



Invited Review

Abiotic methane in continental ultramafic rock systems: Towards a genetic model

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ABSTRACT

Methane (CH₄), often in substantial quantities, is reported for numerous surface manifestations (seeps, springs) and aquifers in continental serpentinized ultramafic rocks, in ophiolites, peridotite massifs and intrusions. Frequently, this gas is considered to have a dominant abiotic origin, with variable, though generally minor, components of biotic gas (thermogenic or microbial). Abiotic CH₄ production through low temperature Fischer-Tropsch Type reactions (FTT) between a carbon (C) compound and H₂ is endorsed by most of scholars, but direct derivation from olivine hydration (serpentinization), magmatic sources and fluid inclusions have also been suggested. Here, we review the application of FTT in geology, discussing the appropriateness of several C compounds (CO₂, CO, formic acid, formate or elemental C) as CH₄ precursors and of aqueous versus gas phase reactions. We examine published gas geochemical and flux data that provide clear constraints on the methane origins. In the analysis we add new isotopic and gas seepage data acquired in surface gas manifestations at Acquasanta, in the Voltri ophiolite (Genova, Italy). Multiple lines of evidence including (a) stable isotope compositions of CH₄, CO₂ and helium, (b) radiocarbon-free CH₄, (c) isotopic disequilibrium between CH₄ and H₂O, (d) low temperatures of CH₄ production based on clumped isotopes and heat flow data, and (e) methane seepage forms and intensities, suggest that CH₄ is not formed directly in water or from magmatic sources or fluid inclusions. Rather, all the lines of evidence taken together are compatible with the hypothesis of low temperature (< 140 °C) Sabatier reactions (CO₂ hydrogenation) in gas-phase and within metal-rich (catalyst) ultramafic rocks. A similar abiotic origin could occur for methane observed in Precambrian shields. Chromitites can support considerable rates of gas generation, potentially higher than those in some shales. In particular, the gas flux intensity and seepage distribution suggest that gas-bearing ultramafic rock systems may be considered analogous to conventional, biotic natural gas systems where, after production in source rocks, CH₄ could migrate, accumulate in reservoir rocks and seep to the surface. Microbial CH₄ generated in water at lower temperatures, generally as minor secondary contributions, may also commingle in these environments.

1. Introduction

Methane (CH₄), the dominant gaseous hydrocarbon exploited as energy source and the most common organic molecule, originates through the microbial or thermal degradation of organic matter, coal, or oil in sedimentary rocks, typically shale and limestone, as described in the petroleum geochemistry literature, e.g., Schoell (1980, 1983), Tissot and Welte (1984), Whiticar et al. (1986), Hunt (1996). Microbial and thermogenic gases are cumulatively termed biotic because of the derivation from biologic compounds, mainly lipids and carbohydrates, in marine (sapropelic) and terrestrial (humic) organic matter. Since the 1980s, considerable amounts of CH₄ have also been discovered in non-

sedimentary systems, in deep boreholes drilled in the crystalline basement of Precambrian shields in South Africa, Canada and Finland (e.g., Sherwood Lollar et al., 1993; Kietäväinen et al., 2017) and in surface manifestations (seeps, hyperalkaline springs with pH > 9) and aquifers in numerous locations in correspondence with serpentinized ultramafic rocks, in ophiolites or peridotite massifs and intrusions (e.g., Lyon et al., 1990; Fritz et al., 1992; Abrajano et al., 1990; Etiope et al., 2011; Etiope et al., 2013a; Szponar et al., 2013; Monnin et al., 2014; Etiope et al., 2016; Etiope et al., 2017; D'Alessandro et al., 2018a, 2018b; Vacquand et al., 2018; see Table 1 for a more complete list of references). Unlike conventional natural gas in sedimentary basins, this non-sediment-sourced CH₄ is typically considered to have predominantly an abiotic

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Table 1

A list of continental serpentinization regions, in ophiolites and peridotite massifs or intrusions, where methane occurrence has been documented (updated January 2019).

Country	Region/Site	Type of manifestation	Gas flux investigated?	Main reference for CH ₄ study
<i>Methane C–H isotopes determined (see Fig. 2)</i>				
Bosnia Herzegovina	Dinaride (e.g., Kulasi, Ljesljani)	Springs	no	Etiope et al. (2017)
Canada	Tablelands	Springs	yes	Szponar et al. (2013); Morissey and Morrill (2017); Morrill et al. (2018)
Greece	Othrys Mt. (Archani, Ekkara)	Springs + vents	yes	Etiope et al. (2013a)
	Argolida (Ermioni)	Spring	no	D'Alessandro et al. (2018b)
Italy	Voltri-Genova (e.g. Acquasanta)	Springs + vents	yes	Boschetti et al. (2013b); this work (Supplementary Material)
	Taro-Ceno	Springs	no	Boschetti et al. (2013a)
	Elba Island (coastal, very shallow seafloor)	Vents	no	Ruff et al. (2016); Sciarra et al. (2019)
Japan	Hakuba-Happo	Springs + wells	no	Suda et al. (2014)
New Zealand	Poison Bay	Spring	no	Lyon et al. (1990)
	Red Hills, Dun Mountain	Springs + vents	yes	Pawson et al. (2014)
Oman	Semail (e.g., Al Khaoud, Nizwa, Bahla, Magniyat)	Springs + wells	no	Fritz et al. (1992); Miller et al. (2016); Vacquand et al. (2018)
Philippines	Zambales (Los Fuegos Eternos, Nagsasa, Mangatarem)	Vents + spring	no	Abrajano et al. (1990); Vacquand et al. (2018)
Portugal	Cabeço de Vide	Springs + wells	yes	Etiope et al. (2013b); Marques et al. (2018)
Spain	Ronda peridotite (e.g. Baños del Puerto, B. del Duque)	Springs + vents	yes	Etiope et al. (2016)
Turkey	Tekirova (Chimaera)	Vents	yes	Hosgormez et al. (2008); Etiope et al. (2011); Vacquand et al. (2018)
	Kizildag, Amik Basin (e.g., Kurtbagi, Tahtakopru)	Springs + vents	no	Yuce et al. (2014); D'Alessandro et al. (2018a)
U.A. Emirates	Al Farfar	Well	no	Etiope et al. (2015)
U.S. California	Coastal Range, The Cedars	Springs + vents	no	Morrill et al. (2013)
	Coastal Range, CROMO	Well	no	Wang et al. (2015)
	Aqua de Ney	Spring	no	Blank et al. (2017)
<i>Incomplete or missing C–H isotope analyses</i>				
Costa Rica	Santa Elena	Springs	no	Sanchez-Murillo et al. (2014)
New Caledonia	Massif du Sud (e.g., Prony Bay, La Crouen)	Springs	no	Monnin et al. (2014); Vacquand et al. (2018)
Norway	Leka	Springs	no	Okland et al. (2012)
Philippines	Palawan (onshore and offshore)	Springs + well	no	Sofer (1985); Cardace et al. (2015)
Serbia	Zlatibor	Springs	no	Milenic et al. (2009)

origin, i.e., it is not the direct result of the diagenetic or catagenic remineralization of organic matter. Certainly, under some conditions abiotic gas can commingle with conventional microbial or thermogenic gases. However in abiotic environments, the admixture of biotic gas generally comprises a minor, albeit variable, constituent (e.g. Etiope and Sherwood Lollar, 2013). Abiotic CH₄ is also observed in geothermal, volcanic-magmatic (sediment-free) systems and fluid inclusions in various igneous rocks (e.g., Welhan, 1988; Gigenbach, 1997; Potter and Konnerup-Madsen, 2003, Etiope et al., 2007; and references therein). Methane in these systems occurs at very low concentrations (typically ppb or ppm by volume of gas) and/or amounts (nmole levels in microscopic inclusions). In contrast, the amounts of abiotic CH₄ in ultramafic rock systems can be considerable (e.g., up to 80–90 vol%) and with migration fluxes in the order of tonnes per year from individual seeps. Such production and migration fluxes rival the rates noted for conventional, biotic, sedimentary natural gas systems (e.g. Etiope, 2015). Understanding the exact abiotic gas formation mechanism generating such quantities of CH₄ has critical implications in microbiology, astrobiology and energy resource exploration. In particular, abiotic CH₄ could play a key role in pre-biotic chemistry and the origin of life (Pedersen, 1997; Russell et al., 2010; Sleep et al., 2011), it may occur on other rocky planets, e.g., Mars (Oze and Sharma, 2005; Atreya et al., 2007; Oehler and Etiope, 2017), and it can “contaminate” conventional biotic natural gas systems (Etiope and Schoell, 2014; Etiope et al., 2015). The main hypothesis proposed in the literature is that abiotic CH₄ in continental ultramafic rock systems originates via Fischer-Tropsch Type reactions (FTT) between molecular hydrogen (H₂) and certain C-bearing compounds. The former is mainly derived from the serpentinization of peridotite (olivine hydration), whereas the carbon could mainly be carbon dioxide (CO₂) from variable sources, such as the atmosphere, or crustal and magmatic rocks, depending on

the geological setting (e.g., Sherwood Lollar et al., 1993; Etiope and Sherwood Lollar, 2013; Etiope and Schoell, 2014; Etiope, 2017; Etiope et al., 2017; Kietäväinen et al., 2017; Vacquand et al., 2018). Since early studies (e.g., Shock, 1990), FTT reactions in geology were generally assumed to occur solely in aqueous phase. More recently, carbon monoxide (CO), formic acid (HCOOH), formate (HCOO⁻) and graphite (C) were also considered to be possible CH₄ precursors (e.g., Taran et al., 2007; McCollom and Seewald, 2003; Fu et al., 2007; Lang et al., 2010; Brovarone et al., 2017; Kietäväinen et al., 2017; Vacquand et al., 2018). Direct CH₄ derivation from serpentinization (without H₂ mediation) was assumed by some authors (e.g., Oze and Sharma, 2005; Suda et al., 2014; Vacquand et al., 2018). However, gas-phase CO₂ hydrogenation (Sabatier reaction) was considered by many to be the only mechanism capable of producing the elevated amounts of CH₄ observed (McCollom, 2016; Etiope and Sherwood Lollar, 2013; Etiope and Ionescu, 2015; Etiope et al., 2017; Etiope et al., 2018). Other authors have suggested that CH₄ may have a magmatic or post-magmatic source, directly from the mantle (De Boer et al., 2007) or derived from fluid inclusions in igneous rocks (Klein et al., 2018; Grozeva, 2018), in analogy with mechanisms proposed for submarine hot springs (McDermott et al., 2015; Wang et al., 2018). The various hypotheses for the formation of abiotic CH₄ are summarised in Fig. 1. We emphasize that our discussion of abiotic methane in continental ultramafic rock systems is totally unrelated to the Russian-Ukrainian and Thomas Gold theories on the mantle origin of petroleum (see Glasby, 2006, for a critical review).

In this paper, we discuss the application and sometimes mis-application of FTT in the geological formation of abiotic CH₄. We treat the potential of CO₂, CO, HCOOH, HCOO⁻ or C as CH₄ precursors and the effectiveness of aqueous vs. gas-phase reactions. The discussion is supported by analysis of published isotope and gas flux data that

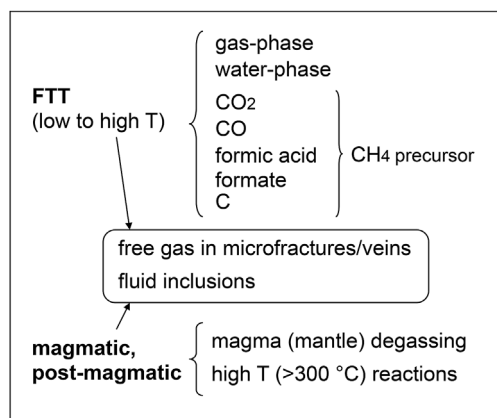


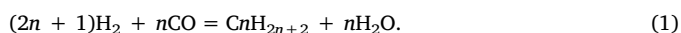
Fig. 1. Summary of the various hypotheses for the formation and origin of abiotic CH₄ observed in continental serpentinized ultramafic rock systems. High T (> 300 °C) reactions include respiciation of C-O-H fluids, carbonate-graphite metamorphism and siderite decomposition, as described in Etiope and Sherwood Lollar (2013).

provide clear constraints on methane origin. This includes the: (a) isotopic composition of CH₄, CO₂ and He, (b) radiocarbon abundance in CH₄, (c) isotopic equilibrium between CH₄ and H₂O, (d) CH₄ production temperatures based on clumped isotopes and heat flow data, and (e) methane seepage forms and intensities. The dataset is integrated with new, unpublished, isotope and CH₄ seepage flux data, including radiocarbon (¹⁴C) analyses of CH₄, acquired in ophiolite-related surface gas manifestations (with hyperalkaline water) at Acquisanta, near Genova, in the Voltri ophiolite (Italy; details provided in the Supplementary Material). We will show that all of the data can be reconciled by only one specific combination of the components summarised in Fig. 1.

2. Use and misuse of FTT reactions in geology

2.1. A brief historical overview

Fischer-Tropsch Type reactions (FTT) are chemical reactions that are widely studied and applied in industrial catalysis for synthetic fuel and chemicals production and CO₂ consumption (e.g., Schulz, 1999; Wang et al., 2011). The Fischer-Tropsch reaction (FT), *sensu strictu*, was developed by Fischer and Tropsch (1926). The general form of the FT reaction is:



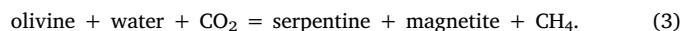
The Sabatier reaction (or CO₂ hydrogenation), is a form of FTT, discovered by Sabatier and Senderens (1902), represented by Eq. (2):



Both the FT and Sabatier reactions are exothermic and thermodynamically spontaneous, but are kinetically limited and have implied heterogeneous catalysis, i.e., the catalyst is in the solid phase, while reagents are in the gaseous phase.

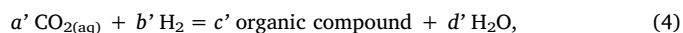
The natural occurrence of FTT in geological environments (in rocks) was initially proposed in early 1960s by Hulston and McCabe (1962) to explain CH₄ in geothermal systems. Analogously, Friedel and Sharkey (1963) and Robinson (1964) invoked FTT as an alternative mechanism for petroleum production, and Studier et al. (1968) proposed it for the origin of organic matter in the solar system. FTT in igneous rocks related to serpentinization of peridotite was suggested by Elanskiy (1966). The first laboratory experiments with isotope analyses were performed by Lancet and Anders (1970), with reference to hydrocarbons in meteorites. A wider hypothesis of FTT as petroleum source was proposed later by Szatmari (1989).

Although FTT synthesis was known to be effective only in gas-phase (H₂O free CO₂-H₂ mixtures), thermodynamic calculations were performed using hydrothermal (aqueous) conditions with dissolved CO₂ (Shock, 1990). Apps (1985) previously calculated thermodynamic feasibility of CH₄ formation via olivine hydration, assuming the following reaction:

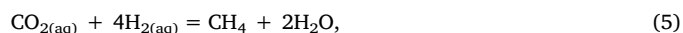


However, the generalized reaction of Eq. (3) masks the true Sabatier synthesis, whereby the H₂ is produced by olivine hydration. Misapplication of Eq. (3), where CH₄ is assumed to derive from H₂O, is discussed in Whiticar and Etiope (2014). Janecky and Seyfried (1986) and Berndt et al. (1996) performed aqueous phase experiments simulating high temperature (300 °C) hydrothermal systems based on the reaction in Eq. (3). Their results, which indicated the formation of CH₄ in reaction cells, were subsequently found by McCollom and Seewald (2001) to be an artefact, as the hydrocarbons were dissolved in the olivine prior to the reaction.

The first explicit formulation of aqueous-FTT was published by Shock and Schulte (1998):



where the mole fraction coefficients *a'*-*d'* depended on the type of organic compound produced. In writing this form of FTT, the authors inappropriately referenced Sullivan et al. (1988) and Silvestri et al. (1990). These earlier papers refer to reactions involving the electrocatalytic CO₂ reduction, a process that can only be generated artificially in laboratory. Nevertheless, Berndt et al. (1996) and Shock and Schulte (1998) initiated a suite of geochemical experiments simulating aqueous-FTT in hydrothermal fluids, e.g., Horita and Berndt (1999), McCollom and Seewald (2001), Foustoukos and Seyfried (2004), Fu et al. (2007), Neubeck et al. (2011) and Okland et al. (2014). Experimental geochemists assumed, then, that in geological environments abiotic CH₄ formation is better represented by aqueous FTT:



where CO_{2(aq)} can be HCO₃⁻ or CO₃²⁻ in hyperalkaline conditions. Several experiments attempted to follow reaction Eq. (3), i.e., without addition of H₂. Other experiments followed FT *sensu strictu* using CO, instead of CO₂, as the potential CH₄ carbon precursor (e.g., Taran et al., 2007). This FT-CO version is frequently mentioned as a possible CH₄ source in geological environments (e.g., Konn et al., 2015).

2.2. Aqueous or gas-phase FTT?

The experiments described above produced ambiguous and sometimes contradicting results. Methane was obtained only in a few cases and the very small amounts reported were questioned (e.g., McCollom, 2013). In the end, a conclusion was that "FTT may not be an important CH₄ generation pathway" (McCollom, 2016). Such a conundrum has been frequently considered in microbiological and serpentinization-related origin-of-life studies, leading some authors to conclude that abiotic CH₄ synthesis on Earth and other planets is both sluggish and trivial compared to a more efficient microbial methanogenesis (e.g., Russell and Nitsche, 2017; Yung et al., 2018). In reality, the statement that FTT is not important in geology should only be applied to aqueous FTT and to experiments that do not follow strict Sabatier reaction rules. It is commonly understood in industrial chemistry that aqueous-based FTT (Eq. (5)) is essentially impossible with heterogeneous catalysis, especially at low temperatures. This is because dissolved C forms are only sparingly chemisorbed onto metal surfaces and the reaction only proceeds sluggishly, if at all, towards the products H₂O and CH₄ (Eq. (5)). In addition, for reactions starting with olivine hydration (Eq. (3)), there may be insufficient H₂ generated to attain the required H₂:CO₂ stoichiometry of ≥ 4 necessary for CH₄ production. In some cases, there

is no control of the catalyst, as this is assumed to form autonomously, for example, as magnetite during serpentinization. Overall, as abundant H₂ seems to be essential for FTT, it is misleading to strictly state that serpentinization produces CH₄.

In catalytic chemistry, the Sabatier reaction involves heterogeneous catalysis and operates only in dry, gas phase conditions, according to Eq. (2). It is known that aqueous FTT can proceed only through homogeneous catalysis (e.g., Bosquain et al., 2007), whereby the catalyst is dissolved and requires the presence of synthetic ligands. These are conditions that should effectively preclude aqueous FTT in natural systems. Methane production has been shown to actually decrease as the partial pressure of H₂O increases (Marwood et al., 1997) and minor amounts of H₂O are tolerated only at T > 250 °C (Miguel et al., 2015). It is understandable that many of the ‘hydrothermal’ aqueous FTT experiments were unable to generate CH₄. It is likely that the minor amounts of CH₄ observed in some experiments were either due to contamination (McCollom, 2013) or possibly obtained as artefacts of gas pockets created in the reactor, particularly at high temperatures.

In contrast, experiments that rigorously follow the Sabatier rules (gas phase, H₂:CO₂ > 4, catalyst available) produced considerably larger amounts of CH₄ over a wide range of temperatures, even < 150 °C (e.g., Taran et al., 2010; Zhang et al., 2013; Medina et al., 2000; Etiope and Ionescu, 2015). These are the temperature conditions that are typically found in continental peridotites, as discussed in Section 4.3. Therefore, it is important to consider that deep geological systems are not necessarily aqueous and that Sabatier synthesis can occur in unsaturated rocks and gas-filled fractures. Examples of water-free rock systems include gas-filled fractures and pores observed: a) in petroleum fields, b) in 3D microscopy of immiscible displacement in rocks (Porter et al., 2015) and c) in gas migration studies of gas columns, slugs and bubbles along fracture networks (e.g., Malmqvist and Kristiansson, 1984; Etiope and Martinelli, 2002). In stagnant, serpentinized systems, Sleep et al. (2004) postulated that under certain conditions H₂ fugacities can exceed saturation. H_{2(gas)} bubbles and gas-filled fractures could exist under such conditions. These gas-filled systems, when hosting CO₂, H₂ and appropriate metal catalysts (nickel, iron, chromium or ruthenium depending on the temperature), can serve as ideal *loci* for CH₄ production, as discussed in Section 6. Seep/spring data discussed in Section 5 (¹⁴C–CH₄; CH₄–H₂O disequilibria; clumped isotopes; seepage forms and intensities) all support the hypothesis that CH₄ is formed by Sabatier synthesis in the free gas phase and not in water.

2.3. Carbon feedstock for CH₄ production: CO₂, CO, formic acid, formate and C

CO₂ is the primary carbon source for CH₄ in the Sabatier reaction (Eq. (2)). Its natural abundance (at percent levels) and multiple potential origins over a range of different geological environments, (atmosphere, crustal C-bearing rocks, magma degassing) make CO₂ a ubiquitous and easily available carbon precursor for abiotic CH₄ formation. Faults at the boundary of ultramafic massifs or ophiolites, which are tectonic contacts with sedimentary or C-bearing rocks (limestones or metasediments), especially those proximal to geothermal basins, may host abundant CO₂. Indeed, all occurrences of CH₄ in continental ultramafic rocks take place just along these marginal faults (e.g., Etiope et al., 2017; Marques et al., 2018). As a consequence of this geological juxtaposition, it is plausible that CO_{2(gas)} plays a key role in the abiotic CH₄ synthesis. Instead of CO_{2(gas)}, however, some laboratory experiments used CO (the FT *sensu strictu*), formic acid (HCOOH) or its conjugate base, formate (HCOO⁻), as carbon source for FTT synthesis (e.g., McCollom and Seewald, 2003; Fu et al., 2007). Formic acid and formate are simple organic acids and acid anions that naturally occur in highly variable concentrations in groundwater and fluids related to peridotite serpentinization. Formate concentrations were reported by Lang et al. (2010) to be < 160 μM in the submarine Lost City hot

spring, and much lower (26 to < 1 μM) or below detection limits in continental peridotite-hosted systems (e.g., Miller et al., 2016; Brazelton et al., 2017; Suda et al., 2017). For comparison, CH₄ concentrations in hyperalkaline water is generally in the order of 10's μM to mM (e.g., Miller et al., 2016; Etiope et al., 2017). Organic acids can serve as CH₄ precursors only in aqueous-FTT that, as discussed above, is not effective in natural heterogeneous catalysis. Therefore, instead of functioning as the primary carbon feedstock for CH₄ synthesis, these organic acids are more likely only intermediate products of FTT. It is also well known that these organic acids are substrates for microbial methanogenesis (e.g., Kohl et al., 2016; Brazelton et al., 2017).

Furthermore, owing to the only very minor amounts of CO present in all geological environments (ppbv or ppmv levels), FT *sensu strictu* using CO is not a plausible geological source of CH₄. CO cannot explain percentage levels of abiotic CH₄ that are actually observed in serpentinized peridotite systems and Precambrian shields. As is the case with organic acids, CO is notoriously observed as intermediate product in the Sabatier reaction. The abundances of these intermediate products strongly depend on the availability and forms of both catalyst (metal) and its support, i.e. the mineral that hosts the catalyst (e.g., Marwood et al., 1997; Wang et al., 2011). The effectiveness of minerals as catalyst is discussed in Section 6.

Although not rigorously a FTT form, geological graphite is also proposed as a carbon source for hydrogenation reactions for abiotic methane, as suggested by Deville and Prinzhofer (2016), Brovarone et al. (2017) and Kietäväinen et al. (2017):



The difficulty with this reaction is that it is extremely sluggish to attain thermodynamic equilibrium at temperatures < 1000 °C (e.g., Hedden, 1962; French, 1966). The reaction is not considered to be feasible at lithospheric conditions and, to our knowledge, there are no published experiments producing CH₄ at lower temperatures. Overall, we conclude that CO, formic acid, formate and graphite are all unlikely candidates as the primary sources of carbon for the considerable amounts of CH₄ observed in ultramafic rock systems.

3. Field data: literature and new data from Voltri ophiolite (Acquasanta, Genova)

Although a detailed review of all studies on methane occurrence in ophiolites and peridotite massifs exceeds the scope of this paper, several case histories will be presented. All of the continental serpentinization sites where CH₄ has been reported in hyperalkaline springs, aquifers or in gas seeps are summarized in Table 1. The mapped locations of these sites are shown in Fig. 2.

For many of these sites, the carbon (¹³C/¹²C) and hydrogen (²H/¹H) stable isotope ratios of methane have been measured. These isotope data are reported using the conventional isotope delta notation (δ¹³C, δ²H):

$$\delta X (\text{‰}) = (R_{\text{sample}}/R_{\text{standard}} - 1) \cdot 1000, \quad (7)$$

where δX = δ¹³C or δ²H and R = ¹³C/¹²C or ²H/¹H, respectively, reported relative to the Vienna PeeDee Belemnite (VPDB for δ¹³C) and Vienna Standard Mean Ocean Water (VSMOW for δ²H) scales. Fig. 3 is the isotopic diagram of δ¹³C–CH₄ vs. δ²H–CH₄ (or CD diagram, where D refers to deuterium, ²H) for the continental serpentinization sites (ultramafic ophiolites and peridotite massifs). The CD diagram shows that CH₄ from ophiolites and peridotite massifs generally have δ¹³C–δ²H isotope signatures that are distinct from biogenic sources. There are a few instances where CH₄ has δ¹³C–δ²H isotope values consistent with microbial methane. Also, some samples partially overlap the thermogenic methane field in the CD diagram (Fig. 3). In conjunction with additional geochemical parameters, e.g., presence of H₂, inverse δ¹³C isotope trends between methane-ethane-propane,

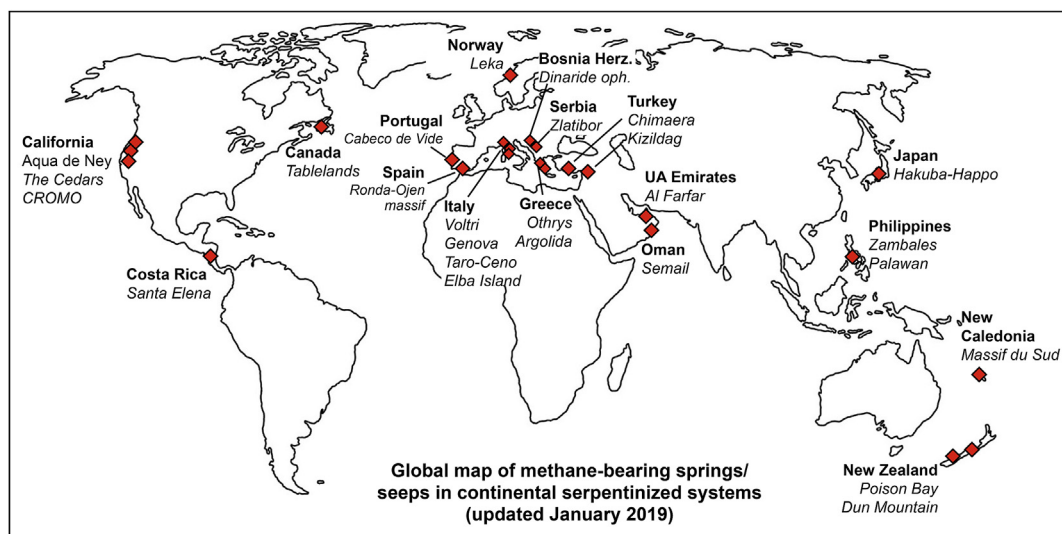


Fig. 2. Global distribution of continental serpentinization sites with seeps, springs or shallow aquifers containing methane.

Schulz-Flory distribution (Etiope and Sherwood Lollar, 2013) and considering the geological settings (e.g., emissions in ultramafic systems in ophiolites or peridotite massifs or intrusions), the $\delta^{13}\text{C}$ – $\delta^2\text{H}$ isotopic field delineated in the CD diagram is diagnostic for abiogenic methane. But because many of the ophiolitic-peridotite samples analysed seem to contain variable, albeit minor, amounts of biotic components, it may be more accurate or rigorous to refer to this $\delta^{13}\text{C}$ – $\delta^2\text{H}$ region in Fig. 3 as ‘predominantly abiogenic’. However, it is important to note, that in comparison with early published isotopic classifications, abiogenic CH_4 is not necessarily ^{13}C -enriched relative to biogenic gases, i.e., abiogenic methane does not have to be $\delta^{13}\text{C}\text{-CH}_4 > -25\text{‰}$. In fact, some abiogenic methane can have $\delta^{13}\text{C}\text{-CH}_4$ values consistent with thermogenic gas (e.g., Etiope and Sherwood Lollar, 2013; Milkov and Etiope, 2018). Fig. 3 includes new $\delta^{13}\text{C}$ – $\delta^2\text{H}$ data obtained at the Acquasanta spring site, in the Voltri ophiolite, near Genova (Italy). At this site, we collected gas from bubbling vents for analysis of stable and radiocarbon (^{14}C) composition of CH_4 . Areal distribution of gas seepage and CH_4 fluxes to the atmosphere were also investigated, as discussed in detail in the Supplementary Material. The results show that the CH_4 at Acquasanta is ^{14}C -free, i.e., the age of the carbon is > 50 ky. This is the same as documented for other serpentinized peridotite sites (see Section 5.1). Methane appears to be released to the surface, also as diffuse gas seepage, along a fault. These are key factors for understanding the relationship between CH_4 and water and the potential origin from fluid

inclusions.

4. Magmatic, high temperature and fluid inclusion origins

Several authors argue that CH_4 in ultramafic rocks systems is derived from magmatic, or post-magmatic processes, or through very high temperature FTT (for a list of the abiogenic mechanisms see Etiope and Sherwood Lollar, 2013). These are either from magma degassing along faults (e.g., De Boer et al., 2007) or from fluid inclusions in minerals (olivine) of mafic–ultramafic rock systems (Klein et al., 2018; Grozeva, 2018). However, we suggest based on a series of observations discussed below that such origins are uncertain.

4.1. General observation of trivial CH_4 amounts in sediment-free geothermal–magmatic systems

A critical point is that magmatic systems, and thus volcanic and geothermal fluids not involving organic matter in sedimentary rocks, have extremely low concentrations of CH_4 , typically in the range of ppbv or ppmv (e.g., Welhan, 1988; Capaccioni et al., 2004; Etiope et al., 2007; Fiebig et al., 2007). Etiope et al. (2007) calculated a median value of 6 ppmv from a dataset of gases from 27 volcanoes. The maintenance of these low CH_4 concentrations in magmatic rocks is a consequence of chemical equilibrium in the C-H-O system at very high

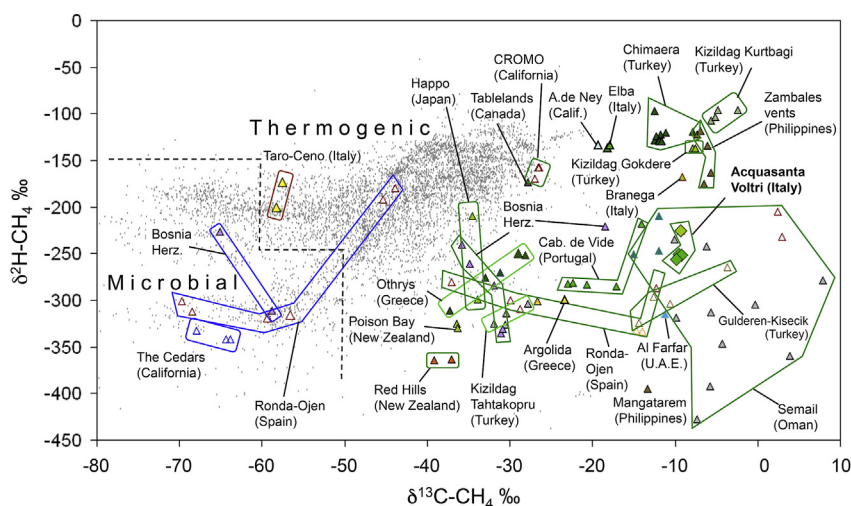


Fig. 3. Stable carbon and hydrogen isotope ratios of methane in continental ultramafic rock systems (ophiolites and peridotite massifs). Data are from the literature listed in Table 1. Acquasanta (Voltri) data (reported in Supplementary Material) refer to analyses performed in 2011 (Boschetti et al., 2013b; light green diamond) and 2014 (this work, dark green diamond). Small grey dots refer to biotic (thermogenic and microbial) gas from sedimentary and petroleum systems (dataset from Milkov and Etiope, 2018). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

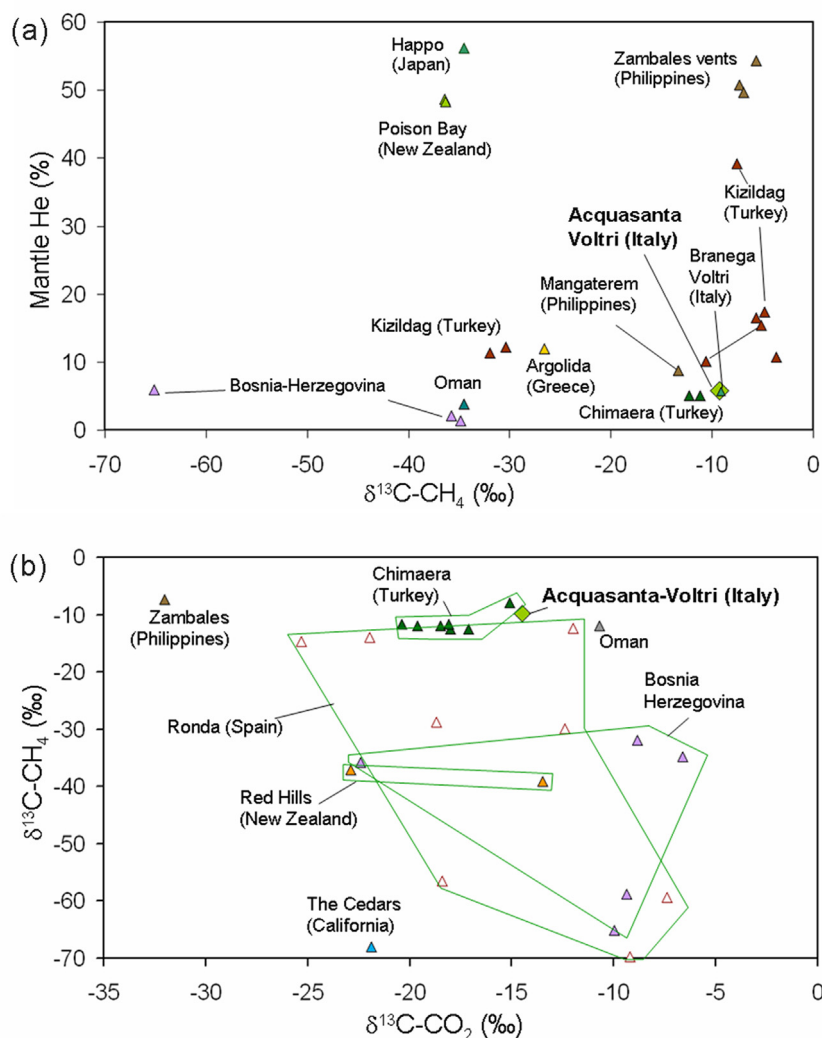


Fig. 4. $\delta^{13}\text{C}\text{-CH}_4$ versus (a) % mantle helium and (b) $\delta^{13}\text{C}\text{-CO}_2$ (b), in gas from ophiolites and peridotite massifs. Data are from the literature listed in Table 1. Acquisanta-Voltri data are in Supplementary Material. The percentage of mantle helium (is estimated assuming MORB (R/Ra: 8) and crustal (R/Ra: 0.01) end-members, as in Etiope and Sherwood Lollar (2013).

temperatures (e.g., Giggenbach, 1997). It is, therefore, not plausible that deep magmatic processes could deliver the large amounts of CH_4 observed in ultramafic rock systems (often exceeding 10–20 vol% and even up to about 90 vol%), with CH_4 migration fluxes in the order of several tonnes per year. The extremely low concentrations of CO_2 in ultramafic rocks further supports a non-magmatic source for this CH_4 .

4.2. CH_4 , CO_2 and He isotopes are not linked

Methane derived from magmatic or post-magmatic sources are expected to have ^{13}C -enriched methane with $\delta^{13}\text{C}\text{-CH}_4$ values that correlate to either mantle-derived CO_2 and/or helium (He). However, there may also be apparent correlations when the carbon in the CH_4 , but not the CH_4 itself, is derived from a magmatic gas, e.g. mantle-derived CO_2 (Etiope and Sherwood Lollar, 2013). It is evident that CH_4 from high temperature hydrothermal systems is ^{13}C -enriched and is directly correlated to mantle CO_2 (the likely CH_4 precursor) and He (see figure 3 reported in Etiope and Sherwood Lollar, 2013). But for gases from ophiolites and peridotite massifs, as shown in Fig. 4, there is no robust correlation between $\delta^{13}\text{C}\text{-CH}_4$, $\delta^{13}\text{C}\text{-CO}_2$ and the percentage of mantle He. Ophiolitic CH_4 can be ^{13}C -depleted and associated with significant mantle He and, vice versa, ^{13}C -enriched CH_4 can also be associated with low mantle He contents (Fig. 4a). Our Acquisanta

samples (Supplementary Material) are examples of ^{13}C -enriched CH_4 associated with low mantle He and non-magmatic CO_2 . The variable mantle He component observed in ophiolites and peridotite massifs, rather than due to direct mantle degassing, is attributed to remnant magmatic sources in the mantle rocks. This was suggested for the ophiolitic gases in the Philippines (Abrajano et al., 1990) and Oman (Sano et al., 1993). Giggenbach et al. (1993) initially observed that helium and carbon systems are often decoupled due to multiple sources of CO_2 and CH_4 and this is particularly true in ultramafic rock systems. Similar reasoning explains the lack of correlation between $\delta^{13}\text{C}\text{-CO}_2$ and $\delta^{13}\text{C}\text{-CH}_4$ from ophiolites and peridotite massifs (Fig. 4b). Carbon dioxide has variable origins, depending on the geological settings, from atmosphere to meteoric water, crustal C-bearing rocks, magmatic sources (Thrasher and Fleet, 1995; Wycherley et al., 1999). In addition, the stable carbon isotope fractionation between CO_2 and CH_4 is depending on factors including temperature, type of catalyst and the degree of reaction of the CO_2 hydrogenation (i.e., CH_4 becomes more ^{13}C -enriched with time during the reaction, e.g. Clark and Fritz, 1997; Etiope and Ionescu, 2015).

4.3. CH₄ production temperature estimates from methane isotopologues and heat flow data

Estimated temperatures of formation provided by CH₄ isotopologues (or clumped isotopes) offer strong and direct indications for a non-magmatic and non-fluid inclusion origin for CH₄ in continental ultramafic rocks. Comparison of doubly-substituted CH₄ isotopologues, namely ¹²CH₂D₂ and ¹³CH₃D, can identify isotopic bond order equilibrium or disequilibrium. In the cases where thermodynamic exchange equilibrium is attained, the temperature of CH₄ formation can be reliably estimated (Young et al., 2017). If the measurement is limited to ¹³CH₃D abundance, without ¹²CH₂D₂, then only apparent temperatures are obtained (e.g., Ono et al., 2014; Douglas et al., 2017). Abiotic reactions typically have low ¹²CH₂D₂ abundances, therefore isotopologue signatures of abiotic methane can easily become contaminated and thus masked by the admixtures of microbial or thermogenic methane (Young et al., 2017). Analyses of gases from ophiolite and peridotite massifs generally point to low temperatures of CH₄ formation (< 140 °C), consistently with low temperature serpentinization (e.g., Bruni et al., 2002; Chavagnac et al., 2013). However, the temperature estimates may be influenced substantially by isotopologue disequilibrium, similar to that observed in some low-temperature serpentinization sites (Young et al., 2017). In particular, in Turkey, at Chimaera, the CH₄ is formed at about 130 °C (Young et al., 2017) and CH₄ of Tablelands in Canada has an apparent temperature of about 80 °C (Morrill et al., 2018). Temperatures calculated for CH₄ released at Cabeço de Vide (Portugal) and Acquasanta (Genova, Italy) also indicate isotopologue disequilibrium (Young et al., 2017). These are similar results to the low temperature CH₄ experiments obtained for laboratory Sabatier experiments and observed in gases from the Precambrian shields. The low temperatures are also consistent with those derived by heat flow data that, in continental peridotite settings, are quite low, typically resulting in temperatures of 100–130 °C at depths of 3–5 km, corresponding to the base of the ophiolite nappe (e.g., Etiope et al., 2013a, 2017). Overall, these low temperatures are not compatible with magmatic or high temperature FTT processes, typical of fluid inclusions (> 200 °C; Salvi and Williams-Jones, 1997; Katayama et al., 2010; Potter et al., 2013). Nevertheless, Klein et al. (2018) and Grozeva (2018) proposed that inclusions in olivine could be the source of methane observed in ophiolitic gas seeps, analogous to the hypothesis of McDermott et al. (2015) and Wang et al. (2018) for methane in submarine hot springs. The methane isotopologue data of ophiolitic CH₄ analysed so far do not support such a hypothesis.

4.4. Methane seepage intensity

The amount and flux intensity of methane released in surface manifestations in ultramafic rock systems is an additional, important factor that is not compatible with a methane origin from olivine fluid inclusions. Several hundred kg CH₄ per year are released from springs and surrounding soil at Othrys (Greece) and Ronda peridotite (Spain) (Etiope et al., 2013a, 2016). Also, the flux measurements performed at Acquasanta near Genova, (see Supplementary Material) show an intense and widespread exhalation of abiotic CH₄. At Acquasanta, diffuse methane fluxes from the ground range from 10² to 10⁴ mg CH₄ m⁻² day⁻¹. Individual vents (bubbling plumes in small pools and along a creek) release from 31 to 200 g of CH₄ per day. We estimated that total CH₄ output from the main seepage site (near the spring) is approximately 500 kg CH₄ per day (Supplementary Material). Lower CH₄ fluxes (3–14 mg CH₄ m⁻² day⁻¹) have been detected in more distant locations along the valley. Considering that water contains about 13.5 mg CH₄/L (Table S1) and that the Spa of Terme di Genova, located close to the seepage site, extracts about 1680 L of water per hour, the amount of CH₄ additionally transported to the surface is approximately 200 kg CH₄ per year.

The Chimaera seep (Tekirova ophiolite, Turkey) has the highest CH₄

emission documented to date from an ophiolite. The site releases several hundred (> 200) tonnes of CH₄ per year from an area of about 5000 m² (Etiope et al., 2011; Etiope, unpublished data). Considering that the seep has been active for at least 2 millennia (it was documented by Pliny the Elder in *Naturalis Historia*, < 79 AD), simple calculations suggest that the total amount of methane emitted over just this period could be around 4 × 10⁵ tonnes or 500 × 10⁶ m³. The original amount of methane stored in the rocks before release (the ultimate reserve) could have been easily on the order of billions m³, i.e., similar to a conventional biotic gas field.

Thus, these amounts of CH₄ stored and emitted are clearly relevant. It is important to assess if fluid inclusions in olivine alone could provide such reserves and sustain such fluxes. We need to assess what the minimum volume of rock, hosting CH₄-rich fluid inclusions, would be necessary to provide continuously such large amounts of gas. Alternatively, we need to address how long-lasting and continuous can a release of gas be guaranteed by a finite volume of fluid inclusions.

Fluid inclusions in olivine and other minerals of ultramafic rocks are in the order of a few micrometers, many of them are gas-free (e.g., Miura et al., 2011) and those containing CH₄ are generally secondary to those filled with saline H₂O and CO₂ (e.g., Kelley and Fruh-Green, 2000), and with the presence of CH₄ in often only trace amounts (e.g., Ferrando et al., 2010). Smith et al. (2017), through Raman and FTIR (Fourier Transform InfraRed) spectroscopy, clearly indicated that olivine cannot be a significant source of methane. The number of fluid inclusions in olivine or other minerals of mafic and ultramafic rocks is extremely variable and, to our knowledge, there are no statistical evaluations. Assuming early estimates of maximum total fluid inclusion volumes of 0.01 vol% of rock (igneous rocks in general) by Roedder (1972), and assuming as an upper bound that all inclusions contain 100 vol% of CH₄, then the minimum volume of rock involved to hold 500 × 10⁶ m³ CH₄ in the Chimaera seep must be 5 × 10¹² m³. Since the Tekirova ophiolite has a thickness of about 3 km, assuming generously that fluid inclusions are spread throughout this thickness, this necessitates area of the gas source to be around 1–2 × 10³ km². Furthermore, this simple calculation does not account for how the gas is quantitatively released from the inclusions, how the gas is focused to an area of ~5000 m² and that the seepage could easily have been flowing longer than 2 millennia. The volumes of CH₄ leached from olivine inclusions are clearly too low to sustain long-lasting, continuous and intense fluxes of many ophiolitic seeps. Fluid mechanics dictate that intense and continuous gas fluxes are advective movements (ruled by Darcy's law) and can only be sustained by pressurised gas accumulations, in analogy with what is observed in conventional biotic gas seeps in petroleum systems (Schrauf and Evans, 1986; Brown, 2000; Etiope and Martinelli, 2002; Etiope, 2015).

5. Evidence for non-aqueous origin of CH₄

5.1. Radiocarbon (¹⁴C) in CH₄

Analyses of ¹⁴C-CH₄ from several serpentinization sites, such as Zambales (Philippines), Ronda (Spain), Chimaera (Turkey), the submarine Lost City (Abrajano et al., 1990; Proskurowski et al., 2008; Etiope and Schoell, 2014; Etiope et al., 2016) and Acquasanta (Voltri, Italy, Supplementary Material), show that the carbon in the methane is fossil, ¹⁴C-free (~0 percent of modern carbon, i.e., the carbon is older than ~50,000 years). In contrast, the carbon dissolved in hyperalkaline springs contains substantial ¹⁴C, dating the water circulation to a few thousand years (Marques et al., 2008; Etiope et al., 2016). Residence times of about 700 years have been estimated for Voltri spring waters (Cipolli et al., 2004). Therefore, methane cannot be sourced from any of the ¹⁴C-bearing carbon dissolved in hyperalkaline waters. This radiometric approach provides a strong independent parameter for the source of the methane carbon.

5.2. General isotopic disequilibrium between CH₄ and H₂O

Hydrogen isotope ($\delta^2\text{H}$) geothermometers (Horibe and Craig, 1995) are a useful tool to assess equilibration temperatures between CH₄, H₂ and H₂O and to verify whether and how these gases interacted in the same system. In serpentinization related hyperalkaline waters, the CH₄-H₂-H₂O system is typically far from the thermodynamic isotope equilibrium distribution expected for high subsurface temperatures. Alternatively, and more likely, the CH₄-H₂-H₂O system has either not attained equilibrium, or it has re-equilibrated at temperatures that are different (generally lower) from the methane generation temperature (Etiope et al., 2017; Young et al., 2017). In many ophiolitic springs, CH₄-H₂O_(aq) equilibrium calculations give unrealistically low temperatures around 0 °C or lower or sometimes too high (> 200 °C). These CH₄-H₂-H₂O system geothermometers do not match the isotopologue and heat-flow derived temperatures (Etiope et al., 2017). The data suggest that CH₄ has not interacted with water for sufficient time to reach isotope equilibrium. This would support the hypothesis that CH₄ is allochthonous, and is not generated *in situ* in the hyperalkaline water.

5.3. Independence of CH₄ from water based on clumped isotopes

Analyses of the CH₄ isotopologues ¹²CH₂D₂ and ¹³CH₃D demonstrate that methane formation in serpentinization systems (continental or submarine) is not connected to circulating fluids. This is basically shown by the difference between equilibrium temperatures calculated using hydrogen isotope geothermometers in the CH₄-H₂O-H₂ system (e.g., Horibe and Craig, 1995) and the isotopologue equilibrium temperature, as observed in the Lost City submarine hydrothermal site (Wang et al., 2018) and in the ophiolitic Chimaera seep (Young et al., 2017). In particular, the estimated high temperature for CH₄ production at Lost City (~270 °C, Wang et al., 2018) is much higher than previously estimated based on isotopic H₂-CH₄ equilibrium (110–150 °C; Proskurowski et al., 2006). This high temperature estimate implies that CH₄ cannot be produced from the formate occurring in this water (Lang et al., 2010).

5.4. Independence of CH₄ from water suggested by gas seepage distribution

Abiotic CH₄ seepage studies find that the gas transport to the surface is not only by migration in hyperalkaline groundwater, but also as discrete gas-phase advection. Gas vents, without water, but with diffuse degassing over relatively wide areas, are common manifestations in ophiolites and peridotite massifs (e.g., Abrajano et al., 1990; Etiope et al., 2011, 2013a; 2016; D'Alessandro et al., 2018a). Our new flux measurements performed at Acquasanta (Voltri, Genova, Supplementary Material), show expansive emissions of abiotic CH₄ decoupled from the hyperalkaline spring. The gas seepage extends outside the spring zone and occurs in association with a fault system (Figs. S1 and S1). Similar decoupled water-CH₄ results were obtained in Turkey, Spain and Greece (Etiope et al., 2011, 2013a; 2016). The extensive distribution of CH₄ seepage suggests that the gas ascends to the surface following tectonic discontinuities permeable to gas, such as faults and fracture systems. This migration is independent of water-based transport and irrespective of the hydrogeological circulation. This is analogous to the well-understood mechanisms of traditional natural gas migration and seepage in petroliferous basins (see Section 7). Seepage data suggest that hyperalkaline waters simply act as gas carrier media, consistent with the interpretation suggested by ¹⁴C data, (Section 5.1). The existence of the springs in a given area is a factor exclusively controlled by local hydrogeology and faults, but CH₄ can also seep to the surface where springs are absent.

6. Natural Sabatier catalysts and CH₄ production rates

6.1. Role and types of catalyst

If gas-phase and low-temperature FTT synthesis is the likely mechanism of abiotic methane formation, then appropriate catalysts are needed in the source rock of the gas to permit methane generation. Iron, nickel, cobalt, chromium and their associated minerals, e.g., magnetite, awaruite, and chromite, are classic metals known to function as catalysts in FTT synthesis. These metals typically occur in common ultramafic rocks (e.g., McCollom, 2013 and references therein). The difficulty with the applicability of these metals as catalysts is that they support FTT only at relatively high temperatures (> 150–200 °C) on at least laboratory time scales (e.g., Wang et al., 2015). FTT experiments using nickel, iron and chromium produced CH₄ only at T > 200 °C (Foustoukos and Seyfried, 2004; Etiope and Ionescu, 2015; Etiope, unpublished data). These temperatures are much higher than the temperatures (< 140 °C) known for methane generation in ophiolites, as indicated by clumped isotopes and heat flow data (Young et al., 2017; Etiope et al., 2018). Rhodium (Rh) (Jacquemin et al., 2010) and ruthenium (Ru) (Thampi et al., 1987) are the only catalysts known to support FTT at low temperatures down to 20–35 °C. Rhodium is an extremely rare element and in ultramafic rocks it is dispersed in roughly ppb concentrations. Although Ru is rare in submarine hydrothermal systems (McCollom and Seewald, 2007; Pašava et al., 2007), within chromitites of continental ophiolites and peridotite massifs it is a dominant platinum group element (PGE), reaching ppm concentrations (e.g., Prichard and Brough, 2009). Ru is mainly held in the form of sulphur minerals, such as laurite (RuS₂), ruthenian pentlandite ((Ni, Fe)₈RuS₈), and Ru-Ir-Os alloy or oxide (RuO₂) (Garuti and Zaccarini, 1997). These are found in either stratiform or podiform chromitites with concentrations in Cr-rich veins up to several ppm (e.g. Bacuta et al., 1990). In ophiolite sequences, Ru enrichments generally occur in crustal dunite, tectonite and Moho transition zones (Prichard and Brough, 2009; Mosier et al., 2012). The potential of ruthenium minerals as FTT catalyst was already discussed in Etiope and Ionescu (2015), but it is useful here to remember the surprising geographic coincidence between the location of surface manifestations of abiotic gas and chromium and PGE mines, as described in detail in Etiope and Ionescu (2015). The Acquasanta-Voltri site is consistent with this rule as chromium-bearing minerals are widespread in the regional ultramafic units, known as 'Formation of Bric del Dente' (Solimano et al., 2014).

The hypothesis of chromitites as methane production rocks is supported by the considerable amounts of methane, hydrogen and other alkanes present, coupled with inverse C isotope trend (typical of abiotic gas) detected in ruthenium-rich chromitites in ophiolites in Greece (Etiope et al., 2018).

FTT synthesis was also considered as the source of abiotic gas in Precambrian shields in South Africa, Canada and Finland (e.g., Sherwood Lollar et al., 1993; Sherwood Lollar et al., 2008; Kietäväinen et al., 2017). A specific study of potential minerals that could act as catalysts in these environments has not yet been done. Sherwood Lollar et al. (1993) assumed that magnetite and hydrated silicates (unspecified), if available in the crystalline rocks, may act as the FTT catalysts. However, these minerals are known to support FTT only at very high temperatures (> 300 °C), whereas the clumped isotope analyses of these Canadian and South African abiotic gas samples reveal a formation temperature well below 100 °C, e.g., around 30 °C for Kidd Creek gas in the Timmins area (Young et al., 2017). The Timmins Basin hosts chromitite (ruthenium-rich) rocks that are extensively mined. The adjacent Sudbury area, where also abiotic gas was studied (e.g., Sherwood Lollar et al., 2008), is located in one of the richest Ru mines in North America (Ames and Farrow, 2007). Furthermore, some Fenoscandian sites with abiotic gas (Juuka, Outokumpu) have serpentinized ultramafic rocks (Kietäväinen et al., 2017) and, therefore, in this case chromium/PGE related catalysts also could play a key role in CH₄

production.

6.2. How much abiotic CH₄ can be produced?

In Section 4.3 we discussed on a mass basis how fluid inclusions could not serve as the origin for relevant amounts of CH₄ in the ultramafic rock systems. But the question is now if the Sabatier reaction, naturally occurring in rocks, could be a source of that CH₄. The Sabatier synthesis in rocks may have limitations for CH₄ production, as discussed below, but even if slow and discontinuous it would represent a long-term, active, generating source of CH₄. This production can then accumulate over geological time in reservoir rocks, analogous to the slow, continual production of natural gas in sedimentary rocks. Fluid inclusions are instead a finite, passive, non-generating gas source: once all inclusions are evacuated the source is exhausted.

The limitation in CH₄ production via Sabatier reactions is essentially related to catalyst abundance, size, dispersion and deactivation over time. These are all controlled by a range of chemical and physical mechanisms (e.g., Forzatti and Lietti, 1999; Wang et al., 2011). Sintering (loss of active surface due to structural modifications) occurs at high temperatures, whereas low temperature Sabatier synthesis is more affected by carbon and H₂O deposition. The catalyst support can have a great influence on catalyst performance, which in natural mineralogic conditions would be the mineral hosting the metal. There are no studies on the performance of naturally occurring catalysts and supports (metals, oxides, minerals). However, the flow of H₂ is an important process that operates naturally in rocks and regenerates the catalyst, thereby ensuring its activity for prolonged times (e.g., Forzatti and Lietti, 1999; Miguel et al., 2015). Similar to industrial Sabatier reactors, a rock receiving a continuous flow H₂ could represent a continuous source of CH₄. Evidence for H₂ flows in chromitites, solely within Ru-bearing minerals, i.e., laurite and Ru-pentlandite, have been reported in several cases (Garuti and Zaccarini, 1997).

Regarding CH₄ production rates, all gas-phase Sabatier experiments show that the CH₄ yield increases with both temperature and catalyst amount. Using ruthenium concentrations similar to those naturally occurring in chromitites, CH₄ production rate at 90 °C was about 1–6 mg CH₄ per gram of ruthenium per day (Etiope and Ionescu, 2015). Taking the concentration of ruthenium in rocks to be 0.1–1 ppm, i.e., the average range observed in chromitites (Economou-Eliopoulos, 1996), this is equates to an average generation rate of 0.3–3 mg CH₄/tonne_{rock}/day, or 0.1–1 g CH₄/tonne_{rock}/year. This assumes that there is sufficient catalyst regeneration (H₂ flow). In comparison with conventional natural gas occurrences in sedimentary rocks from shale source rocks, the abiotic CH₄ generation rate integrated over 10⁸ years can potentially produce comparable amounts of CH₄. For example, gas generation kinetics for Cenomanian source rocks in West Siberian Basin were reported by Schaefer et al. (1999) to have cumulative CH₄ yields of ca. 0.1–1 mg CH₄/g_{TOC}/100 My (average TOC shales of 3 wt.%), which translates to 3–30 × 10⁻⁸ g CH₄/tonne_{rock}/year. Conversely, on geological spatial scale, 1000 tonnes of chromitite with ~220 m³ of rock, and 100–1000 g Ru, permeated by a H₂/CO₂ > 4 mixture, could produce around 10–100 tonnes CH₄ over the course of a million years. Even though these calculations are based on gas generation experiments, their rudimentary results are in the same order of magnitude as that required to support methane generation in chromitites. To refine these calculations, more robust values on abiotic (Sabatier) gas generation kinetics are needed, particularly for a wider range of catalysts and temperatures. In any case, the possibility to form gas accumulations is the key factor for providing the large CH₄ amounts necessary to sustain the fluxes observed on the surface, as discussed in the model proposed in Section 7.

7. Analogy between peridotite-hosted abiotic gas systems and conventional (biotic) gas systems

The amounts of CH₄ migrating to the surface, either transported by groundwater or autonomously in gas-phase, the continuous and long-lasting (at least several thousand years) emissions and their areal distribution may be similar in magnitude to the natural gas seepage in sedimentary petroleum basins. Fluid mechanics dictate that intense and continuous gas fluxes are advective movements driven by pressure gradients that can be sustained only by pressurised gas accumulations (Schrauf and Evans, 1986; Brown, 2000; Etiope and Martinelli, 2002; Etiope, 2015). Such gas accumulations are allochthonous gas, i.e., typically not reservoired in the source rocks where the primary gas is formed. A classical natural gas system is comprised of mature source rocks of either marine lacustrine type (origin of the gas) and a reservoir rock (traps for gas accumulation) that are connected by a migration pathway. In some cases, the source and reservoirs rocks are the same, as in coalbed methane and shale gas plays. In some instances, the gas migration can bypass reservoirs, or there are imperfect traps, such a leaky seals, permeability contrasts and transmissive faults that can allow gas migration to the surface (seepage). We propose that abiotic gas in peridotite systems are analogous to such conventional gas systems (Fig. 5). In an ophiolite or peridotite massif, the source rock, instead of kerogen, would be a rock capable of hosting CO₂, H₂ and metal catalysts, in particular those that support low temperature FTT synthesis. As mentioned, chromitites in Greece have been found to host considerable amounts of methane, hydrogen and other hydrocarbons (Etiope et al., 2018). The gas is contained exclusively in ruthenium-bearing chromitites (or in peridotites in contact with chromitites), and not in other lithotypes (gabbros, serpentinites, basalts) overlying or underlying the chromitites. Essentially, these chromitites are surrounded by methane-free rocks. This suggests that methane in chromitites is autochthonous, i.e. chromitites are the methane source rocks. Microscopic analyses also revealed that the chromitites are highly fractured and permeable (Etiope et al., 2018), a suitable condition to receive gas (H₂ and CO₂) from external systems, such as serpentinized rocks, CO₂-bearing faults or limestones. Evidence for H₂ flow has actually been observed in several cases (Garuti and Zaccarini, 1997). Once generated, the gas can migrate along fractures and faults, along more permeable rocks where it can then be trapped in reservoir rocks. From such reservoirs, the gas can migrate upward along faults or be stripped by circulating water (hyperalkaline at depth). Water, in such cases, would serve only as the gas carrier, as discussed in Section 5. So, the transport and accumulation mechanisms for abiotic systems could be analogous to biotic natural gas seepage systems (Fig. 5).

8. Microbial CH₄ as secondary, shallow process

The presence of microbial CH₄ in waters in some ophiolites or peridotite massifs (in particular in California, Bosnia and Spain) has been suggested on the basis of pronounced ¹²C-enrichment in CH₄, with ¹³C-depleted δ¹³C values as low as -69.7‰ (e.g., Wang et al., 2015; Etiope et al., 2016, 2018). Microbes potentially producing CH₄ (methanogens) have been detected in some cases (The Cedars in California, Voltri in Italy, Semail in Oman and Chimaera seep in Turkey; Kohl et al., 2016; Brazelton et al., 2017; Miller et al., 2018; Zwicker et al., 2018), but not in Portugal and Tablelands in Canada (e.g. Tiago and Verissimo, 2013; Morrill et al., 2014). Most of the sites hosting methanogens have ¹³C-enriched CH₄, with δ¹³C values higher than ~ -20‰ (Oman, Chimaera, Voltri). These gases also have ethane and propane. It is known that only trace amounts of ethane and propane can be produced by microbes and under special conditions in seafloor sediments (Oremland et al., 1988; Hinrichs et al., 2006; Xie et al., 2013). Ethanogens and propanogens have never been detected in hyperalkaline waters. Microbial CH₄ may only be a minor component, and would not dilute or mask the isotope composition of abiotic CH₄. Some

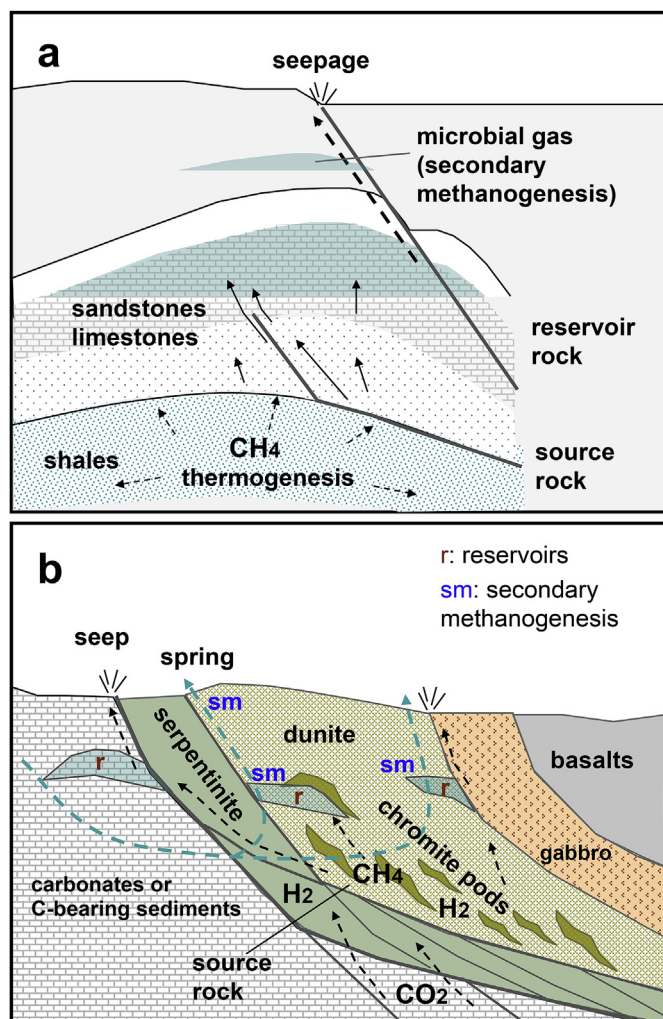


Fig. 5. Possible analogy between (a) sedimentary natural gas systems and (b) continental peridotite-hosted abiotic gas systems (b), including source rocks, reservoir rocks and seepage pathways (faults). In peridotite-hosted systems, chromitites (chromite pods) may represent the source rock, as discussed in Section 6. The gas can migrate along fracture pathways, accumulate in permeable rocks, within the ophiolitic nappe (or peridotite massif) along contacts between the several mafic and ultramafic rocks, and within external sedimentary formations. Seeps and hyperalkaline springs typically occur in correspondence with such contacts (e.g. Chimaera seep in the Tekirova ophiolite, Turkey; springs in the Ronda massif, Spain, Dinaride ophiolite, Bosnia and Herzegovina, Othrys ophiolite, Greece; see related references in Table 1). Light blue dashed arrows indicate circulation of groundwater that becomes hyperalkaline intersecting serpentinized rocks and that can strip methane from source or reservoir rocks. Microbial gas can develop along the water circuit or in shallow reservoirs, in analogy with secondary methanogenesis in conventional natural gas systems. Panel b) is a classic ophiolite scheme, based on a cross section of the Semail ophiolite in Oman, which overlies carbonate rocks of Hawasina formation (e.g., Dilek and Furnes, 2009). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

authors, however, suggest that the microbial component could be more important (if not dominant), because incubation experiments have shown that microbes produce ^{13}C -enriched CH_4 relative to the methanogenic precursor substrate. This is particularly evident if the precursor substrate is ^{13}C -enriched, including conditions of substrate limitation or exhaustion, whereby the residual substrate (e.g., CO_2 or acetate) and product (CH_4) become ^{13}C -enriched as a consequence of kinetic isotope effects (KIE's) associated with methanogenesis (Claypool and Kaplan, 1974; Whiticar, 1999). Similar enrichments have also been observed in

alkaline waters where the substrate availability was controlled by the dissolution of carbonate (Miller et al., 2018). In addition, microbial oxidation of CH_4 is associated with KIE's that lead to ^{13}C -enriched CH_4 of the residual methane (Barker and Fritz, 1981; Whiticar et al., 1986). Methanogens were identified in Voltri hyperalkaline waters, suggesting the presence of microbial gas (Brazelton et al., 2017). Our molecular and isotopic analyses of gas from Acquasanta (Voltri) (Supplementary Material) also detected ethane, propane and butane and an inverse methane-ethane C isotopic trend ($\delta^{13}\text{C}\text{-CH}_4 > \delta^{13}\text{C}\text{-C}_2\text{H}_6$). These are typical signatures of abiotic gas (Etiope and Sherwood Lollar, 2013). If microbial methane exists in the water, it does not appear to be a dominant component based on the molecular composition of the gas. As correctly pointed by Vacquand et al. (2018), methanogens observed in hyperalkaline springs or shallow boreholes are not necessarily representative of the conditions of generation of methane at depth, because there is insufficient carbon in the water flowing from depth. Microbial methane generation observed in water at the surface might instead be a surficial process resulting from a reaction between hydrogen issued from depth and a source of carbon provided by atmospheric CO_2 (Vacquand et al., 2018). The isotopic disequilibrium between CH_4 and H_2O discussed above (Section 5.2) is a key indication that CH_4 is not formed in water, and therefore unlikely to have been produced by microbial processes. We accept that in some situations microbial gas is an additional, minor component commingled with abiotic gas. This is analogous to the situation where secondary microbial methane commingles with thermogenic gas and biodegraded oil in conventional petroleum systems (e.g., Milkov and Dzou, 2007; Milkov and Etiope, 2018), as shown in Fig. 5.

9. Conclusions

Theory, experiments and field data seem to converge on a model of abiotic methane generation based on CO_2 hydrogenation (Sabatier reaction) in a water-free (or unsaturated) rock, at relatively low temperatures, in presence of minerals that can act as FTT catalysts. The fact that among the several ophiolite lithotypes abiotic methane occurs exclusively in chromitites (Etiope et al., 2018), supports the hypothesis of CO_2 hydrogenation catalysed by chromium and/or ruthenium-based minerals. Chromitites (even chromium and ruthenium mines) systematically exist in the areas of all peridotite-hosted gas manifestations (Etiope and Ionescu, 2015; Etiope et al., 2018). A similar abiotic origin may occur for methane observed in Precambrian shields (South Africa, Canada and Finland), but specific geological and mineralogical investigations are required to identify potential catalysts.

Multiple lines of evidence, as depicted by Fig. 6, do not seem to support the hypotheses that the large amounts of CH_4 observed in ophiolites and peridotite massifs on land could be derived from a) high temperature processes (magmatic sources, fluid inclusions in olivine), b) synthesis in water (olivine hydration or aqueous FTT), or c) FTT with carbon compounds other than CO_2 . The arguments leading to this conclusion, albeit controversial, are summarised as follows.

- 1) *No magmatic or high T processes (fluid inclusion hypothesis unlikely):* CH_4 isotopic composition is not related to mantle CO_2 and He isotopes and helium-carbon systems are frequently decoupled. Methane clumped isotopes and seepage continuity and intensity, in particular, indicate high flows of gas produced at low temperatures ($< 140^\circ\text{C}$), which are not compatible with an origin from fluid inclusions in minerals.
- 2) *FTT must be in gas-phase:* FTT theory dictates synthesis in gas-phase and not in water, as known in heterogeneous catalysis chemistry, although some geochemical literature assumed aqueous-FTT. Field data that include the absence of radiocarbon in CH_4 , isotopic $\text{CH}_4\text{-H}_2\text{O}$ disequilibrium, CH_4 clumped isotopes and seepage distribution, all suggest a non-aqueous CH_4 derivation.
- 3) *CO , formate, formic acid or elemental C as CH_4 precursors:* Due to their

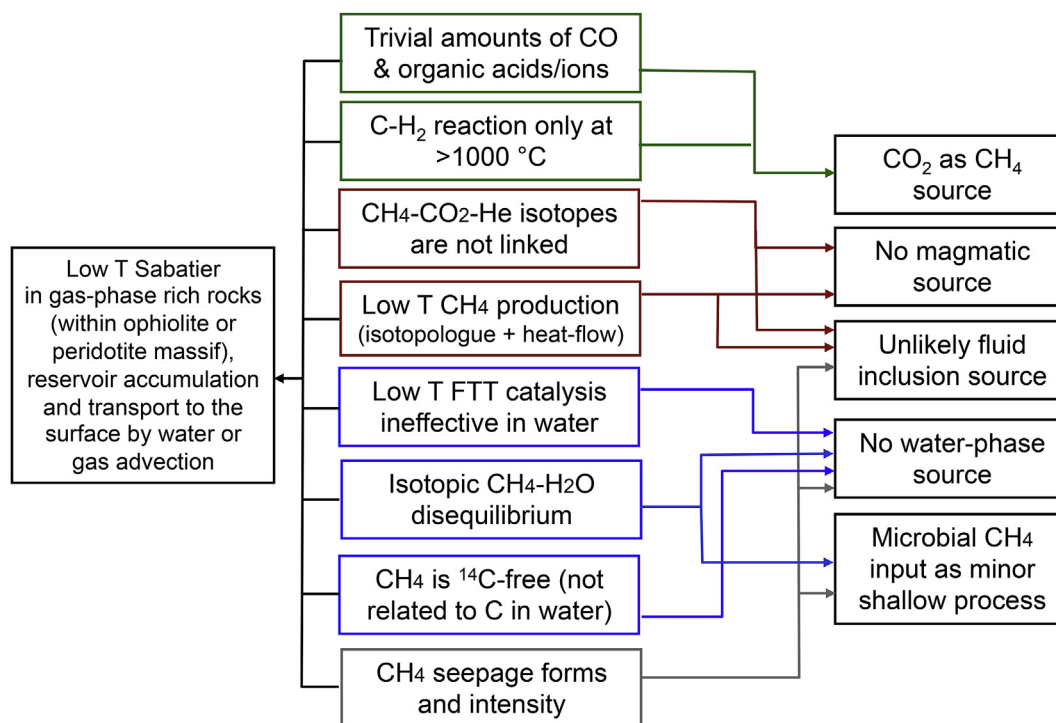


Fig. 6. Flow chart showing multiple lines of incompatibility for methane origin from magmatic, post-magmatic (high T) fluid inclusion sources or production in water, as discussed in Sections 4 and 5. All lines are instead consistent with a process of low T, gas-phase, Sabatier reaction within the ultramafic rock system.

extremely low abundance in natural fluids, CO, formic acid and formate are unlikely to represent primary carbon sources for the large amounts of CH₄ observed in ultramafic rock systems. The reaction between graphite (C) and H₂ is possible only at very high temperatures (> 1000 °C), so graphite cannot be source of CH₄ under crustal conditions, and it is also inconsistent with low temperature CH₄ formation indicated by clumped isotopes.

Regardless the exact CH₄ abiotic formation mechanism, gas flux intensity and seepage distribution suggest that gas-bearing ultramafic rock systems may be analogous to conventional, biotic natural gas systems whereby after production of CH₄ in source rocks, the CH₄ can migrate, accumulate into reservoir rocks and, under certain conditions, leak and seep to the surface. Microbial CH₄ generated under anaerobic, lower temperature aqueous conditions may be added as variable amounts of secondary gas.

The low T, gas-phase Sabatier model emerging in this review is, however, an attempt of reconciling general field and laboratory observations and it may not apply in specific cases. Additional CH₄ isotopologue, isotopic and gas flux data from ophiolitic seeps and springs are needed to validate the model.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.apgeochem.2019.01.012>.

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