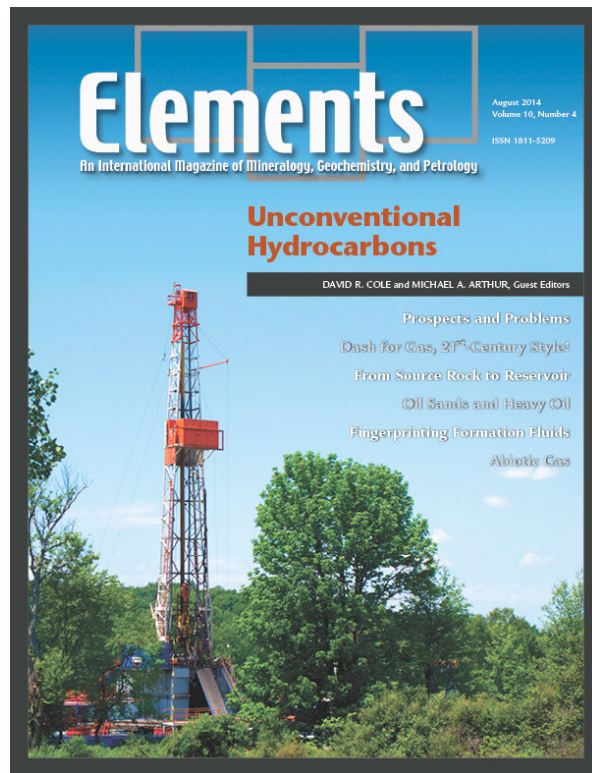


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# Abiotic Gas: Atypical, But Not Rare

Giuseppe Etiope<sup>1,2</sup> and Martin Schoell<sup>3</sup>

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**Abiotic gaseous hydrocarbons comprise a fascinating, but poorly understood, group of Earth fluids generated by magmatic and gas–water–rock reactions that do not directly involve organic matter. At least nine different inorganic mechanisms, including Fischer-Tropsch type reactions, occur over a wide range of temperatures. Trace amounts (typically parts per million by volume) are formed in volcanic and geothermal fluids, but considerable amounts of methane, reaching 80–90 vol%, are now recognized in an increasing number of sites in Precambrian crystalline shields and serpentinized ultramafic rocks. Surface manifestations of abiotic gas related to serpentinization release gas directly to the atmosphere in ways that are similar to seepages of ordinary biotic gas from petroliferous areas. Abiotic methane is more widespread than previously thought. It also likely exists in sites undergoing active serpentinization and may be present in petroleum systems in the vicinity of serpentinized rocks.**

KEYWORDS: abiotic gas, methane, serpentinization, igneous rocks

## INTRODUCTION

The natural gas (methane and light hydrocarbons, including ethane, propane, and butane) we currently exploit originates through the microbial or thermal conversion of organic matter in sedimentary rocks. This gas is termed *biotic* because of its derivation from biologic compounds—mainly lipids and carbohydrates—liberated from marine and terrestrial organic matter. Methane (CH<sub>4</sub>) can also be produced by chemical reactions of inorganically derived gases such as carbon dioxide (CO<sub>2</sub>), carbon monoxide (CO), and hydrogen (H<sub>2</sub>).

The *abiotic* formation of methane was first recognized in 1913 when Paul Sabatier generated methane in the laboratory by reacting CO<sub>2</sub> and H<sub>2</sub> with metal catalysts, a discovery for which he was awarded a Nobel Prize. In 1925, Franz Fischer and Hans Tropsch succeeded in synthesizing more complex hydrocarbons using CO and H<sub>2</sub>. The Sabatier reaction (also known as “hydrogenation of CO<sub>2</sub>”) and the Fischer-Tropsch reaction (with CO) are today cumulatively termed Fischer-Tropsch-type (FTT) reactions.

In pioneering hypotheses, Thayer (1966) and Szatmari (1989) proposed that CO<sub>2</sub> hydrogenation could operate under geologic conditions. Laboratory experiments over

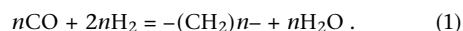
the last 30 years have demonstrated that abiotic methane can form via FTT reactions in conditions similar to those in the Earth’s crust (see review by McCollom 2013). Today, this process is widely invoked to explain the origin of methane-rich gas found in serpentinized peridotites (see review by Etiope and Sherwood Lollar 2013). Serpentinization and Sabatier reaction pathways are now considered fundamental processes that may be linked to the origin of life on Earth and to the production of hydrocarbons on other planets (Atreya et al. 2007; Russell et al. 2010; Etiope et al. 2013b). While the evidence for abiotic generation of methane on Earth cannot be questioned, there is an ongoing controversy related to the formation

of commercial quantities of abiotic natural gas and oil (Glasby 2006 and references therein). Without opening a new debate on this point, we focus on the gaseous hydrocarbons of predominantly abiotic origin that occur in igneous rocks.

## HOW ABIOTIC GAS IS FORMED

The processes of forming abiotic methane fall into two primary classes: (1) magmatic processes and (2) gas–water–rock reactions. TABLE 1 shows that at least nine pathways can be distinguished (Etiope and Sherwood Lollar 2013) and can occur over a wide range of temperatures. At least three processes have origins from primordial gas- and magma-sourced reactions while the other six involve gas–water–rock reactions as inorganic syntheses independent of magma or magma-derived fluids. This classification scheme reveals that magmatic or mantle-derived CH<sub>4</sub> is abiotic, but not all abiotic CH<sub>4</sub> is mantle derived. Field observations suggest, indeed, that the largest quantities of abiotic gas found on Earth’s surface are produced by low-temperature gas–water–rock reactions (Etiope and Sherwood Lollar 2013). Of particular interest are the FTT reactions (B6 in TABLE 1) because they are the most widely invoked mechanisms for generating large quantities of abiotic CH<sub>4</sub> in natural settings.

The FTT process encompasses the Fischer-Tropsch reaction *sensu stricto*, which refers to the catalytic hydrogenation of carbon monoxide (CO) to produce a wide range of linear, long-chain hydrocarbons:



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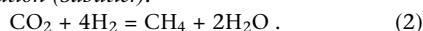
**TABLE 1** CLASSIFICATION SCHEME FOR SOURCES OF ABIOTIC GASES

Magmatic CH <sub>4</sub>
(A1) Primordial gas, delivered by meteorites during accretion of the Earth and preserved in the mantle
(A2) High-temperature (500–1000°C) reactions in the mantle (or magma in the crust), including hydrolysis or hydrogenation of metal carbides and CO, CO <sub>2</sub> , or carbonate reduction with H <sub>2</sub> O
(A3) Late-magmatic (<600°C) redistribution of C–O–H fluids, CO <sub>2</sub> evolution to CH <sub>4</sub> during magma cooling
Gas–water–rock reactions
(B1) High-temperature (~400–500°C) reactions involving carbon and Fe-bearing minerals
(B2) Metamorphism of carbonate–graphite-bearing rocks (with H <sub>2</sub> O at <400°C)
(B3) Carbonate methanation, i.e. thermal decomposition of carbonates and direct reduction (without CO <sub>2</sub> ) to CH <sub>4</sub>
(B4) Iron carbonate (siderite) decomposition
(B5) Uncatalyzed aqueous CO <sub>2</sub> reduction (variable reactions with CO <sub>2</sub> , CO, HCOOH, NaHCO <sub>3</sub> , NaHCOO, and H <sub>2</sub> )
(B6) Fischer-Tropsch-type (FTT) reactions (e.g. Sabatier reaction, see discussion herein)

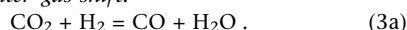
In principle, all FTT reactions can result in the abiotic synthesis of multiple gaseous hydrocarbons, from ethane to butane, and liquid hydrocarbons (starting from pentane), due to polymerization of CH<sub>4</sub> molecules, methylene (-CH<sub>2</sub>), or methyl radicals (-CH<sub>3</sub>) in a chain growth sequence (McCollom 2013).

For this discussion, we consider the catalytic hydrogenation of CO<sub>2</sub>, which produces CH<sub>4</sub> by one-step (Sabatier reaction or methanation) or two-step (reverse water–gas shift) reactions:

*One-step methanation (Sabatier):*



*Two-step reverse water–gas shift:*



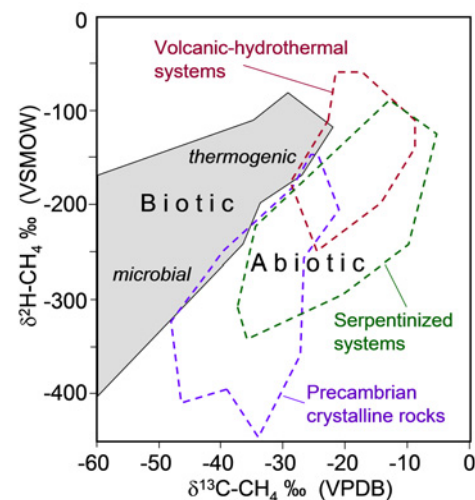
The H<sub>2</sub> necessary for reactions (1) to (3) can be produced by serpentinization (i.e. the hydration of olivine-rich rocks) or other processes (e.g. radiolysis). The CO<sub>2</sub> may originate from the mantle, limestone, or the atmosphere.

All FTT reactions are catalyzed by transition metals (Ni, Fe, Cr, Co) and related oxides, so that the conversion of the gas molecules occurs after adsorption (chemisorption) on the metal surface. Experimentally, FTT synthesis has been observed under hydrothermal conditions, at temperatures above 200°C and high pressures, using Ni, Fe, or Cr (McCollom 2013), which are the most abundant transition metals in ultramafic rocks. An unresolved issue is that methane in land-based serpentinization systems seems to be produced at temperature below 100°C (Etiopie et al. 2011, 2013a; Suda et al. 2014), and catalysis of FTT synthesis by Ni, Fe, or Cr has not yet been shown to proceed in this temperature range (the reader may refer to the wide literature on catalyzed CO<sub>2</sub> hydrogenation, e.g. Wang et al. 2011 and references therein). To understand natural low-temperature systems, we therefore have to assume these catalysts are effective over very long, geologic timescales or involve other catalysts. The only metal catalysts that result in fast methanation at temperatures below 100°C are ruthenium and rhodium (Etiopie et

al. 2013b and references therein). Rhodium is extremely rare and dispersed in parts-per-billion concentrations, but ruthenium can reach concentrations of hundreds of parts per million and forms oxides or sulfur minerals (e.g. laurite) within the chromitites of many continental ophiolites and igneous complexes. Recent laboratory experiments have demonstrated that CH<sub>4</sub> can actually be rapidly produced via the Sabatier reaction at  $T < 100^\circ\text{C}$  by using extremely low amounts of Ru (Etiopie and Ionescu 2014). However, our knowledge about the catalytic role of specific minerals and the potential for low- $T$  serpentinization are poorly constrained and therefore the topic requires more research.

## HOW TO RECOGNIZE ABIOTIC GAS

Methane is the major component of both biotic and abiotic natural gas, and its stable carbon and hydrogen isotope compositions (expressed as  $\delta^{13}\text{C}$  and  $\delta^2\text{H}$  relative to standards VPDB, Vienna Pee Dee Belemnite, and VSMOW, Vienna Standard Mean Ocean Water) is an essential, although sometimes inconclusive, diagnostic property for recognizing the origin (Schoell 1980). Worldwide occurrences of thermogenic and microbial methane have a well-defined distribution of carbon and hydrogen isotopes (e.g. Etiopie et al. 2013b; see the “biotic” field in Fig. 1). Until a few years ago, and based on limited data, the isotopic composition of abiotic gas was considered to be typically enriched in <sup>13</sup>C, with  $\delta^{13}\text{C}$  values higher than -25‰. Today a wider set of isotopic data is available and shows that the  $\delta^{13}\text{C}$  of methane in land-based serpentinized ultramafic rocks can be as light as -37‰ while methane from Precambrian shields can be even lighter (Etiopie and Sherwood Lollar 2013). Interestingly, laboratory experiments have produced abiotic methane with a wide range of  $\delta^{13}\text{C}$  values, including isotopically “light” values once assumed to be indicative of biological activity (e.g. -19 to -53.6‰ by Horita and Berndt 1999; -41 to -142‰ by Etiopie and Ionescu 2014).



**FIGURE 1** Plot of  $\delta^{13}\text{C}$  versus  $\delta^2\text{H}$  for methane, showing four general compositional fields that provide insights into biotic or abiotic origins. Abiotic methane is documented in serpentinized ultramafic rocks (including the submarine Lost City hydrothermal field and land-based active serpentinization sites in the Philippines, Turkey, Oman, New Zealand, Italy, Greece, Japan, and Portugal), Precambrian crystalline shields (South Africa, Canada, and Scandinavia), and volcanic–hydrothermal systems (e.g. East Pacific Rise, Southwest Indian Ridge, Socorro, Milos). The three abiotic isotopic fields are based on data reported by Etiopie and Sherwood Lollar (2013) and Etiopie et al. (2013c). The biotic isotopic field encompasses a global data set, owned by the authors, for microbial and thermogenic gases in petroleum fields (see also Etiopie et al. 2013b).

An updated diagram of  $\delta^{13}\text{C}$  versus  $\delta^2\text{H}$  (known as a “Schoell plot”; FIG. 1) shows four different isotopic fields for methane in geologic systems. These include biotic methanes (thermogenic and microbial) and three abiotic methanes (from volcanic and geothermal systems, Precambrian crystalline rocks, and serpentinization of ultramafic rocks). This diagram provides the first step in determining an abiotic origin of gas and a framework for interpreting isotopic signatures. However, FIGURE 1 cannot reveal if a gas is completely abiotic or mixed with some biotic components. Additional interpretative tools are necessary. These may include the use of noble gases (helium isotopes), assessments of the molecular distribution of the hydrocarbon alkanes (Schulz-Flory distribution tests), the molecular and isotopic composition of associated gases (other hydrocarbons and  $\text{CO}_2$ ), and methane versus ethane mixing plots (Etiopie and Sherwood Lollar 2013). In any case, knowledge of the geological context is an essential precondition for final interpretations. An integration of all these techniques forms the basis of what we call “holistic gas geochemistry”—a comprehensive approach towards understanding the origins and occurrences of methane for energy-resource exploration, environmental issues, and astrobiology.

## WHERE IS ABIOTIC GAS FOUND

The occurrences of abiotic gas in igneous rocks are provided in reviews that reference gas inclusions, deep boreholes, and surface gas manifestations as seeps or springs (Potter and Konnerup-Madsen 2003; Etiopie and Sherwood Lollar 2013). The main global occurrences of abiotic  $\text{CH}_4$ -dominant gas, including recent reports of surface seeps and springs, are presented in FIGURE 2. A geographic list of hydrocarbon occurrences in igneous rocks was provided by Schutter (2003), but the origins of those hydrocarbons are not necessarily abiotic. Here we summarize the key characteristics of dominantly abiotic gas in several geologic environments.

### Volcanic and Geothermal Systems

Active volcanoes, both on land and on the seafloor, release  $\text{CO}_2$ -rich gases with very small amounts of  $\text{CH}_4$  and heavier alkanes (typically in concentrations of a few ppmv or ppbv) (e.g. Welhan 1988). Methane is generally of magmatic origin but, especially along the volcanic flanks, hydrothermal fluids may also contain hydrocarbons from high-temperature (400–500°C) water–rock interactions. These nonmagmatic gases may prevail in many geothermal systems unrelated to active volcanoes, such as the hydrothermal fields in Japan, New Zealand, Greece, and Italy (e.g. Fiebig et al. 2007). Almost-pure abiotic gas was deter-

mined isotopically only in volcanic systems that are less “contaminated” by sediments, such as in the mid-ocean East Pacific Rise and Southwest Indian Ridge (Etiopie and Sherwood Lollar 2013).

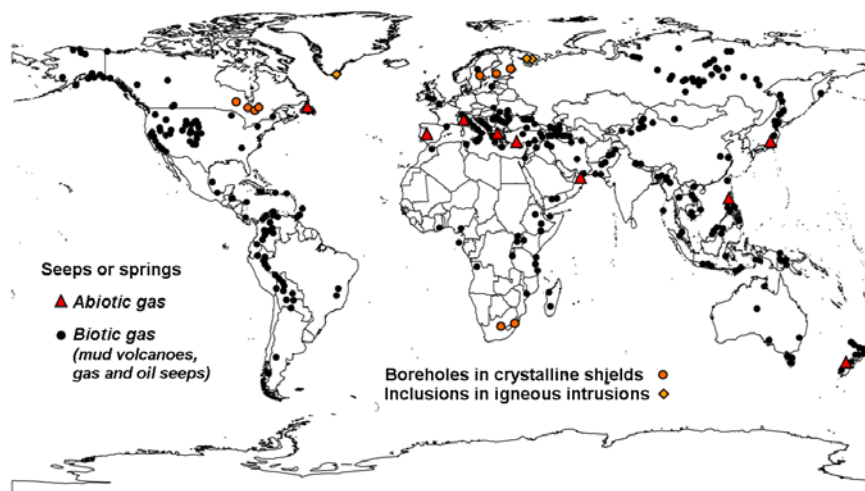
It is important to understand that volcanoes can release more than abiotic and mantle-derived  $\text{CH}_4$ . That is, gas manifestations on volcanic flanks may also release biotic hydrocarbons that originate from the thermal breakdown of organic matter trapped in the sedimentary rocks associated with volcanic plumbing systems. Thus, only a portion of the global volcanic–geothermal  $\text{CH}_4$  emission into the atmosphere should be attributed to a mantle source. This mixing of biotic and abiotic gas can greatly complicate determinations of volcanic–geothermal gas origins in many situations.

### Fluid Inclusions in Igneous Intrusions

Methane (up to 97 vol%) and heavier alkanes (also exceeding 10 vol%) have been identified in fluid inclusions in crystalline rocks, mainly in basic and  $\text{SiO}_2$ -undersaturated alkaline rocks from continental sites and drill cores from the Lovozero, Khibiny (Kola peninsula, Russia), and Ilímaussaq (Greenland) intrusions (e.g. Potter and Konnerup-Madsen 2003; Beeskow et al. 2006). These gases are typically stored in fluid inclusions and rarely as a free phase in rock pores or microfractures (as in Lovozero). The exact abiotic origin of the hydrocarbons is the subject of wide debate, and explanations vary from high- $T$  magmatic processes to FTT reactions. It seems clear, however, that abiotic gas from the margins of the igneous body can mix with thermogenic gas produced in the surrounding sedimentary rocks. Hence, the abiotic fraction increases from the margin to the core of the intrusion (Etiopie and Sherwood Lollar 2013).

### Crystalline Rocks in Precambrian Shields

Significant quantities of hydrocarbons of dominantly abiotic origin have been discovered in crystalline rocks in cratonic shields, accessed by deep boreholes, in Canada, Scandinavia, and South Africa (Sherwood Lollar et al. 2008). The hydrocarbons are typically associated with large quantities of hydrogen, either as free gas (up to 76 vol%  $\text{CH}_4$  and 58 vol%  $\text{H}_2$ ) or dissolved in groundwater (up to millimole levels for both gases). Some sites, such as the Kidd Creek mine (Ontario, Canada), host sections of ultramafic rocks, and the gas may be derived from serpentinization. In the absence of ultramafic rocks, such as in the Witwatersrand Basin (South Africa),  $\text{H}_2$  can be generated by radiolytic decomposition of water.  $\text{CH}_4$  is then likely produced by  $\text{CO}_2$  hydrogenation (Sherwood Lollar et al.



**FIGURE 2** The geographic distribution of onshore abiotic or dominantly abiotic hydrocarbons, where methane is a major gas species.  $\text{CO}_2$ -rich volcanic or geothermal sources, with minor amounts of  $\text{CH}_4$ , are not shown. The locations of surface seeps, including abiotic and biotic (thermogenic or microbial) gas are from the GLOGOS database, [www.gas-consult.com](http://www.gas-consult.com), and Etiopie et al. (2013a, c).

2008). A key additional finding is that these rocks represent a potentially important energy-rich environment for subsurface microbial life (Sherwood Lollar et al. 2007).

### Submarine Serpentinite-Hosted Hydrothermal Fields

The circulation of water in ultramafic rocks (e.g. peridotites) triggers reactions with the original mineral assemblages, summarily called *hydration reactions* or *serpentinization*. Some of these mineral reactions release elemental hydrogen ( $H_2$ ). In the presence of  $CO_2$ , FTT reactions then produce  $CH_4$ . This is the primary mechanism invoked to explain the abundant  $CH_4$  observed in some hydrothermal systems in serpentinites, such as along mid-ocean ridges (e.g. Lost City, Logatchev, and Rainbow in the Atlantic Ocean; Charlou et al. 2002; Proskurowski et al. 2008). In these environments, abiotic gas may mix with microbial gas generated at the seafloor or by extremophiles in  $H_2$ -rich hydrothermal fluids. Thus, evaluating the relative proportion of the two types of gas is often problematic. Although active serpentinization sites are widespread in oceanic settings, including subduction zones and deep submarine mud volcanoes, complete C and H isotopic data for  $CH_4$  are available only for the Lost City and Logatchev hydrothermal fields. Methane was also found in other submarine serpentinite sites (Rainbow, Ashadze, and Nibelungen in the Atlantic Ocean; the Mariana forearc in the Pacific Ocean; and the Central Indian ocean ridge; see Schrenk et al. 2013), but the isotopic data are incomplete (only C) or missing.

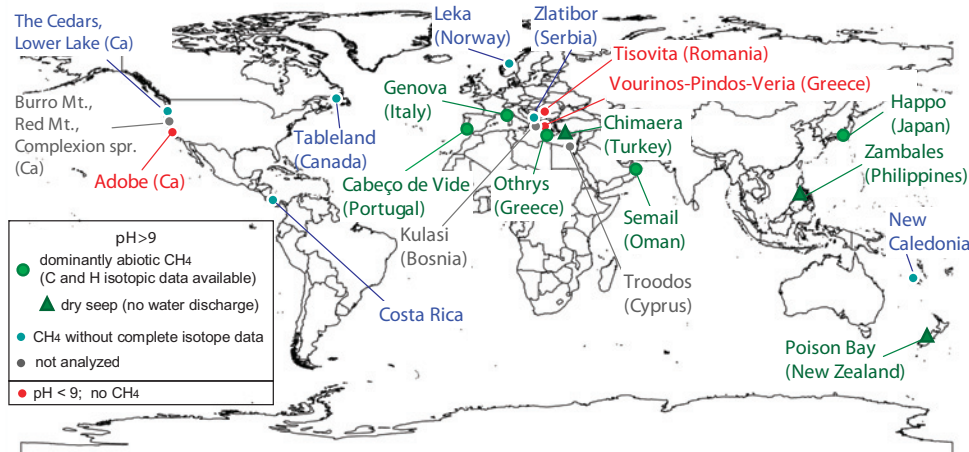
### Land-Based Serpentinization Fluids

On land, serpentinization is driven by meteoric water and is widespread in ophiolites (mantle rocks obducted onto continents), orogenic peridotite massifs, and igneous intrusions. The process is well documented in North America, Europe, Asia, and Oceania (e.g. Barnes et al. 1967; Marques et al. 2008; Schrenk et al. 2013). To date, methane-bearing seeps and springs have been documented, including the C and H isotope compositions of  $CH_4$ , in eight countries: the Philippines, Oman, Turkey, New Zealand, Italy, Greece, Japan, and Portugal (see Etiope and Sherwood Lollar 2013, Etiope et al. 2013c, and Suda et al. 2014). Methane of nonmicrobial origin (as determined by C isotope composition only), probably related to mixing of abiotic and thermogenic methane, is reported in the Tablelands ophiolite (Canada; Szponar et al. 2013).  $CH_4$  concentrations without complete isotopic data are also reported for the Zlatibor ophiolite in Serbia (Etiope and Sherwood Lollar 2013), for Costa Rica (Sánchez-Murillo et al. 2014), and for New Caledonia (Monnin et al. 2014). Abiotic gas in these

systems may, however, be partially mixed with microbial gas, as methanogens may occur in the rocks and thrive in the presence of  $H_2$ . Microbes may produce  $CH_4$  through  $CO_2$  reduction, competing with abiotic FTT synthesis, as was apparently found in The Cedars springs in California (Morrill et al. 2013).

The quantity of methane detected in the onshore serpentinization seeps and spring waters is considerable. Dry seeps, without water discharge, have  $CH_4$  concentrations ranging from ~20 vol% in New Zealand to ~50 vol% at the Zambales seeps in the Philippines, and up to ~90 vol% at the Chimaera seep in Turkey.  $CH_4$  concentrations in springs or groundwaters range from 0.01 to 14 mg/L (normal water in equilibrium with the atmosphere has 0.00003 mg/L). With water-flow rates on the order of 1 L/s (as in springs in Greece and Italy), the total amount of  $CH_4$  transported by individual springs to the surface can reach hundreds of kilograms per year. Methane may also exhale from the soil surrounding the springs (Etiope et al. 2011, 2013a) and far from springs and macroseep sites (Etiope et al. 2011). Although invisible, these microseeps have fluxes similar to those of thermogenic gases in petroliferous sedimentary basins. On a global scale, such abiotic gas microseeps may be widespread and lead to considerable methane emissions into the atmosphere.

"Have olivine, will gas" was the theme of the fundamental work by Oze and Sharma (2005), who studied the potential of serpentinization to produce abiotic  $CH_4$  and  $H_2$ . While the motto is conceptually valid, not all olivine-rich rocks actually produce  $CH_4$ . Olivine hydration is essential to produce  $H_2$ , but may not be sufficient for  $CH_4$  production. Serpentinites on land typically discharge two main types of waters: (1) moderately alkaline (pH ~7–9), Mg-rich bicarbonate-type waters, due to shallow open-system weathering of serpentinized rocks, and (2) hyperalkaline (pH >9) calcium hydroxide ( $Ca^{2+}$ -OH $^-$ ) waters that result from hydrating olivine and pyroxene in deeper closed systems (Barnes et al. 1967; Marques et al. 2008). By analyzing ophiolitic springs in Greece and worldwide, Etiope et al. (2013a) noted that  $CH_4$  occurs only in hyperalkaline waters (Fig. 3). Moderately alkaline, Mg-rich waters, at least on the basis of what has been documented so far, do not contain significant quantities of  $CH_4$ . It appears, then, that  $CH_4$  production is strictly related to active serpentinization, and only deeper meteoric waters, with higher residence times, can take the gas produced in suitable rocks (where FTT reactions occur with sufficient quantities of a suitable catalyst; e.g. Etiope and Ionescu 2014) and carry it to the surface. This leads to the prediction that  $CH_4$  may be found in any hyperalkaline spring in serpentinized rocks on Earth



**FIGURE 3** Geographic distribution of water springs and gas seeps related to active, land-based serpentinization. Among the springs, only those with hyperalkaline (pH >9) water release methane.

(e.g. in Bosnia, Cyprus, Spain) not investigated so far. Thus, an updated motto would be “Have hyperalkaline water, will abiogenic gas.”

### The Extraordinary Case of Chimaera

An outstanding occurrence of dominantly abiogenic methane is that of the Chimaera seep in Turkey, which is probably the biggest onshore abiogenic gas seep on Earth. Chimaera (from the mythological fire-breathing creature described by Homer in *The Iliad*) is an archeological site near Çirali, in the Gulf of Antalya, famous for the natural flames issuing from a fault zone in the serpentinized peridotite of the Tekirova ophiolite (FIG. 4). The gas (~87% CH<sub>4</sub> and 10% H<sub>2</sub>) burns, forming at least 20 large flames that are up to a half meter in height. The methane is dominantly abiogenic ( $\delta^{13}\text{C}$ : -12‰;  $\delta^2\text{H}$ : -129‰), and this gas escapes from visible vents in rock fractures and as invisible seepages throughout the area. At least 190 tonnes of CH<sub>4</sub> are released every year into the atmosphere (Etiope et al. 2011).

In a survey conducted in 2012, in collaboration with Hakan Hosgörmez (Istanbul University), a second site was found, about 300 m from Chimaera, with two actively burning gas vents and numerous burned trees over an area of at least 2000 m<sup>2</sup>. The trees were likely killed by episodic combustion of gas from the ground, as suggested by the surrounding burned soil. The total emission of methane into the atmosphere could be several hundreds of tonnes per year. This flux is higher than that of any other land-based serpentinization seep or spring, and higher than that from large (kilometer-scale) magmatic volcanoes (typically below 100 tonnes per year). Radiocarbon (<sup>14</sup>C) analyses of CH<sub>4</sub> (performed in October 2012 by Isotech Laboratories, Illinois) demonstrated that the gas is older than 50,000 years (-0‰ of modern carbon). Considering that the “eternal flames” have been active for at least 2 millennia (documented by Pliny the Elder in *Naturalis Historia*, <79 AD), the continuous release of hundreds of tonnes of gas per year must be driven by strong pressure gradients. This is possible only if a pressurized gas accumulation exists (by analogy to observations of thermogenic gas seeps). Otherwise the abiogenic synthesis must be very fast and effective in continuously producing an amount of gas equivalent to that released to the atmosphere. Simple calculations suggest that the total amount of methane emitted so far is on the order of 400 million cubic meters. Thus, the original amount of methane stored in the reservoir (the ultimate reserve) could have been on the order of thousands of millions of cubic meters, similar to a conventional biogenic gas field. No studies have been made to assess the present-day reserve.

### Abiotic Gas in Commercial Hydrocarbon Fields

Fractured igneous rocks, including mafic and ultramafic rocks, can act as hydrocarbon reservoirs in atypical and deep petroleum systems (Schutter 2003; Farooqui et al. 2009). Serpentinization reactions, for example, generate large increases in volume (up to 30–40%), inducing increased local strains and stresses that can result in episodic cracking and increased rock permeability. As a consequence, serpentinized rocks form competent reservoirs for many oilfields, such as in Texas, USA, and in Cuba (Smith et al. 2005), and inputs of material from igneous rocks into petroleum pools are possible (e.g. Szatmari et al. 2011). Therefore some abiogenic gases, formed by the FTT reactions described earlier, may contribute to the hydrocarbon pool when located in or adjacent to igneous rocks. Occurrences of minor amounts of abiogenic gas in commercial fields in China (e.g. in the Songliao Basin; Ni et al. 2009) and in the United States (Jenden et al. 1993) have been suggested based upon <sup>13</sup>C enrichments in methane,



FIGURE 4 The Chimaera burning gas (CH<sub>4</sub> and H<sub>2</sub>) in the Gulf of Antalya, Turkey. PHOTOS BY G. ETIOPE AND S. KORDELLA

mantle signatures in the helium isotope composition, and the carbon isotope inverse trend in longer-chained alkane gases. The C<sub>1</sub>-C<sub>4</sub> alkanes become *more* depleted in <sup>13</sup>C with increasing carbon numbers, contrary to what happens in biogenic thermogenic gas. This inverse isotopic trend, however, is not only due to abiogenic synthesis (polymerization) of alkanes, but can also be a result of mixing two different biogenic gases and the recombination of C<sub>n</sub> radicals (e.g. Taran et al. 2007).

As recently as the early 1990s, commercial accumulations of abiogenic CH<sub>4</sub> had not been identified by the petroleum industry, and far less than 1% of CH<sub>4</sub> in most oil and gas fields is abiogenic (Jenden et al. 1993). Nevertheless, these assessments were mainly based on the assumption that abiogenic methane is isotopically enriched in <sup>13</sup>C linked to mantle processes (and thus is enriched in magmatic helium), and they used old versions of the genetic  $\delta^{13}\text{C}$ - $\delta^2\text{H}$  diagram. As discussed above, abiogenic methane may have, instead, a carbon isotope composition that overlaps with that of biogenic gas (FIG. 1), and it is not necessarily associated with magmatic helium (Etiope and Sherwood Lollar 2013). Thus, the origin of gas and the presence of possible abiogenic components in atypical petroleum systems characterized by igneous rocks should be reexamined by using modern geochemical interpretative techniques, with as a reference the geochemistry of the gas in land-based serpentinization systems.

## CONCLUSIONS

The existence of gaseous hydrocarbons of dominant abiotic origin in the crust is more widespread than previously thought. While volcanoes and geothermal systems release only trace quantities of abiotic hydrocarbons, submarine and land-based serpentinized igneous rocks produce gas at percentage levels. In onshore active serpentinization sites, the gas enters the atmosphere via water springs, gas vents, and invisible microseepage from the soil, in quantities and in a way similar to the seepage of ordinary biotic gas in petroliferous areas. This methane seems to be produced via Fischer-Tropsch-type reactions at temperatures below

100°C. Heavier hydrocarbons (from ethane to pentane) are also produced. Abiotic gas is being discovered year after year in different countries, and it may be present in some atypical petroleum systems.

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