal conditions are on the opposing side. In my view, a more reasonable position would be near the center. The facts presented are positive in terms of reactions, and preliminary experimentation with

TABLE III  
Organic synthesis processes in the chemical industry

Process	Typical reaction temperature (°C)	Chemical products	Example references
Wöhler Synthesis	100	Urea	Wöhler (1828)
Strecker Synthesis, many variations	100–200	Amino acids, hydantoins	Strecker (1850, 1854) Mowry (1948)
Fischer-Tropsch (Synthol Process, oxo synthesis)	250–500	Hydrocarbons, oxo-compounds (e.g. aldehydes)	Fischer and Tropsch (1923)
Goldschmidt Reaction	120–200	Formic acid (oxalic acid)	Shreve (1956)
Rothmund Reaction	85–95	Porphyrins (free base)	Rothmund (1935, 193)
Mannich Reaction (aldehydes with amines)	150–200	Numerous natural products (e.g. alkaloids, intermediates)	Reichert (1959)

such syntheses under hydrothermal conditions is encouraging (e.g., Hennes *et al.*, 1992). The high yields of amino acids obtained in two sets of experiments indicate that the hydrothermal experimental conditions favored the Strecker-like reaction at higher rates rather than product destruction (Hennes *et al.*, 1992). These authors point out that the amino acid production vs. destruction rates under the experimental conditions employed need to be elucidated further as a function of temperature. The evidence from the natural hydrothermal systems for organic compound stability has been extensively documented, and new data about the remarkable thermostability of biomolecules is currently appearing (e.g., Aono *et al.*, 1989; Constantino *et al.*, 1990; Deming and Baross, 1993). Furthermore, the various chemical industry processes discussed above set precedents for obvious application in hydrothermal experimentation. Thus, the ideal experimental conditions need to be developed to carry out various syntheses of relevance to prebiotic chemical evolution. The Ventists will persist to test this hypothesis just as the Arcists have done for the past 40 years.

## 6. Conclusion

Hydrothermal alteration of organic matter is a ubiquitous process along the active global rift systems as well as in the off axis areas. The chemistry of organic matter alteration and organic matter synthesis over the temperature spectrum from warm to higher than 400 °C in hydrothermal systems is of great relevance to research on the origin of life, because hydrothermal activity is a phenomenon which has been active over most of geological time. Hydrothermal systems are locales for organic



chemical synthesis because they are strongly reducing. Therefore, they represent an important route to produce organic compounds in the early ocean.

In the contemporary sedimented systems these hydrothermal conditions lead to preservation of labile organic compounds, and to condensation and polymerization reactions. The fluids act as solvents and transport media for the organic products. The mineralogy of the system controls the hydrogen fugacity and possibly catalysis for reactions. Reaction rates are dependent on high temperature/pressure versus brief contact time constraints. Laboratory experiments under hydrothermal conditions are being carried out to elucidate the chemistry of sulfur species and key reactants such as CO, CH<sub>2</sub>O, RCHO, RNH<sub>2</sub>, HCN. The natural systems can then be examined based on the positive results from the laboratory simulations.

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