# Abiotic Synthesis of Organic Compounds in Deep-Sea Hydrothermal Environments

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*Received October 16, 2006*

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## 1. Introduction

Ever since the discovery of deep-sea hydrothermal systems in the late 1970s, there has been keen interest in the potential for abiotic synthesis of organic compounds in these environments. This interest arises, in part, from the ability of methane and other organic compounds in hydrothermal fluids to provide sources of metabolic energy and fixed carbon for biological communities at the seafloor and in the overlying water column.[1,2] In addition, several current theories propose that the origin of life on Earth occurred in submarine hydrothermal systems, and abiotic synthesis may have supplied the prebiotic organic compounds from which life emerged.[3,4]

Generally speaking, organic matter in geologic environments can be broadly attributed to three possible sources: "biogenic" compounds formed by biological organisms as part of their metabolic and biosynthetic activities, "thermogenic" compounds generated by thermal decomposition of living biomass or of biologically derived compounds that have undergone diagenetic processes (e.g., kerogen), and "abiotic" compounds that are formed by purely chemical processes with no participation of biological organisms. For many organic compounds, however, it can be difficult to attribute their origin to one of these sources because they can be generated by more than one process. Common examples include methane and acetate, which can form as a byproduct of microbial metabolism, during thermal decomposition of bioorganic matter, or by abiotic processes such

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10.1021/cr0503660 CCC: $65.00 
Published on Web 01/25/2007

as Fischer−Tropsch synthesis. Although it is increasingly accepted among earth scientists that abiotic compounds are readily synthesized from inorganic precursors in hydrothermal environments, unambiguous identification of those compounds that may have an abiotic source is particularly problematic because of the ubiquitous presence of biological and thermogenic organic matter in surface and near-surface environments. As a consequence, assessments of the potential contribution of abiotic synthesis in these systems have relied heavily on theoretical and experimental studies.

A variety of organic compounds have been identified in deep-sea hydrothermal fluids and accompanying mineral deposits, ranging from simple compounds like methane and ethane to more complex compounds like long-chain hydrocarbons, fatty acids, and polycyclic aromatic hydrocarbons. These compounds are particularly abundant in hydrothermal systems that are overlain by organic-rich sediments, such as Guaymas Basin, Escanaba Trough, and Middle Valley.[5−9] However, the organic matter in these systems is predominantly derived from thermogenic and biologic sources, obscuring any potential contribution from abiotic inputs. As such, these systems provide little information that can be used to assess possible abiotic inputs and are not considered further in the present discussion. Instead, we will focus on unsedimented systems where abiotic sources may contribute a larger (and therefore detectable) fraction of the organic matter found in hydrothermal fluids and mineral deposits.

The abiotic formation of hydrocarbons and other organic compounds in geologic systems involves the reduction of $CO_2$ (or other inorganic carbon sources such as CO and $HCO_3^-$) by $H_2$ produced during fluid−rock interactions. This overall process can be expressed by the general reaction:

$$CO_2 + H_2 \rightarrow CH_4 + C_2H_6 + C_3H_8 + C_nH_{n+2}... + H_2O \quad (1)$$

In natural hydrothermal systems, of course, other reactants are likely to be involved ($H_2S$, $NH_3$, etc.) and might produce a greater variety of organic products than indicated in this reaction (carboxylic acids, amino acids, organosulfur compounds, etc.). However, discussion of abiotic synthesis in deep-sea hydrothermal systems has focused mostly on methane and simple hydrocarbons because they occur at relatively high aqueous concentrations that facilitate quantitative analysis.

Because they are the most abundant and well-studied organic compounds in deep-sea hydrothermal fluids, this review primarily covers the potential for abiotic synthesis of hydrocarbons and discusses recent laboratory experimental studies designed to evaluate abiotic organic synthesis under hydrothermal conditions. We also include a summary of observations of organic compounds in natural systems that place constraints on abiotic inputs. Owing to the potential participation of marine hydrothermal systems in prebiotic chemistry and the origin of life, there have been numerous experimental studies conducted to investigate the abiotic synthesis of biochemically significant compounds such as amino acids, purines, and sugars. The large number of these studies precludes a comprehensive review of that material here, and readers interested in this topic are directed to other reviews covering prebiotic experiments in greater detail.[10,11]

## 2. Geochemical and Thermodynamic Constraints on Abiotic Synthesis

The concept that deep-sea hydrothermal systems are sites of abiotic organic synthesis is based largely on the strongly reducing chemical environments that develop as the result of interactions of circulating seawater with the mafic and ultramafic rocks that make up the ocean crust and underlying mantle.[2,12,13] Generation of reducing conditions (high $H_2$ concentrations) during fluid−rock interactions results from the reaction of water with ferrous Fe-bearing minerals such as olivine, pyroxene, and pyrrhotite. During reaction, Fe(II) is oxidized by water to Fe(III), which precipitates as magnetite or other Fe(III)-bearing minerals, while the hydrogen from water is reduced to $H_2$. The process can be represented by the general reaction:

$$2(FeO)_{rock} + H_2O \rightarrow (Fe_2O_3)_{rock} + H_2 \quad (2)$$

where $(FeO)_{rock}$ refers to the ferrous component of igneous minerals and $(Fe_2O_3)_{rock}$ refers to the ferric component of Fe-bearing alteration products. For example, $H_2$ generation during serpentinization of olivine, the predominant mineral in ultramafic rocks that are common in the oceanic lithosphere, can be expressed as:

$$\underset{\text{olivine (Fo}_{90})}{Mg_{1.8}Fe_{0.2}SiO_4} + 1.37H_2O \rightarrow \underset{\text{serpentine}}{0.5Mg_3Si_2O_5(OH)_4} + \underset{\text{brucite}}{0.3Mg(OH)_2} + \underset{\text{magnetite}}{0.067Fe_3O_4} + 0.067H_2 \quad (3)$$

The $H_2$-producing step (reaction 2) proceeds most effectively in ultramafic rocks because the minerals that form in these relatively silica-poor rocks during hydrothermal alteration (serpentine, brucite) tend to exclude Fe(II) from their metal sites, "forcing" the Fe to oxidize and precipitate as magnetite. As a consequence, deep-sea hydrothermal fluids that circulate through ultramafic rocks are strongly reducing, with $H_2$ concentrations as high as 16 mmol/kg (Table 1). Because of their potential for production of strongly reducing fluids, hydrothermal alteration of olivine-rich rocks such as peridotites is believed to generate particularly favorable environments for abiotic synthesis of organic compounds.[2,4,14−16]

On the other hand, hydrothermal alteration of more silica-rich basalts generates product minerals whose structures more readily allow Fe(II) into their metal sites, so that much of the Fe(II) released during alteration of primary igneous minerals is readily incorporated into secondary alteration phases instead of being oxidized to Fe(III). As a result, hydrothermal alteration of basaltic rocks generally produces less $H_2$ than alteration of ultramafic rocks, even though the Fe(II) content of basalts may be greater. Nevertheless, water−basalt interactions can produce moderately strong reducing conditions with $H_2$ concentrations in hydrothermal fluids up to ~2 mmol/kg (Table 1).

Of course, abiotic synthesis will only proceed if it is thermodynamically favorable. The thermodynamic basis for organic synthesis in deep-sea hydrothermal systems has been most clearly elucidated in a series of papers by Shock and colleagues.[15,17−19] The basic thermodynamic constraints on abiotic organic synthesis are illustrated in Figure 1. The solid curves in the figure represent some mineral assemblages that can buffer oxidation states in geologic systems and span the range of oxidation states that exist in most subsurface environments. Measured concentrations of $H_2$ in high-

**Table 1. Endmember Concentrations and Isotopic Compositions of Dissolved Gases in Representative Unsedimented Hydrothermal Vent Fluids**

| | SW | Rainbow[67] MAR | Logatchev[a] MAR | Lucky Strike[b,l] MAR | Menez Gwen[b] MAR | Broken Spur[c] MAR | TAG[62,d] MAR | Plume Vent[e] JDF | 17−19°S[f] EPR | 21°N[g−j] EPR | Lost City[68,72] |
|---|---|---|---|---|---|---|---|---|---|---|---|
| host rock | | serpentinite | serpentinite | basalt | basalt | basalt | basalt | basalt | basalt | basalt | serpentinite |
| $H_2$ (mM) | 0.0004 | 16 | 12 | 0.02/0.73 | 0.024/0.048 | 0.43/1.03 | 0.15/0.37 | 0.351 | 0.04/1.30 | 0.65/1.5 | <1−15 |
| $CO_2$ (mM) | 2.3 | 16 | 10.1 | 13/28 | 17/20 | 6.0/7.1 | 2.9/3.4 | 3.92 | 8.5/22 | 5.7 | <0.8 |
| $\delta^{13}C_{CO_2}$ (‰) | ∼0 | −3.15 | −4.3 | −7.5/−10.6 | −9.1 | −9.0 | −8.4/−10 | −4.4 | −5.8/−7.9 | −7 | −8 to +3 |
| $CH_4$ (mM) | 0.0003 | 2.5 | 2.1 | 0.50/0.97 | 1.35/2.63 | 0.065/0.13 | 0.12/0.15 | 0.084 | 0.0075/0.133 | 0.06/0.09 | 1−2 |
| $\delta^{13}C_{CH_4}$ (‰) | | −15.8 | −13.6 | −12.7/−13.7 | −18.8/−19.6 | −18/−19 | −8.0/−9.5 | −20.8 | −22/−23.5 | −15/−17.6 | −8.8 to −13.6 |
| $\delta^{2}H_{CH_4}$ (‰) | | | −109 | | | | | | | −102/−126 | −99 to −141 |
| CO ($\mu$M) | 0.0003 | 5 | | | | | | | | 0.110/0.311 | |
| ethane (nM) | | 1097 | | 53/179 | 270/808 | | | 180 | 62/204 | 35/67 | |
| propane (nM) | | 48 | | 7/155 | 15/25 | | | 46 | 7.4−40 | 35/56 | |
| *i*-butane (nM) | | | | | | | | 4.1 | | | |
| *n*-butane (nM) | | | | | | | | 5.7 | | 47 | |
| $T_{equilibrium}$ (°C)[k] | | 590 | 750 | >1070 | 730/690 | 710/770 | | 470 | 440/540 | 850/680 | >680 |

[a] Charlou, J. L.; Donval, J. P.; Douville, E.; Knoery, J.; Fouquet, Y.; Jean-Baptiste, P.; Bourg, C.; Prieur, D.; German, C. *Reun. Sci. Terre RST 98* **1998**, 89. [b] Charlou, J. L.; Donval, J. P.; Douville, E.; Jean-Baptiste, P.; Radford-Knoery, J.; Fouquet, Y.; Dapoigny, A.; Stievenard, M. *Chem. Geol.* **2000**, *171*, 49. [c] Lein, A. Y.; Grichuk, D. V.; Gurvich, E. G.; Bogdanov, Y. A. *Dokl. Earth Sci.* **2000**, *375A*, 1304. [d] Charlou, J. L.; Donval, J. P.; Jean-Baptiste, P.; Dapoigny, A.; *Geophys. Res. Lett.* **1996**, *23*, 3491. [e] Evans, W. C.; White, L. D.; Rapp, J. B. *J. Geophys. Res.* **1988**, *93*, 15305. [f] Charlou, J. L.; Fouquet, Y.; Donval, J. P.; Auzende, J. M.; Jean-Baptiste, P.; Stievenard, M. *J. Geophys. Res.* **1996**, *101*, 15899. [g] Craig, H.; Welhan, J. A.; Kim, K.; Poreda, R.; Lupton, J. E. *EOS Trans. AGU* **1980**, *61*, 992. [h] Lilley, M. D.; Baross, J. A.; Gordon, L. I. In *Hydrothermal Processes at Seafloor Spreading Centers*; Rona, P. A.; et al., Eds.; Plenum Press: New York, 1983; p 411. [i] Welhan, J. A.; Craig, H. In *Hydrothermal Processes at Seafloor Spreading Centers*; Rona, P. A.; et al., Eds.; Plenum Press: New York, 1983; p 391. [j] Welhan, J. A.; Lupton, J. E. *Am. Assoc. Petrol. Geol. Bull.* **1987**, *71*, 215. [k] Equilibrium temperature calculated from measured carbon isotopes for $CO_2$ and $CH_4$ assuming isotopic equilibrium using the $CO_2$–$CH_4$ fractionation curve of: Horita, J. *Geochim. Cosmochim. Acta* **2001**, *65*, 1907. [l] Figures separated by a slash (/) represent measurements the range of values reported for multiple fluids at a particular site; for Lost City, only a range of values are reported. MAR = Mid-Atlantic Ridge, JDF = Juan de Fuca Ridge, EPR = East Pacific Rise.




**Figure 1.** Diagram illustrating mineral-buffered oxidation states, expressed as the fugacity of $H_{2(g)}$, and carbon speciation as a function of temperature. Curves labeled FMQ (fayalite−magnetite−quartz), PPM (pyrite−pyrrhotite−magnetite), and HMP (hematite−magnetite−pyrite) correspond to the oxidation state that would be attained at thermodynamic equilibrium in geologic systems buffered by these mineral assemblages. Dotted lines reflect equilibrium ratios of $CO_2$ to $CH_4$ according to reaction 4. Adapted from ref 18, Copyright 1992, with kind permission of Springer Science and Business Media.

temperature fluids in deep-sea hydrothermal systems indicate oxidation states slightly above to slightly below the pyrite−pyrrhotite−magnetite (PPM) assemblage. At temperatures > ∼450 °C, thermodynamic equilibrium according to the reaction:

$$CO_2 + 4H_2 \leftrightarrow CH_4 + 2H_2O \qquad (4)$$

strongly favors $CO_2$ at oxidation states buffered by naturally occurring mineral assemblages (Figure 1). Thus, hydrothermal fluids that have equilibrated at high temperatures should be dominated by $CO_2$ with trace quantities of $CH_4$. As temperatures decrease, however, $CH_4$ stability dramatically increases, creating a strong thermodynamic drive for the reduction of $CO_2$ in fluids that have cooled subsequent to equilibration at high temperatures.

Formation of other organic compounds (hydrocarbons, carboxylic acids, amino acids, etc.) is similarly favored thermodynamically as temperatures decrease in hydrothermal environments. However, because methane is the most thermodynamically stable organic compound at these conditions, only trace quantities of other organic compounds will form if complete equilibrium is reached. However, experimental and observational studies indicate that kinetic inhibitions to methane formation and to decomposition of organic compounds prevent complete thermodynamic equilibrium from being attained, so that organic compounds other than methane may form and persist in nonequilibrium abundances within hydrothermal environments. Under such conditions, calculations by Shock and colleagues[15,18,19] demonstrate that formation of measurable concentrations of a wide variety of different organic compounds is thermodynamically favored in low-temperature environments within deep-sea hydrothermal systems, such as those created by convective cooling of high-temperature fluids or mixing of hydrothermal fluids with cold seawater.

Based on geological observations as well as theoretical and experimental constraints, there are a variety of environments within hydrothermal systems where abiotic organic synthesis might occur. For example, fluid−rock interactions during heating of seawater in the recharge limb of hydrothermal circulation zones will increase $H_2$ concentrations, favoring reduction of dissolved $CO_2$ (or bicarbonate). During this process, dissolution of magmatic gases trapped within rocks can supply additional $CO_2$ and $H_2$, providing further substrates for synthesis reactions. As fluids approach high-temperature reaction zones in the deeper parts of the system, increased reaction rates may supply additional $H_2$ from reactions with basalt or other rocks, while injection of $CO_2$-dominated magmatic gases into the system will provide additional carbon and increase the thermodynamic drive for abiotic synthesis. This thermodynamic drive will increase further as $CO_2$- and $H_2$-charged high-temperature fluids cool by conduction and/or mixing with seawater during ascent to the seafloor.[18]

While reduction of $CO_2$ and CO by $H_2$ may be thermodynamically favored at temperatures of 350 °C and below in many environments within deep-sea hydrothermal systems, spontaneous reduction of these compounds to methane or other hydrocarbons proceeds only slowly or not at all at these temperatures. Kinetic inhibitions to the reduction of $CO_2$ and CO arise in large part from the configuration of their molecular orbitals, which give the molecules a tendency to not readily accept electrons.[20,21] Rapid reduction of these compounds requires interaction with a catalyst to activate the molecules to promote electron transfer,[21] and, as a consequence, the synthesis of significant amounts of abiotic organic compounds is likely to require the presence of suitable catalysts to facilitate the reaction.

## 3. Pathways for Abiotic Organic Synthesis

The most widely cited mechanism, by far, for the formation of abiotic organic compounds in geologic settings is the Fischer−Tropsch synthesis (FTS). Strictly speaking, Fischer−Tropsch synthesis refers to the formation of organic compounds from a gaseous mixture of CO and $H_2$ in a surface-catalyzed process involving sequential reduction and polymerization of single-carbon units. Within the earth and planetary sciences, however, the term is often used in a broader context to represent any synthesis of organic compounds, often without any specific knowledge of the carbon source or the reaction mechanism involved. The term is also used frequently to refer to the formation of methane alone, even though the Fischer−Tropsch mechanism describes the synthesis of more complex organic compounds through sequential formation of carbon−carbon bonds (the catalyzed reduction of $CO_2$ to methane is more properly referred to as the Sabatier process). In the following discussion, we shall use the term Fischer−Tropsch-type (FTT) synthesis to refer to surface-catalyzed reduction and polymerization of oxidized single carbon compounds ($CO_2$, CO, $CH_3OH$, HCOOH, etc.) to form organic compounds.

It is important to recognize that Fischer−Tropsch-type synthesis is not the only reaction pathway available to produce reduced carbon species under hydrothermal conditions. In particular, production of $CH_4$ and longer-chain hydrocarbons may occur in aqueous solution without the involvement of heterogeneous catalysts. Accordingly, use of the term Fischer−Tropsch synthesis to describe all cases of inorganic carbon reduction to methane and/or longer-chain hydrocarbons should be discouraged, because it may incorrectly imply a reaction mechanism that may not be occurring in the natural system under study.

### 3.1. An Overview of Fischer–Tropsch Synthesis

The chemical process now known as Fischer−Tropsch synthesis was first explored in the 1920s by the German chemists Franz Fischer and Hans Tropsch[22] and was originally developed as a means of converting CO from coal into liquid hydrocarbons that could be used as fuels and lubricants. Although limited in scale relative to conventional oil production, Fischer−Tropsch synthesis continues to be used to produce hydrocarbons in various industrial plants located around the world. Historically, the process has not generally been economically viable, but rising oil demands and prices may make its use more widespread in the future, stimulating continued scientific research on FTS and related reactions.

The Fischer−Tropsch process involves the conversion of CO into organic compounds through sequential reduction and polymerization of carbon on the surface of a solid catalyst.[23,24] Over the years, a number of different mechanisms for the FTS reaction mechanism have been proposed, and, although there continues to be debate over some of the finer points, there is general consensus that the process involves the basic steps outlined in Figure 2. The reaction is initiated

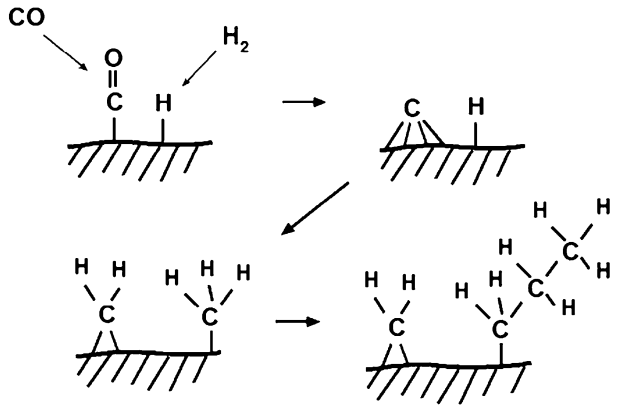


**Figure 2.** Generalized reaction mechanism for Fischer−Tropsch synthesis of hydrocarbons. The reaction is initiated with binding of CO to the catalyst surface to form a carbonyl unit, which then undergoes sequential reduction to surface-bound carbide, methylene, and methyl groups. Chain growth occurs as methylene groups polymerize to one another and terminates when the growing chain combines with a methyl group or surface-bound H rather than another methylene.

when a CO molecule binds to the catalyst surface to form a carbonyl group. The carbonyl then undergoes sequential reduction to form a surface-bound carbide and then methylene ($-CH_{2-}$), which, in some cases, undergoes further reduction to a methyl group ($-CH_3$). Polymerization of methylene groups leads to C−C bond formation and production of alkyl chains. Chain growth terminates when the alkyl chain bonds with a methyl group or surface-bound H rather than an additional methylene, releasing the compound from the surface. Formation of so-called "oxygenates" (alcohols, carboxylic acids, etc.) occurs when the growing alkyl chain terminates by combining with surface-bound carbonyl or OH groups.

Because of the nature of the reaction mechanism, FTS produces a characteristic suite of organic compounds. Chain growth by polymerization, for example, produces almost

exclusively linear alkyl chains, with little branching. As a consequence, FTS products are dominated by methane and a homologous series of normal alkanes (e.g., Figure 3).

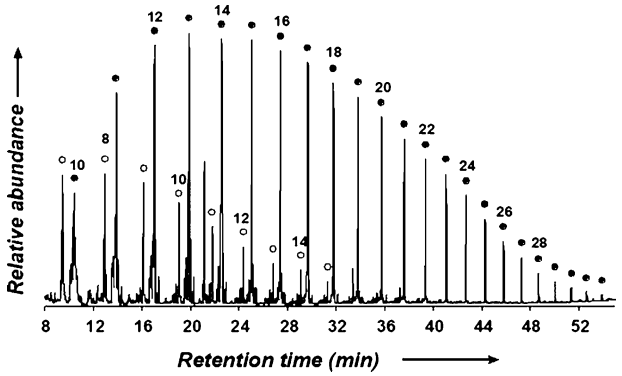


**Figure 3.** Typical nonvolatile reaction products of Fischer–Tropsch-type organic synthesis. The figure shows a total ion chromatogram from gas chromatography/mass spectrometry analysis. The major peaks in the chromatogram correspond to a homologous series of linear saturated hydrocarbons (*n*-alkanes; ●) and alcohols (*n*-1-alkanols; ○). Numbers indicate the carbon chain length of the compounds (only even number of peaks labeled).

Alkenes are typically produced in relatively minor quantities, although ethene and propene may be produced in relatively high abundance under some conditions. Oxygenates (primarily *n*-1-alkanols and *n*-alkanoic acids) are generally produced in lower abundance than hydrocarbons of the same carbon number, although some industrial applications have been developed to optimize the production of acetic acid and ethanol. Other classes of organic compounds, including alkenones, alkanals, and hydroxy acids, are also generated in the process, but in relatively low quantities.

Although CO is primarily used as the carbon source for industrial applications, FTS will also proceed with $CO_2$. Presumably, the first stage in FTS with $CO_2$ as the carbon source involves production of CO through reversal of the so-called "water–gas shift reaction":

$$CO_2 + H_2 \leftrightarrow CO + H_2O \quad (5)$$

Synthesis then proceeds with binding of CO to the catalyst surface (Figure 2).

The relative abundance of reaction products in FTS follows a log-linear decrease in abundance with increasing number of carbon atoms in the alkyl chain, which is commonly known as the Schulz–Flory or Anderson–Schulz–Flory (ASF) distribution[23,24] (Figure 4). The ASF distribution is typical of polymerization processes and arises from the relative probabilities that the growing alkyl chain will bond with an additional methylene group versus some chain-terminating moiety (e.g., methyl, H, OH). The slope of the log-linear relationship, often referred to as the chain growth probability factor ($\alpha$), varies for different catalysts, with some catalysts favoring the production of short-chain products (high $\alpha$) and others favoring longer-chain products (lower $\alpha$).[23,24] In practice, the shorter compounds (i.e., methane and $C_2$–$C_4$ hydrocarbons) often deviate somewhat from the ideal ASF distribution. In addition, product distributions often exhibit a "kink", where longer-chain products have a higher probability for chain growth than the shorter compounds[25–27] (Figure 4). The reason for the kink in product distributions is not well understood, but may be related to the decreased

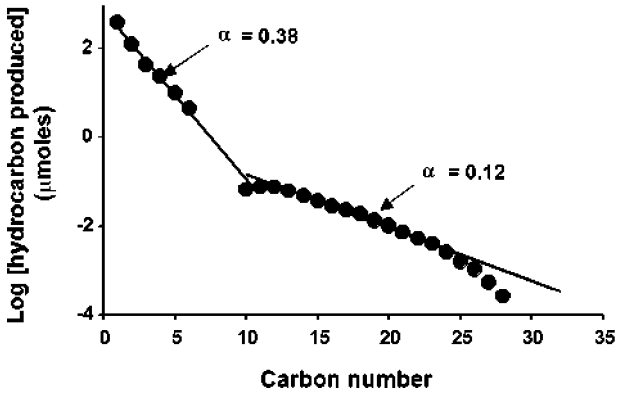


**Figure 4.** Relative abundances of saturated hydrocarbons of different carbon number generated during experimental Fischer–Tropsch-type synthesis (note log scale on vertical axis). In this example, abundances of $C_{10}$ and $C_{11}$ hydrocarbons reflect partial loss of these compounds during sample treatment, and data are unavailable for $C_7$–$C_{10}$ compounds. Data from ref 27.

volatility of longer-chain reaction products or to formation on different catalytic sites.[28,29]

A log-linear decrease in abundance with increasing carbon chain length (i.e., the ASF distribution) has frequently been used as a diagnostic feature for an abiotic origin of hydrocarbon gases. However, it is important to note that thermogenic natural gases often have the same distribution. In the petroleum literature, a log-linear relationship for the relative abundance of thermogenic hydrocarbons is sometimes referred to as the "Kissin slope".[30] A log-linear distribution among hydrocarbons beyond methane would also be attained at thermodynamic equilibrium. Thus, while a log-linear distribution of hydrocarbons may be consistent with formation of hydrocarbons by abiotic synthesis, it is not a characteristic that can be used to distinguish an abiotic origin from thermogenic sources.

## 3.2. Experimental Studies of Fischer–Tropsch-type Synthesis under Hydrothermal Conditions

Because of their use in industrial applications, Fischer–Tropsch synthesis and related chemical processes have been the subject of extensive experimental study (see Anderson[23] and Dry[24] for comprehensive reviews of FTS research). Indeed, a search of the scientific literature reveals several hundred published research papers on this subject in the past decade alone. Unfortunately, the vast majority of this literature is of limited use in interpreting the potential for abiotic synthesis in natural systems because experimental FTS studies are usually performed under conditions with no clear relationship to geologic environments. For example, Figure 5 shows a typical "fluidized bed reactor" employed in many industrial Fischer–Tropsch applications. In this apparatus, a gas with high $H_2$:CO ratio (usually 2–3:1) is bubbled through a liquid (typically molten wax) containing a suspended synthetic catalyst, such as RuO precipitated onto alumina. It is apparent that difficulties are likely to be encountered in translating the results of experiments conducted in this type of apparatus to a geologic environment, such as a deep-sea hydrothermal system, where the fluid medium is water, aqueous $CO_2$ rather than CO gas is the primary carbon source, exotic catalysts like RuO are very rare or absent, and other compounds are present that might interfere with catalyst activity or surface properties.

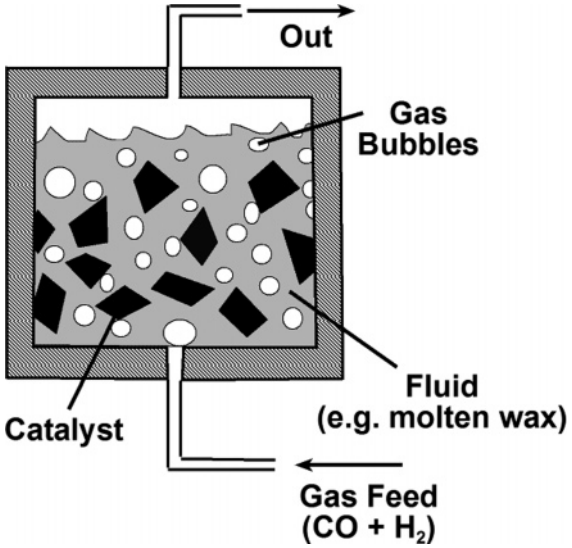


**Figure 5.** Schematic drawing of fluidized bed reactor employed in many industrial FTS applications.

Although there are a number of differences between the conditions present in natural geologic environments and those employed in industrial FTS experiments, three factors are likely to be of particular concern in evaluating potential environments for abiotic synthesis: (1) the presence of water, (2) the nature of potential mineral catalysts, and (3) the presence of high abundances of sulfur compounds. Industrial Fischer−Tropsch syntheses are usually performed with dry gases as the reactants, although small amounts of water are generated as a byproduct of the process through reactions such as:

$$CO + 3H_2 \rightarrow CH_4 + H_2O \quad (6)$$

Results of the relatively few experimental FTS studies that have been performed with water vapor as a component of the feed gas have shown that yields and catalytic activity generally decrease with increasing water activity,[29,31] although this is not always found to be the case.[32] Reasons for the decreased productivity in these experiments are not always clear, but it appears that recrystallization of the catalyst may be involved.

Of course, water is a ubiquitous component of deep-sea hydrothermal systems, so the effect of water on FTS is an important consideration in evaluating abiotic synthesis in these environments. At various locations in the system, water may be present in a wide range of states that includes relatively low-density vapors to higher density liquids. In hydrothermal environments where water is present as a liquid, the state of the carbon source becomes another factor for consideration, because inorganic carbon will be present primarily as dissolved $CO_{2(aq)}$ or $HCO_3^-$ instead of CO or $CO_2$ gas. Because industrial FTS is performed exclusively with gas-phase CO or $CO_2$, the potential for aqueous reactants to undergo synthesis reactions has gone unstudied until recently.

Nearly all industrial FTS applications employ transition metal catalysts, particularly native metals or oxides of Co, Fe, and Ru. The catalyst is typically doped with a few percent of a "promoter", such as $K_2O$ or other alkali oxides, because these impurities improve performance. The catalyst is then precipitated onto a "support" such as alumina, silica, or "kieselguhr" (diatomaceous earth). Most catalysts employed are synthetic and have no natural analogue. The only common naturally occurring mineral regularly employed in industrial FTS applications is magnetite. Several studies have shown, however, that the actual active catalytic sites for FTS when using magnetite are pockets of native Fe and/or Fe-carbides that form on the mineral surface under extremely reducing conditions, rather than the magnetite itself.[25,26,33] For industrial applications, magnetite is usually conditioned prior to use ("fused") by heating in a stream of $H_2$ or CO to create these catalytic sites. It remains unclear whether magnetite precipitated in natural environments would have the same catalytic capacity as treated industrial catalysts. Nevertheless, magnetite is frequently cited as a likely catalyst for FTT syntheses in natural systems.

A third issue relevant to the study of FTS in deep-sea hydrothermal environments concerns the frequent presence of high abundances of sulfur compounds. It is a general rule of thumb that sulfur "poisons" Fischer−Tropsch catalysts, particularly those containing iron,[23,24] although some experimental studies have shown that small amounts of sulfur may actually increase the activity of certain catalysts.[34,35] The exact reason for the negative effects of sulfur has apparently not been explored in detail, but it is likely that reaction with sulfur forms solids on the catalyst surface that interfere with the FTS reaction. It remains unclear to what extent sulfur may affect the catalytic potential of minerals in deep-sea hydrothermal systems, but it has been argued that the presence of sulfur may preclude any significant abiotic synthesis in these environments.[36,37]

The recognition that industrial studies may not be completely applicable to natural environments has recently inspired a few researchers to begin examining FTS under conditions more directly applicable to submarine hot-springs. However, the number of studies that have been performed thus far to understand the behavior of organic compounds in hydrothermal systems remains only a small fraction of the number conducted to investigate inorganic aspects of fluid−rock interactions in these environments. Before proceeding with a discussion of these studies, a brief note on experimental methodology is in order (readers interested in a more in-depth discussion of hydrothermal experimental approaches are directed to the recent review by Holm and Andersson[11]). Experimental studies of FTT synthesis in hydrothermal conditions have generally employed two types of reaction system. The first type are fixed-volume reaction vessels, where reactants together with water are placed into a vessel and heated in a furnace for a certain amount of time, after which the vessel is opened and the products analyzed. The vessels are usually constructed of stainless steel, and experiments are performed with a vapor headspace above the aqueous solution. These conditions often present some problems for data interpretation, because it is difficult to determine whether reactions took place in the aqueous or vapor phases, and the reactor walls can catalyze the reactions under study. However, the reactors are inexpensive and simple to use, and so remain useful in experimental studies despite these limitations.

A second, somewhat more sophisticated, experimental approach has also been employed in which the reactants (aqueous solution, solvents, etc.) are placed inside a flexible reaction cell enclosed within a pressure containment vessel[38] (Figure 6). Typically, the flexible cell is constructed of gold and oxidized titanium, which appear to be noncatalytic for abiotic synthesis reactions. This apparatus provides two

of abiotic $CH_4$ that can contribute to the chemistry of mid-ocean ridge hydrothermal vent fluids, provided that fluids circulating in these deeper portions of the crust interact with those venting at the seafloor. Presently, the extent to which convecting hydrothermal fluids interact with gabbros in crustal layer 3 is poorly constrained, precluding a quantitative assessment of plutonic rocks as an abiotic $CH_4$ source to MOR hot-spring fluids.

Because the chemistry of hydrothermal vent fluids reflects the integrated effects of many different chemical processes occurring over a spectrum of temporal and spatial scales as the fluids circulate through the ocean crust, it is difficult at present to firmly establish the chemical and physical conditions that may be responsible for abiotic $CH_4$ production in the subsurface. One thing that seems clear, however, is that abiotic formation of $CH_4$ is not actively occurring in the majority of MOR vent fluids as they ascend and vent at the seafloor. A thermodynamic assessment of observed volatile abundances reveals that the amount of $CH_4$ present in vent fluids exceeds the amount that is thermodynamically stable for the measured concentrations of $CO_2$ and $H_2$, at observed vent temperatures (Figure 20). In other words, there is no thermodynamic drive for the reduction of $CO_2$ to $CH_4$ at the conditions of venting. Instead, there is an excess of $CH_4$ relative to equilibrium with $CO_2$, indicating that it should be decomposing in this part of the system. Exceptions to this trend are fluids from the Rainbow and Logatchev vent fields where high $H_2$ concentrations produced by serpentinization of olivine create a thermodynamic drive for the reduction of $CO_2$ to $CH_4$ at the measured vent temperatures (Figure 20). Within the context of a model involving reaction of $CO_2$ to $CH_4$ during convective circulation of seawater-derived hydrothermal fluids through the crust, carbon isotope equilibration temperatures point to $CH_4$ synthesis at temperatures substantially higher than measured for the venting fluid, even for the serpentinite-hosted systems. Because of a substantial decrease in the stability of $CH_4$ relative to $CO_2$ with increasing temperature (Figure 1), $CH_4$ formation in hydrothermal vent fluids at temperatures >400 °C would require $H_2$ concentrations that are several orders of magnitude greater than measured at the time of venting. If this were the case, the chemistry of hydrothermal vent fluids would not accurately reflect peak metamorphic conditions experienced during convective circulation.

**Figure 20.** Comparison of measured aqueous $CH_4$ concentrations in high-temperature vent fluids (>300 °C) with values predicted for measured concentrations of $CO_2$ and $H_2$ and temperature assuming chemical equilibrium according to reaction 4. The solid line indicates a 1:1 relationship. Measured values greater than those predicted for equilibrium indicate that there is an excess of $CH_4$ relative to equilibrium and thus no thermodynamic drive for the reduction of $CO_2$ to $CH_4$ at venting conditions.

Although at first glance the isotopic composition of coexisting $CH_4$ and $CO_2$ in vent fluids points to a high temperature origin, the possibility of formation in the down-welling limb of a hydrothermal system at temperatures less than those observed during venting warrants serious consideration. In particular, substantially longer residence times in recharge zones and large increases in the thermodynamic stability of $CH_4$ relative to $CO_2$ with decreasing temperature may enhance abiotic $CH_4$ formation. A key question for such a model is whether low-temperature generation of $CH_4$ during recharge can be reconciled with the isotopic composition of $CH_4$ and $CO_2$ observed in vent fluids. Proskurowski et al.[77] demonstrated that >85% of the carbonate species initially present in seawater source fluids is removed during hydrothermal circulation in the basalt-hosted Endeavor hydrothermal system. Thus, the relatively low concentrations of $CH_4$ observed in many basalt-hosted systems may form from a reservoir of carbonate species that is substantially smaller than that present in seawater. In a closed-system, mass balance constraints require that the $\delta^{13}C$ value of abiotic $CH_4$ increase with reaction progress, and must eventually approach the composition of the starting $CO_2$. Accordingly, variable but substantial amounts of low-temperature reduction of a diminished carbonate pool in down-welling seawater is consistent with the large range of $\delta^{13}C$ values for $CH_4$ that in some cases are depleted relative to marine carbonate (~0‰) by as little as 8‰ (Table 1). Such a scenario implies that the high level of magmatic $CO_2$ observed in vent fluids is added after abiotic synthesis during recharge and has never been in a state of chemical or isotopic equilibrium with coexisting $CH_4$. This would further imply that the isotopic signatures of $CO_2$ and $CH_4$ are decoupled and the apparent high-temperature isotopic equilibrium temperatures are coincidental. Late stage addition of $CO_2$ is consistent with models of convective circulation in which down-welling fluids approach a magmatic heat (and $CO_2$) source just prior to rapid ascent and venting at the seafloor.

Additional perspective in evaluating possible abiotic contributions to the light hydrocarbons in deep-sea hydrothermal systems can be gained by examining hydrocarbon gases from other geologic systems that are also proposed to have an abiotic origin. A number of studies have identified methane with an apparent abiotic origin in crystalline igneous rocks[78−83] and in continental serpentinites.[84,85] In some cases only methane is identified, but in others the methane is accompanied by other hydrocarbons including ethane and propane. These gases occur in geologic settings where significant contributions from thermogenic and biogenic sources appear unlikely. However, the criteria used to support an abiotic origin often include a distinctive isotopic signature. Many of the gases have isotopic signatures that are enriched in $^{13}C$ and depleted in $^{2}H$ relative to typical thermogenic and biogenic gases (Figure 18).

In recent years, gases sampled from a number of crystalline rocks have been shown to follow a carbon isotopic trend for the light hydrocarbons ($C_1$–$C_4$) that is the reverse of that typically observed for thermogenic natural gases.[80−83] That is, whereas thermogenic gases generally become enriched in $^{13}C$ with increasing carbon number ($\delta^{13}C_1 < \delta^{13}C_2 < \delta^{13}C_3$

$< \delta^{13}C_4$), these gases become lighter with increasing number of carbons ($\delta^{13}C_1 > \delta^{13}C_2 > \delta^{13}C_3 > \delta^{13}C_4$). The reversed trend has been attributed to abiotic polymerization reactions that favor the incorporation of $^{12}C$ (ref 80). For instance, Des Marais et al.[63] reported that light hydrocarbons with a reversed C isotopic trend were produced by polymerization of methane gas in a spark discharge experiment. A partially reversed isotopic trend is also observed for light hydrocarbon gases of extraterrestrial origin in the Murchison meteorite,[86] providing additional support that this trend can be generated by abiotic processes in natural systems.

At the same time, however, it must be noted that light hydrocarbons with complete or partial carbon isotope reversals are frequently found in sedimentary basins where they coexist with gases that have more typical thermogenic isotope trends. In these environments, the reversed isotopic trends have been interpreted as originating from conventional thermogenic natural gases though processes such as mixing, microbial inputs, or diffusion through caprocks.[87,88] Furthermore, Du et al.[89] have shown that reversed carbon isotope trends in light hydrocarbon gases can be generated from thermal maturation of biologically derived condensed organic matter under some circumstances, although the mechanism for the reaction has not been determined. Consequently, at the present time it does not appear that a reversed isotopic trend is a characteristic that can uniquely identify an abiotic source for light hydrocarbon gases.

Sherwood Lollar et al.[80,81] have reported hydrocarbon gases in crystalline rocks from deep mines in the Canadian Shield and in South Africa that, in addition to having a reversed carbon isotopic trend, are also strongly depleted in $^2H$ relative to typical thermogenic gases (i.e., $\delta^2H = -430$ to $-230$‰ vs $-220$ to $-130$‰ for typical thermogenic gases). The authors postulated that such large depletions in $^2H$ are the result of polymerization reactions and suggested an abiotic origin for these gases. Although $^2H$ depletions during abiotic synthesis are yet to be demonstrated during laboratory experiments, the occurrence of $^2H$-depleted hydrocarbons with a reversed carbon isotopic trend in crystalline rocks with no apparent thermogenic sources provides persuasive evidence that the gases have an abiotic origin.

To date, there have been no isotopic measurements of hydrocarbons other than methane from deep-sea hydrothermal systems that can be used to test whether they conform to these presumptive abiotic trends. Des Marais et al.[63] found that light hydrocarbons in continental hydrothermal systems at Yellowstone followed a typical thermogenic trend and therefore concluded that they were derived from thermal decomposition of organic matter within the hydrothermal system rather than abiotic synthesis. Further research and measurements along these lines is a promising approach to assess the contribution of abiotic synthesis to hydrocarbons in deep-sea hydrothermal systems.

Few studies have attempted to determine the possible contribution of abiotic sources to more complex organic compounds in hydrothermal settings. However, Holm and Charlou[16] extracted and analyzed organic compounds in high-temperature hydrothermal fluids from a serpentinite-hosted hydrothermal vent at Rainbow, and, although levels were very low, they were able to identify a series of linear saturated hydrocarbons (*n*-alkanes) with 16−29 carbons. Because these compounds resemble those that typically dominate the nonvolatile fraction of organic products generated during Fischer−Tropsch synthesis, the authors proposed that the compounds might have been abiotic in origin. On the other hand, Simoneit et al.[90] investigated organic compounds in hydrothermal chimneys at the same site, and, while they observed the organic extracts of the chimney minerals to be similarly dominated by *n*-alkanes, these hydrocarbons were accompanied by other compounds with a clear biological origin as well as polycyclic aromatic hydrocarbons that are typically produced during high-temperature thermogenic processes. Thus, they concluded that the organic matter in the chimneys was largely derived from biological inputs and pyrolysis of bioorganic matter within the chimney or in deeper parts of the system. If abiotic synthesis products were present in the chimneys, they were obscured by more abundant compounds derived from these other sources. The results of Simoneit et al.[90] for the Rainbow system are similar to those previously reported for mineral deposits in basalt-hosted hydrothermal systems.[69,91]

## 5. Concluding Remarks

The high abundance of methane in high-temperature hydrothermal fluids and fluid inclusions, its isotopic composition, and experiments demonstrating abiotic synthesis under hydrothermal conditions suggest that abiotic methane is present in deep-sea hydrothermal fluids and may even represent the dominant source in many systems, particularly those hosted in serpentinites. The possible contribution of abiotic synthesis to more complex organic matter, however, is less clear. While hydrocarbons and other organic compounds have been observed in hydrothermal fluids and associated mineral deposits, criteria that can be used to differentiate the abiotic compounds from those derived from other sources have not yet emerged. Experimental studies have shown that light hydrocarbons and more complex compounds can be synthesized under certain hydrothermal conditions, while other experiments conducted under similar conditions have failed to produce organic compounds except for methane. It is not yet clear what factors control whether or not synthesis can proceed, making it difficult at this time to identify with certainty those environments within natural hydrothermal systems where abiotic synthesis might be occurring.

Some additional observations could significantly improve understanding of abiotic synthesis in hydrothermal environments. First, more comprehensive analyses of the organic composition of vent fluids and mineral deposits would be helpful. To date, organic analyses of vent fluids in unsedimented systems have been largely limited to methane, and measurements of other compounds would provide additional constraints to evaluate possible abiotic contributions. Isotopic measurements of these compounds are prospectively very useful, given that abiotic organic compounds from other environments appear to exhibit identifiable isotope trends. Second, further experimental studies are required to understand the range of conditions that allow for abiotic synthesis in hydrothermal environments. These experiments should include isotopic analysis of reactants and products to more clearly define the isotopic composition of abiotically synthesized compounds.

Achieving these research objectives will present significant challenges to future researchers. For example, the low abundance of many organic compounds in the highly saline and $H_2S$-rich vent fluids requires development of sampling and analytical methods beyond the capabilities of those currently employed in deep-sea research. From an experimental perspective, the presence of significant levels of

background carbon in natural minerals makes experimental study of isotopic fractionation problematic for hydrothermal conditions where yields of abiotic compounds may be low. Nevertheless, overcoming these challenges will be required to make more precise assessments of the potential contributions of abiotic synthesis to the organic matter of hydrothermal systems.

## 6. Acknowledgments

Our experimental research into abiotic organic synthesis has been supported by the National Science Foundation Earth Science and Ocean Science Directorates through the Chemical Oceanography, Marine Geology and Geophysics, Petrology and Geochemistry, and RIDGE2000 programs.

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CR0503660