

Abiotic Synthesis of Methane and Organic Compounds in Earth's Lithosphere

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ABSTRACT

Accumulation of molecular hydrogen in geologic systems creates conditions energetically favorable for transforming inorganic carbon into methane and other organic compounds. Although hydrocarbons with a potentially abiotic origin have been proposed to form in a number of crustal settings, the ubiquitous presence of organic compounds derived from biological organic matter presents a challenge for unambiguously identifying abiotic organic molecules. In recent years, extensive analysis of methane and other organics in diverse geologic fluids, combined with novel isotope analyses and laboratory simulations, have, however, yielded insights into the distribution of specific abiotic organic molecules in Earth's lithosphere and the likely conditions and pathways under which they form.

KEYWORDS: Abiotic organic synthesis, thermogenesis, origin of life, methane, hydrocarbons, heteroatom compounds

INTRODUCTION

Geologic fluids containing the reducing agent hydrogen (H_2) are intriguing for their propensity to create tremendous thermodynamic driving forces to reduce inorganic carbon into organic molecules in the absence of biological intervention, termed "abiogenesis". Even basic cellular building blocks (e.g., amino acids, nucleotides) are predicted to be stable in warm, H_2 -rich fluids, and their synthesis even yields net chemical energy when formed from inorganic reactants (e.g., CO_2 , H_2 , NH_4^+) (Amend et al. 2011). Implications for prebiotic chemistry, a H_2 -driven origin of life, and early metabolism are tantalizing, motivating extensive research examining the possibilities for organic synthesis in Earth's lithosphere.

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Methane (CH₄), an abundant organic compound in H₂-rich fluids, is of particular interest as a major abiotic “fuel” for microbial life, alongside H₂, in the crust. Recent detection of putative hydrothermal H₂ on Saturn’s moon Enceladus and CH₄ variations in Mars’ atmosphere have again brought abiogenesis to the forefront of solar system astrobiology (see this issue).

Scientists now better understand abiogenesis of CH₄ and some organic compounds in high-temperature crustal fluids (~200–1200+ °C), yet in cooler geologic settings it continues to be debated, particularly the possibility for abiotic production of CH₄ below ~200 °C. Cutting-edge analyses, including measurements of rare temperature-sensitive “clumped” isotopologues of geologic CH₄ (i.e., methane containing two or more heavy isotopes), however, now shed new light on long-debated “hot spots” for abiogenesis. In this article, we review the historical evidence for hydrocarbon abiogenesis and recent findings regarding the origin of these, and other, novel abiotic organic compounds.

HYDROCARBON ABIOGENESIS: CONTROVERSIAL ORIGINS

In line with previous authors (cf. McCollom and Seewald 2007; Etiope and Sherwood Lollar 2013), we use “abiotic” to describe organic compounds formed by purely nonbiological (*abiotic* or *abiogenic*) synthesis reactions not involving complex organic precursors or biological activity, i.e., the inorganic reduction of oxidized carbon. Theories of a deep, global phenomenon of abiotic hydrocarbon production accompanied early petroleum discoveries in Russia in the late 19th century, as expounded by Dmitri Mendeleev, and later by Soviet scientists and by the Austrian-born astrophysicist Thomas Gold (Glasby 2006). Their controversial theories postulated that economic hydrocarbons in crustal settings derive from abiotic CH₄ that polymerized to higher hydrocarbons in the mantle before migrating to Earth’s surface along deep faults. Very detailed biomarker evidence from oils worldwide (molecular “fossils”, e.g., of flowering plants), alongside geological and experimental considerations, continues to strongly refute these theories, instead favoring a principally *thermogenic* petroleum origin, i.e., derived from heat-induced molecular breakdown of biological (*biotic*) organic matter created at Earth’s surface.

However, theory and experimentation now support the idea that CH₄ and other light hydrocarbons (containing 2 to 4 carbons) are stable at deep upper-mantle conditions (beyond ~100–175 km depth) (McCollom 2013 and references therein). But it is questionable whether such deep mantle hydrocarbons would be able to transit the shallow upper mantle where CO₂ becomes much more stable than CH₄ owing to more oxidizing conditions (see McCollom 2013). Degassing magmatic fluids (i.e., high-temperature volcanic

gases) in terrestrial and marine volcanic settings are typically dominated by CO₂ with only trace concentrations of CH₄ (see FIG. 1).

Both lower-temperature terrestrial geothermal and seafloor hydrothermal fluids (typically <450 °C), in contrast, exhibit CH₄/CO₂ ratios much higher than magmatic gases (FIG. 1). Abundant CH₄ and lesser amounts of ethane, propane, butane, and other organics have now been found in many rock-hosted crustal fluids, ranging from seafloor mafic/ultramafic-hosted hydrothermal vents, to low-temperature terrestrial ophiolite springs, to ancient fluids occluded in cratons and igneous intrusions (see McCollom and Seewald 2007; Charlou et al. 2010; Etiope and Sherwood Lollar 2013). Many of these hydrocarbons are widely argued to form abiotically. Below magmatic/upper-mantle temperatures, at the reducing conditions encountered within oceanic or continental crust, reduction of CO₂ to form hydrocarbons is thermodynamically possible. Thus, abiogenesis is most likely a crustal, rather than mantle, phenomenon. Thermodynamic favorability belies, however, the fact that kinetic barriers must still be overcome for abiogenesis to occur.

IDENTIFYING ABIOTIC HYDROCARBONS: LIMITATIONS AND CHALLENGES

How may it be determined if CH₄ and larger hydrocarbons in crustal fluids derive from abiogenesis? Thus far, criteria proposed to identify abiotic hydrocarbons rely heavily on empirical classifications, i.e., comparisons of chemical and isotope ratios of hydrocarbons of unknown origins to those documented as microbial or thermogenic in origin. An abiotic origin was initially proffered for hydrocarbons exhibiting traits strongly deviating from these common biotic sources, often found in crystalline rocks apparently lacking conspicuous organic matter or microbial life. These traits are unfortunately increasingly problematic as our understanding of the unusual systems where abiogenesis is presumed to occur increases.

Signatures of Abiotic Hydrocarbons

The following characteristics have historically been used to identify abiotic CH₄ and co-occurring light hydrocarbons in Earth's crust:

1. *Extreme ¹³C/¹²C and/or ²H/¹H isotope ratios of CH₄.* Welhan and Craig (1983) first reported CH₄ from seafloor hydrothermal vents on the East Pacific Rise (presumably free of sedimentary organic inputs) as having anomalously high ¹³C/¹²C ratios ($\delta^{13}\text{C}_{\text{methane}}$ values) of about -15‰ and suggested that the CH₄ was leached directly from crustal basalt. Similarly, Sherwood Lollar et al. (2002) reported low molecular

weight hydrocarbons found in waters within rock fractures of ancient ultramafic Canadian Shield terranes (e.g., Kidd Creek Mine, Ontario, located in Archean greenstone belt). Relatively low $^2\text{H}/^1\text{H}$ ratios ($\delta^2\text{H}_{\text{methane}}$) in these gases, atypically uncorrelated with $\delta^{13}\text{C}_{\text{methane}}$, strongly deviated from more ^{13}C -depleted, D-enriched biotic CH_4 -rich gases known at the time.

2. *A $^{13}\text{C}/^{12}\text{C}$ isotope "reversal" between CH_4 and ethane.* Thermal decomposition of organic matter in a closed system typically yields light hydrocarbons where $\delta^{13}\text{C}$ increases with the number of carbon atoms owing to more rapid breakage of ^{12}C - ^{12}C bonds than ^{13}C - ^{12}C bonds. Carbon atoms released by bond breaking are thus ^{13}C depleted, but this depletion is diluted in longer chain products by carbon atoms inherited from other sites, distant from the critical bond-breaking reaction. If instead hydrocarbons form by polymerization of CH_4 , ^{12}C - ^{12}C bonds, in theory, should polymerize fastest, leaving residual abiotic CH_4 enriched in ^{13}C relative to product ethane (as well as propane, etc.). Gases from the Kidd Creek Mine first exemplified this unusual pattern (Sherwood Lollar et al. 2002).
3. *Apparent CO_2 - CH_4 chemical and isotopic equilibrium.* Chemical and isotopic equilibrium requires reaction reversibility. Methane abundances and isotopic compositions in terrestrial geothermal gas emissions from Mediterranean subduction-related volcanoes (e.g., Vesuvius and Ischia in Italy; Nisyros in Greece) appear consistent with equilibrium with CO_2 , implying reduction of CO_2 to CH_4 (Fiebig et al. 2007).
4. *Radiocarbon (^{14}C) absence in CH_4 .* Nondetectable ^{14}C (a short-lived cosmogenic radionuclide incorporated into photosynthetic organic matter) in dissolved CH_4 from ultramafic-hosted seafloor hydrothermal vents (e.g., the Lost City hydrothermal field, Mid Atlantic Ridge; the Von Damm vent field at the Mid-Cayman Rise) has been used to argue for a mantle-derived inorganic carbon source (Proskurowski et al. 2008; McDermott et al. 2015).
5. *Alkane $C_1/(C_2 + C_3)$ ratios greater than 100.* Fiebig et al. (2009) used analysis of CH_4 -rich (nonmicrobial) gases from Nisyros Volcano to suggest concentration ratios of CH_4 over the sum of ethane plus propane above 100 (particularly when that CH_4 is ^{13}C -enriched) could reflect admixing of abiotic CH_4 with thermogenic longer-chain hydrocarbons (thermogenic hydrocarbons were considered to have ratios <100).

6. A “Schultz–Flory” relationship between *n*-alkanes: If abundance ratios of homologous *n*-alkane hydrocarbons (e.g., propane/ethane) are nearly constant with increasing chain length, this could reflect probability effects of abiotic carbon chain growth seen during industrial surface-catalyzed syntheses, such as the Fischer–Tropsch process. Etiope and Sherwood Lollar (2013) suggest that thermogenic *n*-alkane mixtures typically have correlation coefficients (r^2 of plotted \log_{10} of alkane mole fractions versus carbon number) of less than 0.9, while *dominantly* and *quasi-pure* abiotic *n*-alkanes should have r^2 values above 0.9 and 0.99, respectively.
7. *Additional geochemical/geological contextual indications.* These include processes such as serpentinization of ultramafic rock (in essence, the aqueous alteration of olivine) producing abundant H_2 (the presumptive reductant), and high values of mantle-derived primordial 3He (a proxy for mantle carbon supply) (Etiope and Sherwood Lollar 2013).

Finding some (or many) of these indicators has led to assertions that low molecular weight hydrocarbons may indeed be abiotic in numerous submarine and terrestrial (e.g., continental, subaerial) crustal settings (Charlou et al. 2010; Etiope and Sherwood Lollar 2013; Etiope and Whiticar 2019).

Problems with Abiotic Signatures

Findings from experiments and natural studies in the last decade suggest that few, if any, of the above criteria, when taken in isolation, provide unambiguous evidence for hydrocarbon abiogenesis. They may be insufficiently convincing even in combination. Significant challenges facing these abiotic indicators include the following:

1. Under alkaline conditions, microbial CH_4 may reach quite high $\delta^{13}C$ values (above -30‰) (Miller et al. 2018). Thermal breakdown of organic matter can also generate $\delta^{13}C_{\text{methane}}$ values up to -15‰ (Milkov and Etiope 2018), with even more positive values (up to -4‰) likely possible under certain 'open system' conditions (Fiebig et al. 2019). Experimental abiotic syntheses also fail to yield CH_4 strongly enriched in ^{13}C relative to thermogenic sources, but is instead typically ^{13}C -depleted relative to CO_2 by $\sim 15\text{‰}$ – 100‰ (McCollom 2013; Milkov and Etiope 2018). As a consequence, experimental abiotic $\delta^{13}C_{\text{methane}}$ values largely overlap the common thermogenic CH_4 range of sedimentary systems ($-75\text{‰} < \delta^{13}C < -15\text{‰}$).
2. Isotope reversals between CH_4 and ethane are rarely obtained in experimental abiotic hydrocarbon formation at hydrothermal conditions (McCollom 2013). Reversals may

also be generated during thermal breakdown of organic matter in an open system, e.g. if CH₄ and ethane are cleaved from different macromolecular precursor sites, and the isotope fractionation associated with CH₄ cleavage is larger than for ethane (Fiebig et al. 2019). A continuous supply of immature organic matter to a heated geologic setting may lead to mixing between thermally mature (¹³C-enriched) and immature (¹³C-depleted) organic matter precursors, just as mixing of CH₄ and other low molecular weight hydrocarbons of distinct maturities may produce apparent reversals without abiogenesis (Fiebig et al. 2019).

3. Definitively proving CH₄ occurs in equilibrium with CO₂ in terrestrial geothermal discharges is challenging. Gas concentration ratios are strongly affected by vapor separation/condensation processes, and redox conditions (i.e., H₂ abundance) at depth are poorly constrained. A reassessment of isotopic compositions of CO₂ and CH₄ in global volcanic–hydrothermal emissions strongly implies apparent CO₂ and CH₄ carbon isotope fractionations only fortuitously correspond to subsurface temperatures (Fiebig et al. 2019).
4. Nondetectable radiocarbon in putative abiotic CH₄ may reflect a biotic carbon origin, if microbial utilization of ¹⁴C-depleted carbon occurs or the carbon formed by photosynthesis >50 ky ago (cf. petroleum gases). Seafloor vent fluids presumably circulate faster than this through oceanic crust, but fluids occluded in fractures or inclusions (in both terrestrial and submarine settings) may be trapped for far longer.
5. Ratios of C₁/(C₂ + C₃) above 100 were recently found in highly mature thermogenic gases. Microbial CH₄ is also characteristically very high on this index. Recent revisions of classification diagrams describing thermogenic versus abiotic regions of δ¹³C_{methane} versus C₁/(C₂ + C₃) space reveal ever-increasing overlap between these two processes (Milkov and Etiope 2018).
6. Schulz–Flory distributions reflect the probability of random polymerization of monomers to form linear chains (polymers), but such effects are identical for random cleavage of preexisting C–C bonds during the thermal decomposition of larger organics. Relatively few terrestrial natural gas sites were used for this empirical classification approach, and the “abiotic” assessment criteria applied to these gases are either debatable (e.g., carbon isotope reversals) or unclear. In mixtures where *r*² deviates from ~1, the test fails to distinguish more complex abiotic hydrocarbon mixtures (e.g. formed by multiple mechanisms) from thermogenic-abiotic hydrocarbon mixtures.

7. Elevated H₂ only indicates extensive reduction of H₂O to H₂ by water–rock reactions (e.g., serpentinization) or by radiation-induced dissociation of water, neither of which need inherently share origins with co-discharged hydrocarbons (i.e., they may not be syngenetic). Mantle ³He is also chemically unrelated to abiogenesis and is, therefore, similarly circumstantial.

EXPERIMENTAL CONSTRAINTS ON ORGANIC ABIOGENESIS

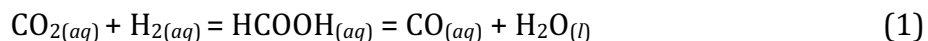
Due to the complexities of natural systems, experimental simulations have been extensively utilized to illuminate abiotic organic transformations in Earth’s crust. We summarize recent salient findings in a historical context here and refer readers to McCollom (2013) and McCollom and Seewald (2007) for more detailed reviews.

Experiments indicate that overall equilibrium between CO₂ and CH₄ (yielding increasingly CH₄-dominated fluids with decreasing temperature) is inhibited at the lower temperature–pressure (*T–P*) conditions of crustal fluids (McCollom 2013). This sluggish overall C–O–H equilibration implies other types of metastable organic carbon can occur, i.e., C in oxidation states less reduced than CH₄ (–IV), such as larger hydrocarbons and heteroatom (N-, S-, O-bearing) compounds (FIG. 2). Thermodynamics predict that abiogenesis of organic compounds other than CH₄ could happen at crustal conditions. But, as for CH₄, kinetic barriers might prevent their formation, even in natural H₂-rich fluids. As such, there has been much experimentation on catalysts that overcome kinetic barriers and that accelerate abiogenesis, with a primary focus on short-chain hydrocarbons.

The role of olivine serpentinization in the abiotic synthesis of light hydrocarbons has been an obvious focus of much experimental study and debate. Early hydrothermal experiments (~300 °C, 500 bar) first suggested reduction of CO₂ could be catalyzed by magnetite, which is a product of serpentinization. The light hydrocarbons that formed, however, evidently derived from preexisting reduced carbon in the olivine or from contaminants. Little or no bona fide abiotic CH₄ (and no larger hydrocarbons) have since been shown to form from ¹³C-labelled inorganic carbon during experimental olivine serpentinization above 200 °C (McCollom 2016), and lower temperature experiments (60–100°C, ~1 atm) similarly produced no detectable CH₄ above background (McCollom and Donaldson 2016 and references therein). Even with abundant dissolved H₂ (0.1 mol/kg_{H₂O} or higher), it now appears that the serpentinization reaction alone is incapable of substantial abiotic hydrocarbon production on laboratory timescales up to the maximum temperatures at which the reaction should occur (~330–400 °C, depending on pressure).

Mineral catalysts besides magnetite must be involved if more rapid and effective hydrocarbon abiogenesis is to occur in reducing crustal environments. Numerous candidates (e.g., chromite, cobalt-enriched magnetite, iron–nickel alloys/sulfides) have been tested under hydrothermal conditions (i.e., aqueous solutions at ~200–400 °C, <50 MPa) (see McCollom 2013). Aqueous CH₄ formation (without production of higher hydrocarbons) occurs rapidly with Ni-enriched alloys, analogous to the ultramafic mineral awaruite (Fe₃Ni). Gaseous CO₂ and H₂ can form CH₄ at 20–90 °C using a dry ruthenium catalyst (Etiope and Ionescu 2015), but the catalytic availability of Ru reaction sites in natural igneous rock is highly uncertain, and may be negligible if shielded by the mineral host or adversely affected by water. Production of bona fide abiotic larger hydrocarbons is possible with other naturally occurring catalysts (e.g., chromite) but is relatively sluggish in experiments at hydrothermal conditions (<0.05% conversion after 45 days at 390 °C, 40 MPa). Native Fe metal, though an efficient catalyst for abiotic synthesis and common in meteorites, is absent in most crustal settings; nevertheless, it has been useful in laboratory experiments to examine C isotope effects of hydrocarbon abiogenesis. At present, despite extensive catalyst testing, no experiment has yet reproduced the δ¹³C values of putative natural abiotic hydrocarbons. This remains a persistent conundrum lacking a satisfactory explanation (McCollom 2013).

While abiotic hydrocarbons have been the focus of many laboratory studies, experiments have also been used to investigate possible abiotic synthesis of other organic compounds. Amino acid abiogenesis has been widely simulated in early Earth studies (see summary in Ménez et al. 2018), but the experiments invariably employed compounds such as cyanides (e.g., HCN, KCN), hydroxylamine, and/or formaldehyde as reactants, which are neither confirmed to exist in appreciable amounts nor demonstrated to be definitively abiotic in hydrothermal fluids. Experiments using ¹³C-labelled inorganic carbon, have, however, shed much light on the abiogenesis of reduced single-carbon molecules (FIG. 2), which often readily form from (and in some cases equilibrate with) CO₂ in solution, without minerals present. These include carbon monoxide (CO), formic acid (HCOOH), methanol (CH₃OH) and methanethiol (CH₃SH). CO₂, for example, rapidly achieves equilibrium with carbon monoxide (CO) and H₂, via HCOOH, in experimental hydrothermal solutions (150–325 °C, 35 MPa) that resemble the “water–gas shift” reaction:



The CO that is formed is far less abundant than CO₂, but HCOOH becomes increasingly abundant at lower temperatures, reaching equilibrium within days to weeks (Seewald et al. 2006). Slower reduction of CO₂ to form CH₃OH proceeds without minerals (homogeneously)

at 300 °C, requiring ~1 y to equilibrate. Even slower homogeneous reduction of CH₃OH by H₂ to form CH₄ occurs over several years at 300–325 °C (35 MPa), with rates dependent on CH₃OH abundance (FIG. 2) (Reeves 2010). The formation of CH₃OH from CO₂ is heavily dictated by available H₂, temperature, and, to a minor extent, pressure. The production of H₂ during serpentinization is predicted to peak at ~200–315°C (at 35 MPa); thus, mineral-free CH₄ formation via CH₃OH could proceed slowly in crustal fluids with long residence times (decadal or greater) under such conditions. Formic acid can form CH₃SH at similar temperatures and pressures in the presence of H₂S (FIG. 2), perhaps via CO, but equilibrium between CO₂ and CH₃SH does not appear to occur (Reeves 2010). The limited experiments on CH₃SH suggest that abiotic alkyl thiols might form rapidly, but that their abundances could be governed by kinetics rather than metastable equilibrium with inorganic carbon.

ORGANIC ABIOGENESIS IN SUBMARINE AND TERRESTRIAL SETTINGS

Submarine Hydrothermal Settings

Seafloor hot springs are complex settings in which to study abiogenesis. Yet, these “natural laboratories” are critical to understanding the phenomenon. These environments are undoubtedly favorable thermodynamic settings for abiogenesis, but elucidating the types and origins of organic molecules present in seafloor hydrothermal fluids is challenging because access to them is infrequent, difficult, and costly. Elevated temperatures, abundant H₂, magmatic CO₂, and/or seawater dissolved inorganic carbon (DIC) (i.e., CO_{2(aq)} + HCO₃⁻ + CO₃²⁻) as reactants, together with possibly catalyst-bearing igneous rocks, create seemingly ideal conditions for organic abiogenesis to occur. Until recently, the reduction of CO₂ to CH₄ (and other, presumably trace, organics) in these fluids was generally assumed to be commonplace. The discovery of cool (<116 °C), CH₄- and H₂-rich fluids venting at the Lost City hydrothermal vent field in the early 2000s did much to shape this conception (Proskurowski et al. 2008), even though the high-pH (>10) fluids there lacked significant DIC to drive abiogenic CH₄ production. However, recent results from the newly discovered CH₄- and H₂-rich Von Damm hydrothermal vent field, which has higher temperatures (up to 226 °C) and moderate pH (~5.5), challenge this paradigm, necessitating a rethinking of presumptions of how subseafloor abiogenesis occurs. Remarkably, the hottest fluids venting at the seafloor at Von Damm have DIC concentrations (and ¹³C/¹²C ratios) that closely resemble seawater values (McDermott et al. 2015), indicating that the fluids have passed through the entire hydrothermal convection system without losing seawater DIC or adding any CO₂, either thermogenic or magmatic. Reduction of inorganic carbon cannot, therefore, be responsible for the abundant dissolved CH₄ observed in the fluids, implying a striking inability to transform CO₂ to CH₄ on hydrothermal timescales, despite the highly favorable

conditions for it to occur. Fluids at other hydrothermal vent fields (e.g., Lucky Strike and Menez Gwen, Mid-Atlantic Ridge), in contrast, contain similarly abundant CH₄, despite the very low H₂ concentrations that make abiogenesis thermodynamically unfavorable, demonstrating that other sources of CH₄ must exist in submarine hydrothermal systems.

Novel measurements of temperature-sensitive “clumped” isotopologues (e.g. ¹³CH₃D) for CH₄ at the Lost City, Rainbow, Von Damm and Lucky Strike vent fields—systems with fluids of diverse temperatures and chemistries—indicate that the CH₄ in all of these systems formed (or isotopically equilibrated with water) at a common, uniformly high temperature, averaging 310 ± ~50 °C (Wang et al. 2018). Collectively, such findings necessitate that abundant CH₄ in many submarine hydrothermal vents, if indeed abiotic, forms independently of chemical compositions and conditions of actively circulating fluids. Methane in these fluids may come from hydrothermal “leaching” of mineral-hosted vesicles (fluid inclusions) containing trapped CH₄ gas, as originally suggested by Welhan and Craig (1983). Klein et al.(2019) propose a model whereby aqueous fluids entering the upper mantle/lower crust are entrapped as secondary fluid inclusions during olivine dissolution-precipitation (>~400 °C). Upon cooling, the walls of these inclusions evidently serpentinize and produce H₂ internally, trapping this H₂ with CO₂ for extremely long time periods (see FIG. 3). This allows sluggish abiotic CO₂ reduction to proceed before hydrothermal fluids can leach the newly formed gas. Analysis of ¹³C/¹²C in CH₄ and ethane trapped in inclusions from rocks near Von Damm reveals isotope ratios overlapping with those of the vent fluids at that site, and at other systems (Grozeva et al. 2020). Such compelling similarity could provide a simple explanation for the uniform isotope signature of hydrothermal CH₄.

Longer-chain hydrocarbons, beyond ethane, are typically only trace components of hydrothermal fluids. Their analyses is therefore challenging and their provenance difficult to decipher, especially when found alongside biomarker molecules that suggest cryptic biological contributions of organics (McCollom et al. 2015). Unusual aromatic (cyclic) amino acids of suggested abiotic origin have recently been detected in subsurface crustal rocks near Lost City (Ménez et al. 2018). Simpler amino acids detected in nearby vent fluids are, however, more consistent with vent microbial sources.

Despite evidence that many complex organics in vent fluids are biological in origin, abiotic CO₂ reduction to single-carbon compounds in vent fluids (HCOOH and CO) (FIG. 2) is supported by experimental, field, and thermodynamic data. Data from diverse settings show almost ubiquitous CO₂-H₂-CO equilibrium in vent fluids (Reeves et al. 2014), consistent with experiments (Seewald et al. 2006). Notable exceptions are the sediment-influenced hydrothermal vents in the Guaymas Basin (Gulf of California, USA), where excess CO relative

to equilibrium with CO₂ suggests thermogenic CO derived from hydrothermal breakdown and/or oxidation of sedimentary organic matter. Widespread CO₂-H₂-CO equilibrium elsewhere implies that the intermediate HCOOH (FIG. 2) should also be commonly found in equilibrium with CO₂, but such equilibrium has only been conclusively demonstrated in Von Damm fluids (McDermott et al. 2015). In contrast, CH₃SH abundances in a variety of hydrothermal fluids show no evidence for equilibrium with DIC (Reeves et al. 2014), which agrees with experimental findings (FIG. 2). Thermogenic CH₃SH sources appear to dominate, likely from the decomposition of cryptic subsurface organic matter (vent biomass, marine organic matter). There is, as yet, still no definitive evidence for CO₂ reduction to CH₃OH in vent fluids. Observations thus far make it difficult to discriminate between kinetically controlled (disequilibrium) abiotic reactions involving single-carbon compounds versus thermogenic production from biomass, because these two processes may share common intermediate species, such as CO or HCOOH. The inability to make substantial (i.e. equilibrium abundance) reduced single carbon compounds by abiogenesis suggests, however, that fluid residence times may be insufficient for them to form in great amounts in the subseafloor.

Terrestrial Crustal Settings

Using some of the criteria noted above, hydrocarbon abiogenesis has been proposed in terrestrial volcanic-hydrothermal systems (Fiebig et al. 2007), alkaline igneous and cratonic rocks (Potter et al. 2004; Sherwood Lollar et al. 2002), and ophiolite/peridotite outcrops (Etiope and Whiticar 2019 and references therein). Abiotic CH₄ generation in these settings has been postulated to occur through the reduction of CO₂ by H₂ at relatively low temperatures in ophiolite/peridotite outcrops and in cratonic rocks (both settings <140 °C), and at somewhat higher temperatures (250°-500°C) in cooling igneous rocks and in hydrothermal systems. Subduction zone metamorphosed carbonates (“ophicarbonates”) have also been implicated in terrestrial abiotic CH₄ production. Vitale Brovarone et al. (2017) demonstrate that the degree of metasomatic alteration of these ophicarbonates tracks ¹³C enrichment in the altered carbonate. This was attributed to carbonate reduction by serpentinization-derived H₂ at 300–450 °C and 1.5–4 MPa, releasing abiotic CH₄ depleted in ¹³C with respect to the primary carbonate. The presence of CH₄- and H₂-bearing fluid inclusions in the altered ophicarbonates supports this possibility.

The above abiotic signatures notwithstanding, global datasets of carbon and hydrogen isotope ratios of methane, ethane, propane and *n*-butane in terrestrial volcanic-hydrothermal fluids are arguably also consistent with the thermal degradation of organic matter under open system conditions (Fiebig et al. 2019). Organic matter may be supplied

by nearby sedimentary rocks or near-surface fluids (meteoric water, seawater) circulating through these systems, perhaps explaining why CH₄ is enriched in hydrothermal emissions relative to magmatic emissions (FIG. 1). The low molecular weight hydrocarbons in magmatic–hydrothermal environments might, thus, better be termed “volcanic-thermogenic” (Fig. 4). Notably, in numerous other terrestrial sites, propane and *n*-butane, argued to be partly or entirely abiotic based on carbon isotope reversals, have δ¹³C values within the range reported for surface organic matter (approximately –15‰ to –30‰, Fiebig et al., 2019).

Taken together, the global survey of Fiebig et al. (2019) and the experiments of McCollom (2016) suggest the possibility that abiotic hydrocarbon formation may occur too slowly in dynamic terrestrial hydrothermal systems to outpace thermogenic production pathways. Abiotic hydrocarbon production may, however, become significant, and even overwhelm thermogenic pathways, under stagnant hydrothermal conditions such as those encountered in entrapped fluid inclusions (e.g., Vitale Brovarone et al. 2017; Klein et al. 2019). Under such closed system conditions, inorganic carbon in entrapped hydrothermal fluids may have sufficient time to react with H₂ and form CH₄ and other light hydrocarbons slowly over time.

Recent measurements of CH₄ clumped isotopologues (both ¹³CH₃D and ¹²CH₂D₂) from gas discharges at terrestrial sites of suspected abiogenesis have deepened interpretations of hydrocarbon formation there (Young et al. 2017). Originally assumed to be of low temperature (≤50 °C) abiotic origin, the Chimaera “flaming rock” ophiolite CH₄ seep in Turkey, for example, evidently comprises CH₄ isotopologues that internally equilibrated at ~120–140 °C. These temperatures are much hotter than regional constraints indicate should occur in the subsurface at the site, and the gas is likely a mixture of both abiotic and thermogenic CH₄. Strong depletions in the heavier isotopologues ¹²CH₂D₂ and ¹³CH₃D (relative to a purely random “stochastic” isotope ordering) are emerging as unusual patterns showing up in low temperature CH₄ emissions from terrestrial mafic–ultramafic igneous settings (Cabeço de Vide, Spain; Kidd Creek Mine, Canada). Such “anti-clumped” behavior may be due to quantum tunneling effects by D or H atoms that confound classical kinetic isotope theory, based on limited experimentation (gas-phase CH₄ production catalyzed by dry ruthenium). Applying the signature as an unequivocal tracer of abiotic CH₄ in these sites is, however, problematic, given that microbial processes also produce such effects, as well as potentially overprint them (Young et al. 2017). The availability and role of Ru in many of these water-rich environments is also debatable.

CONCLUDING REMARKS

Unambiguous evidence that hydrocarbons and other organics in crustal fluids are abiogenic is unfortunately scarcer now than previously assumed. Future attempts to identify abiogenic organics can nonetheless avail of a remarkably wide array of techniques: these include the multiply substituted and site-specific isotopologues, theoretical models of the thermodynamic constraints on abundance, and diverse existing datasets for natural systems. In order to quantitatively assess the importance of abiogenic hydrocarbon formation in natural systems, the fate of the organic matter that is supplied to crustal rocks by seawater and meteoric water needs to be better understood. Further experiments on the C-, H-, clumped and site-specific isotope systematics of microbial, abiogenic, and hydrothermal thermogenic CH₄ production, especially under diverse (but realistic) natural conditions, will be critical in the coming decade.

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FIGURES CAPTIONS

Figure 1 Molar CH_4/CO_2 ratios versus discharge temperatures in diverse terrestrial geothermal fluids (from New Zealand, Iceland, the Mediterranean) and selected submarine hydrothermal vent fluids (SuSu Knolls, Manus Basin, Papua New Guinea), relative to magmatic fluids (red dots, yellow squares). Magmatic fluid emissions contain acid components such as SO_2 , HCl and HF and are almost all depleted in CH_4 relative to lower temperature convective hydrothermal fluids (lacking acid components; white, blue and black dots, black squares). Seafloor hydrothermal fluids from SuSu Knolls are enriched in CH_4 relative to locally venting magmatic fluids, but this CH_4 is thermogenic in origin.

Figure 2 Summary of abiogenic carbon transformations demonstrated in experimental aqueous hydrothermal solutions (heated oceanic crust conditions), based on ^{13}C -label tracking. Potential reaction intermediates that were not measured are not shown. Bidirectional arrows (blue) denote aqueous reactions where observed chemical equilibrium (reversibility) in the absence of minerals has been confirmed by thermodynamic calculations

(using all reactants and products). Unidirectional arrows denote reactions where equilibrium has not been shown.

Figure 3 (A) Thin section photomicrographs of fluid inclusions rich in H₂ and/or CH₄ trapped in olivine within peridotitic and gabbroic rocks from ultraslow-spreading mid-ocean ridge settings (Gakkel and Southwest Indian Ridges, Mid-Cayman Rise), a slow-spreading setting (Mid-Atlantic Ridge, MAR) to a fast-spreading setting (East Pacific Rise, EPR) **(B)** False-color Raman maps of an olivine-hosted inclusion showing the distribution of brucite, CH₄, H₂ and the serpentine mineral chrysotile. Figures adapted from Klein et al.(2019) and reproduced with permission.

Figure 4 Global summary of CH₄ hydrogen (δD) versus carbon isotope ratios ($\delta^{13}C$) attributed to various methane-producing processes (indicated) from Fiebig et al. (2019) and references therein. Ranges for sedimentary thermogenic CH₄ production and microbial CO₂ reduction/fermentation pathways are from Milkov and Etiope (2018) and Miller et al. (2018). The “volcanic-thermogenic” field (in red) is proposed to be consistent with organic matter pyrolysis: it substantially overlaps the range of values for CH₄ argued to be potentially abiotic. Abbreviations: VPDB = Vienna Pee Dee belemnite; VSMOW = Vienna standard mean ocean water; red'n = reduction.

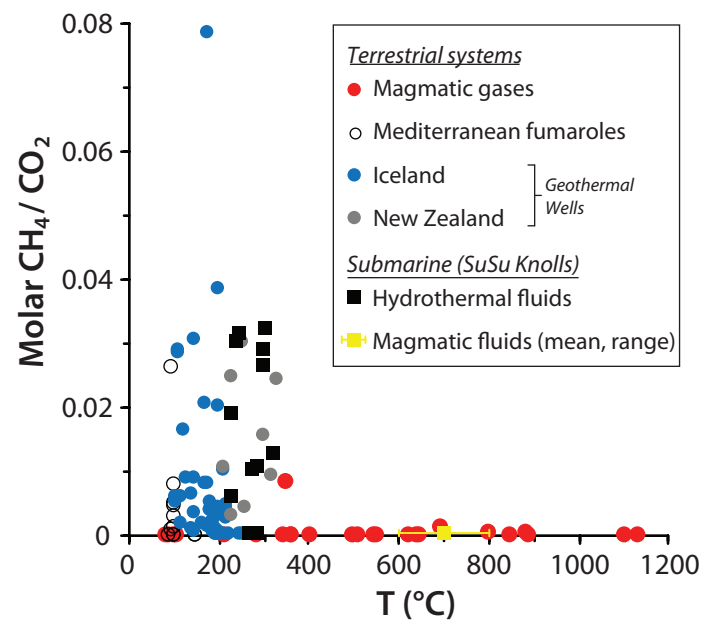


Figure 1

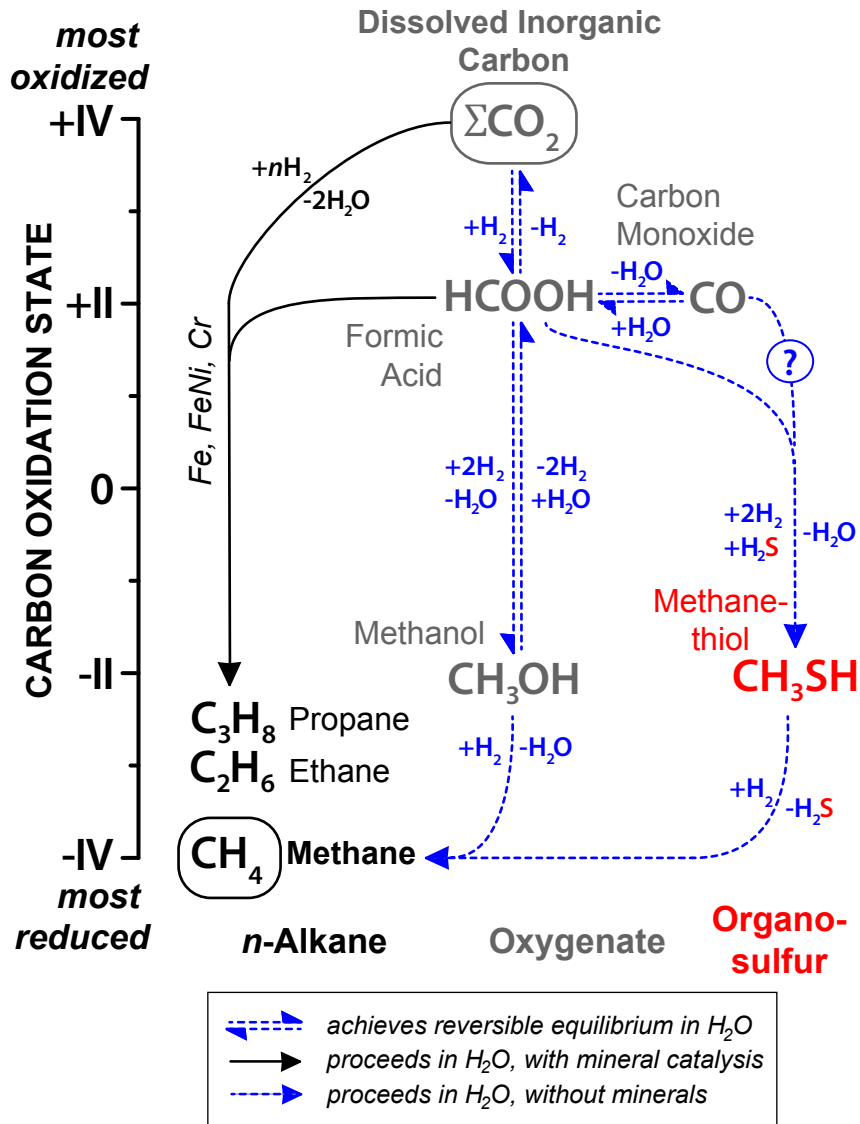


Figure 2

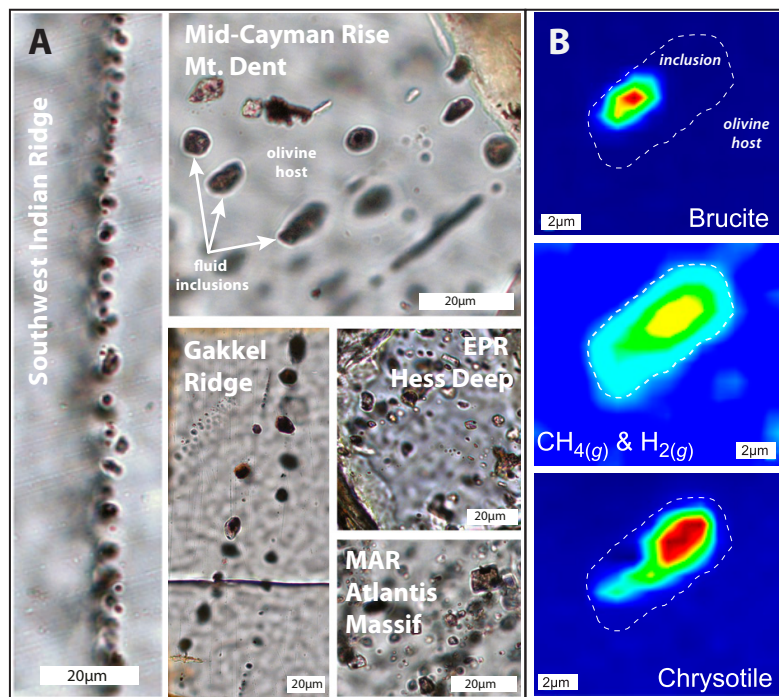


Figure 3

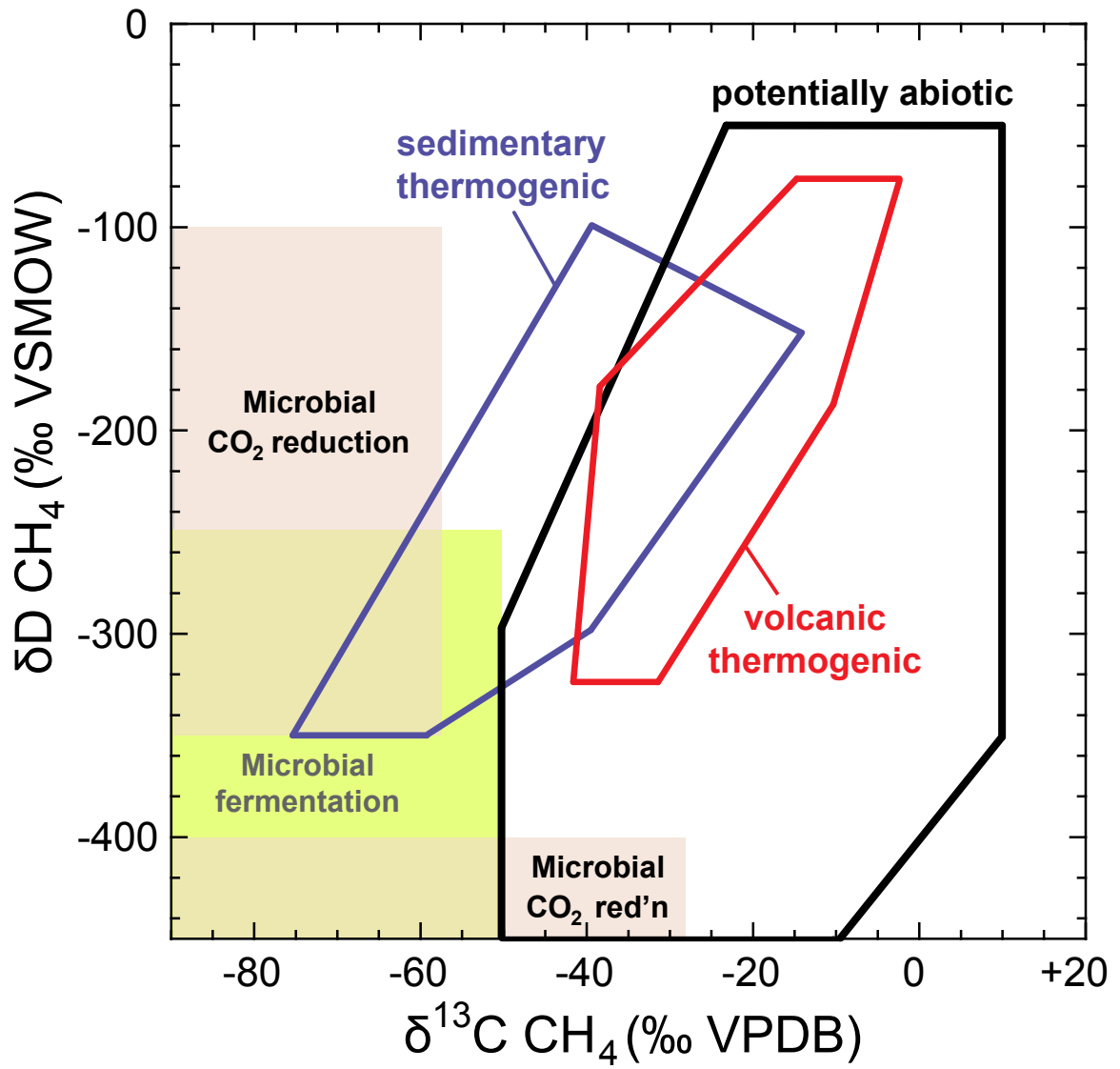


Figure 4