

Abiotic Synthesis of Organic Compounds in Deep-Sea Hydrothermal Environments

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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

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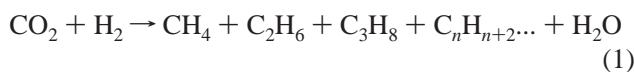
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can be generated by more than one process. Common examples include methane and acetate, which can form as a byproduct of microbial metabolism, during thermal decomposition of bioorganic matter, or by abiotic processes such

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 biogenic 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 CO₂ (or other inorganic carbon sources such as CO and HCO₃[−]) by H₂ produced during fluid–rock interactions. This overall process can be expressed by the general reaction:

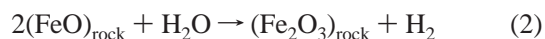


In natural hydrothermal systems, of course, other reactants are likely to be involved (H₂S, NH₃, etc.) and might produce a greater variety of organic products than indicated in this reaction (carboxylic acids, amino acids, organosulfur compounds, etc.). However, discussion of abiotic synthesis in deep-sea hydrothermal systems has focused mostly on methane and simple hydrocarbons because they occur at relatively high aqueous concentrations that facilitate quantitative analysis.

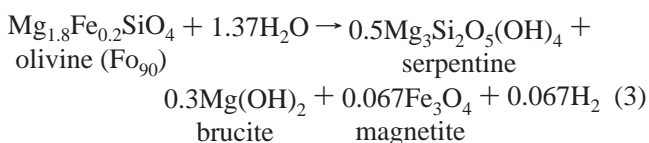
Because they are the most abundant and well-studied organic compounds in deep-sea hydrothermal fluids, this review primarily covers the potential for abiotic synthesis of hydrocarbons and discusses recent laboratory experimental studies designed to evaluate abiotic organic synthesis under hydrothermal 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 H₂ 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 H₂. The process can be represented by the general reaction:



where (FeO)_{rock} refers to the ferrous component of igneous minerals and (Fe₂O₃)_{rock} refers to the ferric component of Fe-bearing alteration products. For example, H₂ generation during serpentinization of olivine, the predominant mineral in ultramafic rocks that are common in the oceanic lithosphere, can be expressed as:



The H₂-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 H₂ 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 H₂ 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 H₂ 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 H₂ 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
δ ¹³ C _{CO₂} (‰)	~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
δ ¹³ C _{CH₄} (‰)		-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
δ ² H _{CH₄} (‰)			-109							-102/-126	-99 to -141
CO (μM)	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>i</i> -butane (nM)								4.1			
<i>n</i> -butane (nM)								5.7			
<i>T</i> _{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 CO₂ and CH₄ assuming isotopic equilibrium using the CO₂-CH₄ 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.

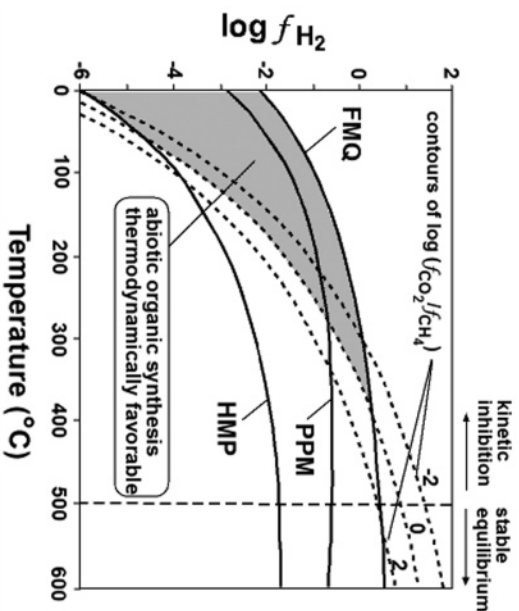
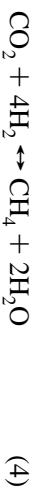


Figure 1. Diagram illustrating mineral-buffered oxidation states, expressed as the fugacity of H₂(*f*_{H₂}) and carbon speciation as a function of temperature. Curves labeled FMQ (fayalite–magnetite–quartz), PPM (pyrite–pyrrhotite–magnetite), and HMP (hematite–magnetite–pyrite) correspond to the oxidation state that would be attained at thermodynamic equilibrium in geologic systems buffered by these mineral assemblages. Dotted lines reflect equilibrium ratios of CO₂ to CH₄ 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:



strongly favors CO₂ at oxidation states buffered by naturally occurring mineral assemblages (Figure 1). Thus, hydrothermal fluids that have equilibrated at high temperatures should be dominated by CO₂ with trace quantities of CH₄. As temperatures decrease, however, CH₄ stability dramatically increases, creating a strong thermodynamic drive for the reduction of CO₂ 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 Tropsch²² 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

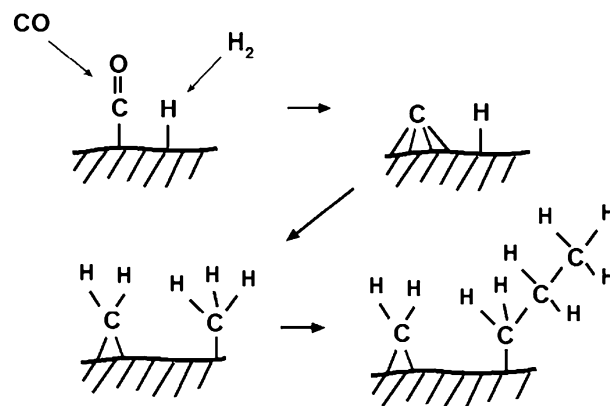


Figure 2. Generalized reaction mechanism for Fischer–Tropsch synthesis of hydrocarbons. The reaction is initiated with binding of CO to the catalyst surface to form a carbonyl unit, which then undergoes sequential reduction to surface-bound carbide, methylene, and methyl groups. Chain growth occurs as 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).

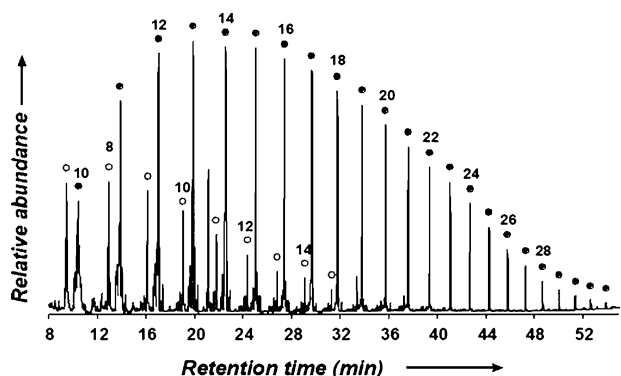
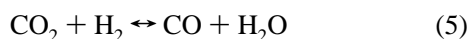


Figure 3. Typical nonvolatile reaction products of Fischer–Tropsch-type organic synthesis. The figure shows a total ion chromatogram from gas chromatography/mass spectrometry analysis. The major peaks in the chromatogram correspond to a homologous series of linear saturated hydrocarbons (*n*-alkanes; ●) 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 CO₂. Presumably, the first stage in FTS with CO₂ as the carbon source involves production of CO through reversal of the so-called “water–gas shift reaction”:



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 (α), varies for different catalysts, with some catalysts favoring the production of short-chain products (high α) and others favoring longer-chain products (lower α).^{23,24} In practice, the shorter compounds (i.e., methane and C₂–C₄ 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

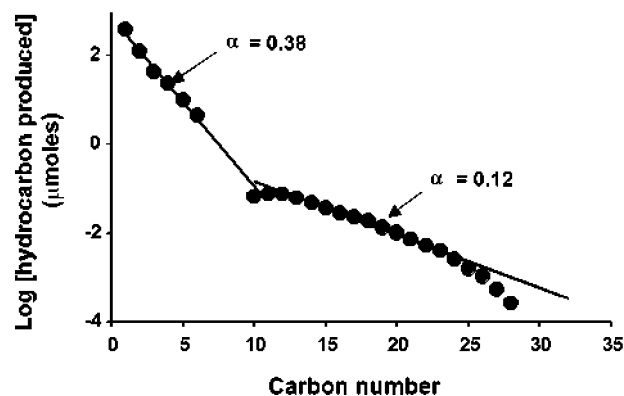


Figure 4. Relative abundances of saturated hydrocarbons of different carbon number generated during experimental Fischer–Tropsch-type synthesis (note log scale on vertical axis). In this example, abundances of C₁₀ and C₁₁ hydrocarbons reflect partial loss of these compounds during sample treatment, and data are unavailable for C₇–C₁₀ 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 Anderson²³ and Dry²⁴ 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 H₂: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 CO₂ 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.

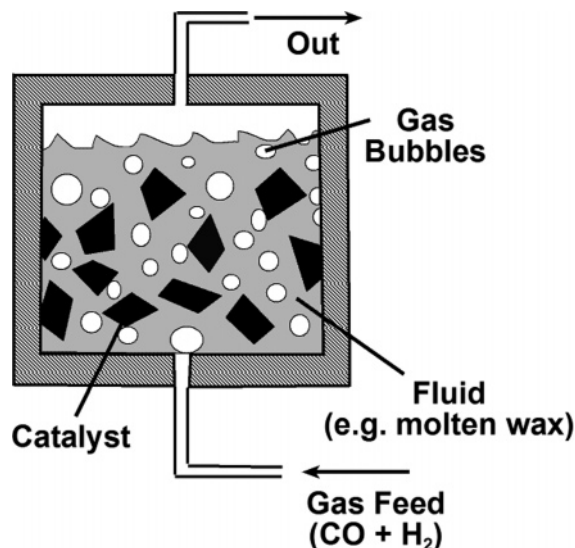
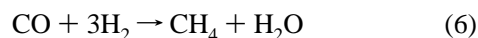


Figure 5. Schematic drawing of fluidized bed reactor employed in many industrial FTS applications.

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:



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 $\text{CO}_{2(\text{aq})}$ 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 FTS 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 Andersson¹¹). Experimental studies of FTS 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 vessel³⁸ (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

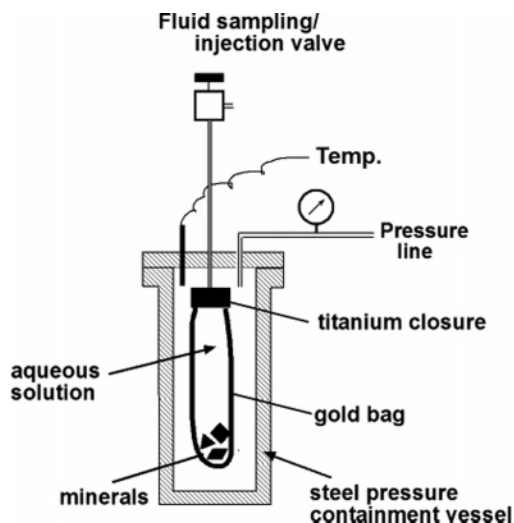


Figure 6. Schematic drawing of flexible-cell reaction system employed in many hydrothermal experiments.

distinct advantages for experimental hydrothermal studies. First, external pressure applied to the flexible reaction cell allows experiments to be performed without a vapor head-space, ensuring all reactants are present as dissolved compounds. Second, attachment of a sampling valve to the reaction cell allows samples of the fluid to be obtained over time so that progress of the reactions can be monitored. While this apparatus has certain advantages, it is also expensive as well as somewhat difficult and time-consuming to operate, providing some limitations on its utility in experimental studies.

In one of the first experimental attempts to examine abiotic organic synthesis at conditions that more closely approximate those of deep-sea hydrothermal systems, Berndt et al.¹⁴ reacted an aqueous bicarbonate-bearing solution with olivine at elevated temperature and pressure (300 °C, 50 MPa) in a flexible-cell system, and monitored production of H₂ and light hydrocarbons over time (Figure 7). As noted earlier,

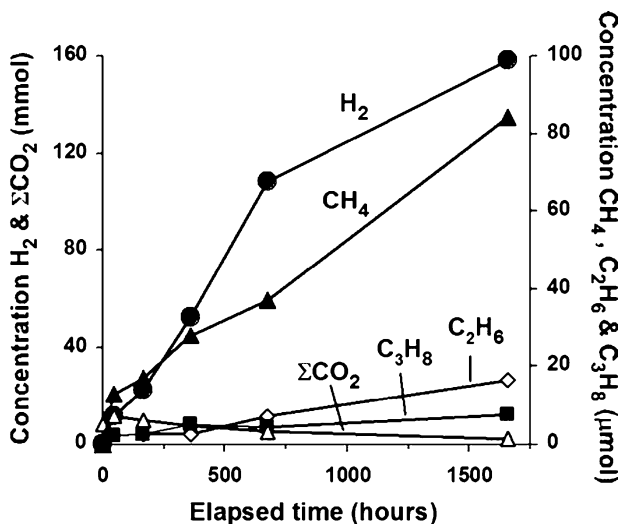


Figure 7. Dissolved concentrations of H₂, ΣCO₂, and light hydrocarbons during reaction with serpentinized olivine in the experimental study of Berndt et al.¹⁴

serpentinization of olivine-rich ultramafic rocks is thought to produce particularly favorable environments for abiotic organic synthesis because of the strongly reducing conditions that develop during alteration (reaction 3). As the experiment

proceeded, serpentinization of the reactant olivine generated high concentrations of H₂ in solution, reaching 158 mmol/kg after 69 days (Figure 7). Gradual accumulations of micromolar concentrations of aqueous methane, ethane, and propane over the course of the experiment were interpreted by the authors to be products of dissolved bicarbonate reduction by Fischer–Tropsch synthesis. Magnetite formed during the serpentinization process was suggested as the active catalyst. Berndt et al. also reported the presence of bi-lobed, carbonaceous particles among the solid reaction products that were also interpreted to be high-molecular weight products of FTT synthesis, but these particles were subsequently identified as pine pollen that was inadvertently introduced into the reaction products during sample handling.³⁹

The results of Berndt et al. initially appeared to indicate that naturally formed magnetite could serve as an effective Fischer–Tropsch catalyst and that the process could take place in aqueous conditions with a dissolved carbon source. The conclusions of their study, however, were called into doubt in a subsequent set of experiments by McCullom and Seewald.⁴⁰ In their study, the experiment of Berndt et al. was repeated, but with the carbon source replaced with ¹³C-labeled bicarbonate (H¹³CO₃⁻) that allowed the source of carbon in organic reaction products to be traced. Although yields of H₂ as well as C₁–C₃ hydrocarbons in the experiment were similar to those previously reported by Berndt et al., isotopic analysis of the products indicated that only a small fraction of the methane generated had incorporated the ¹³C label, and none of the ethane and propane was labeled. This result indicated that, except for a small fraction of methane, the hydrocarbons generated in the experiment were not the product of reduction of dissolved bicarbonate, but were instead generated from thermal decomposition of organic matter already present in the reactants at the start of the experiment. Consequently, the potential for abiotic synthesis of hydrocarbons during serpentinization under the experimental conditions is substantially more limited than had been indicated by the previous results.

Similar results were observed in a further series of experiments conducted by McCullom and Seewald.⁴¹ In a set of three experiments, aqueous solutions containing elevated concentrations of H₂ and a ¹³C-labeled carbon source (¹³CO₂, H¹³CO₃⁻, and/or H¹³COOH) were heated in the presence of mineral substrates at 175–260 °C, 35 MPa for prolonged periods (250 to >6000 h). Minerals included in the three experiments were: (1) NiFe-alloy plus magnetite, (2) olivine that underwent alteration to serpentine, brucite, magnetite, and trace chromite (reaction 3), and (3) magnetite plus hematite. In the experiments, reduction of bicarbonate to formate was found to proceed rapidly even at temperatures of 175 °C. However, further reduction to hydrocarbons, as monitored by the production of ¹³C-labeled reaction products, was limited to formation of small amounts of methane in the NiFe-alloy/magnetite experiment and was not observed in the other experiments. Although micromolar concentrations of ethane and propane were produced in each of the experiments, none of the ¹³C from the dissolved carbon sources was observed in these compounds, indicating that they were derived from thermal decomposition of background organic matter present at the start of the experiment rather than abiotic organic synthesis. Methane generated from background sources was also observed in each of the experiments.

The results of McCollom and Seewald^{40,41} introduced a couple of important concepts into the experimental study of abiotic synthesis of organic compounds under hydrothermal conditions. First, minerals and other reactants employed in abiotic synthesis experiments can release significant quantities of background organic compounds that can be easily mistaken for synthesis products, particularly under conditions where yields of abiotic products may be low or nonexistent. Accordingly, it is critical in experimental studies to ascertain the levels of background contributions before concluding that reaction products are formed by abiotic synthesis. Conversely, experimental studies of abiotic synthesis yielding small amounts of organic products should be viewed with some degree of skepticism if the possible contribution from background has not been assessed. Second, use of ¹³C-labeled carbon sources is a straightforward and effective means of differentiating between bona fide synthesis products and compounds from background sources.

Because of the absence of synthesized compounds containing more than one carbon during their experiments, McCollom and Seewald⁴¹ speculated that the aqueous environment might prevent formation of C–C bonds from dissolved reactants. Soon afterward, however, Foustoukos and Seyfried⁴² showed that abiotic synthesis of ethane and propane could in fact proceed under hydrothermal conditions by reacting an aqueous solution containing ¹³CO₂ and H¹³CO₃[−] at 390 °C and 40 MPa in the presence of either chromite (FeCr₂O₄) plus magnetite or magnetite alone in a flexible-cell reaction system. Production of ¹³CH₄ and ¹³C₃H₈ at micromolar levels demonstrated that these compounds were synthesized in the experiment (Figure 8). The authors

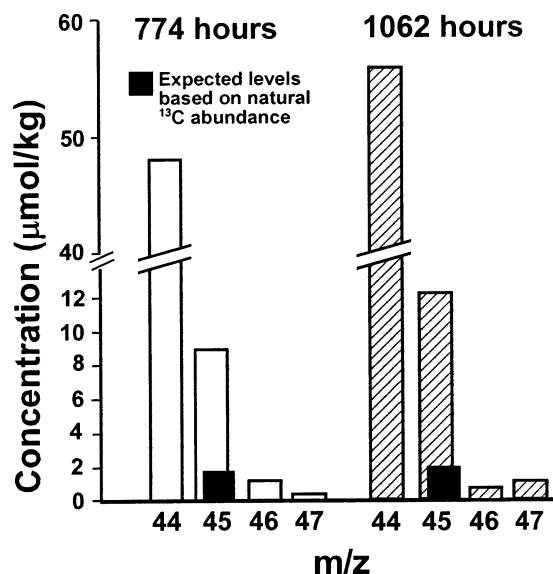


Figure 8. Isotopic measurements of propane formed during hydrothermal reaction of ¹³CO₂ in the presence of chromite plus magnetite in an experiment by Foustoukos and Seyfried.⁴² Shown are measured abundances of propane with mass/charge ratios (*m/z*) of 44, 45, 46, and 47, corresponding to molecular ions for ¹²C₃H₈, ¹²C₂¹³CH₈, ¹²C¹³C₂H₈, and ¹³C₃H₈, respectively. ¹³C-bearing compounds represent products synthesized of reduction of ¹³CO₂ during the experiments, while ¹²C is derived from background sources of organic matter. The black bar represents the amount of ¹²C¹³CH₈ expected for natural abundances of ¹³C based on the abundance of ¹²C₃H₈.

attributed their production to FTT synthesis that was catalyzed by the minerals included in the reaction vessel. Partially labeled compounds were also observed (¹²C¹³CH₆

and ¹²C₂¹³CH₈), indicating that background carbon sources participated in some synthesis reactions, perhaps from incorporation of residual unlabeled alkyl groups present on the surfaces of the reactant minerals at the start of the experiment.⁴²

On the basis of the observation that labeled hydrocarbon production was ~70% slower in the experiment without chromite (i.e., magnetite only), Foustoukos and Seyfried⁴² concluded that hydrocarbon formation was more effectively catalyzed by chromite relative to magnetite. However, alternative interpretations of the data are also possible, because the substantially higher in situ pH (8.8 vs 4.8) and lower aqueous H₂ during the chromite-free experiment may have influenced fluid speciation and reaction kinetics, especially for aqueous carbonate species. Accordingly, the relative catalytic roles of magnetite and chromite during these experiments are presently unclear. In the absence of unequivocal evidence to support a surface-catalyzed reaction mechanism, other synthesis mechanisms such as homogeneous CO₂ reduction or CH₄ polymerization in the aqueous phase should be considered as possibilities and need to be assessed through further experiments.

Whatever the actual mechanism, the results of Foustoukos and Seyfried⁴² demonstrate that reaction pathways exist for C–C bond formation and hydrocarbon synthesis from dissolved inorganic compounds under hydrothermal conditions, which has significant implications for identifying environments within deep-sea hydrothermal systems where abiotic synthesis might proceed. It is not immediately apparent why synthesis of ethane and propane occurred during their experiments but not in other hydrothermal experiments that also included magnetite and comparable levels of dissolved reactants (CO₂ and H₂).^{40,41} A likely possibility is that rate of carbon reduction under hydrothermal conditions is strongly temperature dependent, and the relatively short durations and lower temperatures (175–300 °C vs 390 °C in the Foustoukos and Seyfried experiments) of the other experiments precluded accumulation of synthesis products in solution at detectable levels. Another possibility is that the lower density or smaller dielectric constant of water at the higher temperature of the Foustoukos and Seyfried experiments allowed greater interaction of reactants with the catalyst surface and/or with each other in the aqueous phase.

It is worth emphasizing that in each of the above hydrothermal experiments the formation of methane and other hydrocarbons from reduction of dissolved CO₂ is strongly favored by thermodynamics. Indeed, at the H₂ levels present in each of these experiments, essentially all of the carbon should have been converted to dissolved methane at equilibrium. While gradual methane synthesis was observed in several of the experiments, only a small fraction of the available CO₂ was converted to methane despite the strong thermodynamic drive and extended reaction times (e.g., ~0.5% conversion in 1062 h of heating at 390 °C,⁴² ~0.5% conversion during 2086 h at 260 °C⁴¹). In addition, each of the above experiments was conducted at H₂ concentrations that are significantly higher than those measured in deep-sea hydrothermal environments, and, because the reaction rates are likely to be a function of H₂ concentration, even slower conversion would probably have occurred at H₂ levels found in natural hydrothermal systems. These results demonstrate that formation of methane was kinetically inhibited on laboratory time scales for the conditions studied.

In sharp contrast to the experiments described above, however, Horita and Berndt⁴³ reported rapid conversion of dissolved ΣCO_2 ($\text{CO}_{2,\text{aq}} + \text{HCO}_3^-$) to methane in hydrothermal experiments performed at 200–400 °C and 50 MPa in the presence of NiFe-alloy (awaruite) and magnetite in a flexible-cell system. In their experiments, essentially complete conversion of 12 mmolal ΣCO_2 to methane occurred in less than 350 h at 300 °C (Figure 9). Furthermore, the

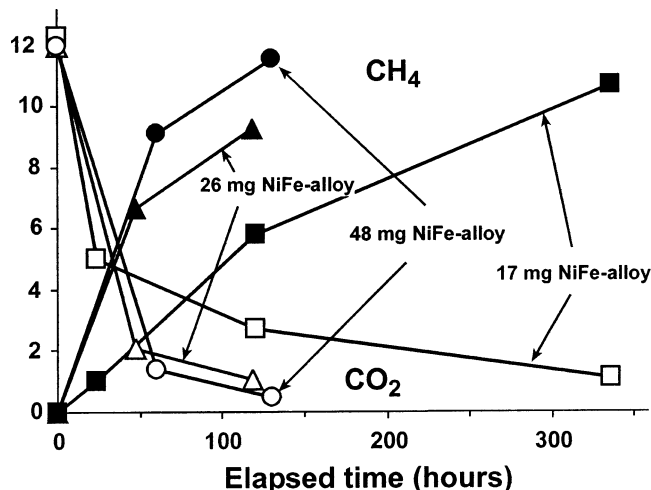


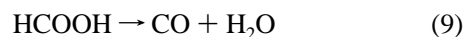
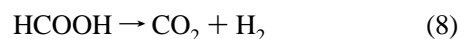
Figure 9. Composition of hydrothermal fluids during formation of methane from reduction of CO_2 catalyzed by varying amounts of NiFe-alloy (Horita and Berndt⁴³). Experiments shown were performed at 300 °C.

rate of the reaction increased with increasing amounts of the NiFe-alloy, demonstrating catalysis of the reaction by the NiFe-alloy rather than magnetite. The reaction also proceeded rapidly at 400 °C in the early stages of the experiments, but slowed over time. Horita and Berndt did not suggest an explanation for the latter observation, but it may be attributable to passivation of the catalytic properties of the NiFe-alloy during reaction with water. A particularly noteworthy feature of the NiFe-alloy-catalyzed reaction observed by Horita and Berndt is that it appeared to be exclusive for methane synthesis, because ethane and propane were not observed at the detection limits of the analyses. This result is in general agreement with industrial synthesis experiments where Ni-bearing catalysts typically produce methane as the exclusive or strongly predominant synthesis product.²³ It should also be noted that, because the reaction did not produce higher hydrocarbons, it is not related to Fischer–Tropsch synthesis but instead probably corresponds to an aqueous version of the Ni-catalyzed Sabatier process.

The results of Horita and Berndt⁴³ indicate that, in some circumstances, kinetic barriers to methane formation may be overcome by mineral catalysis, even with dissolved reactants. In natural systems, NiFe-alloys are only formed under very strongly reducing conditions, but such conditions are sometimes attained in subseafloor environments during hydrothermal alteration of ultramafic rocks, where olivine provides a source of Ni and serpentinization produces high concentrations of H_2 .^{44,45} Serpentinite-hosted seafloor hydrothermal systems such as Lost City and Rainbow (Table 1) may reach sufficiently reducing conditions to stabilize NiFe-alloy, and the elevated methane concentrations observed in those systems could well be the product of NiFe-alloy-catalyzed synthesis from dissolved CO_2 . On the other hand, catalysis of methane formation by NiFe-alloy is highly

unlikely in basalt-hosted systems because redox conditions are not sufficiently reducing to stabilize native metal alloys.

Several studies have demonstrated that a hydrothermal environment in and of itself is also not a barrier to rapid synthesis of more complex organic compounds by FTS synthesis. McCullom and colleagues⁴⁶ reacted aqueous solutions of formic acid (HCOOH) or oxalic acid (HOOC-COOH) in fixed-volume stainless steel reactors at 175 °C for 72 h and analyzed nonvolatile organic compounds in solvent extracts of the reaction vessel. Reaction products included long-chain linear alkanes, alkanols, and alkanolic acids, which are typical of the higher molecular weight fraction of FTS. Presumably, synthesis of these compounds occurred in the reactor headspace from CO , CO_2 , and H_2 produced from decomposition of the formic and oxalic acids according to the reactions:



with the reaction catalyzed by the walls of the stainless steel reactors.

These experiments were followed up by Rushdi and Simoneit,⁴⁷ who used similar methods to investigate the impact of temperature on the distribution of synthesis products. They conducted a series of experiments heating water and oxalic acid for 2 days at temperatures ranging from 100 to 400 °C in stainless steel reactors. The authors observed that yields of synthesis products were greatest in their 200 °C experiment and fell off significantly with both increasing and decreasing temperatures. In addition to the reaction products reported in the previous experiments,⁴⁶ Rushdi and Simoneit⁴⁷ identified minor amounts of alkanals, alkenones, and methyl-branched alkanes. Aromatic compounds (alkyl-benzenes and polycyclic aromatic hydrocarbons) were also found in the 400 °C experiment, which were interpreted to be formed through high-temperature reprocessing (“cracking”) of FTS products. The authors attributed the decrease in product yields with increasing temperatures above 200 °C to increased competition of cracking processes with synthesis reactions, but another possibility is that the high temperatures favored formation of greater proportions of volatile reaction products (methane, ethane, etc.) that were not monitored in the experiments. No explanation was provided for the lower yields at temperatures below 200 °C. However, because decomposition of aqueous formic acid is very slow at temperatures below 175 °C,⁴¹ it is likely that very little of the carbon substrates employed would have decomposed in the short duration of the experiments. If CO and H_2 formed during decomposition of these carbon sources is required for synthesis to occur (reactions 8 and 9), product formation by FTS may have been limited. It should be noted that temperatures of 150 °C and below are not generally a barrier to FTS because synthesis experiments are frequently conducted at lower temperatures.^{23,24}

In another set of experiments, Rushdi and Simoneit⁴⁸ included ammonia among the reactants to assess formation of nitrogenous compounds during FTS. Water, ammonium bicarbonate, and oxalic acid were heated at 300 °C for 72 h in a stainless steel vessel. In addition to typical FTS products such as alkanes and alkanolic acids, nitrogenous products

identified included alkyl amides and alkyl amines, demonstrating incorporation of N into synthesis products is possible.

McCullom and Seewald²⁷ investigated these reactions at higher pressure by heating an aqueous solution of formic acid in the presence of powdered Fe at 250 °C and 32.5 MPa in a flexible-cell reaction vessel. During heating, the Fe was rapidly oxidized to magnetite, generating abundant H₂ in the process, and HCOOH decomposed to produce CO₂, CO, and additional H₂ (reactions 8 and 9). Substantial organic synthesis was observed, with >10% of the source carbon converted to hydrocarbons after 44 h. Organic compounds formed in the experiment were typical of Fe-catalyzed Fischer–Tropsch products, dominated by saturated, linear hydrocarbons (*n*-alkanes) with lesser amounts of alkenes and 1-alkanols (Figure 3), with the characteristic log-linear decrease in abundance with increasing carbon number (Figure 4).

It is not immediately apparent which factors allowed FTT synthesis to proceed rapidly in this experiment even though it was performed under conditions similar to those employed in other experiments where little or no organic synthesis of compounds other than methane was observed.^{14,40–43} Because powdered Fe was one of the initial reactants in the experiment, it is possible that native Fe, or other compounds such as Fe-carbides formed on its surface, was the catalyst for the organic synthesis reaction, and analogous catalysts did not form in the other experiments. Alternatively, the high amounts of H₂ attained in the experiments from decomposition of Fe and HCOOH exceeded the aqueous solubility at the experimental conditions, so an H₂-, CO-, and CO₂-rich gas phase may have formed in the experiments during heating, allowing FTS to proceed from gaseous reactants rather than dissolved compounds. Either of these interpretations would restrict the sorts of environments within hydrothermal systems where the experimental results would be applicable, and a better understanding of the conditions allowing synthesis will be needed before applying the results to specific environments within natural systems. Nevertheless, these and other results^{46–48} indicate that FTT synthesis can proceed rapidly in hydrothermal environments if the right conditions are met.

The speciation of single carbon compounds in natural hydrothermal environments is likely to have a significant impact on the potential for abiotic organic synthesis. Although FTT synthesis can proceed from CO₂, it appears that CO is the actual substrate for the reaction, so that CO₂ must first be converted to CO for synthesis to occur (reaction 5). At equilibrium, CO constitutes only a small fraction of dissolved carbon species in hydrothermal fluids,⁴⁹ and analyses of vent fluids indicate that CO concentrations are very low relative to CO₂ (Table 1). If the rates of synthesis are dependent on CO concentration, the low levels may create a bottleneck for formation of abiotic compounds in natural systems. The dependence of FTT synthesis on carbon speciation can be demonstrated experimentally. Figure 10 shows results for hydrocarbon production in two abiotic synthesis experiments performed under essentially identical conditions except that either CO or CO₂ is utilized as the initial carbon source. Significant hydrocarbon synthesis took place in the CO experiment, but only very small amounts of hydrocarbons were produced with CO₂. Measured CO concentrations were very low in the CO₂ experiments (<0.25 mmolal), which may have been the limiting factor in organic synthesis.

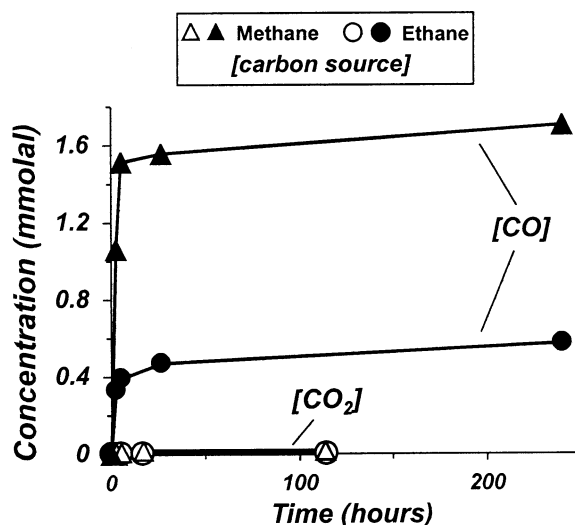


Figure 10. Concentrations of methane and ethane produced in hydrothermal abiotic synthesis experiments performed under essentially identical conditions except that either CO or CO₂ is used as the carbon source (McCullom, unpublished results). The experiments were conducted by heating the carbon source with Fe and water in a closed-system reactor at 250 °C and 200 bar, using procedures similar to those in McCullom and Seewald.²⁷ Concentrations of H₂ (350–400 mmolal) and the carbon source (50–80 mmolal) were comparable in both experiments, so the differences are attributable to carbon source.

In an effort to simulate conditions produced on the seafloor as intruding dikes release magmatic volatiles, Voglesonger and colleagues⁵⁰ reacted a mixture of 63 mol % H₂, 27 mol % CO₂, and 10 mol % H₂O in a stainless steel flow-through reactor at temperatures of 200–360 °C for reaction times of 10–30 s. The authors focused on the production of alcohols. Initially, they observed production of C₁–C₅ alcohols that they attributed to catalysis by the steel reactor walls. Over time, however, the reactor walls appeared to passivate, and no further production of these compounds was observed in blank experiments. However, production of small amounts of methanol was observed when TiO₂-rich magnetite was included within the deactivated reaction vessel in experiments at 300 °C and above. Other products, such as methane and other light hydrocarbons, amorphous carbon, or organic acids, were not found. Methanol formation in the magnetite experiment appeared to be a vapor-phase process that decreased over time, indicating the reaction was surface catalyzed and that the surface of the catalyst passivated with exposure to the reactants. The maximum rate of CO₂ conversion to methanol was $\sim 6 \times 10^{-4}$ mol % CO₂ per hour.

3.3. Isotope Fractionation during FTT Synthesis

Efforts to determine the source of methane and other organic compounds in natural systems have relied heavily on the isotopic compositions of individual compounds. The ability to use isotopes to identify abiotic compounds could be strengthened if the direction and magnitude of isotopic fractionation associated with abiotic organic synthesis pathways were well constrained. To date, however, there have been only a handful of experimental studies that have reported the isotopic composition of Fischer–Tropsch synthesis products, and most of these were conducted under conditions typical of industrial applications (see recent review by Horita⁵¹). Furthermore, all of these experiments have focused on carbon isotopes, and there are at present no

published data on the H isotope composition of FTT synthesis products. As a consequence, the isotopic fractionating steps during abiotic synthesis are poorly known. Recognition of this gap in our knowledge and the potential utility of isotopic data to identify sources of hydrocarbons have recently induced a flurry of experimental activity on this subject, and there is likely to be a significant improvement in our understanding of isotopic fractionation during abiotic synthesis in the near future.

Lancet and Anders⁵² were the first to report isotopic compositions of Fischer–Tropsch synthesis products. They heated a gas mixture composed of equimolar CO and H₂ in the presence of a cobalt catalyst at 137 °C, 0.1 MPa in a closed-system glass reaction vessel, and monitored the abundance and carbon isotopic composition of CO₂, CH₄, and total C₂₊ volatile hydrocarbon products (Figure 11). The

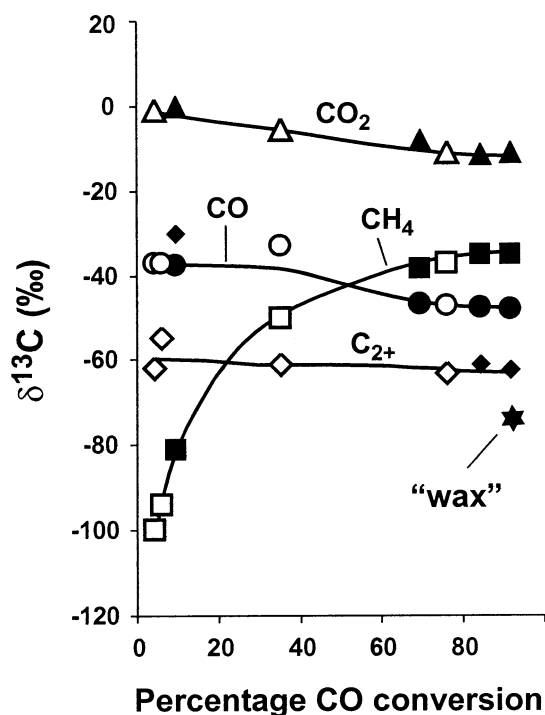


Figure 11. Carbon isotopic composition of CO₂ and hydrocarbons generated during Fischer–Tropsch synthesis on a Co catalyst at 137 °C (Lancet and Anders⁵²). Closed and open symbols represent results of two replicate experiments.

predominant reaction product was methane, with minor amounts of C₂₊ hydrocarbons and CO₂ (<1% of total gas). Relative to the starting CO ($\delta^{13}\text{C} = -38.6\text{‰}$), product CO₂ was enriched in ¹³C by ~35–38‰. Methane was strongly depleted in ¹³C relative to CO in the early stages of the reaction, but became steadily more enriched with increasing conversion of CO such that the methane present in the latter stages of the experiment was enriched in ¹³C by ~10–13‰. Heavier volatile hydrocarbons (C₂₊) were depleted in ¹³C by ~12–18‰ with respect to CO, and nonvolatile hydrocarbons (“wax”) were even more strongly depleted in ¹³C, with a depletion of ~33‰. It is worth noting that mass balance indicates that a significant fraction of carbon from the initial CO reactant is unaccounted for among reaction products, and this “missing” carbon may have had a role in the evolution of the isotopic composition of methane.

Yuen et al.⁵³ also measured the carbon isotope composition of FTS products in a series of experiments; however, the results are reported only in an extended abstract with few

details given on the isotopic measurements or experimental procedures. The experiments were conducted at 250–500 °C with a CO/H₂ gas mixture in both closed-system and flow-through reactors, using three different (but undescribed) iron-bearing catalysts. They found that saturated hydrocarbons and nonvolatile compounds deposited on the catalyst surface were depleted in ¹³C by ~11–35‰ relative to the reactant CO. In contrast to results reported by Lancet and Anders,⁵² however, CO₂ generated was also depleted in ¹³C (by ~2–13‰) while the CO became enriched in ¹³C relative to its starting composition by ~2–23‰ during the course of the experiments. The authors state that no systematic isotopic variation with carbon number was observed among the major saturated hydrocarbon products, but the evidence for this statement was not provided.

Hu et al.⁵⁴ were apparently the first to report the isotopic composition of individual C₂₊ hydrocarbon gases produced by Fischer–Tropsch synthesis. These authors reported the carbon isotopic composition of CO₂, CH₄, and C₂–C₄ hydrocarbons produced during reaction of a CO/H₂ gas mixture using magnetite or cobalt-iron carbonyl [CoFe₃(CO)₁₃] as the catalyst at 280–300 °C, 0.7–2.0 MPa, and reaction times varying from 1 to 105 h (Figure 12). The

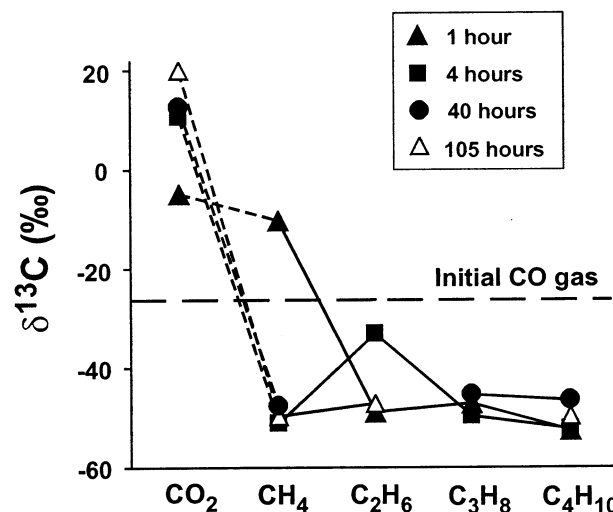


Figure 12. Carbon isotopic composition of CO₂ and hydrocarbons generated during Fischer–Tropsch synthesis from CO reported by Hu et al.⁵⁴ Results shown are for experiments conducted at 280 or 282 °C with magnetite as the catalyst.

isotopic composition of CO₂ produced in the experiments was enriched in ¹³C by ~20–45‰ relative to the initial reactant CO, while methane was enriched by 16‰ in the shortest experiment (1 h), but depleted by 21–25‰ in longer duration experiments. This trend is exactly opposite to that reported by Lancet and Anders,⁵² whereby methane was initially depleted in ¹³C relative to CO in the initial stages of their experiments, but became increasingly enriched with continued reaction time (Figure 11). Except for ethane in one experiment, the C₂–C₄ hydrocarbons exhibited ¹³C depletions of 20–26‰ relative to the initial CO, similar to methane. The C₂–C₄ hydrocarbons exhibited a general isotopic trend of decreasing ¹³C content with increasing carbon number ($\delta^{13}\text{C}_{\text{C}_2\text{H}_6} > \delta^{13}\text{C}_{\text{C}_3\text{H}_8} > \delta^{13}\text{C}_{\text{C}_4\text{H}_{10}}$), although the differences are small and inconsistent among the experiments (Figure 12). Hydrocarbons in the single experiment using CoFe₃(CO)₁₃ as catalyst were slightly less depleted in ¹³C than the magnetite-catalyzed products.

All of the experiments discussed above were performed using typical industrial FTS conditions that include a dry CO/H₂ feed gas and synthetic Co and Fe catalysts. Perhaps more directly relevant to isotopic fractionation in deep-sea hydrothermal environments are the experiments of Horita and Berndt⁴³ described earlier, in which dissolved ΣCO₂ was reduced to methane using an NiFe-alloy catalyst (Figure 9). These authors monitored the carbon isotopic composition of ΣCO₂ and methane over time as the reaction proceeded and found that the methane produced was depleted in ¹³C by 50–66‰ relative to ΣCO₂ during reaction at 200 °C and by 35–40‰ at 300 °C.

McCollom and Seewald²⁷ measured the carbon isotope composition of individual compounds (hydrocarbons and alcohols) generated by FTT synthesis under hydrothermal conditions (see previous section). With the exception of the C₂–C₄ alkanes, all of the hydrocarbons had similar isotopic compositions that were depleted in ¹³C by ~36‰ relative to dissolved CO₂ and ~31‰ relative to siderite (an iron carbonate mineral, FeCO₃) that precipitated during the experiment (Figure 13). Ethane, propane, and butane were

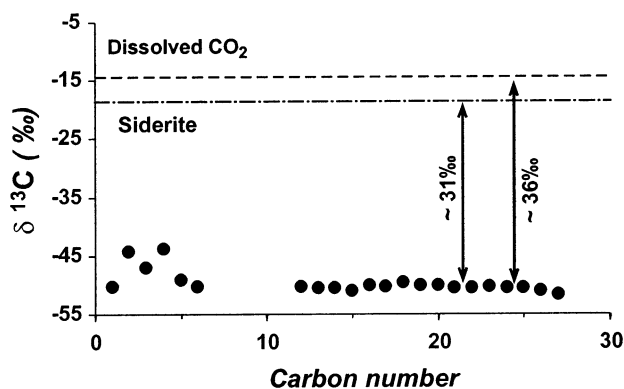


Figure 13. Carbon isotopic composition of hydrocarbons generated during hydrothermal Fischer–Tropsch-type synthesis (McCollom and Seewald²⁷). Horizontal lines represent isotopic composition of dissolved CO₂ and siderite (FeCO₃) that precipitated during the experiment. Data for C₇–C₁₁ compounds not available.

slightly enriched in ¹³C (3–6‰) relative to the other hydrocarbons, but it is possible that the isotopic compositions of these compounds were affected by secondary reactions such as reduction of alkenes that were also produced during synthesis.

Although the experiments performed to date provide a limited perspective on isotopic behavior during FTT synthesis, a couple of tentative conclusions can be drawn. First, the data indicate that organic matter produced by FTT synthesis is likely to be substantially depleted in ¹³C relative to inorganic precursors. The magnitude of this depletion could potentially be useful for interpreting the source of organic compounds in natural systems. The experiments of Lancet and Anders⁴⁸ and Hu et al.⁵⁰ yielded hydrocarbons that were depleted in ¹³C by 50–70‰ relative to CO₂, but McCollom and Seewald²³ observed a substantially smaller isotope difference between dissolved CO₂ and hydrocarbons (~36‰) under hydrothermal conditions. If the latter value is representative of abiotic synthesis under hydrothermal conditions, it suggests that carbon isotope compositions may not be an effective tool to differentiate between abiotic synthesis and other sources of hydrocarbons because the magnitude of the isotope difference is very similar to that produced during carbon fixation by photosynthesis. For

instance, lipids in marine sediments as well as hydrocarbons in petroleum typically have carbon isotopic signatures in the –25‰ to –35‰ range. However, it must be considered that the CO₂ and hydrocarbons in these experiments are both generated from CO, whereas hydrocarbons in natural systems are likely to arise from reduction of CO₂, which may not produce the same isotopic differences between CO₂ and hydrocarbons as those generated in the experiments. Consequently, it remains uncertain whether the experimentally determined isotopic differences are appropriate for hydrothermal systems.

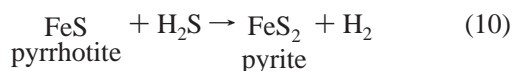
Assessing the likely isotopic composition of Fischer–Tropsch reaction products in natural systems with greater certainty will require additional experimentation to gain a better understanding of the isotopic fractionating steps and how the fractionation varies with environmental factors such as temperature and catalyst composition. While the available data are not yet sufficient to determine what reaction steps are responsible for the observed fractionation during FTS, some inferences are possible. The observation that hydrocarbons with increasing carbon number have the same isotopic composition^{27,53} (Figure 13) suggests that no fractionation occurs during polymerization of methylene units (step 3 in Figure 2). Also, based on the large carbon isotope differences between hydrocarbon products and the initial carbon source,^{27,52–54} it is apparent that significant fractionation occurs between reactant CO and formation of surface-bound methylene units, either as CO attaches to the catalyst or as surface carbonyl units are reduced to methylene.

3.4. Alternative Pathways to Organic Synthesis in Hydrothermal Systems

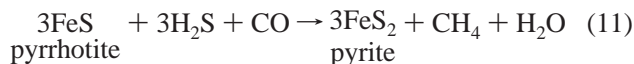
Although Fischer–Tropsch-type synthesis is the most widely discussed pathway for abiotic synthesis of organic matter in deep-sea hydrothermal systems, other reaction pathways might also contribute to production of organic compounds. One such pathway has been investigated by Williams et al.,⁵⁵ who reported formation of organic compounds during reaction of aqueous methanol solutions with clay minerals at 300 °C and 100 MPa. Major products of the reaction were CH₄, CO₂, and dimethylether (a condensation product of two methanol molecules). Minor identified products included C₂–C₆ alkanes and alkenes as well as an assortment of alkylated cyclic aromatic compounds such as alkylbenzenes, alkylphenols, alkyl-naphthalenes, and alkyl-naphthols. The predominance of alkylated aromatic compounds among the higher molecular weight reaction products distinguishes them from the linear saturated alkanes that are characteristic of FTT synthesis (Figure 3), suggesting either a different mechanism is involved or that alkanes were generated first and underwent secondary reactions to form aromatic compounds. While the mechanism of the reaction remains to be determined, Williams et al.⁵⁴ hypothesized that the organic compounds may have formed within the interlayers of the clay structure, indicating that clays may provide unique microenvironments for organic synthesis. Although not abundant, clays that may be capable of promoting such reactions occur in hydrothermal vent chimneys and hydrothermally altered basalts.

The potential participation of hydrothermal systems in prebiotic organic syntheses leading to the origin of life has inspired a host of experimental studies.^{10,11} Considerable attention has been given to the so-called “pyrite-pulled” chemoautotrophic hypothesis for the origin of life.^{56–58} In

this scenario, prebiotic organic synthesis is driven by reducing environments created by reaction of pyrrhotite with H_2S to form pyrite, which can be generalized by the reaction:

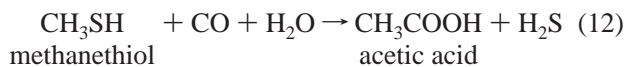


Reduction of carbon compounds might proceed from the H_2 produced by this reaction, or might involve direct electron transfer to carbon compounds,⁵⁴ which can be portrayed by reactions such as:

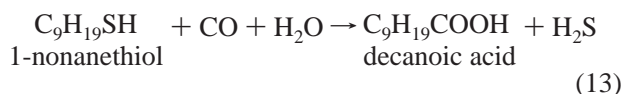


Heinen and Lauwers⁵⁹ tested the potential for organic synthesis in an iron- and sulfide-rich system by reacting synthetic FeS, H_2S , water, and CO_2 gas at 75–90 °C in glass serum bottles, and monitoring the headspace for production of organosulfur compounds. The major identified reaction products were CS_2 and a series of alkylthiols ranging from C_1 (methanethiol) to C_5 (pentanethiol). The mechanism for the formation of the alkylthiols was not determined, but one possibility is that the alkyl moieties were produced by a typical Fischer–Tropsch polymerization process on the surface of the minerals, which was then terminated by a thiol group. Because the source of the carbon in the alkyl chains was not determined, it is also possible that these products are derived from reaction of H_2S with background contaminants (e.g., formation of butanethiol from reaction of contaminant butane; $\text{C}_4\text{H}_{10} + \text{H}_2\text{S} \rightarrow \text{C}_4\text{H}_9\text{SH} + \text{H}_2$).

However, another possibility is that these compounds represent a distinctly different sort of abiotic organic synthesis pathway in which organosulfur compounds play a central role. The critical stage in any reaction pathway for synthesis of complex organic compounds is the formation of C–C bonds. In a further experimental investigation of prebiotic organic synthesis in sulfur-rich systems, Huber and Wächtershäuser⁶⁰ reported formation of acetic acid during reaction of aqueous solutions of methanethiol with CO gas at 100 °C in the presence of metal sulfides. The overall reaction can be expressed as:



Cody et al.^{61,62} explored this type of reaction further by reacting nonanethiol ($\text{C}_9\text{H}_{19}\text{SH}$) with CO, CO_2 , and water (supplied by the thermal decomposition of an aqueous formic acid solution, reactions 8 and 9) in the presence of a variety of different transition metal sulfide minerals. Although a broad spectrum of products was observed, one major reaction product was decanoic acid, apparently formed through the overall reaction:



Reactions 12 and 13 both involve the formation of C–C bonds to generate the carboxylic acid. Yields of carboxylic acids were dependent on the composition and surface area of the metal sulfide minerals, indicating that the reaction was surface catalyzed.⁶² Figure 14 shows a possible mechanism for the reaction, involving adsorption of CO and the alkyl moiety of the alkylthiol to the mineral surface, followed by

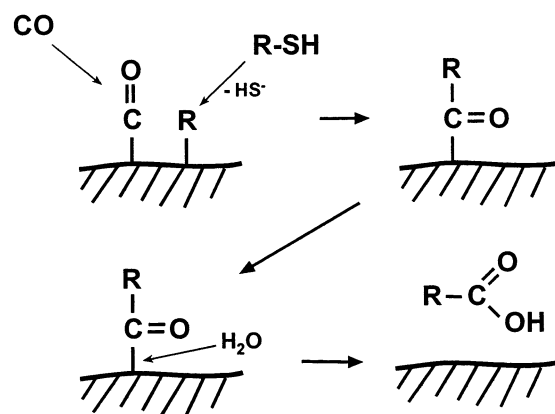


Figure 14. Schematic drawing of potential reaction mechanism for surface-catalyzed reaction of CO and an alkylthiol to form an alkanolic acid (modified after Cody et al.⁶²). R represents an alkyl group. Adapted from ref 62, Copyright 2004, with permission from Elsevier.

formation of the C–C bond by migration to the carbonyl, and terminated by release from the surface as a carboxylic acid. If the carboxylic acid product undergoes reduction to an alcohol followed by exchange with H_2S to form another thiol, progressive iterations of this mechanism could lead to the formation of multiple C–C bonds, generating compounds with elongated alkyl chains (Figure 15). This pathway could

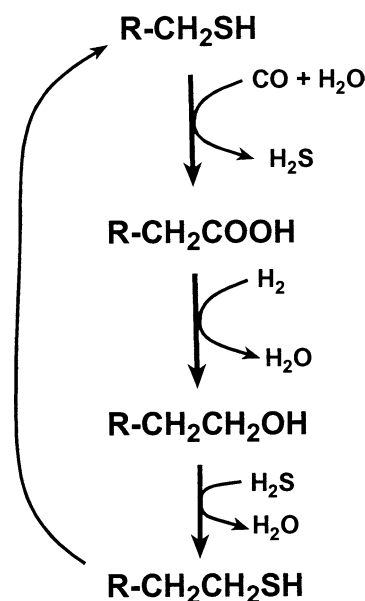
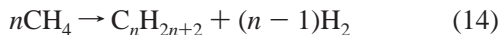


Figure 15. Hypothetical reaction scheme for the progressive elongation of alkyl carbon chains and formation of complex organic compounds through involvement of a thiol intermediate. R represents an alkyl group.

account for the formation of C_1 – C_5 alkylthiols in the experiments of Heinen and Lauwers⁵⁹ and also account for the observation of C_{11} – C_{13} carboxylic acids in the nonanethiol experiments of Cody et al.⁶² Conceivably, this is a potential mechanism to convert simple organic compounds (e.g., methanol) to complex organic matter in sulfur-rich hydrothermal environments. Regardless of the actual reaction pathway, the experiments of Heinen and Lauwers⁵⁹ and others^{60–62} demonstrate that a potential for abiotic synthesis of complex organic compounds exists in hydrothermal systems even under sulfur-rich conditions where Fischer–Tropsch synthesis has been claimed to be ineffective.^{36,37}

Another potential pathway for hydrocarbon synthesis in hydrothermal systems that has so far remained largely unexplored involves the polymerization of methane, which can be represented by the general reaction:



Des Marais et al.⁶³ formed hydrocarbons in this manner by passing electric sparks through methane gas, but the conditions of this experiment clearly preclude direct application to hydrothermal systems. However, in a preliminary set of experiments, performed by heating ¹³C-labeled methane gas (99% ¹³CH₄), water vapor, and magnetite in fixed-volume reactors constructed of either steel or surface-oxidized titanium at 350 °C for 8 weeks, formation of labeled C₂–C₅ hydrocarbons was observed (Figure 16), suggesting similar

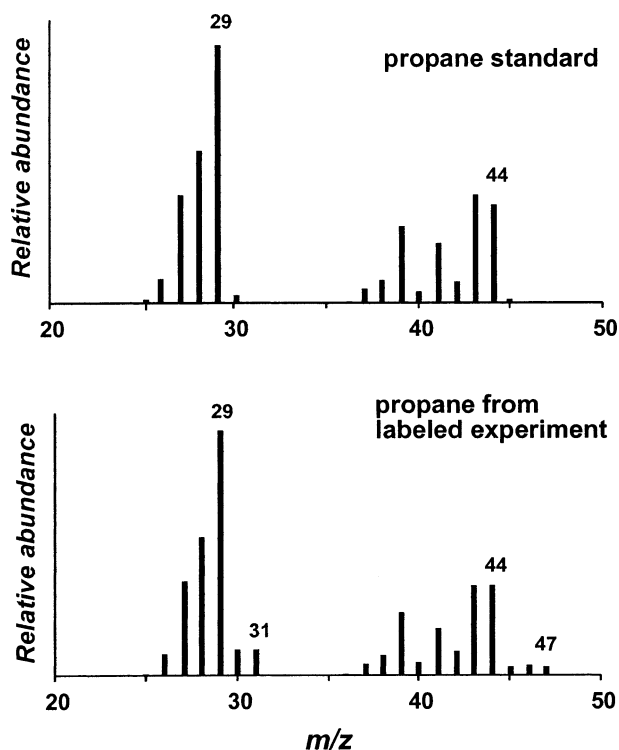


Figure 16. Mass spectrum of propane produced during heating of ¹³C-labeled methane (>99% ¹³CH₄) for 8 weeks at 350 °C (m/z = mass to charge ratio) (McCollom, unpublished data). The spectra compare a propane standard (top) with propane produced in the experiment (bottom). Although the experimental spectrum includes a significant contribution from unlabeled, background carbon sources, ~15% of the propane is composed of ¹³C (¹³C₃H₈), demonstrating it was synthesized from the reactant ¹³CH₄. Note increased abundance of ions with m/z = 30, 31, 45, 46, and 47 in the lower spectrum, corresponding to mass fragments ¹³C₂H₄⁺, ¹³C₂H₅⁺, ¹³C₃H₆⁺, ¹³C₃H₇⁺, and ¹³C₃H₈⁺, respectively.

reactions could take place in geologic environments (McCollom, manuscript in preparation). Although production of unlabeled hydrocarbons indicated that background sources of carbon were present in the experiments, labeled compounds composed entirely of ¹³C were produced (e.g., ¹³C₃H₈ rather than mixed labeled compounds such as ¹³C¹²C₂H₈), demonstrating complete synthesis from polymerization of the ¹³CH₄ reactant. Of course, more experimental work is required to place constraints on the progress of these reactions, such as whether they can occur with methane dissolved in water.

In addition to the surface-catalyzed reactions such as the Fischer–Tropsch synthesis that may be responsible for the occurrence of reduced carbon compounds in hydrothermal systems, there are numerous reactions that produce reduced carbon compounds in aqueous solution without the involvement of a heterogeneous catalyst or gas phase. Laboratory experiments have demonstrated reduction of CO₂ to methanol via a series of sequential aqueous reactions that produce formic acid and CO as reaction intermediaries^{37,45} (Figure 17). Each of the reactions that lead to methanol formation

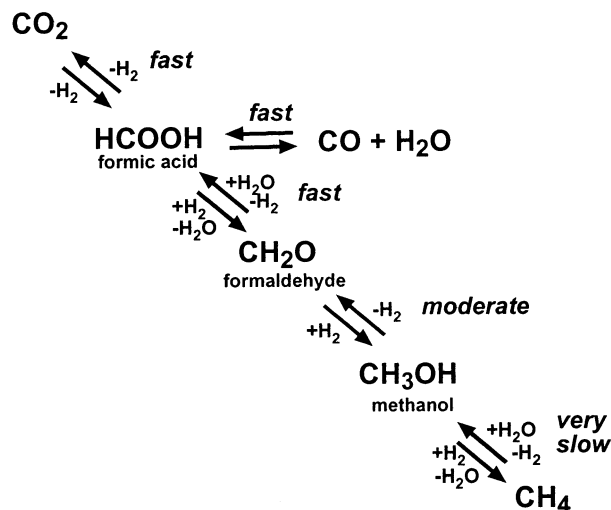


Figure 17. Reaction scheme for the sequential reduction of CO₂ to methane (modified after Seewald et al.⁴⁹). Reprinted from ref 49, Copyright 2006, with permission from Elsevier.

is reversible, allowing CO₂, CO, formic acid, methanol, and H₂ to attain states of redox-dependent metastable thermodynamic equilibrium on a laboratory time scale. Relatively rapid reaction kinetics for these single carbon compounds suggests that their abundance may vary systematically as a function of CO₂ concentration, pH, redox, and temperature in hydrothermal systems. Thus, the low measured concentrations of formic acid and methanol in CO₂-rich environments may reflect the thermodynamic controls on their abundance at the prevailing chemical conditions, and not the absence of a reaction mechanism necessary for their formation. Stepwise aqueous reduction of CO₂ to form methanol represents a substantially different reaction mechanism from that proposed by Vogelsonger et al.,⁵⁰ which requires a gas phase and magnetite catalyst, and demonstrates that methanol may be generated in CO₂-rich vent fluids regardless of whether a gas phase or suitable mineral catalyst is present.

Complete reduction of aqueous CO₂ to CH₄ has also been observed during laboratory experiments without added catalysts at 200–300 °C, but at a substantially slower rate than observed for formation of other C₁ compounds, precluding attainment of thermodynamic equilibrium on laboratory time scales.⁴⁹ Whether aqueous CH₄ formation occurs via methanol reduction (Figure 17) or some other reaction path is presently unknown. The extent of homogeneous CH₄ formation in natural systems will be strongly influenced by residence times for hydrothermal fluids in high-temperature reaction zones. In general, residence times for hydrothermal fluids are poorly constrained, but for high-temperature fluids (>200 °C) along the Juan de Fuca Ridge, available data indicate residence times of ≤3 years.^{64–66} A 3 year time frame is comparable to the duration of laboratory experiments

and suggests that homogeneous CH_4 production might be an important process in ridge-crest hydrothermal systems.

4. Geochemical Evidence for Abiotic Organic Compounds in Hydrothermal Fluids

The organic geochemistry of deep-sea hydrothermal fluids and mineral deposits provides additional data that can be examined for evidence of abiotic synthesis. However, as compared to the extensive analyses that have been made of the inorganic compositions of fluids and rocks from hydrothermal systems, analyses of organic compounds from these environments have been fairly limited, and primarily restricted to hydrocarbons. Methane is by far the most abundant organic compound observed in mid-ocean ridge (MOR) hydrothermal fluids, with measured concentrations in unsedimented systems ranging up to 2.5 mmolal (Table 1). Methane concentrations in these fluids are well above seawater levels of 0.3 nmolal, indicating that methane must be added to the fluids during circulation through the crust. Methane concentrations are especially elevated in serpentinite-hosted hydrothermal systems, such as Rainbow⁶⁷ and Lost City.⁶⁸ In a few instances, other volatile hydrocarbons (ethene, ethane, propane, and butane) have also been detected in these fluids at very low levels, with reported C_1/C_{2+} ratios ranging from ~ 100 to >8000 (Table 1). There have been only a few reports of extraction and analysis of more complex hydrocarbons in hydrothermal vent fluids in unsedimented systems,^{16,69} and these are dominated by linear aliphatic hydrocarbons (*n*-alkanes) ranging up to C_{35} . To date, there have been no published reports on the possible presence and abundance of other classes of organic compounds (e.g., organic acids, amino acids, saccharides) in unsedimented deep-sea hydrothermal fluids, which is likely attributable to the difficulties involved in measuring low concentrations of these compounds in salt- and H_2S -rich fluids.

A variety of sources are possible contributors to the methane and other hydrocarbons found in vent fluids, including biological inputs, thermal degradation of organic matter, direct injection of magmatic gases, extraction of magmatic gases trapped within basalt, and abiotic synthesis from reduction of CO_2 during hydrothermal circulation.⁷⁰ Of course, because many of these fluids are discharged from the seafloor at very high temperatures, any methane present that was derived from biological processes such as methanogenesis would have to be formed in the lower temperature parts of the system and be entrained by high-temperature fluids.

Several criteria have been proposed to differentiate among potential sources of methane and light hydrocarbon gases in geologic systems. One such approach combines the C and H isotopic signatures of methane⁷¹ (Figure 18). Based on empirical observations of natural gases, methane from thermogenic and biogenic sources appears to be well separated in terms of its C and H isotopic signatures. The biogenic field can be further divided into methane derived from fermentation of organic matter and methane derived from reduction of CO_2 . Values of $\delta^{13}\text{C}$ and $\delta^2\text{H}$ for CH_4 in high-temperature fluids from unsedimented ridges where both isotopes have been measured vary from -13 to -24‰ and -109 to -126‰ , respectively, although data are presently available for only a few locations. Methane in fluids from the off-axis, serpentinite-hosted Lost City hydrothermal system is slightly enriched in ^{13}C and slightly depleted in ^2H relative to MOR values (Table 1). All of these

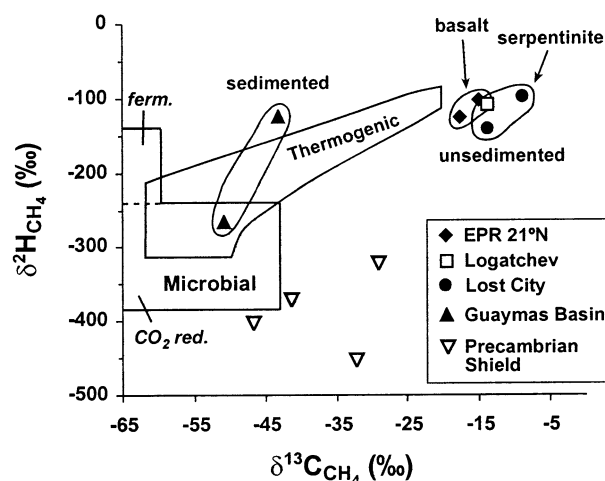


Figure 18. Carbon and hydrogen isotopic compositions of methane in vent fluids from unsedimented and sedimented deep-sea hydrothermal environments. The unsedimented measurements include both basalt-hosted (EPR) and serpentinite-hosted (Logatchev, Lost City) systems. Also shown for reference are fields encompassing typical isotopic compositions of microbial and thermogenic methane (after Schoell⁷¹) and methane proposed to have an abiotic origin in crystalline Precambrian Shield rocks.⁸¹

fluids are located at one extreme of the thermogenic trend in Figure 18.

Hydrocarbons from unsedimented ridges can be further distinguished from typical thermogenic hydrocarbons by substantially higher C_1/C_{2+} ratios. On a plot of C_1/C_{2+} versus $\delta^{13}\text{C}$, light hydrocarbons in unsedimented deep-sea hydrothermal systems are clearly distinct from both biogenic and thermogenic sources (Figure 19). At the same time, hydro-

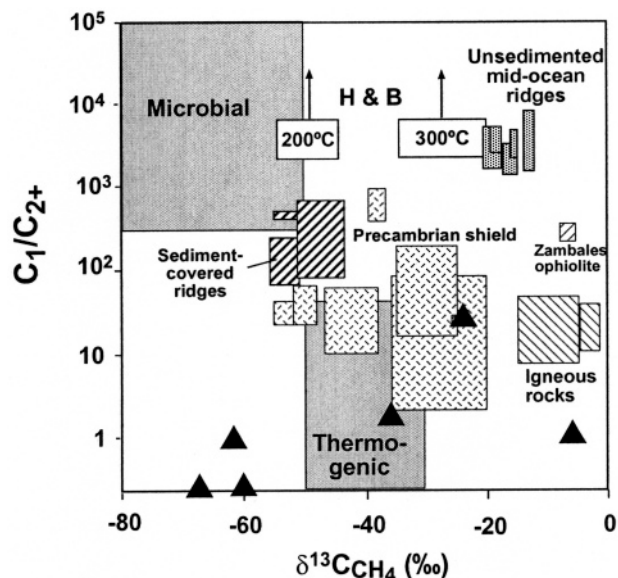


Figure 19. Carbon isotopic composition of methane and C_1/C_{2+} ratios for volatile hydrocarbons in high-temperature fluids from mid-ocean ridge hydrothermal systems. Shown in gray is the range of values observed for typical microbial and thermogenic hydrocarbon gases. Also shown for comparison are values for gases proposed to have an abiotic origin in Precambrian shield rocks, igneous rocks, and gases venting from a continental serpentinite (Zambales ophiolite). The fields marked "H & B" are abiotic methane generated in hydrothermal experiments of Horita and Berndt⁴³ (C_1/C_{2+} values are minimums because C_{2+} compounds were below detection limits). \blacktriangle represent hydrocarbons formed in Fischer-Tropsch synthesis experiments.^{27,52,54} Adapted with permission from ref 43. Copyright 1999 AAAS (<http://www.aaas.org>).

carbons in fluids from sediment-covered ridges are intermediate between thermogenic and biogenic fields, consistent with the dominant inputs from microbial methanogenesis and thermal maturation of sedimentary organic matter in these systems. These criteria indicate that the methane from many unsedimented deep-sea hydrothermal systems is compositionally and isotopically distinct from typical biogenic and thermogenic sources, supporting the possibility that it may be abiotic in origin. However, it remains uncertain where in the system and under what conditions the methane might have formed.

An additional constraint on the possible origin of methane is provided by experimental carbon isotope studies. In their experiments catalyzed by NiFe-alloy, Horita and Berndt³⁹ reported formation of methane depleted in ^{13}C by 50–66% relative to ΣCO_2 during reaction at 200 °C and by 35–40% at 300 °C. The isotopic differences between ΣCO_2 and methane ($\Delta^{13}\text{C}_{\Sigma\text{CO}_2-\text{CH}_4}$) at 200 °C are particularly noteworthy because they are similar in magnitude to isotopic fractionation during microbial methane formation (Figure 19). These experiments also produced methane with no detectable ethane or propane, similar to the high C_1/C_{2+} ratios generated during microbial methanogenesis. Together, these results indicate that, under some circumstances, abiotic processes are capable of producing methane with chemical and isotopic characteristics that have traditionally been ascribed to a microbial origin (Figure 19), suggesting that it may be difficult to unequivocally differentiate between microbial and abiotic sources of methane in certain environments. Because abiotic methane meeting these criteria has only been generated in experiments with NiFe-alloy catalysis, this concern may be most relevant to serpentinite-hosted hydrothermal systems where NiFe-alloy is stable. Light hydrocarbons from unsedimented deep-sea hydrothermal systems have isotopic signatures and compositions similar to the 300 °C results of Horita and Berndt,⁴³ and the correspondence may be even closer if the experimental results are extrapolated to the higher temperatures of the venting fluids (~350–400 °C) (Figure 19). This correspondence provides additional evidence that the light hydrocarbon composition of the fluids is consistent with an abiotic source, particularly for the serpentinite-hosted systems like Rainbow and Logatchev where NiFe-alloy may be stable in subsurface reaction zones.

Although the chemical and isotopic compositions of light hydrocarbons in deep-sea hydrothermal environments are consistent with an abiotic origin, they are significantly different from those generated in FTT synthesis experiments to date (Figure 19). These experiments generally produce hydrocarbons with C_1/C_{2+} ratios much lower than those observed in vent fluids, and most have isotopic signatures substantially more depleted in ^{13}C . It is also apparent from Figure 19 that the experiments performed to date have produced a wide range of isotopic values and C_1/C_{2+} ratios reflecting different experimental conditions, with no clear trend in the data. Because most of these experiments are performed under conditions with uncertain relevance to natural hydrothermal systems, it is not yet clear which of these experiments, if any, are most applicable to abiotic synthesis in hydrothermal environments. However, if the experimental values are at all representative of those that might occur in hydrothermal environments, it is clear that any contribution of FTT synthesis to the light hydrocarbons in unsedimented systems must be accompanied by additional

sources of ^{13}C -enriched methane to be consistent with the measured compositions of the fluids.

Stable isotope geothermometry can be used to place further constraints on the origin of CH_4 in hydrothermal systems. A critical factor that influences the success of such an approach is the rate of isotopic reequilibration that may preclude “quenching” of high-temperature signals as fluids cool. Hydrogen isotopes, for example, are of limited use for differentiating magmatic CH_4 from other possible sources in high-temperature vent fluids because rapid exchange results in isotopic reequilibration at measured vent temperatures.^{70,72} Carbon isotopes, on the other hand, are more effective at recording high-temperature processes because reequilibration during subsequent cooling appears to be kinetically inhibited, locking the high-temperature signature in place. Temperatures calculated assuming isotopic equilibrium between coexisting CO_2 and CH_4 in vent fluids range from 400 °C to magmatic conditions (~1250 °C), although the majority are <1000 °C (Table 1). Carbon isotope equilibration temperatures in this range are consistent with abiotic reduction of CO_2 to CH_4 during cooling of magmatic volatiles. Synthesis of CH_4 may occur after magmatic CO_2 is entrained in convecting hydrothermal fluids as it streams off a degassing magma chamber or while cooling in gabbro-hosted fluids inclusions prior to leaching by hydrothermal fluids. Estimated temperatures for isotopic equilibration that are substantially lower than magmatic conditions suggest direct infiltration of CH_4 formed at magmatic conditions is not an important process. Indeed, a thermodynamic assessment of CH_4 stability indicates that only trace quantities of CH_4 are stable at the temperatures and oxidation states of mid-ocean ridge basaltic magmas,⁷³ resulting in CO_2/CH_4 ratios that are substantially greater than those observed in hydrothermal vent fluids. Moreover, chemical analyses of magmatic volatiles trapped in basalt vesicles confirm that basaltic magmas are characterized by very high CO_2/CH_4 ratios.⁷⁴

Additional evidence that respeciation of carbon occurs during cooling of magmatic volatiles is provided by the chemical and isotopic composition of fluid inclusions entrapped in gabbros that form in the lower portion of the oceanic crust (layer 3) at the Southwest Indian Ridge.^{75,76} One type of fluid inclusion found in these rocks formed at super-solidus to greenschist facies metamorphic conditions and contain CO_2 - CH_4 - H_2O -rich fluids with CH_4 concentrations up to 43 mol %. A second set of CH_4 - H_2O - H_2 -bearing inclusions with CH_4 concentrations >40 mol % is inferred to have formed under a more limited temperature range near 400 °C. High CH_4 abundances are attributed to reduction of magmatic CO_2 under conditions of high H_2 activity created by precipitation of graphite during cooling and/or serpentinization of olivine during circulation of hydrothermal fluids.^{75,76} The carbon isotope composition of CH_4 in the inclusions that resulted from reequilibration of carbon species during cooling of magmatic volatiles varied from -9.1 to -33.8‰ and encompasses the range of values observed for CH_4 in vent fluids from unsedimented hot springs. Trapped CO_2 is characterized by less variability with an average value of -4.7‰ that is similar to the isotopic composition of vent fluid CO_2 . Carbon isotope geothermometry yields temperatures that are consistent with abiotic formation of CH_4 at temperatures of ~500–800 °C.⁷⁶ The CH_4 -rich nature of the fluid inclusions in gabbros from the Southwest Indian Ridge suggests that plutonic rocks may represent a major reservoir

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

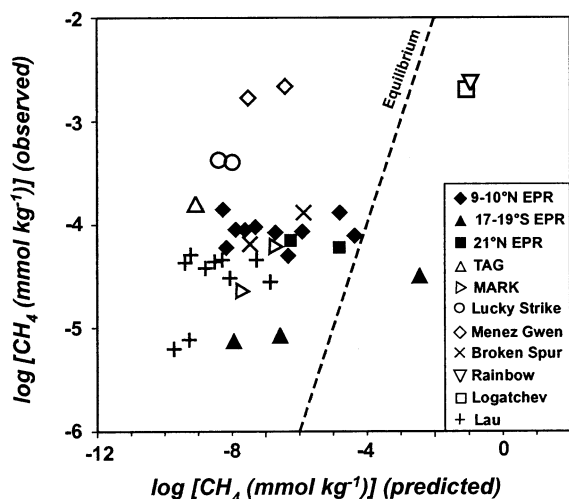


Figure 20. Comparison of measured aqueous CH_4 concentrations in high-temperature vent fluids ($>300\text{ }^\circ\text{C}$) with values predicted for measured concentrations of CO_2 and H_2 and temperature assuming chemical equilibrium according to reaction 4. The solid line indicates a 1:1 relationship. 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.

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 $>400\text{ }^\circ\text{C}$ 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.

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 $\delta^{13}\text{C}$ 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 $\delta^{13}\text{C}$ values for CH_4 that in some cases are depleted relative to marine carbonate ($\sim 0\%$) 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 ^2H 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 ($\text{C}_1\text{--C}_4$) 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 ($\delta^{13}\text{C}_1 < \delta^{13}\text{C}_2 < \delta^{13}\text{C}_3$

$< \delta^{13}\text{C}_4$), these gases become lighter with increasing number of carbons ($\delta^{13}\text{C}_1 > \delta^{13}\text{C}_2 > \delta^{13}\text{C}_3 > \delta^{13}\text{C}_4$). 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 through 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., $\delta^2\text{H} = -430$ 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 Charlou¹⁶ 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.

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