

Low temperature production and exhalation of methane from serpentinized rocks on Earth: A potential analog for methane production on Mars

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ABSTRACT

We evaluate, based on terrestrial analogs, the potential flux, origin and isotopic signature of methane (CH₄) from serpentinized or serpentinizing rocks on Mars. The Tekirova ophiolites, in Turkey, have been shown to release, either via focused vents or through diffuse microseepage, substantial amounts of CH₄ which could be produced via catalyzed abiotic methanation (Sabatier reaction) at low temperatures (<50 °C). Serpentinized ultramafic rocks on Mars are likely to have necessary chemical constituents for methane production and fractures for release of gas to the atmosphere, similar to those on Earth. A simple, first-order estimation gas-advection model suggests that methane fluxes on the order of several mg m⁻² d⁻¹, similar to microseepage observed in terrestrial ophiolites, could occur in martian rocks. High temperature, hydrothermal conditions may not be necessary for abiotic CH₄ synthesis on Mars: low temperature (<50 °C) methanation is possible in the presence of catalysts like ruthenium, rhodium or, more commonly, chromium minerals, which occur in terrestrial ophiolites as in martian mantle meteorites. The terrestrial analog environment of abiotic microseepage may thus explain production of methane on Mars in the ancient past or at present. The wide range of martian ¹²C/¹³C and D/H ratios and the potential secondary alteration of CH₄ by abiotic oxidation, as observed on Earth, could result in large isotope variations of methane on Mars. CH₄ isotopic composition alone may not allow definitive determination of biotic vs. abiotic gas origin. Using our terrestrial vs. martian analysis as guide to future Mars exploration we propose that direct methane and ethane gas detection and isotopic measurements on the ground over serpentinized/serpentinizing rocks should be considered in developing future strategies for unraveling the source and origin of methane on Mars.

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1. Introduction

The detection of ~10–20 ppb of methane (CH₄) in Mars atmosphere (Mumma et al., 2003; Formisano et al., 2004; Krasnopolsky et al., 2004) suggested the existence of an active gas source. If confirmed, the CH₄ plume observed by telescopic measurements in the Northern Summer 2003 would indicate an emission from the martian ground of ~19,000 tons CH₄ yr⁻¹ (Mumma et al., 2009) or ~150,000 tons CH₄ yr⁻¹ (Lefevre and Forget, 2009) and possibly up to ~570,000 tons CH₄ yr⁻¹ (Chizek et al., 2010). The occurrence of CH₄ on Mars has been recently questioned because atmospheric photochemistry and transport models make short-lived methane plumes implausible and ground-based observations of methane are heavily affected by telluric interference (Zahnle et al., 2011).

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Nevertheless, an intriguing aspect of the Northern Summer 2003 plume (Mumma et al., 2009) is that some of the elevated CH₄ concentrations were detected over olivine-bearing rocks, sometimes serpentinized, in the martian regions of Syrtis Major, Terra Sirenum and Nili Fossae (Hoefen et al., 2003; Ehlmann et al., 2010). This would be consistent with the hypothesis that abiotic CH₄ synthesis in serpentinizing rocks may be a past and/or present source of CH₄ on Mars (Oze and Sharma, 2005; Atreya et al., 2007). Accordingly, terrestrial outcrops of actively serpentinizing ultramafic rocks, especially several ophiolites exposed on the continents, are important analog sites to understand production and exhalation fluxes of abiotic methane in olivine-rich rocks on Mars (Blank et al., 2009; Szponar et al., 2010; Etiope et al., 2011c).

On Mars, methane could be produced by various processes such as (i) serpentinization of olivine-rich materials, (ii) volcanic activity, (iii) water–rock reactions in magmatic dikes, (iv) exogenous sources such as meteorites, and (v) biological activity (Lyons et al., 2005; Atreya et al., 2007). The first process, serpentinization,

is favored by most workers (Oze and Sharma, 2005; Atreya et al., 2007), implying that methane would mainly be produced by methanation (also known as Sabatier reaction) which is a Fischer–Tropsch-type synthesis, resulting from the release of hydrogen during the hydration of olivine and oxidation of iron (Abrajano et al., 1988; Oze and Sharma, 2005; Etiope et al., 2011c). Serpentinization may or may not be the source for present-day observed methane, but the recent orbital detection of outcrops of serpentine-bearing, Noachian-aged materials at the Mars surface is evidence that serpentinization was active on early Mars and could have generated hydrogen, and eventually methane, in the past (Ehlmann et al., 2010). Methanation can however be independent of serpentinization if H_2 produced by other mechanisms (e.g., radiolysis, magma degassing) is available.

The formation and exhalation of abiotic gas from serpentinizing terrestrial ophiolites represent fundamental reference processes for understanding possible degassing pathways of methane on Mars. Only recently, however, has methane degassing from terrestrial ophiolites been directly measured (Etiope et al., 2011c): the serpentinized Tekirova ophiolites in Turkey release considerable amounts of abiotic methane, both from focused vents (the Chimaera macro-seep with the so-called “eternal fires”) and through invisible, diffuse exhalation, called miniseepage and microseepage (see definitions in Etiope et al. (2011b,c)), from exposed ophiolitic rocky ground. Preliminary calculations suggest that even if only low fluxes of microseepage occur in the serpentinized ultra-mafic rocks on Mars, they could supply more than enough to sustain the methane levels apparently detected in the atmosphere (Etiope et al., 2011c).

In this work, we examine the terrestrial analog of serpentinizing Tekirova ophiolites and discuss controls on fluxes and isotopic signatures of methane that might have been produced by similar processes on Mars. This geologic site is different from other serpentinizing systems because serpentinization occurs at relatively low temperatures, the ultramafic rocks are in contact with carbonates (limestones), which may provide CO_2 for methanation, and the principal gas emitted is methane rather than hydrogen. We use the methane seepage data and the main gas-transport and gas-generation properties of the terrestrial serpentinized rocks (Sections 2.1 and 3.1) to assess if similar release rates per area and genetic processes could be realistically expected for martian rocks (Sections 2.2 and 3.2). In contrast to previous models of abiotic methane generation in ultramafic rocks on Mars (Lyons et al., 2005; Oze and Sharma, 2005), we discuss the potential for catalyzed CH_4 generation at very low temperatures ($<50^\circ C$) as may be occurring or have occurred in the martian shallow crust. The isotopic signatures of CH_4 formed by abiotic synthesis in terrestrial serpentinized rocks are examined (Section 4.1). Considering possible post-genetic isotopic modifications (e.g., extreme deuterium enrichments in the CH_4 molecule, recently discovered in a thermogenic gas on Earth; Etiope et al., 2011a), we provide a range of C and H isotopic values that could potentially be measured on Mars (Section 4.2). The potential for abiotic CH_4 production and microseepage, and the recognition of some interpretative limits of the classical genetic CH_4 isotopic zonation offer new geochemical arguments that should be considered in future strategies for unraveling the source and origin of methane on Mars (Section 5).

2. Methane exhalation from exposed serpentinized ultramafic rocks

2.1. Evidence from terrestrial ophiolites

Methane exhalation into the atmosphere from low temperature ($<100^\circ C$) serpentinization in continental ophiolites is documented

in four countries – the Philippines, Oman, New Zealand, and Turkey (Abrajano et al., 1988; Fritz et al., 1992; Sano et al., 1993; Lyon et al., 1990). Gas-bearing ophiolites with indications of CH_4 in hyperalkaline water springs and H_2 in boreholes, are known in several places (e.g., California, Canada, Italy, Romania; e.g., O’Neil and Barnes, 1971; Filipescu and Humă, 1979; Cardace et al., 2009; Monnin et al., 2011). Hydrogen gas has been reported in ophiolites at several sites; however, methane flux from ophiolites has been directly measured only in Turkey, at Çirali, in the Gulf of Antalya (Fig. 1; Etiope et al., 2011c). The Çirali ophiolites belong to the Tekirova Unit (Upper Cretaceous), which is part of the Neotethyan ophiolite complex exposed across the circum-Mediterranean region. The Çirali ophiolitic block has a thickness of about 3 km and is an assemblage of peridotite and gabbro that includes serpentinized harzburgites with minor lherzolite, podiform dunites and chromitites, with a degree of serpentinization ranging from ~30% to 65% (Aldanmaz et al., 2009). This block is in contact, along a fault, with Mesozoic limestones. Gas is issuing just in correspondence with this fault.

By using a closed-chamber system linked to a portable methane sensor (Fig. 1D; for details of the technology see Etiope et al., 2011b,c), two types of abiotic methane seepage were recognised from the Tekirova ophiolites: (i) focused release of gas (vents) from fractures or cracks in the exposed rock, individually releasing up to several tons of CH_4 per year (macro-seepage), and (ii) invisible but pervasive, diffuse exhalation from the ground with methane fluxes ranging from tens to thousands of $mg\ m^{-2}\ d^{-1}$ (called miniseepage when it is within or around a macro-seepage zone and microseepage when it is far from and independent of macro-seep occurrence).

The macro-seepage in the Tekirova ophiolites is known as “the Chimaera seep”, which is probably the biggest onshore abiotic gas seep on Earth. It is a system of more than 50 gas vents issuing from fractures in a 5000 m^2 wide ophiolitic outcrop (Fig. 1). At least 20 vents burn continuously, producing flames up to a half meter in height. There are no water discharges, so all fractures emit only gas composed of 87% of CH_4 and around 10% of H_2 (plus minor amounts of N_2 , CO_2 , ethane and propane). While H_2 is very likely produced by serpentinization in the ultramafic rocks, methane ($\delta^{13}C \sim -12\text{‰}$; $\delta D \sim -129\text{‰}$) could be produced by an abiotic synthesis as discussed in Section 3.

Measured diffuse methane fluxes range from 32 to 95,000 $mg\ CH_4\ m^{-2}\ d^{-1}$. The gas exhalation, causing rapid accumulation of methane in a 10 L chamber, occurred even in correspondence with exposed rock which is apparently unfractured and homogeneous (Figs. 2 and 3A and B).

The Chimaera macro-seepage and miniseepage release in total at least 150–190 tons of CH_4 annually into the atmosphere (Etiope et al., 2011c). Abiotic methane microseepage was also detected about 3 km away from the Chimaera seep but over the same ophiolitic formation along a fault at the Çirali beach (Figs. 1D and 3C). Methane fluxes ranged from 68 to 1040 $mg\ m^{-2}\ d^{-1}$. For the lowest flux detected, CH_4 concentration in the chamber increased from ambient air level ($\sim 2\text{ ppmv}$) up to 7 ppmv in 5.6 min with a rate of 0.015 ppmv/s (Fig. 4A). For the highest microseepage flux, CH_4 build-up was about 0.2 ppmv/s (up to 21 ppmv in less than 2 min; Fig. 4B). These flux values are similar to those reported for traditional microseepage of thermogenic gas, produced by thermal degradation of organic matter, in various sedimentary basins (Etiope and Klusman, 2010).

Given the significant fluxes and rapid pressure build-up in the chamber, the gas movement in the rock is mainly due to advection, driven by a pressure gradient (Darcy’s law), rather than diffusion, which is controlled by concentration gradients (Fick’s law). The exhalation must take place through diffuse microfractures in the rock (Fig. 3). In general, small-scale permeability of partially

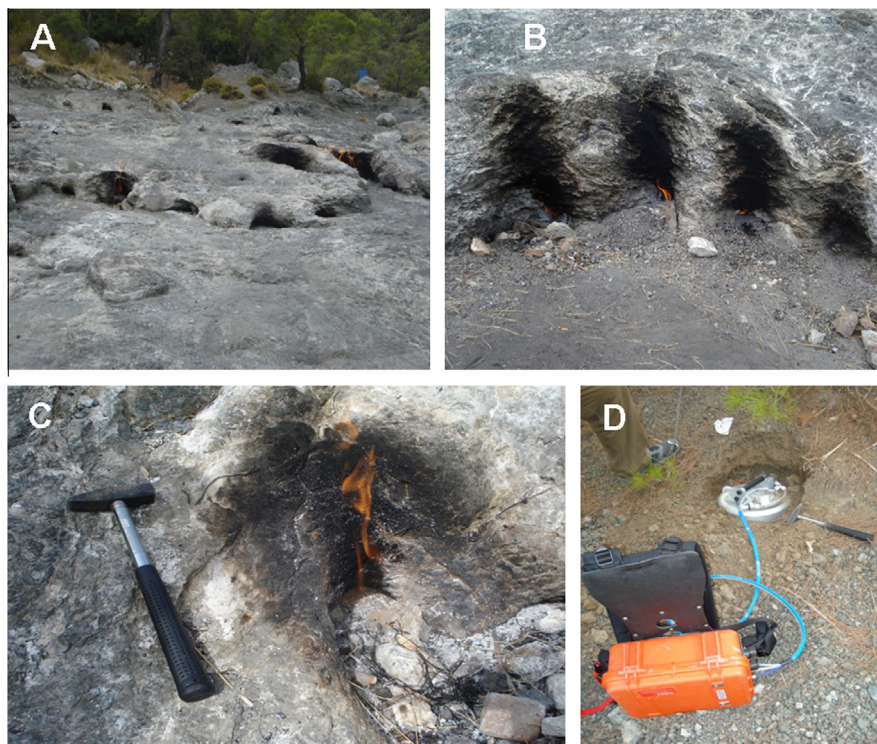


Fig. 1. Images of Chimaera seep: partial view of the ophiolite outcrop (A), and examples of clusters (B) and isolated burning vents (C). Gas miniseepage (invisible, diffuse exhalation around the vents, 10^1 – 10^4 mg m $^{-2}$ d $^{-1}$) is pervasive throughout the outcrop. (D) measurement of CH $_4$ microseepage (diffuse fluxes $\leq 10^3$ mg m $^{-2}$ d $^{-1}$) at the Çirali beach by closed-chamber technique.

serpentinized peridotites is comparable to permeability of shaley materials, but olivine hydration generates large volume changes and thus high local strains and stresses with episodic cracking (Macdonald and Fyfe, 1985). In the Tekirova ophiolite micro-scale fractures are pervasive throughout the peridotite outcrop and are often mineralized by carbonates (Fig. 3A and B). The outcrop is, however, also characterized by larger joints and faults (Fig. 3C) as a result of the tectonic overthrusting above the sedimentary Mesozoic and Cenozoic sequence (Etiope et al., 2011c). The serpentinization-related microfractures and the tectonic fractures are, therefore, important escape pathways for methane generated inside the Çirali ultra-mafic block. On Mars, permeability due to fracturing during the serpentinization of olivine-rich rocks may be the most important gas pathway in absence of tectonic activity.

2.2. Gas migration potential in martian serpentinized rocks

The Northern Summer 2003 episodic emission of $\sim 19,000$ tons CH $_4$ yr $^{-1}$ (Mumma et al., 2009) or $\sim 150,000$ tons CH $_4$ yr $^{-1}$ (Lefevre and Forget, 2009) could be supplied by one hundred to one thousand macro-seeps like Chimaera (Etiope et al., 2010, 2011c). On Mars, however, this kind of macro-seep is improbable; at least on Earth, Chimaera represents a rare phenomenon. Rather, an easier and more probable degassing scenario on Mars could be that of diffuse microseepage (Etiope et al., 2011c). A diffuse flux of ~ 100 – 1000 mg m $^{-2}$ d $^{-1}$ from an area of 500 to 5000 km 2 would be sufficient to support the estimated martian CH $_4$ emission. If the entire 30,000 km 2 of olivine-rich outcrop at the Nili Fossae (Hoefen et al., 2003) is assumed to exhale, then a microseepage ~ 15 mg m $^{-2}$ d $^{-1}$, i.e. 4–5 times lower than the minimum detected at Çirali, could account for the observed martian CH $_4$ plume. Recent modeling of CH $_4$ release on Mars indeed suggests that the Northern Summer 2003 plume was formed by a broad source rather than a point emission (Mischna et al., 2011). Microseepage can be either

episodic (as required by the martian model of Mischna et al. (2011)), seasonal (as required by Geminale et al. (2008)) or quasi-permanent, depending on the underground gas pressure gradients, the migration mechanisms, and changes of exogenic (atmospheric) factors (Etiope and Klusman, 2010; Etiope et al., 2011c).

The ability of methane produced in the martian subsurface to reach the surface should depend on the physical properties of the substrate, including water occurrence, permeability, porosity, pressure and thermal gradients, according to advection and diffusion migration processes (see Etiope and Martinelli (2002) for a general overview and bibliography of these mechanisms in terrestrial rocks). In general, martian terrains seem to have good gas-transport properties. Vapor–ice deposition models for ice distribution predict that the upper tens to hundreds of meters of Mars' subsurface exchange with the atmosphere (e.g. Mellon et al., 1997) and large-scale aquifer models predict fluid migration through pores at several kilometers depth (e.g. Clifford, 1993; Hanna and Phillips, 2005; Grimm and Painter, 2009). For a granular material, the depth of compaction for pore-sealing does not occur until ~ 11 km (Clifford, 1993). So, Mars surface properties, including those in more fractured, serpentinized rock, would allow migration of gases produced at depth.

On Earth, advection is the most important mechanism of gas migration in the subsoil, being able to transport large amounts of gas for long distances in short time (Brown, 2000; Etiope and Martinelli, 2002). Gas advection can take place in two forms, depending on the presence of water. In dry porous or fractured media gas flows through interstitial or fissure space (gas-phase advection). In saturated porous or fractured media two possible phenomena may be distinguished: gas dissolves and is transported by groundwater (water-phase advection) or gas flows displacing water (gas-phase advection). In the first case, gas moves at the same velocity as water; in the second case gas must have a

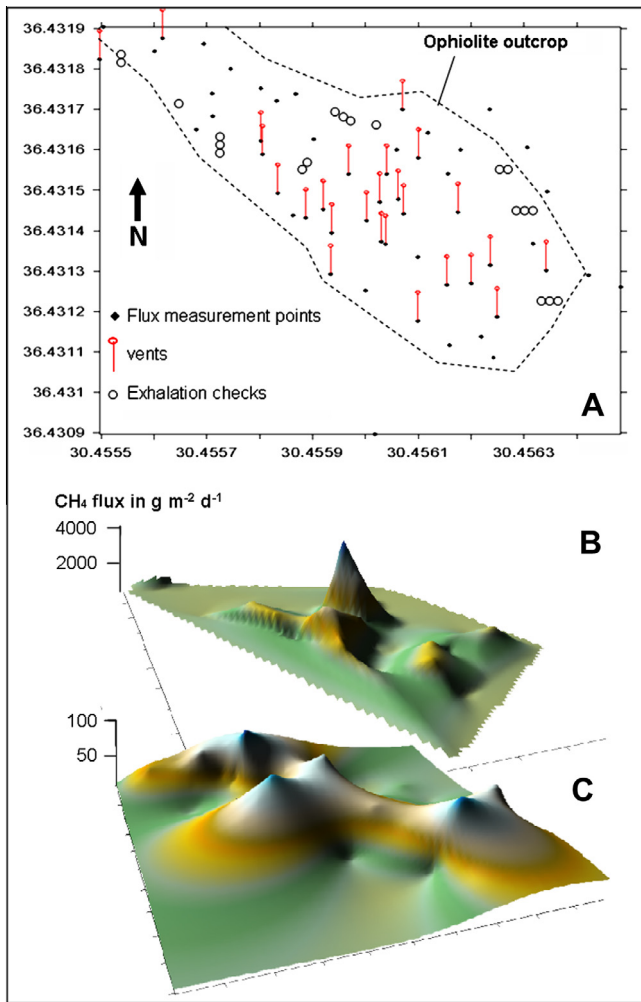


Fig. 2. Distribution of exhalation detection points within the ophiolite outcrop at the Chimaera seep (A), and 3D visualization of vent macro-seep flux (B, “Natural neighbour” interpolation) and miniseepage (C, “Kriging” interpolation).

pressure (P_g) above the sum of hydrostatic pressure (P_w) plus capillary pressure (P_c). Water displacement can then be in form of bubbles or slugs (Etiope and Martinelli, 2002).

At the equatorial and mid-latitudes on the Mars surface today, water is typically only stable in the gas phase (Haberle et al., 2001). However, near-surface salts and thin-film type weathering point to small amounts of surface water in the geologically recent past (Arvidson et al., 2010). Availability of subsurface water remains a subject of active research. Subsurface water was available in the past, causing chemical alteration (McLennan et al., 2005; Okubo and McEwen, 2007; Ehlmann et al., 2010). Subsurface ice from vapor–ice deposition exists near the surface at high latitudes and may also be present at greater depths in lower latitudes (Mellon et al., 1997; Byrne et al., 2009). Radar investigations have not revealed a subsurface aquifer (Farrell et al., 2009; Nunes et al., 2010), but modern seepage of brines shows the potential for episodic subsurface water availability on some places on Mars (McEwen et al., 2011). Liquid H₂O in the martian crust is estimated to be stable from 4 km to 15 km, and liquid water could exist as a brine at depths shallower than 4 km (Oze and Sharma, 2005). Subsurface ice may act as a barrier for advection of gases to the surface; however, evidence for seasonal melting/sublimation offers a mechanism whereby water–rock reactions could produce methane, and gases trapped by ice-filled pore spaces could occasionally be released.

It is likely, then, that the most frequent form of gas advection on Mars, at least at relatively shallow depths, could be the gas-phase in dry fractured media. Under these conditions gas velocity may range in the order of 10^0 – 10^3 m/day; for high permeability, fractured rock, whose fracture aperture or voids are in the order of several mm, gas plumes may reach velocities of the order of 10^3 – 10^4 m/day (Etiope and Martinelli, 2002). Advection is dependent on permeability and pressure gradients according to Darcy’s law. No direct measurements of these parameters on Mars exist but some models suggest that near the surface, permeability may range from 10^{-9} to 10^{-11} m², similar to terrestrial basaltic aquifers, decreasing to 10^{-17} m² at depth (Grimm and Painter, 2009; Hanna and Phillips, 2005 and references therein). Gas advection is mainly driven by secondary permeability due to fracturing. It is known that the martian crust is fractured at multiple scales (Fig. 5), e.g. from repeated meteorite impacts and fracturing during cooling of lavas.

Additional fracturing can be due to serpentinization, as discussed above, so that the olivine-bearing rocks may have higher secondary permeability in comparison with non-serpentinized areas. In these various fracture-generating processes the actual permeability (k_f , m²) of the ground can be estimated by the ‘cubic law’ model (Schrauf and Evans, 1986):

$$k_f = a^3/6d \quad (1)$$

where a is the average fracture width (m) and d the average fracture spacing (m). As measured in the Semail ophiolite in Oman, fracture width in serpentinized peridotite is typically in the range of 0.001–0.01 m and the fracture spacing is more frequently in the range of 0.03–0.5 m (consistent with our observations in the Tekirova ophiolite), leading to permeabilities in the order of 10^{-6} – 10^{-9} m² (Nehlig, 1994). The advective gas flux (F , kg m⁻² s⁻¹) along fractures, in absence of liquid water (as we may assume in shallow rocks on Mars), in one-dimensional form, along the z -axis, is then determined by the gas concentration (C , kg m⁻³), dynamic gas viscosity (μ , kg m⁻¹ s⁻¹), fracture permeability (k_f , m²) and the pressure difference (ΔP , kg m⁻¹ s⁻²) between two points spaced at distance Z (m) (Etiope and Martinelli, 2002):

$$F = Ck_f\Delta P\mu^{-1}Z^{-1} \quad (2)$$

For either past gas generation during Noachian serpentinization or present serpentinization fed by unknown water sources, we may assume conservatively that abiotic methane in the martian serpentinized ultramafic rocks would be at low concentrations (<1% v/v or <1 kg m⁻³). In the martian shallow underground, CO₂ is probably the most frequent or abundant gas, as in the atmosphere, so it can act as a carrier of trace gases. As such, it determines the pressure gradient driving the advective flow. Special cases of trace gas transport by carrier gas on Mars could be those related to CO₂-vapor outgassing processes from condensed CO₂, which however probably occur only in polar regions (Stewart and Nimmo, 2002). Then, the following highly simplified, one-dimensional model based on Eq. (2) can be adopted for a first-order estimation of the methane flux at the martian surface, assuming:

- a gas (CO₂ + CH₄) source 100 m deep at ~1 MPa with rock density of 3000 kg m⁻³;
- CO₂ viscosity μ : 15 kg m⁻¹ s⁻¹, from Fenghour et al. (1998), at 1 MPa and temperatures of 280–300 K derived by using the geotherms of Stewart and Nimmo (2002) and surface temperatures in the near-equatorial summer (~240 K), where the Northern Summer 2003 CH₄ plume was detected (Spanovich et al., 2006);
- serpentinized rock permeability $k_f \sim 10^{-6}$ m², with even higher values reported by Nehlig (1994).

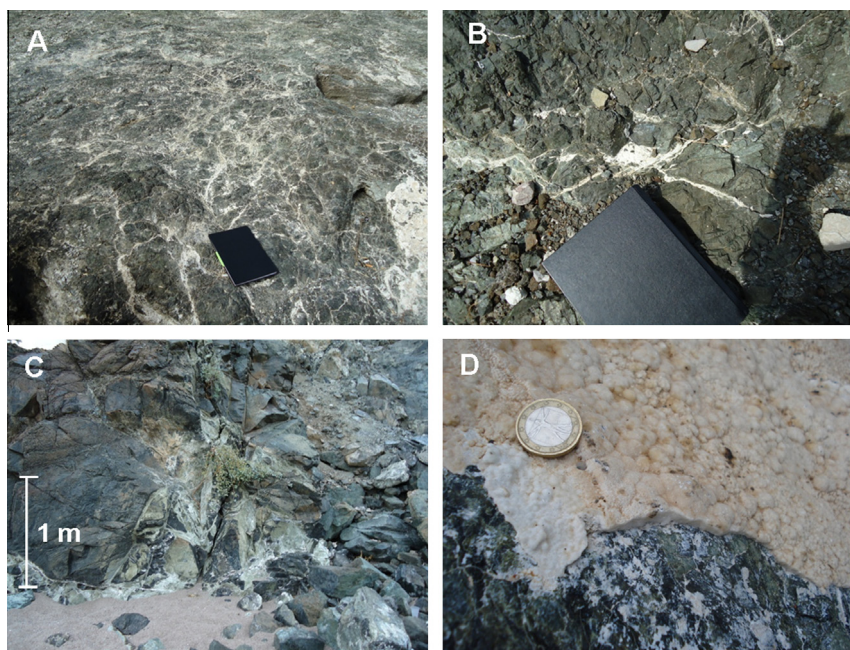


Fig. 3. The ophiolite outcrop at Chimaera (A and B) and Çirali beach (C and D) showing fractures and carbonate filled veins. Methane exhalation is diffuse throughout the exposed rocky ground (A and B) and at the base of the faulted scarp in Çirali (C). The carbonate (D) is pure calcite with $\delta^{13}\text{C} = -11.2\text{‰}$ (VPDB).

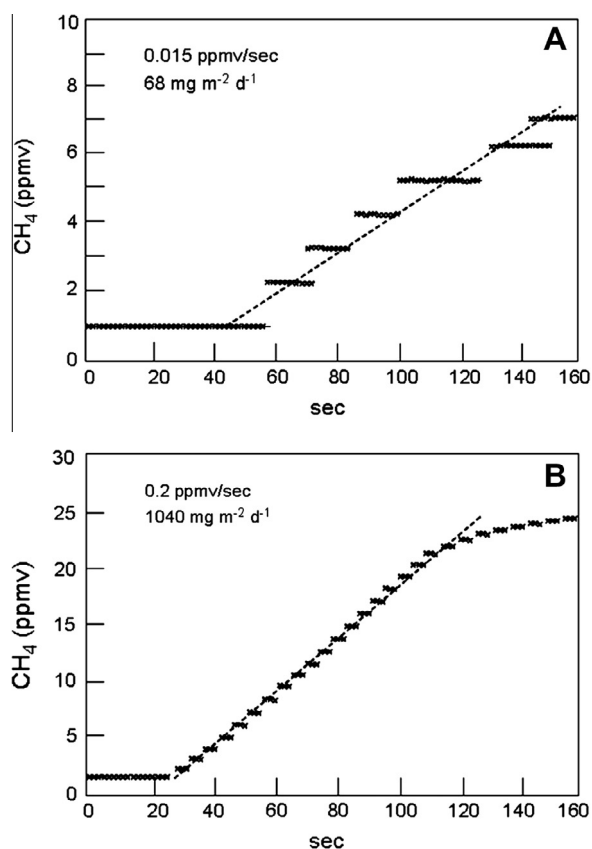


Fig. 4. Minimum and maximum methane microseepage flux measured over Tekirova ophiolites by closed-chamber technique, as recorded by the West System flux meter software. Details of the chamber and measurement procedures are reported in Etiope et al. (2011b,c).

With these parameters, methane fluxes $>10^{-11} \text{ kg m}^{-2} \text{ s}^{-1}$ ($>10 \text{ mg m}^{-2} \text{ d}^{-1}$, similar to the microseepage observed in the

Tekirova ophiolite) can occur for CH_4 concentrations of only 0.02% v/v in the source at 100 m depth even with trivial pressure differences $\Delta P \sim 10 \text{ kg m}^{-1} \text{ s}^{-2}$. This is equivalent to 0.01 kPa, that is 1/100 of atmospheric martian pressure. Higher CO_2 pressures, such as those expected during condensed CO_2 outgassing (Stewart and Nimmo, 2002) may lead to significant CH_4 fluxes even for CH_4 concentrations at ppmv levels. These calculations are a first rough estimation to verify the potential occurrence on Mars of methane fluxes with the same order of magnitude of those observed on Earth; more rigorous modeling and calculations are needed to actually test the flux in a wider range of rock permeabilities, temperatures and pressures. Furthermore, better understanding of subsurface ice and, potentially, liquid water distribution would be a critical input for more refined models at different latitudes and greater depths.

3. A potential CH_4 origin on Mars: low temperature methanation

3.1. Evidence of low temperature methanation on Earth

The molecular and isotopic composition of C_1 – C_5 alkanes, CO_2 , and N_2 of Chimaera gas, combined with source rock maturity data and thermogenic gas formation modeling suggest a dominant abiogenic component (~ 80 – 90%) mixed with thermogenic gas (Etiope et al., 2011c). The gas-geochemical data and the geologic boundary conditions, namely the presence of limestones in contact with the ultra-mafic rocks and the low geothermal gradient ($<80^\circ \text{C}$ at 3 km depth, which is the base of the ophiolitic block; Etiope et al., 2011c), together suggest that the abiogenic methane was likely produced by a Fischer–Tropsch type reaction, similar to that invoked for other abiogenic gas seeps associated with serpentinized rocks such as in the Lost City Atlantic ridge, in the Philippines, Oman and New Zealand (Proskurowski et al., 2008; Bradley and Summons, 2010; Abrajano et al., 1988; Fritz et al., 1992; Sano et al., 1993; Lyon et al., 1990). Chimaera gas, however, seems to have formed at very low temperatures. CH_4 isotopic composition

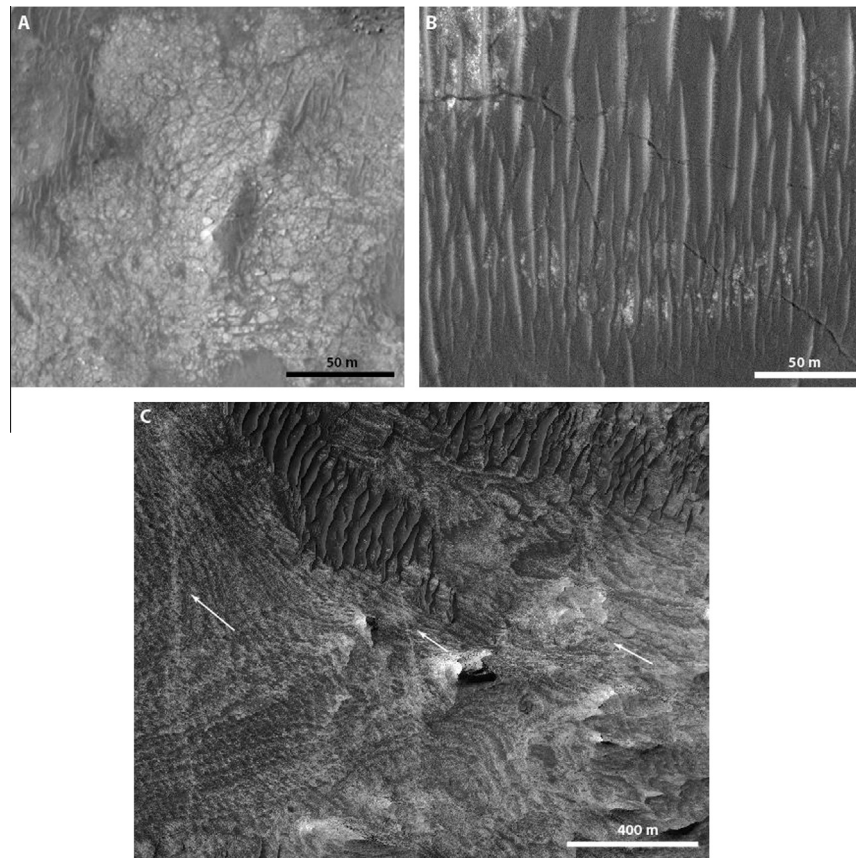


Fig. 5. Fractures and ridges that may represent past or present sites of gas seepage or fluid flow in (A) fractured, olivine-rich rocks northeast of Syrtis Major and south of the Nili Fossae (HiRISE ESP_016931_1980; [Ehlmann et al., 2010](#)); (B) sand-covered bedrock near Nili Fossae (PSP_003086_2015; [Wray and Ehlmann, 2011](#)); (C) sedimentary layered rocks in Candor Chasma within Valles Marineris (TRA_000836_1740; [Okubo and McEwen, 2007](#)).

and the low deuterium/hydrogen isotopic ratio of H_2 (δD_{H_2} : -720‰) suggest that gas is produced at about 50°C or less, consistent with the low geothermal gradient of the area. This temperature is lower than that estimated at other serpentinization sites. Chimaera gas temperatures would be, however, similar to those estimated for deep (630–1000 m) accumulations of hydrogen gas in Kansas with δD_{H_2} : -740‰ to -836‰ , where CH_4 was found only in trace amounts ([Coveney et al., 1987](#)).

Chimaera gas data suggest that low temperature methanation may occur naturally in shallow (<3 km) geologic conditions; this significantly expands the environments of potential generation of methane. The low temperature synthesis of abiotic gas in Chimaera must be very fast and effective in continuously producing an amount of gas equivalent to the long-lasting (>2 millennia) emission of >100 tons CH_4 yr^{-1} , otherwise pressurized gas accumulation must exist.

The easiest and most thermodynamically favorable reaction at low temperatures would be the Sabatier reaction, also named “methanation” or “ CO_2 hydrogenation”: $CO_2 + 4H_2 = CH_4 + 2H_2O$. Rapid methanation (CH_4 generation after a few hours) at room temperature ($<50^\circ\text{C}$) and atmospheric pressure was demonstrated in the laboratory with ruthenium and rhodium catalysts ([Thampi et al., 1987](#); [Jacquemin et al., 2010](#)). These Platinum Group Elements (PGEs) are common in chromitites of many continental ophiolitic outcrops, including those of Oman and the Philippines where methane seepage occurs ([Page et al., 1982](#); [Bacuta et al., 1990](#)). [Thampi et al. \(1987\)](#) demonstrated that CH_4 can be generated at a rate of about $20\text{ }\mu\text{L/h}$ (~ 0.3 mg/day) at temperatures below 50°C using a ruthenium catalyst (Ru/TiO_2) in presence of H_2 and CO_2 . [Jacquemin et al. \(2010\)](#) obtained methane in a similar way at room temperature

and atmospheric pressure using a $Rh/\gamma\text{-}Al_2O_3$ catalyst. It is likely, therefore, that ruthenium and rhodium minerals and alloys in the serpentinized ultramafic rocks play a key role in the methane production. However, also chromium, which is a potent FTT catalyst ([Foustoukos and Seyfried, 2004](#)), much more abundant in ultramafic rocks than PGE, could support low temperature methanation over longer time scales (months, years), especially when associated to other metal minerals (e.g., Ni, Fe, Mg oxides or alloys in chromitites); such a slow methanation is theoretically possible but not yet experimentally demonstrated in laboratory.

3.2. Potential low temperature methanation on Mars

[Oze and Sharma \(2005\)](#) proposed a model for methane production via serpentinization and $H_2 + CO_2$ mixing on Mars. In the past, with a higher geothermal gradient and more abundant water, H_2 produced during serpentinization would have been possible at a range of depths in the martian crust. On Mars today, H_2 may be available from present-day serpentinization in deep rocks (>4 km), where liquid water is potentially stable ([Oze and Sharma, 2005](#)). We also cannot exclude that H_2 might be produced, disregarding serpentinization, by other mechanisms, such as radiolysis, cataclasis of silicates in fault zones or magmatic degassing ([Smith et al., 2005](#); [Onstott et al., 2006](#)). In either case, accumulations of H_2 -rich gas could exist in the martian underground, as on Earth ([Coveney et al., 1987](#); [Smith et al., 2005](#)). CO_2 can derive from atmosphere or magmatic degassing as discussed by [Oze and Sharma \(2005\)](#) or from carbonate material, such as that closely associated with olivine-rich rocks near the Nili Fossae ([Ehlmann et al., 2008](#)).

The proposed $H_2 + CO_2$ mixing models (e.g., Oze and Sharma, 2005), however, typically infer hydrothermal temperatures, based on the fact that some Fischer–Tropsch reactions, and in particular the Sabatier reaction (methanation), are exothermic, thermodynamically favorable at temperatures $<600\text{ K}$ ($<325\text{ °C}$) and occur in the presence of Cr–Fe–Ni catalysts. These catalysts are actually known to be effective at temperatures above 200 °C on short time scales (hours or days; Foustoukos and Seyfried, 2004; Wang and Gong, 2011). Here we can add that Oze and Sharma's model may be valid even at temperatures $<50\text{ °C}$, as observed on Earth (Etiope et al., 2011c) and as described in Section 3.1, assuming the occurrence of chromites or specific low- T methanation catalysts, such as ruthenium and rhodium, in the martian ultramafic rocks. Indeed, these siderophile elements, associated to chromium minerals, seem to be particularly enriched in martian mantle rocks (Jones et al., 2003). About 16 ppb of Ru were detected in the Chassigny meteorite (Jones et al., 2003), belonging to the SNC (Shergotty, Nakhla, Chassigny) meteorites, which are derived from martian mantle. Such a concentration is within the typical range observed in terrestrial chromitites, including those in methane-bearing ultramafic rocks in Oman and the Philippines (Page et al., 1982; Bacuta et al., 1990). Taken together, these observations support the notion that low temperature methanation may occur in martian serpentinized ultramafic rocks.

4. Potential abiotic CH_4 isotopic signatures on Earth and Mars

4.1. C–H isotopic signatures of abiotic CH_4 on Earth

The C–H isotopic diagram in Fig. 6 summarizes the isotopic genetic zonation of biotic (microbial and thermogenic) vs. abiotic CH_4

based on terrestrial data acquired so far. The diagram is updated, and more complete, with respect to that reported by Onstott et al. (2006) as it includes the isotopic data of abiotic methane from deep crystalline rocks (C-FTT), higher temperature geothermal systems (G-FTT) and lower temperature serpentinization systems in which methane is probably produced by Fischer–Tropsch Type reactions as discussed above, i.e. at Chimaera and within other ultra-mafic rocks (S-FTT). It also shows a peculiar thermogenic (biotic) gas, recently discovered in Romania (Homorod seep) with unusual deuterium enrichment in methane whereby the most positive $\delta D-CH_4$ of $+124\text{‰}$, represents the highest value of $\delta D-CH_4$ ever found on Earth (Etiope et al., 2011a). This extreme deuterium enrichment in CH_4 is interpreted to result from abiogenic oxidation, mediated by metal oxides, of thermogenic methane. While microbial oxidation of methane produces $\delta^{13}C_{CH_4}-\delta D_{CH_4}$ correlated variations with fractionation factor $\Delta H/\Delta C \sim 8-9$ (Coleman et al., 1981; Kinnaman et al., 2007), abiogenic oxidation follows a slope of $\Delta H/\Delta C \sim 21$ (Kiyosu and Imaizumi, 1996), so that the deuterium enrichment can be larger than that induced by microbial oxidation. Microbial oxidation would result in a different trend with lighter δD_{CH_4} .

Methane can be oxidized abiogenically due to temperature increases (e.g., increased heat flow related to igneous intrusions) in metal-rich (Fe_2O_3 , MnO_2 , CuO) mafic rocks (Kiyosu and Imaizumi, 1996; Etiope et al., 2011a). The abiotic CH_4 field (represented by the dashed red line in Fig. 6) denotes the potential isotopic signatures resulting from abiogenic oxidation, based on the deuterium enrichment observed in the Homorod natural gas, starting from any original abiotic gas.

Biotic and abiotic fields have considerable overlap, however. It is important to note that the Chimaera methane, despite its clear position in the “abiotic realm” of the $\delta^{13}C$ vs. δD diagram (Fig. 6),

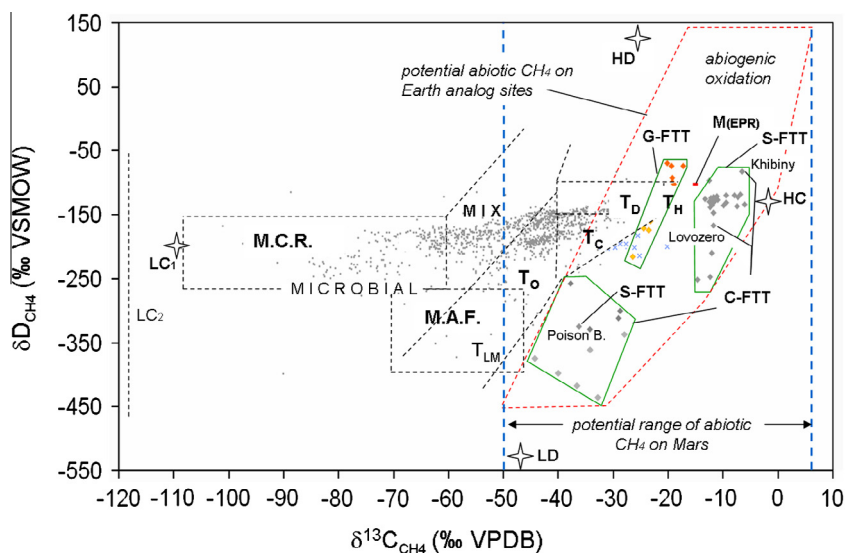


Fig. 6. Revised CH_4 genetic zonation based on deuterium and carbon isotopic data. Black dashed lines are the traditional fields of biotic (microbial and thermogenic) gas: MCR: Microbial CO_2 Reduction; MAF: Microbial Acetate Fermentation; T_o : thermogenic with oil; T_c : thermogenic with condensate; T_d : dry thermogenic; T_h : thermogenic with high-temperature CO_2-CH_4 equilibration; T_{LM} : thermogenic low maturity (Schoell, 1988; Welhan, 1988; Hunt, 1996; Milkov and Dzou, 2007; Etiope et al., 2011a). Small gray dots are reservoir data from a global data-set owned by the authors. The white stars are the four “records” of highest and lowest $\delta^{13}C_{CH_4}$ and δD_{CH_4} found in natural gas systems (Etiope et al., 2011a and references therein): HC: Highest $\delta^{13}C_{CH_4}$, Illimaussaq inclusions, Greenland; LC1: lowest $\delta^{13}C_{CH_4}$, microbial gas in Antarctica sediments, and LC2: an unpublished lowest $\delta^{13}C_{CH_4}$, (vertical dashed line, the δD value is unknown) offshore Eastern Indonesia; LD, Lowest δD_{CH_4} from Big Soda Lake, Nevada; HD, Highest δD value, Homorod mud volcano, Romania. These four extreme biotic methanes are due to microbial or abiogenic oxidation (Etiope et al., 2011a). Abiotic gas is represented by mantle gas (M_{EPR} , East Pacific Rise, Welhan and Craig, 1983) and gas potentially derived by Fischer–Tropsch Type reactions (green line fields) in geothermal systems (G-FTT: Socorro (red) Taran et al., 2010, and Salton Sea (orange), Mazzini et al., 2011), deep crystalline rocks (C-FTT: Lovozero and Khibiny as reported by Etiope et al. (2011c); Pre-Cambrian shields in Canada and South Africa; Sherwood Lollar et al., 2006) and serpentinization of ultramafic rocks (S-FTT including data from Lost City, Chimaera, Zambales, Oman, Poison Bay as reported by Etiope et al. (2011c)). Small blue crosses are data from abiotic–thermogenic mixed gas of Songliao, China (from Etiope et al. (2011c)). The red dashed line encompasses the “potential” abiotic field of CH_4 in serpentinization analog sites and includes isotopic signatures (positive δD_{CH_4} values) derivable by abiogenic oxidation observed in a natural gas (Etiope et al., 2011a). $\delta^{13}C$ and δD ranges of this field may be valid for Mars only assuming that the precursor C and H have isotopic signatures similar to those on Earth (martian non-fractionated atmospheric or magmatic C, and martian olivine H; see text). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

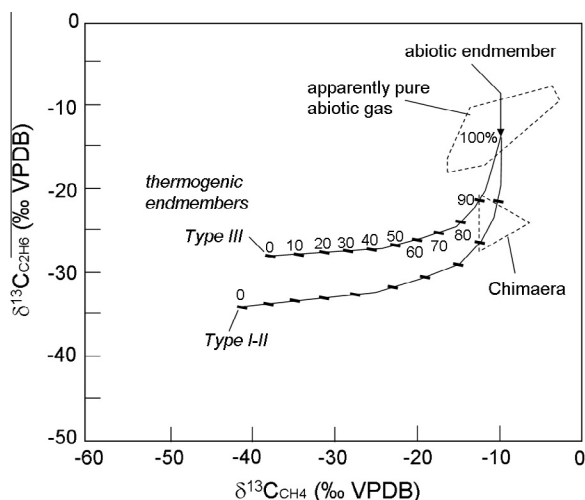


Fig. 7. A $\delta^{13}\text{C}_1$ (methane) vs. $\delta^{13}\text{C}_2$ (ethane) plot with mixing lines between two thermogenic endmembers (represented by natural gas from marine Type I–II and terrestrial Type III organic matter like that potentially located below the Chimaera ophiolitic rocks; Etiope et al., 2011c) and an abiotic endmember given by the average of the $\delta^{13}\text{C}_1$ and $\delta^{13}\text{C}_2$ values in gas considered to be derived by Fischer–Tropsch type processes in igneous inclusions and serpentinized ultra-mafic rocks (Lovozero, Khibiny, Lost City, and Oman, after Etiope et al. (2011c)). The plot shows that the presence of small (<10%) fractions of biotic gas mixed with abiotic gas does not significantly change the carbon isotopic composition of CH_4 , but is distinguished by the isotopic composition of ethane.

is actually mixed with a minor (10–20%) thermogenic (biotic) gas component, as suggested by the isotopic composition of ethane (C_2H_6) and carbon dioxide (Etiope et al., 2011c). Small amounts (<10%) of biotic CH_4 have little effect on the overall $\delta^{13}\text{C}_{\text{CH}_4}$ value, as evidenced in a CH_4 vs. C_2H_6 mixing plot (Fig. 7; Etiope et al., 2011c). The isotopic composition of ethane should then be used in conjunction with that of CH_4 to determine more precisely the occurrence of minor amounts of biotic gas.

The $\delta^{13}\text{C}$ vs. δD diagram alone does not allow recognition of the existence of minor biotic components in the abiotic genetic field; consequently, the presence of some biotic CH_4 cannot be excluded

for any terrestrial CH_4 isotopic signature typically considered abiogenic. Detection of ethane and its isotopic composition would be critical to unravel the gas origin

4.2. Potential C–H isotopic signatures of abiotic CH_4 on Mars

On Mars, the isotopic carbon signature of methane produced by Fischer–Tropsch type synthesis could be similar to that observed on Earth. The possible main CH_4 precursor on Mars is unfractionated atmospheric and/or magmatic CO_2 (Oze and Sharma, 2005), which would have $\delta^{13}\text{C}$ values in a range (–20‰ to 0‰; Niles et al., 2010), similar to that of CO_2 found in terrestrial serpentinized rocks (from –36‰ at Zambales, Abrajano et al., 1988; to ~–3‰ at Socorro; Taran et al., 2010).

In contrast, the hydrogen isotopic composition of martian CH_4 could have a much wider range than that on Earth (Chassefière and Leblanc, 2011). Hydrogen in the martian atmosphere and in minerals analyzed from martian meteorites is extremely enriched in deuterium (δD up to ~4000‰; Leshin, 2000; Sugiura and Hoshino, 2000). However, such enrichments are likely the result of atmospheric escape fractionation processes and may not be representative of all igneous rocks, magmas, or subsurface waters. Gillet et al. (2002) reported negative δD values ranging from –60‰ to –280‰ in martian olivine; moreover, magmatic glass in melt inclusions suggests that the δD of martian magma was low and that the initial H isotope signature of Mars may be similar to that of Earth (Boctor et al., 2003; Lunine et al., 2003).

Hence, a wide range of H isotopic values could be measured for martian CH_4 , and abiotically produced martian methane could be very deuterium-enriched, far outside terrestrial variations depicted in Fig. 6. However, martian δD – CH_4 values could be within the terrestrial range if the precursor hydrogen derives from primordial, unfractionated, magmatic gas (Boctor et al., 2003) or is similar to that of martian olivine (Gillet et al., 2002). As on Earth, low δD and δC values might imply the existence of microbes on Mars; this would open a wider discussion which is beyond the scope of this work.

5. Conclusions

Fig. 8 is a conceptualized sketch of the hypothesis made in this work. Terrestrial ophiolitic rocks, with on-going serpentinization and associated carbonate material, may generate considerable methane through low temperature abiotic synthesis in the presence of H_2 and CO_2 and metal catalysts, and have favorable gas-transport properties due to fracturing induced by serpentinization itself.

We have documented that serpentinized ultramafic rocks on Mars have some similar properties to terrestrial ones and may possess or have possessed favorable features for methane production and release to the martian atmosphere. Serpentinization-driven microfractures could provide enhanced pathways for methane generated within martian ultramafic rocks even in absence of tectonic activity. Like terrestrial serpentinized rock, martian serpentinized rock may be micro-fractured, e.g. olivine-bearing rocks near Terra Sirenum and near Syrtis Major and the Nili Fossae (where the Northern Summer 2003 CH_4 plume was reported; Mumma et al., 2009) may have higher secondary permeability in comparison with non-serpentinized areas. Thus, diffuse methane microseepage on the order of several $\text{mg m}^{-2} \text{d}^{-1}$, like that observed in terrestrial ophiolites, could occur in the serpentinized olivine-rich rock on Mars.

In the martian subsurface, methane can be produced at low temperatures (<50 °C) by a catalyzed reaction between H_2 and CO_2 . Low temperature reaction of olivine to produce the serpentine observed in some Noachian terrains could have resulted in past

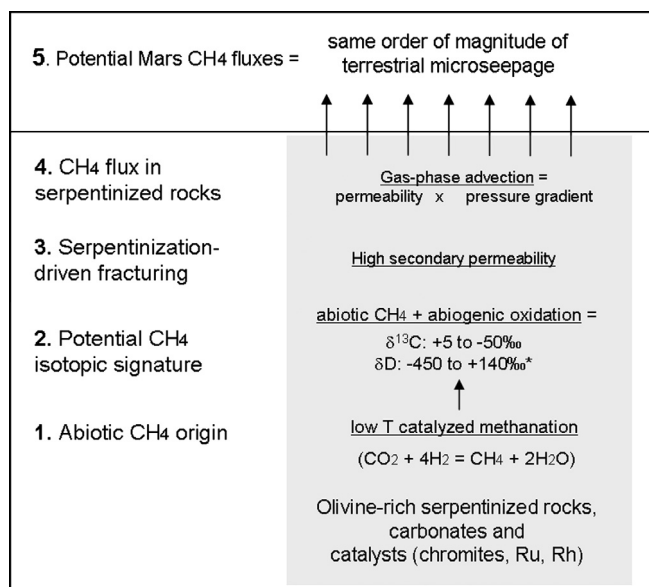


Fig. 8. Conceptual sketch of low temperature abiotic CH_4 production and exhalation potentially occurring on Mars based on terrestrial analogs. The $\delta^{13}\text{C}$ and δD ranges may be valid for Mars as discussed in Fig. 6.

methane production. On modern Mars, hydrogen gas could still be produced by present-day serpentinization if liquid water is available at depth; alternatively, the hydrogen may be a trapped, relict product of past serpentinization or other geologic processes. Carbon dioxide may derive from the atmosphere, magma degassing or carbonate material associated with the olivine-rich rocks.

Future rovers and landers may provide key elements to test the hypothesis proposed in this work. Regions of past serpentinization may be revealed by serpentine minerals exposed near the surface. If serpentinization is ongoing at depth, the released, reduced H₂-rich or CH₄-rich gases could result in the precipitation of carbonate minerals as well as reaction with iron oxides near the vent (Almeida-Filho et al., 2002). These zones might be spectroscopically distinct and mappable by remote mineralogic instruments. Chemical instruments can detect in situ evidence of fractionation of elements caused by rock reactions with reduced gases, and examination of the isotopic compositions of carbonate phases could indicate the nature of the formation process. Furthermore, low temperature methanation catalysts, such as ruthenium and rhodium, (so far identified only in martian meteorites) should be searched for in the olivine-rich outcrops, as they could be the key to allow for methane synthesis at the low temperature conditions characteristic of modern Mars.

However, only direct in situ detection of methane flux at an altered, mineralized site would definitively indicate a presently-ongoing methane production process. Instruments such as the gas chromatograph/quadrupole mass spectrometer/tunable laser spectrometer, comprising the Sample Analysis on Mars (SAM) instrument suite on the Mars Science Laboratory (Webster and Mahaffy, 2011), might be able to detect such gas production. The SAM Tunable Laser Spectrometer will search for atmospheric methane and measure its isotopic value. Nevertheless, the ideal system to detect methane (and other alkanes) would be a closed system, where gas can accumulate during exhalation from the ground, like in the closed-chamber (Fig. 1D), and isotopic composition measured before release to the atmosphere.

A wide range of C and H isotopic values could be measured in the CH₄ molecule on Mars, but the C isotopic composition may potentially be similar to that observed in terrestrial serpentinized rocks. On Earth, extremely positive δD values in CH₄ (beyond +100‰) are compatible with biotic gas origin (as discussed in Section 4.1; Etiope et al., 2011a). Although the D/H ratio is considered a fundamental biomarker, because biological systems prefer hydrogen (H) to deuterium (2H), samples from a natural gas in Romania (Etiope et al., 2011a) indicate that this preference can be masked by abiogenic oxidation, occurring in the absence of oxygen. As outlined by Onstott et al. (2006), the C and H isotopic ratio of CH₄ alone will not necessarily determine the gas origin. The Chimaera analog site suggests that the detection of ethane and its isotopic composition would be critical to unravel the gas origin on Mars.

Further studies of low temperature serpentinization analog sites on Earth are needed to understand better the mechanisms of methane production. Why are some ophiolites producing abundant gases and why are some “sterile”? What precisely controls whether or not CH₄, rather than H₂, is produced at low temperatures? It is essential to understand the role of low temperature methanation catalysts and the diagnostic signatures of biotic vs. abiotic processes. Connecting results from future terrestrial studies of serpentinizing systems with data from Mars exploration may yet reveal fundamental insights on the nature of serpentinizing systems and methane gas production on modern or ancient Mars.

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