

# ABIOTIC METHANE ON EARTH

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[1] Over the last 30 years, geochemical research has demonstrated that abiotic methane (CH<sub>4</sub>), formed by chemical reactions which do not directly involve organic matter, occurs on Earth in several specific geologic environments. It can be produced by either high-temperature magmatic processes in volcanic and geothermal areas, or via low-temperature (<100°C) gas-water-rock reactions in continental settings, even at shallow depths. The isotopic composition of C and H is a first step in distinguishing abiotic from biotic (including either microbial or thermogenic) CH<sub>4</sub>. Herein we demonstrate that integrated geochemical diagnostic techniques, based on molecular composition of associated gases, noble gas isotopes,

mixing models, and a detailed knowledge of the geologic and hydrogeologic context are necessary to confirm the occurrence of abiotic CH<sub>4</sub> in natural gases, which are frequently mixtures of multiple sources. Although it has been traditionally assumed that abiotic CH<sub>4</sub> is mainly related to mantle-derived or magmatic processes, a new generation of data is showing that low-temperature synthesis related to gas-water-rock reactions is more common than previously thought. This paper reviews the major sources of abiotic CH<sub>4</sub> and the primary approaches for differentiating abiotic from biotic CH<sub>4</sub>, including novel potential tools such as clumped isotope geochemistry. A diagnostic approach for differentiation is proposed.

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## 1. INTRODUCTION

[2] Biotic methane (CH<sub>4</sub>), produced either by microbial processes or by thermogenic degradation of organic matter in sedimentary rocks, is widespread on Earth and forms the major commercial natural gas reservoirs driving the global economy. Abiotic (or abiogenic) CH<sub>4</sub>, formed by chemical reactions that do not directly include organic matter, is produced in much smaller amounts on a global scale, and is not found in economically exploitable reservoirs, apart from rare and controversial exceptions [e.g., Dai *et al.*, 2005; Ni *et al.*, 2009; Jin *et al.*, 2009]. In most geologic environments biotic and abiotic gases are mixed, and notwithstanding the modern molecular and isotopic analytical and interpretative tools, in many cases it is not easy (or even possible) to distinguish them. Nevertheless, unraveling abiotic from biotic CH<sub>4</sub> would be extremely important in a wide range of scientific fields. Besides the more traditional issues of organic geochemistry and petroleum exploration [e.g., Jenden *et al.*, 1993], the problem of determining the

existence and origin of abiotic CH<sub>4</sub> in natural systems spans the disciplines of deep subsurface microbiology and the origin of life [e.g., Russell *et al.*, 2010]; hydrocarbon synthesis in oil industry and space-based applications [Lunde and Kester, 1974; Szatmari, 1989]; and astrobiology and planetary exploration (e.g., the formation of CH<sub>4</sub> on Mars, Titan, and Enceladus [Tobie *et al.*, 2006; Atreya *et al.*, 2007; Mousis *et al.*, 2009; Mumma *et al.*, 2009; Etiope *et al.*, 2013a]).

[3] This paper is an updated review of abiotic CH<sub>4</sub> on Earth, providing new data and concepts that seek to make identification of abiotic CH<sub>4</sub> less ambiguous. We do not discuss the possible abiotic origin of petroleum, meaning crude oil or complex gaseous hydrocarbons, proposed in the Russian-Ukrainian theory and the Thomas Gold theory [Kudryavtsev, 1951; Gold, 1979; Kenney *et al.*, 2002; Kolesnikov *et al.*, 2009] and which was already reviewed by Glasby [2006] and, in this journal, by Kutcherov and Krayushkin [2010]. We focus on CH<sub>4</sub> only, the simplest and most widespread hydrocarbon, whose possible abiotic origin is not questioned. To date, no comprehensive review on abiotic CH<sub>4</sub> generation mechanisms has appeared, despite major changes in our knowledge based on both field and experimental studies of CH<sub>4</sub> since reviews published many years ago [e.g., Welhan, 1988; Whiticar, 1990; Potter and Konnerup-Madsen, 2003]. This work also seeks to resolve some confusion that still exists in the terminology

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used in nonspecialized literature to describe the various types of abiotic CH<sub>4</sub>. A confusion that may foster misunderstandings concerning its distribution and importance on Earth or other planets. For example, a critical point that is often lost in the debate is the distinction between magmatic (mantle-derived) CH<sub>4</sub> and other possible sources of abiotic CH<sub>4</sub> such as water-rock and gas-rock reactions (e.g., serpentinization and CO<sub>2</sub> hydrogenation). Magmatic or mantle-derived CH<sub>4</sub> is abiotic, but not all abiotic CH<sub>4</sub> is mantle-derived. These terms and categories are clarified herein.

[4] We propose a coherent classification of abiotic CH<sub>4</sub> sources and, for each source, describe the basic production mechanisms (section 2). Occurrences of abiotic CH<sub>4</sub> in various geologic environments and its flux into the atmosphere are reviewed (section 3). The stable isotopic composition of carbon and hydrogen of CH<sub>4</sub> (expressed as  $\delta^{13}\text{C}$  and  $\delta^2\text{H}$ ) is fundamental information necessary, but often not in itself sufficient, to define the origin of CH<sub>4</sub>. We review the isotopic data of CH<sub>4</sub> found on Earth and chronicle the main steps of using the traditional isotopic diagram (CD – carbon-deuterium, or  $\delta^{13}\text{C}$  vs  $\delta^2\text{H}$  diagram, also known as Schoell's plot; Schoell [1980]) for genetic zonation of CH<sub>4</sub> (section 4.1). We then develop a more comprehensive and updated version of this diagram (section 4.2) and further show how noble gases, specifically helium isotopic composition, may help in deciphering abiotic CH<sub>4</sub> data sets (section 4.3). We discuss the techniques/principles of determining an abiotic origin (sections 5.1–5.2), propose their integrated approach (section 5.3), and test a specific technique—the Schulz-Flory distribution—on selected data sets (section 5.4). Finally, future directions for potential research are introduced—with clumped isotopes as a specific example (section 5.5).

## 2. CLASSIFICATION OF ABIOTIC ORIGINS OF CH<sub>4</sub>

[5] Most of the works published during the last century about abiotic CH<sub>4</sub>, or hydrocarbons in general, discussed the occurrence of abiotic gas in a given environment, trying to define possible gas generation pathways. Along this line were the numerous papers by Russian or Scandinavian researchers about hydrocarbons in igneous rocks [e.g., Petersilie, 1962; Porfir'ev, 1974; Nivin *et al.*, 1995]. In the same way, Welhan [1988] focused on hydrothermal systems, and reported that “...the principal source of methane in most subaerial hydrothermal systems is from thermocatalysis of organic matter (thermogenesis). (...) However, abiogenesis represents the principal methane source in high-temperature rock-dominated mid-ocean-ridge hydrothermal systems, in which methane is derived from the rock itself.” It was recognized that hydrothermal fluids largely release a form of biotic (specifically thermogenic) CH<sub>4</sub>, instead of abiotic gas, because of the involvement of crustal sediments (rich in organic matter) in the hydrothermal systems. This was a fundamental understanding, but the global picture of all possible abiotic origins of CH<sub>4</sub> was not completely clear yet. A rough classification of abiotic CH<sub>4</sub> in Welhan

[1988] was limited to: (1) primordial CH<sub>4</sub>, with juvenile carbon from the mantle, and (2) inorganic synthesis in reactions at high temperatures (>300–400°C), involving CO<sub>2</sub> and H<sub>2</sub> or other C-H molecules. The second category is quite generic and Welhan [1988] did not consider that inorganic synthesis can also take place at temperatures below 200°C, as discussed in sections 2.9 and 3.1. More recently, Potter and Konnerup-Madsen [2003] distinguished mantle, late magmatic and postmagmatic processes, but the category of postmagmatic processes was limited to Fischer-Tropsch type reactions. In fact this category may embrace a wide set of gas generation mechanisms.

[6] On the basis of theoretical and experimental lines of evidence, at least nine specific mechanisms of abiotic CH<sub>4</sub> production appear in the scientific literature, distinguished into two main major classes: magmatic processes and gas-water-rock reactions (Table 1).

[7] Magmatic CH<sub>4</sub> includes: (1) Primordial gas (2) High-temperature reactions in the mantle (or magma in the crust) and mineral phase transition (3) Late magmatic (<600°C) respeciation of C-O-H fluids during magma cooling.

[8] Gas-water-rock reactions are inorganic syntheses independent of the presence of magma or magma-derived fluids (the term “postmagmatic” was used by Potter and Konnerup-Madsen [2003]) and include: (4) High *T* reactions (5) Metamorphism of carbonate-graphite bearing rocks (6) Iron carbonate decomposition (7) Carbonate methanation (8) Uncatalyzed aqueous CO<sub>2</sub> reduction (9) Fischer-Tropsch Type (FTT) reactions (e.g., Sabatier reaction, after or independent of serpentinization).

### 2.1. Primordial CH<sub>4</sub>

[9] Conceptually, primordial CH<sub>4</sub> was delivered by meteorites during accretion of the Earth and preserved in the mantle; somewhat similar to juvenile He [Craig and Lupton, 1976]. This source was postulated by Gold [1979], probably stemming from ideas of the British astronomer Fred Hoyle who hypothesized the presence of hydrocarbons in chondritic material that contributed to form the Earth [Hoyle, 1955]. While the occurrence of hydrocarbons in meteorites has been verified by several studies [e.g., Yuen *et al.*, 1984], to date there is no compelling evidence that such a primordial CH<sub>4</sub> still exists in significant amounts in the Earth's interior. Certainly the isotopic signature of CH<sub>4</sub> ( $\delta^{13}\text{C}$  and  $\delta^2\text{H}$ ) attributable to a primordial CH<sub>4</sub> end-member has never been confirmed (see also section 4). Thus, this type of origin is theoretically reasonable, but speculative from an experimental and observational viewpoint, and we will not address further.

### 2.2. High-Temperature Reactions in the Mantle

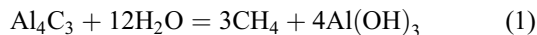
[10] One of the first major theories of inorganic synthesis of hydrocarbons in the Earth's mantle was proposed by Mendeleev [1877], based on hydrolysis of metal carbides (see Glossary). In industrial chemistry it is well

TABLE 1. Abiotic Methane Origins in Geologic Environments

| Class                    | Process/mechanism                                                                                                                                                         | Main reactions                                                                                                                                                                                                                                                                                                                                                                         | Examples of occurrence                                                                                                                                                                                                                  | Reference |
|--------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------|
| MAGMATIC                 | 1. Primordial;<br>delivered by meteorites during Earth's accretion                                                                                                        | extraterrestrial CH <sub>4</sub> synthesis                                                                                                                                                                                                                                                                                                                                             |                                                                                                                                                                                                                                         | (1-2)     |
|                          | 2. High T reactions in the mantle;<br>hydrolysis or hydrogenation of metal carbides;<br>CO, CO <sub>2</sub> , carbonates reduction with H <sub>2</sub> O<br>(500-1500 °C) | $\text{Al}_4\text{C}_3 + 12\text{H}_2\text{O} = 3\text{CH}_4 + 4\text{Al}(\text{OH})_3$ $\text{Fe}_3\text{C} + 4\text{H}^+ = 3\text{Fe} + \text{CH}_4$ $8\text{FeO} + \text{CaCO}_3 + 2\text{H}_2\text{O} = 4\text{Fe}_2\text{O}_3 + \text{CH}_4 + \text{CaO}$                                                                                                                         | Khibiny inclusions (4) (7), East Pacific Rise (6)                                                                                                                                                                                       | (1) (3-9) |
| LATE-MAGMATIC            | 3. Respeciation of C-O-H fluids;<br>CO <sub>2</sub> evolution to CH <sub>4</sub> during magma cooling<br>(<500-600 °C)                                                    | $\text{CO}_2 + 2\text{H}_2\text{O} = \text{CH}_4 + 2\text{O}_2$                                                                                                                                                                                                                                                                                                                        | SW Indian Ridge gabbro inclusions (10) Ilimaussaq inclusions (11)                                                                                                                                                                       | (10-19)   |
| GAS-WATER-ROCK REACTIONS | 4. Post-magmatic high T reactions (400-500 °C)                                                                                                                            | $\text{CO}_2 + 2\text{H}_2\text{O} = \text{CH}_4 + 2\text{O}_2$ $8\text{FeO} + 2\text{H}_2\text{O} + \text{CO}_2 = 4\text{Fe}_2\text{O}_3 + \text{CH}_4$ $2\text{C} + 2\text{H}_2\text{O} = \text{CO}_2 + \text{CH}_4$                                                                                                                                                                 | New Zealand and Japan geothermal systems (20-21)                                                                                                                                                                                        | (20-21)   |
|                          | 5. Carbonate-graphite metamorphism; reduction of graphite with H <sub>2</sub> O (<400 °C)                                                                                 | $\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2 + 3\text{CaCO}_3 + 6\text{C} + 5\text{H}_2\text{O} = 3\text{CaMg}(\text{CO}_3)_2 + 4\text{SiO}_2 + 3\text{CH}_4$                                                                                                                                                                                                                     |                                                                                                                                                                                                                                         | (22-23)   |
|                          | 6. Iron carbonate decomposition; siderite decomposition with H <sub>2</sub> O (300 °C)                                                                                    | $3\text{FeCO}_3 + w\text{H}_2\text{O} = \text{Fe}_3\text{O}_4 + x\text{CO}_2 + y\text{CO} + z\text{H}_2 + \text{HCs}$                                                                                                                                                                                                                                                                  | Meteorites (24)                                                                                                                                                                                                                         | (24)      |
|                          | 7. Carbonate methanation; thermal decomposition of carbonates and direct reduction (without CO <sub>2</sub> ) to CH <sub>4</sub> (250-870 °C)                             | $\text{CaCO}_3 + 4\text{H}_2 = \text{CH}_4 + \text{Ca}(\text{OH})_2 + \text{H}_2\text{O}$ $4\text{H}_2 = \text{CH}_4 + \text{Ca}(\text{OH})_2 + \text{H}_2\text{O}$ $\text{FeCO}_3 + 5\text{H}_2 = \text{CH}_4 + \text{FeO} + 2\text{H}_2\text{O}$                                                                                                                                     |                                                                                                                                                                                                                                         | (25-28)   |
|                          | 8. Uncatalyzed aqueous CO <sub>2</sub> reduction (150-300 °C)                                                                                                             | Variable reactions with CO <sub>2</sub> , CO, HCOOH, NaHCO <sub>3</sub> , NaHCOO, and H <sub>2</sub>                                                                                                                                                                                                                                                                                   |                                                                                                                                                                                                                                         | (29)      |
|                          | 9. Fischer-Tropsch Type (FTT) reactions; surface-catalysed CO <sub>2</sub> hydrogenation in gas or aqueous phase (25 to 500 °C)                                           | One-step methanation (Sabatier)<br>$\text{CO}_2 + 4\text{H}_2 = \text{CH}_4 + 2\text{H}_2\text{O}$<br>Two-steps reverse water-gas shift + FT<br>$\text{CO}_2 + \text{H}_2 = \text{CO} + \text{H}_2\text{O}$<br>$\text{CO} + 3\text{H}_2 = \text{CH}_4 + \text{H}_2\text{O}$<br>In aqueous solution: $\text{CO}_3^{2-} + 4\text{H}_2 = \text{CH}_4 + \text{H}_2\text{O} + 2\text{OH}^-$ | MOR, continental volcanoes - geothermal systems SWIR, (10), Vesuvius, Ischia, Nysiros (43) serpentinized ultramafic rocks at seafloor and ophiolites (34, 35, 44); alkaline igneous intrusions: Lovozero (41) Strange Lake, Quebec (38) | (29-44)   |

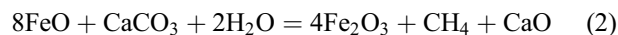
(1) Gold [1979]; (2) Sugisaki and Mimura [1994]; (3) Scott *et al.* [2004]; (4) Petersilie [1962]; (5) Petersilie and Sorensen [1970]; (6) Welhan and Craig [1983]; (7) Beeskov *et al.* [2006]; (8) Manveev *et al.* [1997]; (9) Zhang and Duan [2009]; (10) Kelley and Frith-Green [1999]; (11) Konnerup-Madsen [2001]; (12) Gerlach [1980]; (13) Konnerup-Madsen [2003]; (14) Kogarko *et al.* [1987]; (15) Karzhavin and Vendillo [1970]; (16) Samson and Williams-Jones [1991] (17) Cesare [1995]; (18) Andersen and Burke [1996]; (19) Potter and Konnerup-Madsen [2003]; (20) Giggensch [1997]; (21) Kiyosu *et al.* [1992]; (22) Holloway [1984]; (23) Kenney *et al.* [2002]; (24) McCollom [2013]; (25) Giardini and Salotti [1969]; (26) Reller *et al.* [1987]; (27) Jagadeesan *et al.* [2009]; (28) Yoshida *et al.* [1999]; (29) Seewald *et al.* [2006]; (30) Horita and Berndt [1999]; (31) Foustoukos and Seyfried [2004]; (32) McCollom and Seewald [2006]; (33) Taran *et al.* [2007]; (34) Proskowski *et al.* [2008]; (35) Abrajano *et al.* [1988]; (36) Sherwood Lollar *et al.* [1993]; (37) Kelley [1996]; (38) Salvi and Williams-Jones [1997]; (39) Charlou *et al.* [2002]; (40) Szatmari [1989]; (41) Potter *et al.* [2004]; (42) Oze and Sharma [2005]; (43) Fiebig *et al.* [2007]; (44) Etiope *et al.* [2011b].

known that metal carbides, such as aluminum and beryllium carbides, may react with water and produce CH<sub>4</sub> via reactions like



[11] Iron carbides may form CH<sub>4</sub> by reaction with hydrogen atoms [Lai, 2007]. Although metal carbides have been discovered in meteorites and terrestrial mantle minerals [e. g., Kaminsky, and Wirth, 2011], there is no evidence that they are particularly abundant in the Earth's mantle, and there are no systematic, modern experimental or modeling studies on reaction (1).

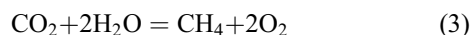
[12] Synthesis of CH<sub>4</sub> in the mantle from CO and/or CO<sub>2</sub> at very high temperatures (around 1000°C) has been proposed. In particular, CH<sub>4</sub> formed by carbonate reduction in the upper mantle from FeO, CaCO<sub>3</sub> (calcite), and water at pressures between 5 and 11 GPa and temperatures ranging from 500 to 1500°C was suggested by Scott *et al.* [2004] via the reaction



[13] A similar process was invoked by Petersilie *et al.* [1961] and Beeskow *et al.* [2006] to explain CH<sub>4</sub> observed in fluid inclusions from the Khibiny complex (Kola peninsula, Russia). Magmatic CH<sub>4</sub> can also be observed in trace amounts in volcanoes and, in particular, in the East Pacific Rise (EPR), which is the only magmatic or almost-pure magmatic CH<sub>4</sub> end-member analyzed to date in terms of isotopic composition [Welhan and Craig, 1983]. Sugisaki and Mimura [1994] invoked FTT reactions in the mantle, but this is widely considered unlikely, as FTT synthesis is thermodynamically favorable only below 600°C (see section 2.9).

### 2.3. Respeciation of C-O-H Fluids

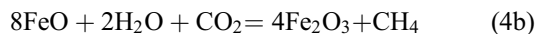
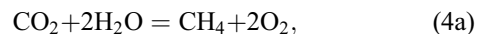
[14] During magma cooling, at temperatures <500–600°C, carbon, oxygen and hydrogen atoms (C, O, H) may reorganize forming CH<sub>4</sub> commonly referred to as “late magmatic.” Phase relations in the C-O-H system and potential CH<sub>4</sub> generation from CO<sub>2</sub>-rich or H<sub>2</sub>-rich fluids were discussed in detail by Potter and Konnerup-Madsen [2003, and references therein]. Here we do not repeat the specific chemical equilibria conditions [see Potter and Konnerup-Madsen, 2003, Figure 2], but simply note that a CH<sub>4</sub>-rich fluid can easily evolve in a closed system by re-equilibration of a magmatic CO<sub>2</sub>-H<sub>2</sub>O fluid below about 500°C through reactions such as



[15] Such an origin was invoked for CH<sub>4</sub> sampled at the Niragongo volcano in Africa [Gerlach, 1980]; in the Ilimaussaq inclusions in Greenland [Konnerup-Madsen, 2001]; in inclusions in quartz in south Norway [Andersen and Burke, 1996]; and in the Southwest Indian Ridge (SWIR) [Kelley and Fröh-Green, 1999].

### 2.4. Postmagmatic High T Reaction

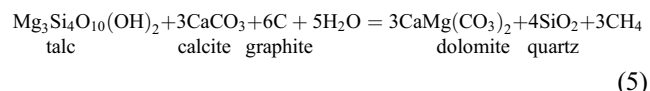
[16] Once magma is solidified and igneous rocks are formed, a series of reactions involving CO<sub>2</sub>, H<sub>2</sub>O and metal oxides can occur between 200 and 500°C, leading to production of CH<sub>4</sub> via reactions such as



[17] These reactions are typically identified in geothermal systems [Giggenbach, 1997; Kiyosu *et al.*, 1992]. Giggenbach [1997] is a fundamental work which describes chemical and isotopic equilibria between CO<sub>2</sub> and CH<sub>4</sub> under these postmagmatic conditions. The main finding is that in high-heat flow (>80 mW/m<sup>2</sup>) geothermal systems, CH<sub>4</sub>, and CO<sub>2</sub> approach both chemical and carbon isotopic equilibrium. This equilibrium is subsequently lost as temperature decreases. Relative concentrations of CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub> (ethane), and C<sub>3</sub>H<sub>8</sub> (propane) follow a Schulz-Flory distribution resulting from random breakage of C-C bonds of more complex molecules [Flory, 1936]. This relationship (described in more detail in section 5.4) seems to be typical of abiotic hydrocarbon synthesis, and may be an important (but not definitive) concept to recognize abiotic gas.

### 2.5. Metamorphism of Carbonate-Graphite Bearing Rocks

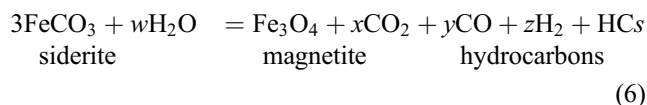
[18] Below 400°C the presence of graphite (widespread in metamorphic rocks) in contact with C-O-H fluids (CO<sub>2</sub>, H<sub>2</sub>O) plays a crucial role in determining unmixing and separation of CO<sub>2</sub> or CH<sub>4</sub> rich fluids [Holloway, 1984]. In particular, CH<sub>4</sub> can be produced during retrograde metamorphism of a graphite-bearing rock by a reaction of the type



[19] CH<sub>4</sub> can exist as a stable species under geologically common oxidation conditions at temperatures below 400°C. Below about 325°C, graphite-bearing rocks may contain nearly pure and immiscible H<sub>2</sub>O and CH<sub>4</sub> fluids, rather than CO<sub>2</sub> [Holloway, 1984]. This may explain CH<sub>4</sub> observed in some low-grade metamorphic rocks [Huff and Nabelek, 2007, and references therein]. It is important to note that because graphite may result from metamorphism of sedimentary rocks, the carbon precursor of CH<sub>4</sub> in such an example is ultimately organic (i.e., from marine carbonates, kerogen or dispersed organic matter). The resulting CH<sub>4</sub> may be considered “abiotic” however if the reaction mechanism of its production is entirely inorganic (see the Glossary for a short discussion on this point).

### 2.6. Iron-Carbonate Decomposition

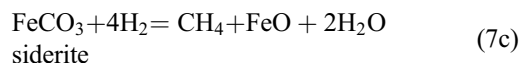
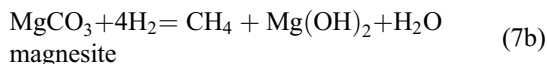
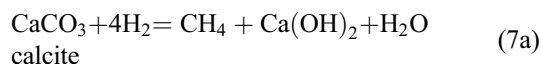
[20] A specific abiotic CH<sub>4</sub> production mechanism was proposed by McCollom [2003] in the presence of iron carbonates (siderite) and water, at ~300°C. The basic reaction proposed was



[21] Such a reaction, verified by laboratory experiments on meteorite samples [McCollom, 2003], generated a variety of organic products dominated by alkylated and hydroxylated aromatic compounds as well as  $\text{CH}_4$ . McCollom [2003] suggested this process could account for some of the reduced carbon observed in metasedimentary rocks from the early Earth.

## 2.7. Carbonate Methanation

[22] In a wide range of temperatures between 250 and 800°C, carbonate minerals (calcite, magnesite, siderite) can react directly with hydrogen ( $\text{H}_2$ ) and produce  $\text{CH}_4$  [Giardini *et al.*, 1968; Giardini and Salotti, 1969; Reller *et al.*, 1987; Yoshida *et al.*, 1999]. This process, called carbonate methanation, is a direct carbonate surface-gas reaction and can be described by the reactions

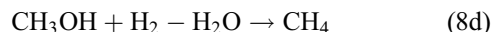
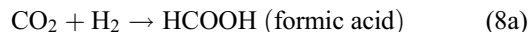


[23] The temperature of decomposition actually decreases as  $\text{H}_2$  concentration increases [Reller *et al.*, 1987] especially in the presence of suitable catalysts (e.g., Co and Ni). This means that in  $\text{H}_2$ -rich environments, carbonate starts to decompose at lower temperatures. This process is quite interesting because it produces  $\text{CH}_4$  through one step, directly from the solid carbonate, without mediation of gaseous  $\text{CO}_2$  (as typically happens in the catalytic hydrogenation or FTT reaction, discussed below). The occurrence of reactions (7a–7c) was confirmed by laboratory experiments: very rapidly (instantaneously) at 250°C in  $\text{H}_2$  atmosphere with mixed alkaline-Earth metal/transition metal carbonates including Mg, Ca, Co, Ni, and Cu [Reller *et al.*, 1987]; with similar metal carbonates at 550°C, in five hours [Jagadeesan *et al.*, 2009]; and at 300–400°C with Ir-Pd catalysts, in 100 min time scale [Yoshida *et al.*, 1999]. There are currently no studies to our knowledge at lower temperatures and over longer time scales.

## 2.8. Uncatalyzed Aqueous $\text{CO}_2$ Reduction

[24] At relatively high temperatures (>150°C), and in presence of  $\text{CO}_2$ , CO, and  $\text{H}_2$ , production of  $\text{CH}_4$  may occur in aqueous solution without the involvement of a heterogeneous catalyst or gas phase. In laboratory experiments, Seewald *et al.* [2006] observed rapid  $\text{CH}_4$  generation due to  $\text{CO}_2$  reduction in aqueous solution at 200°C.  $\text{CH}_4$  was associated with methanol, which indicates that formation of  $\text{CH}_4$  from  $\text{CO}_2$  may not involve a heterogeneously

catalyzed FTT reaction, but instead may occur via a series of redox reactions that produce formic acid, and possibly formaldehyde and methanol as intermediaries, according to the sequential reactions

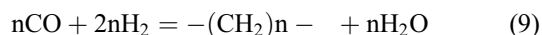


[25] Such abiotic reactions involving aqueous carbon compounds in hydrothermal conditions may influence metabolic pathways utilized by organisms that inhabit submarine vent environments [Seewald *et al.*, 2006].

## 2.9. Fischer-Tropsch Type Reactions

[26] The FTT reactions are probably the most widely invoked mechanism for generation of abiotic  $\text{CH}_4$  in natural settings, especially with reference to serpentinized ultramafic rocks [e.g., Szatmari, 1989; Horita and Berndt, 1999; Sherwood Lollar *et al.*, 1993; Charlou *et al.*, 2002; Foustoukos and Seyfried, 2004; McCollom and Seewald, 2006; Taran *et al.*, 2007; Proskurowski *et al.*, 2008; Etiope *et al.*, 2011b]. Serpentinization, that is hydration of olivine and/or pyroxene, produces  $\text{H}_2$  which then may react with C-gases ( $\text{CO}_2$  or CO) forming  $\text{CH}_4$ . The FTT synthesis, however, may be independent of serpentinization, whereby  $\text{H}_2$  in many rocks can derive from other processes, such as radiolysis, cataclasis of silicates in fault zones, or magmatic degassing [Smith *et al.*, 2005; Onstott *et al.*, 2006].

[27] The FTT term broadly includes the specific Fischer-Tropsch reaction *in sensu stricto*, which refers to the catalytic hydrogenation of carbon monoxide (CO) to produce a wide range of linear, long-chain hydrocarbons [e.g., Anderson, 1984; Schulz, 1999]

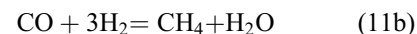
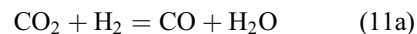


and the catalytic hydrogenation of carbon dioxide ( $\text{CO}_2$ ), which produces  $\text{CH}_4$  by one step (Sabatier reaction or methanation) or two steps (reverse water-gas shift) reactions [e.g., Anderson, 1984; Wang *et al.*, 2011]:

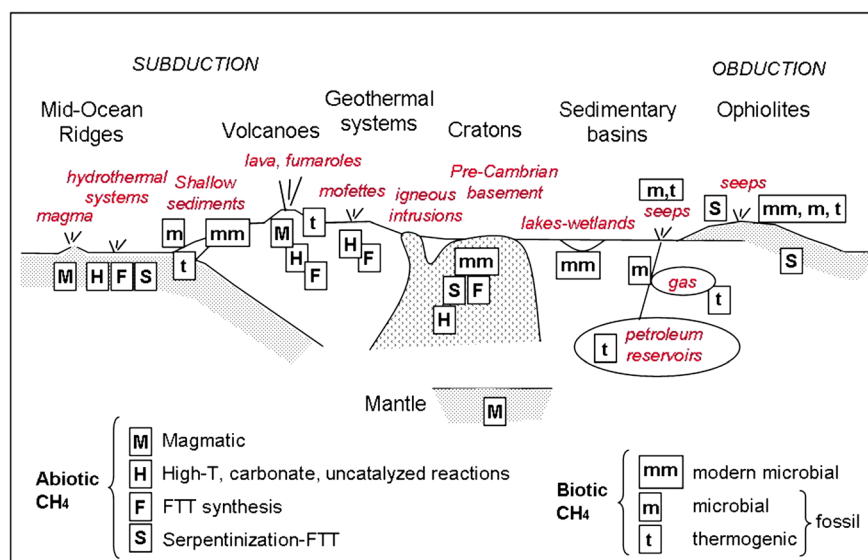
One-step methanation (Sabatier):



Two-steps reverse water-gas shift:



[28] All FTT reactions are catalyzed by transition metals (Ni, Fe, Co, Cr, Ru) and related oxides, so that the conversion of the gas molecules occurs on the metal surface. The Sabatier reaction, the simplest FTT form, is reversible, exothermic ( $H = -167 \text{ kJ/mol}$ ) and proceeds spontaneously and catalytically at relatively low temperatures. Experimentally, FTT synthesis has been widely reported under hydrothermal



**Figure 1.** Sketch of abiotic CH<sub>4</sub> occurrences on Earth. High-*T*, carbonate, uncatalyzed reactions (H) refer to all processes described in sections 2.4 to 2.8 (from high-temperature reactions to uncatalyzed CO<sub>2</sub> reduction; see Table 1); Fischer-Tropsch Type (FTT) synthesis (F) can be independent of serpentinization or associated with serpentinization of ultramafic rocks (S). Typical biotic CH<sub>4</sub> occurrences are also shown. The sizes of the geologic environments are not to scale.

conditions, at temperatures above 200°C and high pressures, using Ni, Fe Cr, which are the most abundant transition metals in ultramafic rocks [e.g., *Foustoukos and Seyfried*, 2004; *McCollom and Seewald*, 2006; *Taran et al.*, 2007]. CH<sub>4</sub> production was observed over hours to days time scales. The kinetics of methanation at lower temperatures (<100°C) is theoretically much slower, but a fast (a few hours) methanation at room temperatures (<50°C) and atmospheric pressure has been proven with ruthenium and rhodium based catalysts [*Thampi et al.*, 1987; *Jacquemin et al.*, 2010]. These platinum group elements, however, occur in ultramafic rocks only in trace amounts (orders of hundreds of ppb), so their catalytic role in nature should be verified. The most abundant catalysts available in ultramafic rocks, like chromium (e.g., chromitites in peridotites), iron (magnetite) and nickel (e.g., in awaruite) could support low temperature methanation over longer time scales (months, years). Such a slow methanation is theoretically possible but not yet experimentally demonstrated in the laboratory. Analyses of natural gas released from a seep in serpentinized ophiolites in Turkey (Chimaera seep) revealed that the gas (11% H<sub>2</sub> and 86% CH<sub>4</sub>) was likely produced abiotically by low temperature methanation. Geothermometers based on the isotopic composition of CH<sub>4</sub> and H<sub>2</sub>, as well as the low geothermal gradient (max. 80°C at 3 km depth, the base of the ophiolitic block) suggest that the gas was mainly formed at temperature <50°C [*Etioppe et al.*, 2011b]. It is likely then, that low temperature methanation reactions may occur naturally under wider geologic conditions, even at low pressure conditions, expanding the environments of generation of CH<sub>4</sub>. This process may have relevant implications both for environmental issues, due to the ability of such a reaction to consume CO<sub>2</sub> (CO<sub>2</sub> sequestration, CO<sub>2</sub> removal in spacecraft cabin) and for energy-related issues for CH<sub>4</sub> synthesis.

Furthermore, Sabatier methanation could be a mechanism involved in the origin of CH<sub>4</sub> reported in the Mars atmosphere [e.g., *Oze and Sharma*, 2005; *Etioppe et al.*, 2011b, 2013a].

### 3. NATURAL OCCURRENCES OF ABIOTIC CH<sub>4</sub> AND EMISSIONS INTO THE ATMOSPHERE

#### 3.1. Occurrence and Abundance of Abiotic CH<sub>4</sub>

[29] Figure 1 summarizes the occurrences on Earth of several main classes of abiotic CH<sub>4</sub>. Despite the sometimes erroneous concept that volcanoes emit only abiotic and mantle-derived CH<sub>4</sub>, it is well known that volcanic flanks and related gas manifestations frequently release mainly hydrocarbons from postmagmatic processes, and also biotic gas originating from thermal breakdown of organic matter trapped in sedimentary rocks involved in the volcanic plumbing system or soils [e.g., *Etioppe et al.*, 2007]. Accordingly, only part of the global volcanic-geothermal CH<sub>4</sub> emission into the atmosphere (3–7 Mt/yr) [*Etioppe et al.*, 2008] should be attributed to a mantle source. A significant component of abiotic CH<sub>4</sub> production and release is independent of volcanism. Gases from geothermal systems (independent from volcanoes) result mainly from late-magmatic or postmagmatic origins, but often also incorporate biotic CH<sub>4</sub> originating from thermal breakdown of organic matter in sedimentary rocks. Abiotic synthesis by gas-water-rock reactions generally provide higher amounts of hydrocarbons (even % levels) compared to magma degassing (few units of ppmv or ppbv).

[30] In recent years there has been growing interest in the role of serpentinization of ultramafic rocks, either on land or seafloor, and abiotic synthesis of CH<sub>4</sub>. Abiotic CH<sub>4</sub> at the Earth's surface has been found to be related to low temperature (<150°C) serpentinization in ultramafic rocks such as in

the submarine Lost City Hydrothermal field (LCHF) and, on land, in ophiolites or igneous intrusions in the Philippines, Oman, New Zealand, Turkey, Italy, Greece, and Japan, [e.g., *Etioppe et al.*, 2011b and references therein; *Boschetti et al.*, 2013; *Etioppe et al.*, 2013b; *Suda*, 2013]. CH<sub>4</sub> has also been measured at other sites with active serpentinization, but the data necessary to determine the CH<sub>4</sub> origin are incomplete or not available. Nonmicrobial CH<sub>4</sub>, possibly related to abiotic-thermogenic mixing was reported in the Tablelands ophiolite (Canada) [*Szponar et al.*, 2013]. CH<sub>4</sub> concentrations without isotopic data are also available for the Zlatibor ophiolite in Serbia [*Milenic et al.*, 2009]. Abiotic gas may however be partially mixed with biotic gas, and methanogens may occur in the rocks and thrive on the presence of H<sub>2</sub> amounts. Microbes may produce CH<sub>4</sub> through CO<sub>2</sub> reduction, competing with abiotic FTT synthesis [*Sherwood Lollar et al.*, 2002; *Sleep et al.*, 2004]. An apparent major microbial component has been reported in ophiolitic springs in California [*Morrill et al.*, 2013].

[31] On land, gas vents or gas-bearing water springs are often located in correspondence with faults or fractures in peridotites affected by present-day, meteoric-water driven, serpentinization. CH<sub>4</sub> is often, but not always, associated with large amounts of H<sub>2</sub> [*Abrajano et al.*, 1988; *Fritz et al.*, 1992; *Sherwood Lollar et al.*, 2007; *Boschetti et al.*, 2013; *Etioppe et al.*, 2011b, 2013b]. Present-day serpentinization is typically revealed by the occurrence of hyperalkaline (pH > 10) and calcium-hydroxide (Ca<sup>2+</sup>-OH<sup>-</sup>) waters of meteoric origin, resulting from the release of OH<sup>-</sup> and Ca<sup>2+</sup> during hydration of olivine and pyroxenes [*Barnes et al.*, 1967; *Neal and Stanger*, 1983]. Wherever these waters are, there is high potential to find abiotic CH<sub>4</sub>.

[32] The temperature of serpentinization and of subsequent abiotic CH<sub>4</sub> production at these sites is always below 100°C, often around 40–60°C [*Etioppe et al.*, 2011b; *Boschetti et al.*, 2013; *Etioppe et al.*, 2013b; *Suda*, 2013]. This means that whatever the CH<sub>4</sub> production mechanism is, it took place in a temperature field which is much lower than that considered in traditional hydrothermal systems and laboratory experiments on abiotic gas synthesis [*Berndt et al.*, 1996; *Foustoukos and Seyfried*, 2004; *McCollom and Seewald*, 2006; *McCollom*, 2013].

[33] Concerning the presence of abiotic CH<sub>4</sub> in oil-gas fields in sedimentary basins, few and uncertain data are available worldwide. A systematic review by *Jenden et al.* [1993] shows that, at least up to the early 1990s, commercial accumulations of abiotic CH<sub>4</sub> have not been discovered by the petroleum industry, and that far less than 1% of CH<sub>4</sub> in most oil and gas fields is abiotic. Uncertain and contrasting results are published about the Songliao Basin in China; while most of gas is thermogenic [*Huang et al.*, 2004], deep strata may host some abiotic gas [*Jin et al.*, 2009], but there is no consensus on the amount compared to biotic gas.

### 3.2. Abiotic CH<sub>4</sub> Fluxes Into the Atmosphere

[34] While typical fluxes (emission factors) and global emissions to the atmosphere of biotic (thermogenic and

microbial) CH<sub>4</sub> have been widely investigated and assessed (~60 Mt CH<sub>4</sub>/yr globally; *Etioppe et al.*, 2008; *Etioppe*, 2012], the global emission of abiotic CH<sub>4</sub> is unknown. Theoretical estimates were proposed by *Emmanuel and Ague* [2007] (~2.3 Mt/yr) but they mostly refer to hypothetical fluxes to the oceans from the mid-ocean ridges (not to the atmosphere) and are not constrained by direct measurements.

[35] Fluxes of CH<sub>4</sub> were measured in continental CO<sub>2</sub>-rich volcanic-geothermal manifestations (see the review by *Etioppe et al.* [2007]) but are based on gas emissions of mixed abiotic and biotic origin. Global CH<sub>4</sub> emission from these systems is estimated in the order of 3–6 Tg/yr [*Etioppe et al.*, 2008] with the actual abiotic fraction unknown. Fluxes of abiotic CH<sub>4</sub> from serpentinized ultramafic rocks on land (ophiolites) have been documented only recently [*Etioppe et al.*, 2011b; *Boschetti et al.*, 2013; *Etioppe et al.*, 2013b] including CH<sub>4</sub> microseepage (see Glossary) from some peridotite outcrops, similar to traditional microseepage in petroleum fields [orders of 10<sup>1</sup>–10<sup>3</sup> mg m<sup>-2</sup> d<sup>-1</sup>; *Etioppe and Klusman*, 2010]. The output into the atmosphere of abiotic CH<sub>4</sub> released by hyperalkaline springs depends on the water flow rate and the dissolved CH<sub>4</sub> concentration. Gas flux measurements in Greece and Italy are in the order of a few kilograms of CH<sub>4</sub> per year from individual springs, and several tens of kilograms of CH<sub>4</sub> per year including degassing from the surrounding soil [*Boschetti et al.*, 2013; *Etioppe et al.*, 2013b]. The biggest abiotic gas seep in the world known so far, Chimaera in Turkey [*Etioppe et al.*, 2011b] is not associated with water springs and annually releases at least 150 tons of abiotic CH<sub>4</sub> from an ophiolitic outcrop 5000 m<sup>2</sup> wide. This flux is higher than that from large (kilometer-scale) magmatic volcanoes (e.g., CH<sub>4</sub> emissions from Mt. Etna and from most Icelandic volcanoes are lower than 100 tons yr<sup>-1</sup>; *Etioppe et al.* [2007]). Further studies are necessary to develop a reliable estimate of global CH<sub>4</sub> emission from ophiolites. In particular, similar studies are required for other proposed sources of abiotic CH<sub>4</sub>, such crystalline shield rocks (see section 4), as to date little or no estimates exist of potential flux from these systems.

## 4. THE STABLE CARBON AND HYDROGEN ISOTOPIC COMPOSITION

### 4.1. History of Abiotic CH<sub>4</sub> Zonation in the C-H Isotopic Diagram

[36] The genetic zonation of CH<sub>4</sub> based on the isotopic composition of carbon (<sup>13</sup>C/<sup>12</sup>C) and hydrogen (<sup>2</sup>H/<sup>1</sup>H) was introduced by *Schoell* [1980]. The δ<sup>13</sup>C vs δ<sup>2</sup>H diagram or CD diagram [e.g., *Tissot and Welte*, 1984; *Whiticar*, 1999], has provided a fundamental framework to evaluate the origin of CH<sub>4</sub>, although inherently empirically based. As such, the proposed genetic zones have and continue to expand as a function of three main developments. The first is the inevitable expansion that occurs with incorporation of a wider variety of gas occurrences worldwide beyond the focus on sedimentary basin gases, marine sediments and marine hydrothermal systems on which the original framework was developed. The second and third developments are linked. The increased sensitivity of compound

specific continuous flow isotope mass spectrometry for carbon and hydrogen isotopes has enabled an unprecedented series of experimental data sets that have expanded the range of possible isotopic signatures for CH<sub>4</sub>. This includes both CH<sub>4</sub> production by microbes, especially under extreme conditions of growth phase, temperature, pressure and substrate availability [Valentine *et al.*, 2004a, 2004b; Templeton *et al.*, 2006]. In parallel, experiments on abiotic synthesis of CH<sub>4</sub> have demonstrated a range of possible carbon and hydrogen isotope signatures almost overlapping with those traditionally associated with biotic (microbial and thermogenic) gases, with  $\delta^{13}\text{C}$  values as depleted as  $-57\text{‰}$ , well within the range of isotopically “light” values once assumed to be a “biomarker” [Horita and Berndt, 1999; McCollom and Seewald, 2006; McCollom *et al.*, 2010; Taran *et al.*, 2007]. While many developments have been incorporated into revised genetic fields for biotic origin [e.g., Schoell, 1980; Whiticar, 1999; Milkov, 2011; Etiope *et al.*, 2011a], considerable uncertainty remains regarding the appropriate  $\delta^{13}\text{C}$  and  $\delta^2\text{H}$  range for an abiotic field in such a diagram.

[37] Schoell [1988] and Welhan [1988] were the first to include abiotic gas in the CD diagram by showing the isotopic data of the EPR [Welhan and Craig, 1983], the Zambales ophiolite gas [Abrajano *et al.*, 1988], Canadian shield gases [Sherwood *et al.*, 1988] and isotopic fields for “geothermal” (by Schoell) or “hydrothermal” (by Welhan) gas from the USA, Mexico, and New Zealand (data were from Hulston and McCabe [1962], Gunter and Musgrave [1971], Lyon [1974], Welhan and Craig [1983], Lyon and Hulston [1984], Welhan and Lupton, 1987, and Des Marais *et al.* [1981], who did not report  $\delta^2\text{H}$  values, however). Both the “geothermal”, “hydrothermal”, and shield gas, however, included substantial components of biotic gas (as in the Guaymas Basin or Salton Sea sediment-hosted hydrothermal fields) so their distribution in the CD diagram was not representative of an abiotic CH<sub>4</sub> end-member. Similarly, Whiticar [1990] included isotopic CH<sub>4</sub> data from deep crystalline rocks in the Siljan Ring [Schmitt, 1987] and inclusions from Ilimaussaq in Greenland [Konnerup-Madsen *et al.*, 1988], which appeared to be the most  $^{13}\text{C}$ -enriched CH<sub>4</sub> to that point. Whiticar [1990] then wrote: “Considering all the crystalline data, it appears that there is an end-member (abiotic) gas type situated in the general isotope range of  $\delta^{13}\text{C}$ -CH<sub>4</sub>:  $-0$  to  $-15\text{‰}$  and  $\delta^2\text{H}$ -CH<sub>4</sub>:  $-100$  to  $-150\text{‰}$ . The mechanism of formation remains to be resolved.” Kelley and Frih-Green [1999] reported complete isotopic CH<sub>4</sub> data from inclusions in gabbros of a sediment-free, igneous host system of the SWIR. The isotopic ratios were quite variable, with  $\delta^{13}\text{C}$  from  $-9.1$  to  $-33.8\text{‰}$ , and  $\delta^2\text{H}$  from  $-99$  to  $-244\text{‰}$ , overlapping partially the thermogenic isotopic field.

[38] Successively, many papers adopted CD diagrams showing a generic “geothermal-hydrothermal-crystalline” field after Whiticar [1999]. Anyone who has eventually considered this field as representative of “abiotic” CH<sub>4</sub> failed. It is obvious that the terms “geothermal” or “hydrothermal” or “crystalline” CH<sub>4</sub> refer to the environment or setting in which gas is occurring, rather than to its genetic origin. In each of these environments we may find varying mixtures of abiotic

magmatic (or mantle-derived CH<sub>4</sub>); abiotic postmagmatic CH<sub>4</sub> due to hydrothermal or gas-water-rock interactions, and biotic (thermogenic and microbial) CH<sub>4</sub>. Indeed, addressing the complexities introduced by gas occurrences that in fact represent mixtures of CH<sub>4</sub> of different genetic origins remains an ongoing challenge for the use of carbon and hydrogen isotopic signatures as diagnostic parameters.

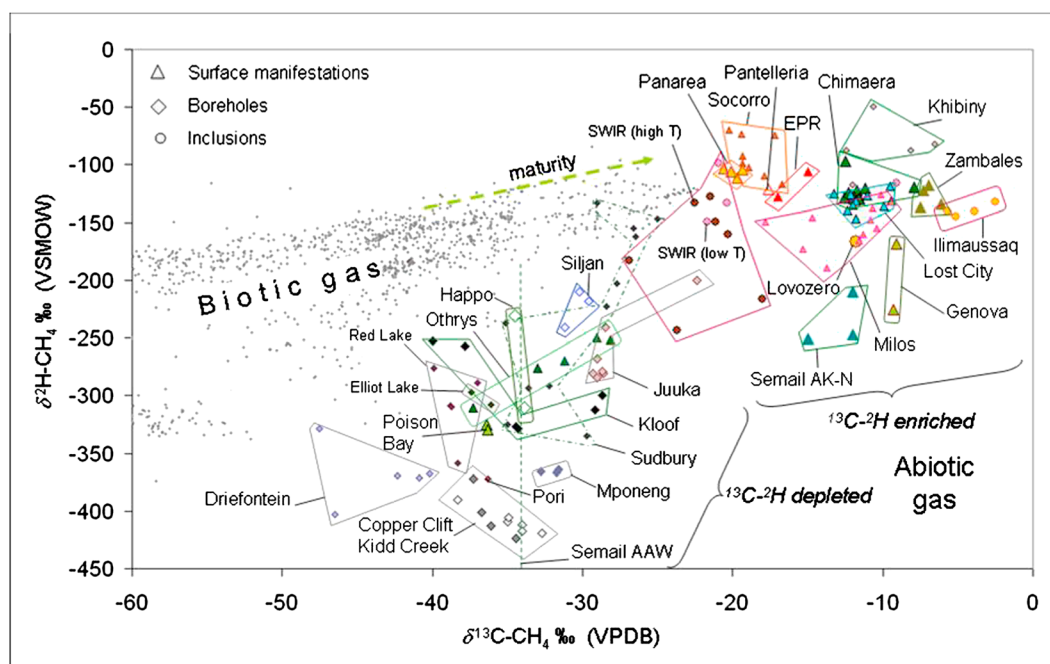
## 4.2. An Updated CD Diagram

[39] As a starting point, this review plots for the first time a revised version of the CD diagram that reflects, to our knowledge, all available literature from field investigations that proposed a major abiotic CH<sub>4</sub> contribution. It is surprising to admit that even today, we have no isotopic CH<sub>4</sub> data clearly attributable to a pure magmatic CH<sub>4</sub>. CH<sub>4</sub> closest to a pure magmatic source is probably that of the “sediment-free” EPR [Welhan and Craig, 1983]. SWIR CH<sub>4</sub> is apparently not magmatic, but representative of late-magmatic and postmagmatic processes, including respeciation of magmatic CO<sub>2</sub>, graphite precipitation and FTT reactions [Kelley and Frih-Green, 1999]. The lack of isotopic data from a truly magmatic CH<sub>4</sub> such as the mid-oceanic ridge popping rock samples [Staudacher *et al.*, 1989] is partially due to the difficulty of analyzing  $\delta^{13}\text{C}$  and  $\delta^2\text{H}$  of the very low CH<sub>4</sub> concentrations occurring in magmatic exhalations (typically in the order of ppbv or a few ppmv).

[40] Figure 2 incorporates a wide range of reported carbon and hydrogen isotopic values for gas for which a primarily abiotic origin, or a substantial contribution of abiotic CH<sub>4</sub>, have been reported (150 data, 28 sites). As a first step, we make no distinction between those two categories. The field settings fall into four main groups: (1) surface manifestations in serpentinized ultramafic rocks; (2) boreholes in deep Precambrian shield crystalline rocks; (3) fluid inclusions in crystalline intrusions; and (4) volcanic and high temperature hydrothermal systems.

[41] 1. Abiotic CH<sub>4</sub>, assumed to be related to FTT reactions has been reported at several sites with serpentinized ultramafic rocks, both on continents (ophiolites in Oman [Fritz *et al.*, 1992; Sano *et al.*, 1993], New Zealand [Lyon and Giggenbach, 1994], and Turkey [Hosgormez *et al.*, 2008; Etiope *et al.*, 2011b]) and at mid-ocean ridges [e.g., Charlou *et al.*, 2002] and off-axis spreading centers [Kelley *et al.*, 2005; Proskurowski *et al.*, 2008]. In the last few years, isotopic data were reported for CH<sub>4</sub> dissolved in hyperalkaline springs in Greece (Othrys) [Etiope *et al.*, 2013b], Italy (Genova) [Boschetti *et al.*, 2013], Japan (Happo) [Suda, 2013], Canada [Szponar *et al.*, 2013] and California [Morrill *et al.*, 2013]. In all cases for which both carbon and hydrogen isotope values are available, these have been added to Figure 2.

[42] 2. A second major group includes isotopic data of CH<sub>4</sub> occurring in fracture waters in deep crystalline rocks accessed via boreholes in Canada, Scandinavia and South Africa by Sherwood Lollar *et al.* [1993, 2002, 2006, 2008], Lyon and Giggenbach, [1994]. Included in Figure 2 are only those sites that have been suggested to have a predominant or at least significant contribution of abiotic CH<sub>4</sub>. Not included in Figure 2 are the many sites where geochemical and isotopic evidence,



**Figure 2.** Values of  $\delta^{13}\text{C}$  vs  $\delta^2\text{H}$  for  $\text{CH}_4$  gases which are considered to have a dominant abiogenic component, from volcanic-hydrothermal systems little affected by organic matter in sediments (EPR: East Pacific Rise, SWIR: Southwest Indian Ridge; Socorro, Milos, Pantelleria, Panarea) (sediment-hosted hydrothermal fields, like Guaymas Basin and Salton Sea, are not considered), serpentinized ultramafic rocks (Chimaera-Turkey; Semail-Oman AK-N: Al-Khoud and Nizwa; AAW: Ain-Al-Waddah; Zambales-Philippines; Poison Bay-New Zealand; Othrys-Greece; Genova-Italy; Haplo-Japan), and in submarine hydrothermal fields (Lost City); inclusions in igneous rocks in Russia and Greenland (Lovozero, Khibiny, Ilimaussaq); and from deep boreholes in crystalline igneous rocks in South Africa, Canada and Scandinavia (Sudbury, Juuka, Kloorf, Mponeng, Pori, Copper Cliff, Driefontein, Elliot Lake, Red Lake, Siljan Ring Gravberg-1 well). Data from: Abrajano *et al.* [1988], Botz *et al.* [1996], Boschetti *et al.* [2013], Etiope *et al.* [2011b, 2013b], Fritz *et al.* [1992], Kelley and Fröh-Green [1999], Lyon and Giggenbach [1994], Potter *et al.* [2004], Proskurowski *et al.* [2008], Sherwood *et al.* [1988], Sherwood Lollar *et al.* [1993, 2006], Sano *et al.* [1993], Suda [2013], Taran *et al.* [2010a], Tassi *et al.* [2012], Welhan and Craig [1983], Whiticar [1990]. Small grey dots are from a global data set [Etiope *et al.*, 2013a] of biotic (microbial and thermogenic) natural gases in sedimentary basin petroleum fields.

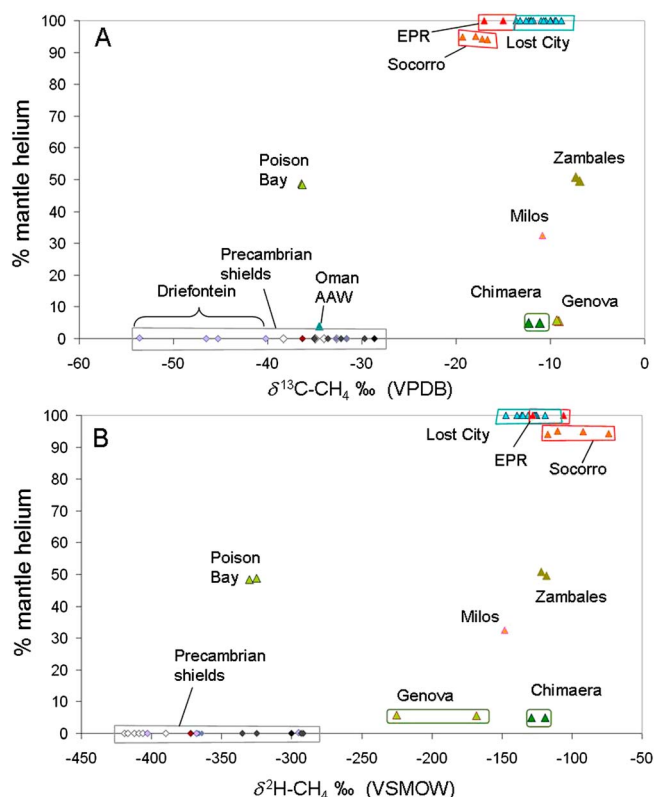
as well as confirmation from culture-based and molecular microbiology supports a predominantly microbial origin for the  $\text{CH}_4$  [Ward *et al.*, 2004; Sherwood Lollar *et al.*, 1993].

[43] 3. A third major group includes  $\text{CH}_4$  from fluid inclusions in crystalline rocks from continental sites and drill cores from Lovozero, Khibiny (Kola peninsula, Russia) and Ilimaussaq (Greenland) intrusions by Nivin *et al.* [1995], Beeskov *et al.* [2006; reporting however old data by Yerokhin [1978]], and Konnerup-Madsen [2001]. Other works on  $\text{CH}_4$  in crystalline rocks reported only carbon isotopic data [e.g., Laier and Nytoft, 2012 and references therein] and cannot be included at this time. These however generally show similar ranges of  $\delta^{13}\text{C}$  values for  $\text{CH}_4$ , although Laier and Nytoft [2012] suggest that Ilimaussaq gas is biotic and its  $^{13}\text{C}$  enrichment is due to isotopic fractionation by diffusion. We will discuss in detail this point in section 5.4.

[44] 4. Finally,  $\text{CH}_4$  isotopic data are available from several volcanic and hydrothermal systems but, as mentioned previously, many of these include mixtures of varying amounts of  $\text{CH}_4$  thermogenic and even microbial origin. In Figure 2, in addition to EPR and SWIR ridge systems, we have chosen to include only the volcanic-hydrothermal gases considered

to be less affected by organic matter, and for which both  $\delta^{13}\text{C}$  and  $\delta^2\text{H}$  data are available: i.e., Socorro, Mexico [Taran *et al.*, 2010a; Lyon and Giggenbach, 1994], Panarea and Pantelleria, Italy [Tassi *et al.*, 2012], and Milos, Greece [Botz *et al.*, 1996]. As noted earlier, gases from the Songliao Basin have not been included in this figure because although an abiogenic origin has been suggested for some of the deepest samples, the majority of the gases are of mixed or thermogenic origin [Jin *et al.*, 2009].

[45] We observe that the abiogenic (or dominantly abiogenic)  $\text{CH}_4$  plotted in Figure 2 has a wide range of  $\delta^{13}\text{C}$  and  $\delta^2\text{H}$  values, and although overlapping with parts of both the microbial and thermogenic fields for certain specific samples, these data are distinguished from biotic gas fields by an overall shift toward more  $^{13}\text{C}$ -enriched values. Within this data, there is an apparent trend toward more  $^{13}\text{C}$ - $^2\text{H}$  enriched values (we may call it “heavy” abiogenic  $\text{CH}_4$ ), in the high temperature volcanic-hydrothermal systems, and in the serpentinized ultramafic rocks of Lost City, Chimaera, Zambales, Semail, and Genova. In contrast, more  $^{13}\text{C}$ - $^2\text{H}$  depleted (“light” abiogenic  $\text{CH}_4$ ) appears to be more closely associated with gases found in the Precambrian crystalline igneous rocks of South Africa,



**Figure 3.** Percentage of mantle helium versus  $\delta^{13}\text{C}$  (A) and  $\delta^2\text{H}$  (B) of  $\text{CH}_4$  in the subset of samples reported in Figure 2 for which all these isotope measurements are available for the same sample. Noble gas samples are evaluated for air contamination by a variety of methods including measurement of the  $^4\text{He}/^{20}\text{Ne}$  value, which for air is 0.288. If values are significantly higher, then air contamination can be discounted and the remaining helium attributed to a two component mixture between mantle-derived helium and helium derived from crustal radiogenic processes [Ballentine and Burnard, 2002, and references therein]. Measured  $^3\text{He}/^4\text{He}$  ratios ( $R$ ) are typically normalized to the atmospheric ratio ( $R_a = 1.4 \times 10^{-6}$ ) and expressed as  $R/R_a$  values. Assuming an average  $R/R_a$  value for the mantle of 8, and  $R/R_a$  of 0.01 for crustal radiogenic He, then the % contribution of mantle-derived helium to any measured sample can be calculated.

Canada and Scandinavia, and in the present-day serpentinization seeps of Poison Bay (New Zealand), Othrys (Greece) and Happo (Japan). Greenland igneous intrusions in continental rocks plot close to the high temperature hydrothermal fluids, and both high and low temperature SWIR samples plot in approximately the same position.

#### 4.3. Integrating $\text{CH}_4$ Isotopes With Noble Gases

[46] A more robust differentiation within these sample groups is only possible by introducing an additional diagnostic parameter—specifically a parameter that unlike  $\text{CH}_4$ , is conservative and hence preserves information about the carbon and hydrogen feedstock materials supporting abiotic methanogenesis. The inert noble gases have been used extensively in geochemistry as a powerful means of investigating the origin of gases and fluids [see Ballentine and

Burnard, 2002, and references therein]. Nonetheless, their applications to organic geochemistry, petroleum exploration and astrobiology have to date been much less developed [Sherwood Lollar and Ballentine, 2009]. Figure 3 demonstrates how integrating these conservative tracers with the information on reactions and cycling provided by carbon and hydrogen isotopic signatures can play a critical role in deciphering the data set from Figure 2. Figures 3a and 3b show the subset of samples from Figure 2 for which helium isotope values as well as carbon and hydrogen isotope measurements are available for the same sample. What is immediately clear from Figure 3a is the strong relationship between carbon isotope values and the presence of a significant component of mantle-derived helium. Those samples with at least 5% mantle helium (e.g., Chimera, Genova), to almost pure mantle helium (e.g., LCHF, Socorro and EPR) have  $\delta^{13}\text{C}\text{-CH}_4$  values more enriched than approximately  $-20\text{‰}$ . The same pattern is observed for  $\delta^2\text{H}$  values as this same suite of samples (with the exception of one of the Genova springs and Poison Bay) all have  $\delta^2\text{H}$  values for  $\text{CH}_4$  more enriched than approximately  $-200\text{‰}$ . These ranges are similar to those of the presumed pure abiotic  $\text{CH}_4$  end-member at the EPR ( $-15$  to  $-17\text{‰}$ ; and  $-100$  to  $-128\text{‰}$ ). The reverse is also evident. For all samples with  $\delta^{13}\text{C}$  values more depleted than approximately  $-20\text{‰}$  and  $\delta^2\text{H}$  values more depleted than approximately  $-200\text{‰}$  (again with the exception of one Genova spring and Poison Bay), helium isotopic signatures rule out any significant mantle input.

[47] Whereas helium contributions are restricted to three sources (atmospheric, radiogenic-crustal, mantle) that mix conservatively, there are a myriad of carbon sources and sinks in the crust that may both contribute to the  $\text{CH}_4$  pool through mixing, as well as change the carbon and hydrogen isotope composition of the  $\text{CH}_4$  due to fractionation during postformation reactions. Hence it is not uncommon for helium and carbon-based gases such as  $\text{CO}_2$  or  $\text{CH}_4$  to become decoupled and it is not impossible to have a mantle helium signature and no component of mantle-derived carbon in either  $\text{CO}_2$  or  $\text{CH}_4$ . Nonetheless, the patterns that emerge from Figure 3 strongly support the case that the set of samples with the more  $^{13}\text{C}$ - and  $^2\text{H}$ -enriched signatures in Figure 2 reflect a significant mantle contribution to both the helium and the  $\text{CH}_4$ . Because the question of  $\text{CH}_4$  from the mantle remains controversial, we adopt the traditional convention of referring to this component only as mantle-derived  $\text{CH}_4$ —that is,  $\text{CH}_4$  produced from a carbon source that originated from a mantle or magmatic carbon input into the crust, likely originally in the form of  $\text{CO}_2$ . For many of these sites (e.g., LCHF, EPR, Socorro) this is supported by  $^{13}\text{C}$ -enriched values for  $\text{CO}_2$  (approximately  $-5\text{‰}$ ) and in some cases  $\text{CO}_2/^3\text{He}$  ratios on the order of  $1\text{--}6 \times 10^9$  consistent with a mantle-derived origin for both gases [Marty and Jambon, 1987]. As described in section 2, the specific  $\text{CH}_4$  forming reactions may vary as a function of the geologic setting and mineralogy, fugacity, temperature etc., but Figure 3 demonstrates the important role of the isotopic composition of the feedstock in determining the overall range of  $\delta^{13}\text{C}$

and  $\delta^2\text{H}$  values in the resulting  $\text{CH}_4$  at these sites. While an abiotic origin has been suggested for the Nisyros Volcano in Greece [Fiebig *et al.*, 2004], no  $\delta^2\text{H}$  values are available for the  $\text{CH}_4$  and hence this data has not been included in Figure 3. That said, their inclusion would not change the above analysis and patterns significantly, as both a large mantle-derived helium component (approximately 70%) and a very enriched range of  $\delta^{13}\text{C}$  values for  $\text{CH}_4$  (ranging from  $-16.4$  to  $-24.8\text{‰}$ ) are reported in that study.

[48] A few samples/studies require some additional discussion in the above analysis. For instance, the one sample from Sano *et al.* [1993] for  $\text{CH}_4$  from the Oman (Semail) ophiolite springs, while containing some mantle helium (3.9%) has a more  $^{13}\text{C}$ -depleted value ( $-34.5\text{‰}$ ) than any of the other samples discussed above. Notably, this value is inconsistent with previous work published for nearby springs by Fritz *et al.* [1992], which reported  $\delta^{13}\text{C}$  values between  $-12$  to  $-15\text{‰}$ . It is not possible to comment further at this time, but it is notable that the 1992 values would place these samples within the same range as the other samples in Figure 3a with a significant mantle-derived component. Fritz *et al.* [1992] note that there may be substantial variability in  $\text{CH}_4$  production at the springs due to reconfiguration of the system for irrigation of date palms. While data from the Lovozero and Khibiny complexes on the Kola peninsula, and from the Ilimaussaq in Greenland are included in Figure 2, there are not to our knowledge directly corresponding samples for which helium isotopes have been characterized. Nivin [2008] and Tolstikhin *et al.* [2002] in separate studies analyzed noble gas isotopes for these systems—demonstrating a wide variety of signatures reflecting variable proportions of mantle, crustal, and atmospheric components reflecting the complex evolution of these systems. Without the ability to directly relate the noble gas data to the carbon and hydrogen isotope signatures, these systems could not at this time be incorporated into the analysis in Figure 3.

[49] The two samples from Poison Bay, New Zealand are anomalous in that they contain both significant mantle-derived helium but relatively depleted  $\delta^{13}\text{C}$  values ( $\sim -36\text{‰}$ ) [Lyon and Giggenbach, 1994]. While these samples had been reported to have a significant component of abiotic  $\text{CH}_4$ , a closer reading of the original publications [Lyon and Giggenbach, 1994; Giggenbach *et al.*, 1993; Hoke *et al.*, 2000] reveals that these occur in a region where some mixing of  $\text{CH}_4$  sources may occur—including both thermogenic and in some cases microbially generated  $\text{CH}_4$ . Giggenbach *et al.* [1993] specifically comments that helium and carbon systems are likely decoupled due to multiple sources of  $\text{CO}_2$  and  $\text{CH}_4$  as well as loss of the carbon gases due to secondary reaction. Such situations may not be unusual for the case of  $\text{CH}_4$  in ultramafic rock obducted on continents (i.e., ophiolites) where additional sources of enriched carbon from decomposition of limestone or incorporation of atmospheric  $\text{CO}_2$  via circulating meteoric waters may introduce multiple carbon sources. Similarly near surface circulation of meteoric waters through these fractured rocks may introduce more depleted carbon sources from microbial or fossil organic matter [Szponar *et al.*,

2013]. Additionally, mantle helium may not be preserved in highly disrupted and fractured ophiolites like those of Poison Bay [Hoke *et al.*, 2000], or may be related to local tectonics favoring “seismic pumping” of deep mantle fluids toward the surface as suggested by Giggenbach *et al.* [1993]. Certainly surface exposures of ultramafic rocks will provide some of the most complex systems to interpret, as they are impacted by present day serpentinization driven by circulating meteoric water and many near-surface and local carbon sources.

[50] As noted previously, in both Figures 2 and 3 we sought to include only those gases that had been suggested in the literature to be either predominantly abiotic or at least contain a major contribution of abiotic  $\text{CH}_4$ , if some mixing could not be ruled out. Occurrences known or suspected to be significant mixtures of  $\text{CH}_4$  from different sources were not included in the analysis. This approach was deliberately chosen so that we might use the resulting plots to help establish the most promising diagnostic parameters. As a subsequent step, then we may test these parameters by applying them to more complex or mixed systems in which the contribution of abiotic  $\text{CH}_4$  is more controversial. An initial test of this approach can be made with our own data from some of the South African gold mines. One aspect of Figure 3a that becomes clear is the extent to which the most depleted  $\delta^{13}\text{C}$  values (all those in fact more depleted than  $-40\text{‰}$ ) for  $\text{CH}_4$  are all from one mine, the Driefontein site in South Africa. If the Driefontein samples are not included, the range of observed  $\delta^{13}\text{C}$  values tightens considerably (although the same is not true for  $\delta^2\text{H}$  values). In some ways this is not a new insight, as the original publications emphasized that of all the sites in South Africa for which an abiotic  $\text{CH}_4$  component was suggested, the Driefontein mine was most likely to be in fact a mixture of abiotic and microbial  $\text{CH}_4$  end-members [Sherwood Lollar *et al.*, 2006]. Figure 3 now provides more quantitative support for this interpretation, and indicates that in fact the contribution of microbial  $\text{CH}_4$  to the Driefontein samples may have been even larger than originally estimated [Sherwood Lollar *et al.*, 2006].

[51] In summary, incorporating the conservative helium tracer in Figure 3 demonstrates the controlling factor of feedstock in the resulting abiotic  $\text{CH}_4$ . In the presence of a significant contribution from mantle- or magmatic-derived helium, abiotic  $\text{CH}_4$  has a range of carbon and hydrogen isotope values that reflect a more  $^{13}\text{C}$ - and  $^2\text{H}$ -enriched source, similar to that first observed at the EPR. In contrast, in the absence of a significant contribution of mantle-derived helium, carbon and hydrogen isotope values for abiotic occurrences of  $\text{CH}_4$  occupy a much more depleted range. If the Driefontein samples are recognized to in fact represent a significant mixture of microbial  $\text{CH}_4$  and are not included, then this second group of abiotic  $\text{CH}_4$  appears to fall in a range of  $\delta^{13}\text{C}$  values between  $\sim -20$  and  $-40\text{‰}$  and  $\delta^2\text{H}$  values between  $\sim -200$  and  $-425\text{‰}$ , likely reflecting the  $^{13}\text{C}$ -depleted nature of the crustal carbon sources feeding abiotic  $\text{CH}_4$  generation reactions in these lower temperature crustal settings.

[52] More widespread use of tools based on integration of stable isotope and gas geochemistry with noble gases is an essential step in advancing the field of investigation of abiotic CH<sub>4</sub>. Incorporation of conservative noble gas tracers such as helium provides the initial criteria to resolve the controlling influence of feedstock on the observed carbon and hydrogen isotope signatures for CH<sub>4</sub> (and associated gases such as CO<sub>2</sub>, if present). Recent studies are demonstrating how additional noble gases (Ne, Ar, Kr, Xe) can provide further insight [Sherwood Lollar and Ballentine, 2009; Lippmann-Pipke, *et al.*, 2011; Holland *et al.*, 2013], but are beyond the scope of this review. Only having first resolved this overriding controlling factor of feedstock isotopic composition, is it then possible to move forward with interpretation of the details of carbon and hydrogen isotope variation within each data set to investigate additional information that may reflect fractionation during specific reaction mechanisms and conditions, and to determine the role of secondary processes such as oxidation or mixing. A new framework for undertaking such a diagnostic approach is the subject of section 5

## 5. UNRAVELING BIOTIC VERSUS ABIOTIC CH<sub>4</sub>

### 5.1. Rationale and State-of-the-Art

[53] The challenge of developing effective diagnostic frameworks to evaluate the origin of CH<sub>4</sub> is an ongoing one. While debates around the Gold hypothesis have largely faded [Gold, 1979], distinguishing between abiotic and biotic origins of CH<sub>4</sub> are central to current interpretations regarding the evolution of metabolic pathways [Ueno *et al.*, 2006], the role of CH<sub>4</sub>-powered chemolithotrophic microbial communities at the hydrothermal vents [Kelley *et al.*, 2005], and may play an important role in constraining the biologic versus geologic origin of CH<sub>4</sub> reported to occur in the Mars atmosphere [e.g., Krasnopolsky *et al.*, 2004; Mumma *et al.*, 2009]. In the area of environment and resources, the ability to reliably differentiate between microbial CH<sub>4</sub> in near surface soils, sediments and aquifers, and CH<sub>4</sub> from deeper reservoirs under economic development through shale gas production [Osborn *et al.*, 2011; Kirk *et al.*, 2012] is at the core of the current “fracking” controversy.

[54] As discussed in section 4.1, the longstanding interpretational frameworks developed by pioneers such as Schoell [1980], Tissot and Welte [1984], Whiticar [1990], and Bernard *et al.*, [1978] have undergone and continue to undergo substantial expansion and revision in the past decade. This process has been driven not only by increasingly novel geologic and biogeochemical settings that are being investigated, beyond the original empirical foundation of these frameworks (largely based on shallow marine sediments), but by technological developments. The increase in sensitivity of isotopic analysis by several orders of magnitude made possible by continuous flow compound specific mass spectrometry [Sessions, 2006 and references therein] has not only revolutionized the spatial and temporal scale at which isotopic signatures can be investigated, but

facilitated multi-isotope investigations incorporating stable carbon, hydrogen, oxygen, nitrogen and sulfur analysis. Furthermore, continuous flow techniques have facilitated coupling of isotopic measurements to microbiological and abiotic experiments specifically designed to push the limits of knowledge of isotopic fractionation factors and to provide a conceptual foundation that reflects not just the “typical” range of observed phenomenon but what could be called “fractionation at the extreme.” Specific examples are provided below.

### 5.2. Reevaluation of Traditional Frameworks

[55] The range of possible carbon and hydrogen isotope fractionation effects involved in microbial methanogenesis have undergone substantial reexamination recently based on field [Tazaz *et al.*, 2013] and laboratory experiments investigating growth phase and substrate availability [e.g., House *et al.*, 2003; Valentine *et al.*, 2004a], and the role of enzymatically induced hydrogen isotope exchange reactions [e.g., Chidthaisong *et al.*, 2002; Valentine *et al.*, 2004b]. Temperature and pressure effects on fractionation are being evaluated, and demonstrating that for instance, thermophiles produce a smaller carbon kinetic isotope effect during methanogenesis from CO<sub>2</sub> than previously understood [e.g., House *et al.*, 2003; Valentine *et al.*, 2004a; Takai *et al.*, 2008]. For methanotrophs, Templeton *et al.* [2006] demonstrated substantial differences in carbon isotope effects related to changes in cell density during aerobic bacterial oxidation of CH<sub>4</sub>.

[56] Simultaneously, novel experimental efforts in abiotic organic synthesis of CH<sub>4</sub> have, very recently, made significant strides in characterizing carbon (and in a more limited number of cases hydrogen) isotope fractionation effects associated with chemical synthesis of CH<sub>4</sub> and associated higher hydrocarbons by reactions such as surface-catalyzed polymerization from reduction of CO or CO<sub>2</sub> in a Fischer-Tropsch type synthesis [McCollom and Seewald, 2006; Taran *et al.*, 2007, 2010b; McCollom *et al.*, 2010]; heating or metamorphism of graphite- or carbonate-bearing rocks [McCollom and Bach, 2009]; and other gas-water-rock reactions associated with serpentinization [McCollom and Seewald, 2001]. Significantly, several experimental studies have shown that abiotic CH<sub>4</sub> derived by gas-water-rock reactions can result in  $\delta^{13}\text{C}$  values as depleted as  $-57\%$ , comparable to the isotopically “light” values that were once assumed to be an indication of biological activity [Horita and Berndt, 1999; McCollom and Seewald, 2006; Taran *et al.*, 2007, 2010b; McCollom *et al.*, 2010]. In addition, it has become evident that the carbon isotope “inverse” trend first proposed by Des Marais *et al.* [1981] as a diagnostic feature of abiotic CH<sub>4</sub>, ethane (C<sub>2</sub>H<sub>6</sub>), and higher hydrocarbons, is not observed in all cases and alone is insufficient to support an abiotic origin [Taran *et al.*, 2007; McCollom *et al.*, 2010, and references therein]. Increasingly, such studies are incorporating not only an examination of the isotopic signatures of CH<sub>4</sub>, but those of the other products of hydrocarbon synthesis for deeper insight into the specific reaction mechanisms. For instance, a comparison of field [Sherwood Lollar *et al.*, 2008] and laboratory-derived abiotic

hydrocarbons [McCollom *et al.*, 2010; Taran *et al.*, 2010b] suggests that during polymerization, the specific extent of the carbon and hydrogen isotope fractionation between CH<sub>4</sub> and C<sub>2</sub>H<sub>6</sub> varies as a function of different reaction mechanisms and parameters such as catalysts or conversion ratio. In contrast, for the higher hydrocarbons, the rapid rate of abiotic chain polymerization is such that any net isotopic fractionation associated with subsequent carbon addition steps is negligible. The  $\delta^{13}\text{C}$  values of C<sub>2</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>8</sub> and higher straight chain alkanes produced by abiotic polymerization may be predicted by simple mass balance from the  $\delta^{13}\text{C}$  values of the lower molecular weight precursors, independent of the fractionation associated with the first step [Sherwood Lollar *et al.*, 2008; McCollom *et al.*, 2010].

[57] Hydrogen isotopic composition of FTT reactions was studied in a very limited number of laboratory experiments and only at temperatures above 250°C [Fu *et al.*, 2007; Taran *et al.*, 2010b; McCollom *et al.*, 2010]. The data show that CH<sub>4</sub> is depleted in <sup>2</sup>H by −35 to −80‰ relative to the initial H<sub>2</sub>. Experimental isotopic fractionation factors at 400°C between H<sub>2</sub>O, H<sub>2</sub> and CH<sub>4</sub> [Fu *et al.*, 2007], compared with theoretical isotopic equilibrium values [Horibe and Craig, 1995], show complete isotopic equilibrium between H<sub>2</sub>O-H<sub>2</sub> but only partial equilibrium for H<sub>2</sub>O-CH<sub>4</sub> and H<sub>2</sub>-CH<sub>4</sub>. Sherwood Lollar *et al.* [2007] demonstrated that the very depleted  $\delta^2\text{H}$  values for H<sub>2</sub>(g) typically found associated with abiotic CH<sub>4</sub> is likely controlled by relatively rapid H<sub>2</sub>-H<sub>2</sub>O isotopic exchange and hence provides little information on the primary  $\delta^2\text{H}$  values of the H<sub>2</sub> in these systems. As CH<sub>4</sub>-H<sub>2</sub> and especially CH<sub>4</sub>-H<sub>2</sub>O isotopic equilibration is thought to be significantly slower, and at low temperatures may require long geologic timescales, the effect of isotopic re-equilibration on  $\delta^2\text{H}$  signatures for CH<sub>4</sub> remains an area of investigation [Sessions *et al.*, 2004]. There are no FTT experiments with isotopic determinations at lower temperatures, such as those occurring in continental serpentinization sites (generally <100°C). Natural gas samples from ophiolites and deep crystalline rocks show  $\delta^2\text{H}$  of H<sub>2</sub> in the range −580 to −730‰ and  $\delta^2\text{H}$  of CH<sub>4</sub> is always more enriched than −450‰, up to around −110‰ [e.g., Etiope *et al.*, 2011b; Sherwood Lollar *et al.*, 2007].

### 5.3. Integrated Approach Incorporating Multiple Lines of Evidence

[58] A key conclusion from this review of recent work is that some of the confusion around resolving the origin of CH<sub>4</sub> occurrences has arisen due to an over-reliance on using isotope geochemistry in isolation. In contrast the most successful studies have integrated multiple lines of evidence to constrain and inform the isotopic parameters. Drawing on the concepts and discussion from the previous sections (sections 1–4), we suggest here an integrated diagnostic approach to resolve biotic versus abiotic CH<sub>4</sub>.

#### 5.3.1. Characterization of the Entire Reaction Spectrum (Reactants and Products)

[59] As is apparent from the discussion to this point, interpretation of a carbon isotope signature for CH<sub>4</sub> (or even a coupled carbon and hydrogen isotope set) in isolation has

limitations. Comparison of the  $\Delta^{13}\text{C} = \delta_{\text{reactant}}^{13}\text{C} - \delta_{\text{product}}^{13}\text{C}$  (e.g.,  $\Delta^{13}\text{C} = \delta^{13}\text{C}_{\text{CO}_2} - \delta^{13}\text{C}_{\text{CH}_4}$ ; or  $\Delta^2\text{H} = \delta^2\text{H}_{\text{H}_2\text{O}} - \delta^2\text{H}_{\text{CH}_4}$ ) is essential information, at a minimum. Research in this area remains an exciting area of discovery as, for instance, the role of different substrates in methanogenesis impacts not only the “source” signature (initial isotopic signature of the carbon and hydrogen substrates entering the reaction in question), but the fractionation associated with methanogenesis [Penning and Conrad, 2006 and references therein]. Particularly in the case of  $\delta^2\text{H}$  signatures, characterization of the H sources contributing to biosynthetic reactions has been essential to the evaluation of microbially catalyzed hydrogen isotope exchange as well as isotopic re-equilibration postreaction [Chidthaisong *et al.*, 2002; Valentine *et al.*, 2004a, 2004b]. Equally, as has been demonstrated by the abiotic organic synthesis experiments described above, deciphering reaction mechanisms has required comparison of all products in a reaction series (e.g., not simply CH<sub>4</sub> but C<sub>2</sub>-C<sub>6</sub> alkanes and higher molecular weight hydrocarbons as well) [Taran *et al.*, 2007; Sherwood Lollar *et al.*, 2008; McCollom *et al.*, 2010].

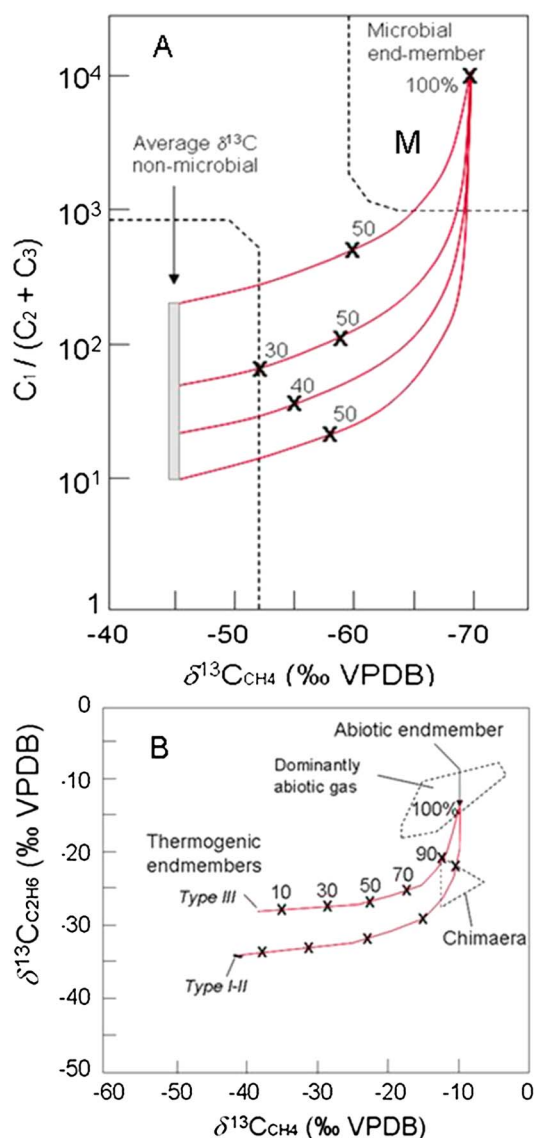
#### 5.3.2. Associated Species

[60] In addition to associated species involved as either reactants or products in direct reaction with CH<sub>4</sub>, the above discussion has highlighted the critical information that can be gained from other associated species. Such information might include: the presence or absence of other reactive gases indicative of a biological origin (e.g., methyl mercaptan, dimethyl sulfide; Allen *et al.* [2006]); gases associated with an abiotic water-rock reaction such as serpentinization (e.g., high concentrations of H<sub>2(g)</sub>; Sherwood Lollar *et al.* [2007]); or with other geologic sources (e.g., nonhydrocarbon reactive gases such as N<sub>2</sub> or CO<sub>2</sub>; Ballentine and Sherwood Lollar *et al.* [2002]; Gilfillan *et al.* [2009]). While most of this information does not constrain the origin of CH<sub>4</sub> forming processes directly—and may be decoupled from CH<sub>4</sub> formation processes even in the same setting—the cumulative contextual information can nonetheless be important additional lines of evidence.

[61] As has been demonstrated in this review, this is particularly true for the noble gases. Combined with information from the reactive gases, the conservative noble gases provide a unique ability to both identify and quantify the relative contribution of mantle/magmatic, crustal-derived, and atmospheric-derived fluids and gases. This review demonstrated the role of helium isotope signatures in constraining the carbon feedstock for abiotic synthesis of CH<sub>4</sub> (Figure 3). The use of multiple isotope systems (including He, Ne, Ar, Kr, Xe) can also provide residence time estimates for fluids associated with CH<sub>4</sub> [Holland *et al.*, 2013]; constrain paleo-recharge conditions for groundwaters or formation waters in which CH<sub>4</sub> is found; or establish the role and ratio of water/gas or oil/gas phase interactions [Ballentine and Burnard, 2002, and references therein].

#### 5.3.3. Geologic and Hydrogeologic Context

[62] Sherwood Lollar and Ballentine [2009] reviewed of the role of noble gases in constraining the source and cycling of carbon in the subsurface. That work also provided multiple examples of a critical dimension in the recommended

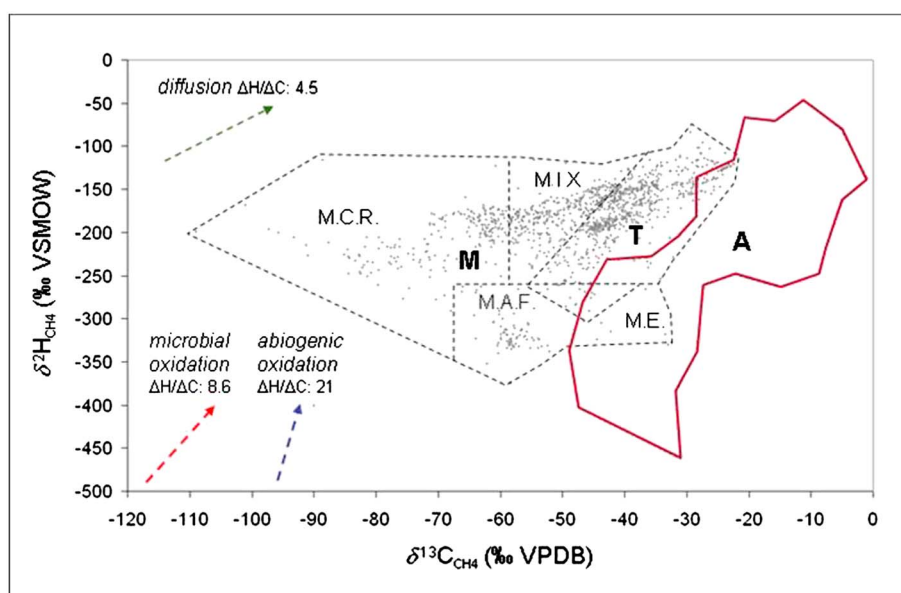


**Figure 4.** (A)  $C_1/(C_2 + C_3)$  versus  $\delta^{13}C_{CH_4}$  for hydrocarbon gases after Bernard *et al.* [1978]. Range of typical values of microbial  $CH_4$  (M), and for a nonmicrobial end-member (appropriate for either thermogenic or abiogenic cases) are indicated. X indicates for each theoretical line, the percentage (%) of mixing contribution from a microbial  $CH_4$ , with a nonmicrobial end-member with an average value of  $\delta^{13}C$  of -45‰ and a range of possible  $C_1/(C_2 + C_3)$  ratios between 10 and 500 for the purposes of the mixing calculations. The example illustrates cases wherein up to 50–60% mixing with a microbial  $CH_4$  can occur with minimal shifting of the location of the data along the y axis. In the absence of a series of data points that lie along the curve due to increasing proportions of mixing ratios, such shifts are difficult or impossible to identify. (B)  $\delta^{13}C_{CH_4}$  vs.  $\delta^{13}C_{C_2H_6}$  plot with mixing lines between two thermogenic end-members (represented by natural gas from marine Type I–II and terrestrial Type III organic matter) and an end-member considered to be dominantly abiotic from igneous inclusions and serpentinized ultramafic rocks given by the average of the  $\delta^{13}C_1$  and  $\delta^{13}C_2$  values in the gas. The plot shows that the presence of small (<10%) fractions of biotic gas mixed with abiotic gas do not significantly change the carbon isotopic composition of  $CH_4$ , but can be distinguished by the isotopic composition of ethane (redrawn from Etiope *et al.* [2013a]).

integrated approach—the integration of all of the above lines of evidence into a detailed geologic and hydrogeologic model. While characterization of the geologic context for  $CH_4$  gas studies is typically routine, integration of hydrogeologic constraints sometimes receives less emphasis. Given the intimate association of gases with fluids—both aqueous and nonaqueous (e.g., petroleum; supercritical  $CO_2$ ), establishing the origin of  $CH_4$  can be most effectively constrained if the degree of interaction and transport with the fluid phases are incorporated in the diagnostic strategy from the onset of investigation. A clear example is also given by the association of abiogenic  $CH_4$  and hyperalkaline (pH > 9) Ca-OH type waters in continental serpentinized ultramafic rocks, described in section 3.1 [e.g., Neal and Stanger, 1983; Boschetti *et al.*, 2013; Etiope *et al.*, 2013b]. Understanding why and when abiogenic  $CH_4$  may originate in those environments requires an understanding of the hydrogeologic factors leading to the genesis of the hyperalkaline waters and the geologic setting and history.

#### 5.3.4. Evaluation of Potential for Mixing

[63] As discussed extensively, one of the major goals of this review of diagnostic approaches was to attempt to clarify parameter space by restricting our analysis as much as possible to gases thought to be dominantly abiogenic. Some of the confusion in the literature we feel has arisen due to the tendency, perhaps due to the novelty or controversy around abiogenic  $CH_4$ , to characterize gas occurrences with even partial abiogenic components as “abiogenic” and to deemphasize the mixed contributions. In many cases, as noted, careful reading of the original publications, or reevaluation of the carbon and hydrogen isotope data in the light of new parameters such as helium isotope signatures, have revealed that some reported abiogenic occurrences are in fact likely gases of mixed origin. The importance of a quantitative evaluation of mixing cannot be over-emphasized. A major limit of the CD diagram and other traditional framework plots is that they are relatively insensitive to mixing. This is due to uncertainty and overlap in the  $\delta^{13}C$  of the microbial, thermogenic or abiogenic end-members. In addition, a large degree of mixing may be required before the mixing effect on  $\delta^{13}C$  of  $CH_4$  is readily apparent. Figure 4a illustrates this for the example of mixing of a microbial  $CH_4$  end-member with a nonmicrobial end-member with an average  $\delta^{13}C$  of -45‰ and a range of possible  $C_1/(C_2 + C_3)$  ratios between 10 and 500 for the purposes of the mixing calculations. The example clearly demonstrates that up to 50% mixing with a microbial  $CH_4$  can occur with minimal shifting of the location of the data along the y axis. In the absence of a series of data points that lie along the curve due to increasing proportions of mixing ratios, such shifts are difficult or impossible to identify. Figure 4b provides another example in the case of Chimaera gas, where a minor biotic component was recognized only by using mixing models based on  $CH_4$  and  $C_2H_6$  isotopic composition [Etiope *et al.*, 2011b], as the effects of mixing are much more readily apparent in the latter. Figure 4b shows that the presence of small (<10%) fractions of biotic gas mixed with abiotic gas does not significantly change the carbon isotopic composition of  $CH_4$ , but is distinguished by the isotopic composition of  $C_2H_6$ .



**Figure 5.** Synoptic CD diagram including biotic  $\text{CH}_4$  observed in subsoil petroleum systems (T: thermogenic; M: microbial; M.C.R.: microbial from carbonate reduction; M.A.F.: microbial from acetate fermentation (small grey dots are the same of Figure 2, from a database after *Etiope et al.* [2013a]), microbial  $\text{CH}_4$  in special ecosystems (M.E., microbial evaporitic; *Tazaz et al.* [2013]) and dominantly abiogenic  $\text{CH}_4$  reviewed in this work (A). The red line encompasses the data reported in Figure 2. Isotopic fractionation slope due to microbial oxidation is the average of the values reported by *Coleman et al.* [1981] and *Kinnaman et al.*, [2007]; abiogenic oxidation fractionation slope after *Etiope et al.* [2011a]; diffusion fractionation slope (for the residual gas) after *Runge* [1980] and *Schoell* [1983].

### 5.3.5. Role of Postgenetic Alteration Processes

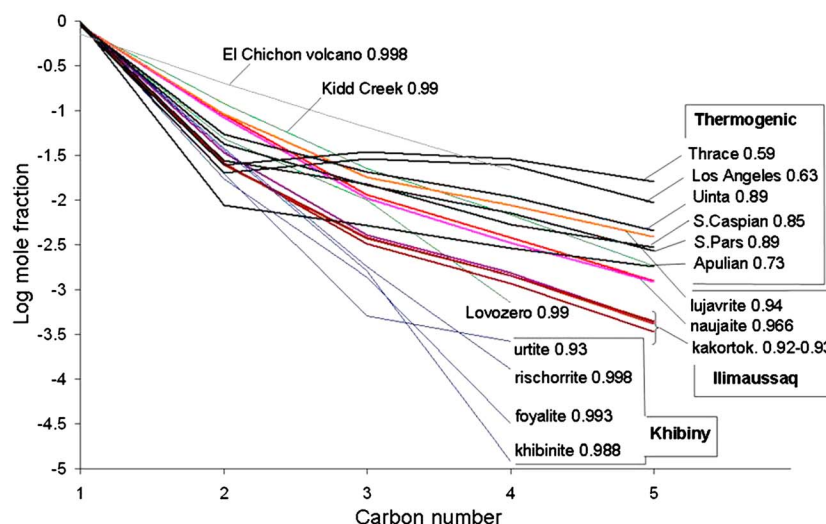
[64] Postgenetic processes may affect molecular and isotopic composition of  $\text{CH}_4$  after its formation and during its migration, so that the gas sampled in surface manifestations, boreholes or secondary inclusions may be different from the original gas at the source. These secondary processes include microbial oxidation, abiogenic oxidation, isotopic fractionation by diffusion, molecular fractionation by advection and, typically in oil-prone sedimentary basins, the anaerobic biodegradation of heavy hydrocarbons with secondary methanogenesis. These processes are extensively described by, among others, *Coleman et al.* [1981], *Schoell* [1983], *Whiticar* [1999], *Kinnaman et al.* [2007], *Etiope et al.* [2009], *Etiope et al.* [2011a], and references therein.

[65] Figure 5 is the synoptic result of the review of the CD diagram made in sections 4.1 and 4.2, considering the isotopic range of microbial  $\text{CH}_4$  observed in subsoil rocks; microbial  $\text{CH}_4$  recently observed in particular ecosystems (evaporitic hypersaline environment; *Tazaz et al.* [2013], is added for completeness. It is important to emphasize that any gas sampled far from its source, and plotted in the CD diagram, may be altered so that its isotopic signature may not correspond to its genetic process. In particular, microbial or abiogenic oxidation produce  $^{13}\text{C}$  and  $^2\text{H}$  enrichments according to fractionation slopes reported by *Coleman et al.* [1981], *Kinnaman et al.* [2007], and *Etiope et al.* [2011a], shown in Figure 5. Gas diffusion, driven by concentration gradients according to Fick's law, may produce  $^{13}\text{C}$  and  $^2\text{H}$  depletion in the diffusing gas, but the residual gas will be  $^{13}\text{C}$  and  $^2\text{H}$  enriched. Although the effect of

diffusion on the isotopic signature of  $\text{CH}_4$  has been demonstrated in the laboratory for carbon, it must be noted there are few examples to date where these effects have been identified in field samples [e.g., *Runge*, 1980]. In Figure 5 we assume the  $\Delta\text{H}/\Delta\text{C}$  fractionation slope observed in some petroleum systems [*Runge*, 1980; *Schoell*, 1983]. The three fractionation slopes (microbial oxidation, abiogenic oxidation and diffusion) can be used to predict isotopic compositions that are unlikely to result from postgenetic alteration of a biotic gas. For example, it is unlikely that a gas with isotopic composition of  $\delta^{13}\text{C}$ :  $-30\text{‰}$  and  $\delta^2\text{H}$ :  $-350\text{‰}$ , or  $\delta^{13}\text{C}$ :  $-10\text{‰}$  and  $\delta^2\text{H}$ :  $-250\text{‰}$  is an oxidized or residual (after diffusion) gas of microbial origin, unless there is some microbial  $\text{CH}_4$  with an isotopic range wider than that reported in Figure 5.

### 5.4. Testing the Schulz-Flory Distribution

[66] The possible abiotic origin of  $\text{CH}_4$  can be further evaluated by checking the Schulz-Flory distribution of its hydrocarbon homologs. The Schulz-Flory distribution is a molecular distribution of the hydrocarbon alkanes that is controlled by chain growth probability factor for abiotic stepwise polymerization where  $(\text{C}_n + 1/\text{C}_n)$  is approximately constant ( $\text{C}_n$  is the concentration in mole units). Such a distribution seems to be typical (even if not exclusive) of abiotic synthesis [e.g., *Sherwood Lollar et al.*, 2008]. As pointed out by *Giggenbach* [1997], however, the similarity in the distribution of hydrocarbons in natural gases to that in synthetic gas cannot be used to distinguish between FTT-synthesis and thermogenic decay of organic matter,



**Figure 6.** Evaluation of the Schulz-Flory distribution coefficient,  $r^2$ , on selected pure, nonmixed, thermogenic gas (Thrace Basin, Turkey: *Gürgey et al.* [2005]; Los Angeles and Uinta basins, U.S.: *Jeffrey et al.* [1991]; *Rice et al.* [1992]; South Caspian basin, Azerbaijan: *Katz et al.* [2002], South Pars gas field, Iran: *Aali et al.* [2006]; Apulian basin, Italy: *Ricchiuto and Schoell* [1988]) and presumed abiotic gas (not significantly mixed with biotic gas) from Ilimaussaq and Khibiny intrusions [*Potter and Konnerup-Madsen*, 2003; *Beeskow et al.*, 2006], Kidd Creek boreholes in Precambrian shield [*Sherwood Lollar et al.*, 2008], and El Chichon volcano [*Capaccioni et al.*, 2004]. Thermogenic gas is typically characterized by a correlation coefficient  $r^2 < 0.9$ , while  $r^2$  is  $> 0.9$  for dominantly abiotic gas and  $> 0.99$  for quasi-pure abiotic gas.

because the “size distribution of polymers resulting from random formation of linkages is identical to that for random breaking of linkages.”

[67] We tested the Schulz-Flory distribution on selected thermogenic gas (whose origin is not considered mixed with microbial gas and for which at least  $\text{CH}_4$  to butane ( $\text{C}_4\text{H}_{10}$ ) concentrations are available), and presumed abiotic gas (not significantly mixed with biotic gas) from Ilimaussaq and Khibiny intrusions and El Chichon volcano. *Sherwood Lollar et al.* [2008] already tested the distribution on HCs from Kidd Creek and other South Africa and Canadian shield sites.

[68] The test showed that thermogenic gas is typically characterized by a correlation coefficient  $r^2 < 0.9$ , while  $r^2$  is typically  $> 0.99$  for quasi-pure abiotic gas. An evaluation of  $r^2$  for different types of gases is summarized in Figure 6. Thermogenic gas (black lines) typically have  $r^2 < 0.9$ . Pure abiotic gas such as that measured in the crater of the El Chichon volcano exhibits a  $r^2$  close to 1 (0.998). Kidd Creek and Lovozero gases, considered abiotic, show  $r^2$ : 0.99. Khibiny gas (blue lines)  $r^2$  ranges from 0.93 to 0.998. In the Khibiny massif  $\delta^{13}\text{C}$  of  $\text{CH}_4$  increases from the margin to the core of the intrusion, suggesting that margin rocks are contaminated by biotic  $\text{CH}_4$  from the surrounding sedimentary rocks [*Beeskow et al.*, 2006]. We have also verified that the correlation coefficient  $r^2$  of the Schulz-Flory distribution increases from margin to core (Figure 7a). The coefficient  $r^2$  is  $> 0.99$  only for the more internal rocks, rischorrite and foyelite. This further supports the hypothesis of abiotic origin of hydrocarbons inside the Khibiny intrusion, and slight mixing with biotic gas in the external rocks.

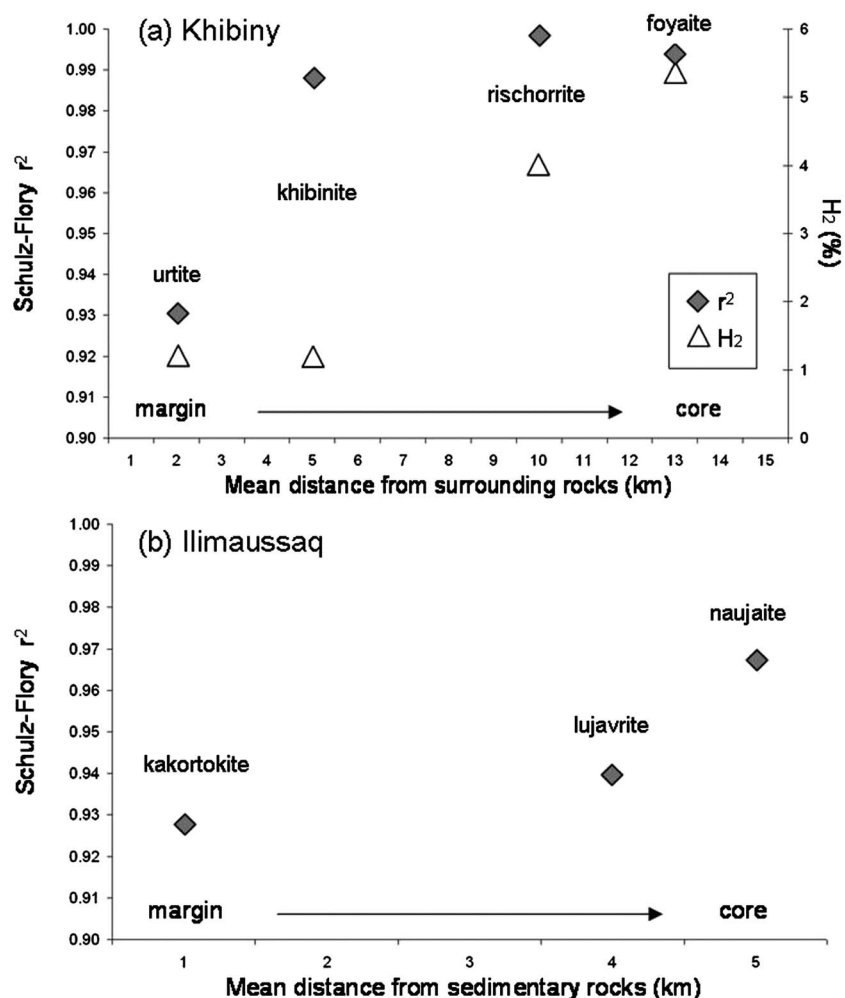
[69] The same exercise has been made for the Ilimaussaq intrusion (brown, red, orange lines in Figure 6) where  $r^2$

ranges from 0.92 to 0.97. Hydrocarbons in the internal (core) rocks have higher  $r^2$  (Figure 7b). This suggests that for Ilimaussaq as well there may be mixing with biotic gas at the margins of the igneous block. In contrast *Laier and Nytoft* [2012] suggested that all gas in Ilimaussaq is biotic and its  $^{13}\text{C}$  enrichment is related to isotopic fractionation by diffusion. In the case of diffusion, however, the  $\delta^2\text{H}$  values of  $\text{CH}_4$  would also be fractionated. Assuming the H/C fractionation slope of *Runge* [1980] (Figure 5), for an enrichment of 10‰ in  $\delta^{13}\text{C}$ ,  $\delta^2\text{H}$  would increase by 45‰. If so, residual thermogenic  $\text{CH}_4$  after diffusion should be characterized by  $\delta^2\text{H}$  values roughly in the range  $-75$  to  $0$ ‰. Ilimaussaq  $\delta^2\text{H}$  values range instead from  $-132$  to  $-145$ ‰ [*Konnerup-Madsen*, 2001]. As suggested by Figure 2, if Ilimaussaq  $\text{CH}_4$  is the residual of gas diffusion, the original  $\text{CH}_4$  would have been still abiotic, similar to Lovozero.

[70] In summary, the Schulz-Flory distribution, although is not a decisive diagnostic tool to identify an abiotic origin of  $\text{CH}_4$ , can offer a good test. Correlation coefficient ( $r^2$ ) values  $> 0.9$  may indicate a dominant abiotic component; values  $> 0.99$  likely refer to almost pure abiotic gas. This parameter should be interpreted with caution for surface gas seeps, which may be affected by molecular fractionation (more  $\text{CH}_4$ , less  $\text{C}_{2+}$ ) with respect to the original gas in the deep source.

### 5.5. Clumped Isotopes

[71] A major new frontier in  $\text{CH}_4$  isotope geochemistry is opening up with the development of new analytical systems for measuring clumped isotopes of  $\text{CH}_4$  and other hydrocarbons. Clumped isotopologues are those rare subsets of a population of a given compound, such



**Figure 7.** Schulz-Flory distribution correlation coefficient  $r^2$  versus distance from the margin of Khibiny (A) and Ilimaussaq (B) igneous intrusions. Variation of  $H_2$  concentration is also reported for Khibiny (data from Potter and Konnerup-Madsen [2003] and Beeskow *et al.* [2006]). Minimum distance between sample and surrounding volcano-sedimentary rock is derived from Beeskow *et al.* [2006] and Layer and Nytoft [2012]. Although khibinite is generally the most external rock in the Khibiny massif, its sample location is more distant from the surrounding rock with respect to the urtite sample.

as  $CH_4$ , that contain both a heavy carbon isotope ( $^{13}C$ ) and a heavy hydrogen ( $^2H$ , or  $D$ ) and hence form highly stable bonds. The field has been extensively developed for  $CO_2$  for paleoclimate research [Eiler and Schauble, 2004], and is currently being explored for the basis of a novel geothermometer based on  $CH_4$  [Wang *et al.*, 2004; Ma *et al.*, 2008]. As for  $CO_2$ , the principle for  $CH_4$  is that the presence of two heavy isotopes makes the bond extremely stable. Formation of the highly stable bonds is favored at lower temperatures, and theoretical calculations predict a correlation of decreasing frequency of the doubly substituted molecules as formation temperatures increase [Wang *et al.*, 2004; Ma *et al.*, 2008].

[72] The approach offers insight into the temperature at which  $CH_4$  molecules were formed, and hence an indirect additional line of evidence regarding  $CH_4$  origin, rather than a direct diagnostic parameter. Specifically, a robust differentiation between microbially produced  $CH_4$  formed at temperatures  $< 80^\circ C$  and magmatic  $CH_4$  produced by abiotic

organic synthesis at a high temperature hydrothermal vent may be possible. However, as with conventional carbon and hydrogen isotope signatures, there will be areas of significant overlap in predicted signatures. Distinguishing low temperature methanogenesis via diagenesis of organic matter, from microbial  $CH_4$  production by thermophiles, or from abiotic  $CH_4$  synthesis via low temperature-water rock reactions in continental ultramafic rocks [Etiope *et al.*, 2011b; Boschetti *et al.*, 2013] might be difficult as they all may occur at  $< 100^\circ C$ . Abiotic organic synthesis of  $CH_4$  poses a specific challenge. There may be considerable overlap between highly mature thermogenically produced  $CH_4$  and the range of possible temperatures for abiotic synthesis. In particular, abiotic organic synthesis via water-rock reactions can occur over a wide range of temperatures (e. g., FTT or Sabatier reaction synthesis, depending on the catalyst, can occur both below  $100^\circ C$  and up to at least  $450^\circ C$  [Etiope *et al.*, 2011b; Boschetti *et al.*, 2013; McCollom and Seewald, 2006, 2007; Mims and McCandlish, 1985]).

[73] Consistent with the conclusions of this review, no single approach provides a silver bullet. The clumped isotope approach is an exciting new avenue for specific data on temperatures of formation, and hence an important additional line of evidence on reaction mechanisms. In addition if both mass 18 rare isotopologues can be measured, the approach holds promise for clearly identifying gases of mixed origin, due to deviation from the expected isotopologue distributions (E. Young, 2013, pers. comm.) As for conventional carbon and hydrogen isotope approaches however, this new tool will be most powerful when embedded in a coherent set of supporting data and geologic and hydrogeologic contextual evidence. The range of temperature under which FTT reactions can occur, and the extensive experimental literature for FTT are likely unparalleled, therefore making these experiments a strategic and feasible initial set of geothermal calibration experiments for clumped isotope investigations.

## 6. CONCLUSIONS

[74] Abiotic CH<sub>4</sub> can be produced in different geologic environments under a wide range of temperature and pressure. The production mechanisms can be divided into two main classes, magmatic processes, generally in volcanic and high temperature hydrothermal settings, and gas-water-rock interactions (or postmagmatic processes), at lower temperatures. In total, at least nine specific gas production mechanisms (or group of mechanisms) are defined. This review emphasizes that abiotic CH<sub>4</sub> includes more than just mantle-derived gas, and that elevated temperatures are not necessary for its synthesis. Recently occurrences of abiotic or dominantly abiotic CH<sub>4</sub> have been documented, so far, in surface seeps and water springs related to serpentinization of ultramafic rocks (peridotites) at temperature below 150°C and in deep subsurface fracture waters in Precambrian cratons and igneous complexes. On land, present-day serpentinization in ultramafic rocks, driven by meteoric water, results in associated abiotic CH<sub>4</sub> at sites in Turkey, Oman, Philippines, New Zealand, Greece, Italy, Japan, and very likely it also occurs in Cyprus, Portugal, Serbia, and other settings where there is evidence of present-day serpentinization (e.g., hyperalkaline, pH >10, and Ca-OH type waters). Such a low temperature serpentinization may be the origin of CH<sub>4</sub> discovered in the atmosphere of Mars.

[75] The increased number of studies and analyses of gas from these systems allows, today, to draw a global diagram of isotopic composition of CH<sub>4</sub> ( $\delta^{13}\text{C}$  vs  $\delta^2\text{H}$ ), which shows that abiotic, or dominantly abiotic, CH<sub>4</sub> is generally isotopically offset from typical biotic (microbial or thermogenic) gas, although complexities arise due to overlap, and due to the fact that the <sup>13</sup>C and <sup>2</sup>H composition can be relatively insensitive to mixing. Abiotic CH<sub>4</sub> may be either <sup>13</sup>C- and <sup>2</sup>H- enriched ( $\delta^{13}\text{C} > -20\text{‰}$  and  $\delta^2\text{H} > -200\text{‰}$ ) or depleted ( $\delta^{13}\text{C}$  between  $-30$  and  $-47\text{‰}$  and  $\delta^2\text{H} < -200\text{‰}$ ). This may reflect variable carbon feedstock (mantle versus crustal) and fractionation between CO<sub>2</sub> and CH<sub>4</sub>. In any case, the CD diagram (also known as “Schoell plot”) remains a useful

initial survey tool to spot a possible dominantly abiotic gas. Further diagnostic techniques are however necessary to better assess the abiotic CH<sub>4</sub> origin, especially in cases where sedimentary rocks, with their potential organic matter feedstock, can contribute to the production of the gas. Noble gases, mixing models and the Schulz-Flory distribution are the best complementary tools. Complete isotopic analyses and modeling of gases associated with CH<sub>4</sub> (e.g., CO<sub>2</sub>, H<sub>2</sub>, C<sub>1</sub>-C<sub>5</sub> alkanes, when available) and clumped isotope analyses may, in the near future, offer new interpretative techniques. However, a detailed knowledge of the geologic context, including hydrogeologic, structural and petrographic factors, is always necessary. Integration of these aspects is today allowing researchers to recognize abiotic CH<sub>4</sub> in an increasing number of sites suggesting that low temperature (<100°C) abiotic CH<sub>4</sub> synthesis is more common than previously thought. A similar investigative approach may be required to study the origin of CH<sub>4</sub> on other planets, as in the case of Mars.

## GLOSSARY

**Abiogenic (methane):** Synonymous with abiotic

**Abiotic (methane):** Produced by nonorganic reactions or mechanisms. CH<sub>4</sub> precursor can however be organic (e.g., inorganic reactions on graphite, which is derived by organic material, may produce abiotic CH<sub>4</sub>). This may be matter of debate, because some authors prefer to assume that abiotic CH<sub>4</sub> is only that derived from inorganic starting material. This makes the story more complex, however, because subduction and recycling of crustal rocks may bear “organic” carbon into deep, mantle fluid systems, where the distinction between organic and inorganic carbon is lost.

**Bacterial (methane):** Term widely used to define CH<sub>4</sub> produced by microbial activity. However, it should be stressed that bacteria do not produce CH<sub>4</sub>; CH<sub>4</sub> is generated by microorganisms belonging to the group (or domain) of Archaea which is quite distinct from the bacterial domain.

**Biogenic (methane):** Generic term initially used to define CH<sub>4</sub> produced by microbial activity (synonymous with microbial CH<sub>4</sub>); however, it is also used by astrobiology community as synonymous with biotic CH<sub>4</sub> (see below), including both microbial and thermogenic CH<sub>4</sub>. To avoid misunderstandings the use of this term is not used in the review.

**Biotic (methane):** Produced by degradation of organic matter, by microbes (Archaea) at low temperature (microbial CH<sub>4</sub>), or by thermal decomposition of high molecular weight organic matter (kerogen) or oil (thermogenic CH<sub>4</sub>).

**Carbides:** Binary compounds consisting of carbon and a more electropositive element. Naturally occurring metal carbides are minerals, such as cohenite, (Fe,Ni,Co)<sub>3</sub>C or yarlongite (Fe,Cr,Ni)<sub>9</sub>C<sub>4</sub>, found so far in meteorites and in inclusions in mantle-derived kimberlite and ophiolitic chromitites [e.g., Kaminsky and Wirth, 2011].

**Fischer-Tropsch:** A set of chemical reactions invented by the German scientists Franz Fischer and Hans Tropsch in the 1920s for the production of hydrocarbons as described in section 2.9. See Schulz [1999] for a historical review.

**Hydrothermal:** Some confusion persists around the term “hydrothermal.” Though often used or assumed to refer only to magmatic or high temperature reactions such as that occurring in mid-ocean ridges or spreading centers, the term in fact refers more generally to water-rock reactions at any range of temperatures.

**Microbial (methane):** Produced by microbial (Archaea) communities (methanogens).

**Microseepage:** Pervasive, low CH<sub>4</sub> fluxes from soil (typically units up to hundreds of mg m<sup>-2</sup> d<sup>-1</sup>), distant from macro-seeps or independent of their occurrence, generally occurring in petroleum fields. Microseepage can induce secondary mineralization and methanotrophic bacterial activity in the soil.

**Serpentinization:** Alteration by hydration of olivine and pyroxene minerals, in low-silica mafic and ultramafic rocks, typically peridotite, with production of serpentine, brucite, magnetite, and other minerals. The anaerobic oxidation of Fe<sup>2+</sup> by the protons of water leads to the formation of H<sub>2</sub>. Serpentinization may occur at the seafloor (hydration by seawater in or around mid ocean ridges) and in mountain belts (present-day hydration by meteoric water in ophiolites or intrusive igneous massifs).

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