Abiotic methane flux from the Chimaera seep and Tekirova ophiolites (Turkey): Understanding gas exhalation from low temperature serpentinization and implications for Mars

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A B S T R A C T

The emission of abiotic methane (CH4) into the atmosphere from low temperature serpentinization in ophiolitic rocks is documented to date only in four countries, the Philippines, Oman, New Zealand, and Turkey. Serpentinization produces large amounts of hydrogen (H2) which in theory may react with CO2 or CO to form hydrocarbons (Fischer–Tropsch Type synthesis, FTI). Similar mechanisms have been invoked to explain the CH4 detected on Mars, so that understanding flux and exhalation modality of ophiolitic gas on Earth may contribute to decipher the potential degassing on Mars. This work reports the first direct measurements of gas (CH4, CO2) flux ever done on onshore ophiolites with present-day serpentinization. We investigated the Tekirova ophiolites at Çirali, in Turkey, hosting the Chimaera seep, a system of gas vents issuing from fractures in a 5000 m² wide ophiolite outcrop. At this site at least 150–190 t of CH4 is annually released into the atmosphere. The molecular and isotopic compositions of C1–C5 alkanes, CO2, and N2 combined with source rock maturity data and thermogenic gas formation modelling suggested a dominant abiotic component (~80–90%) mixed with thermogenic gas. Abiotic H2-rich gas is likely formed at temperatures below 50 °C, suggested by the low deuterium/hydrogen isotopic ratio of H2 (δD/H: ~70‰), consistent with the low geothermal gradient of the area. Abiotic gas synthesis must be very fast and effective in continuously producing an amount of gas equivalent to the long-lasting (~2 millennia) emission of >100 t CH4 yr−1, otherwise pressurised gas accumulation must exist. Over the same ophiolitic formation, 3 km away from Chimaera, we detected an invisible microseepage of abiotic CH4 with fluxes from 0.07 to 1 g m−2 d−1. On Mars similar fluxes could be able to sustain the CH4 plume apparently recognised in the Northern Summer 2003 (106 or 108 t CH4 yr−1) over the wide olivine bedrock and outcrops of hydrated silicates in the Syrtis Major and Nili Fossae; just one seep like Chimaera or, more realistically, a weak, spatially sporadic microseepage, would be sufficient to maintain the atmospheric CH4 level on Mars.

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1. Introduction

While the exhalation of abiotic methane (CH4) in high temperature (>150–200 °C), volcanic or hydrothermal settings is quite common on Earth (e.g., Charlou et al., 2002; Fiebig et al., 2007; Taran et al., 2010; Welhan and Craig, 1983), the surface seepage of abiotic hydrocarbons in low temperature (<100–150 °C) environments was identified to date only in the Atlantic Lost City hydrothermal system (Bradley and Summons, 2010; Proskurowski et al., 2008) and, on land, in four countries — the Philippines, Oman, New Zealand, and Turkey, in correspondence with ophiolitic outcrops characterised by present-day serpentinization of ultramafic rocks (Abrajano et al., 1988; Fritz et al., 1992; Hosgürmez et al., 2008; Lyon et al., 1990; Sano et al., 1993). Methane-bearing ophiolites, however, may be more widespread and indications of active serpentinization on land (e.g., occurrence of H2, hyperalkaline springs) are known in several places (e.g., California, Canada, Italy, Romania; Barnes et al., 1967; Blank et al., 2009; Cardace et al., 2009; Filipescu and Humă, 1979; Monnin et al., 2011; O’Neil and Barnes, 1971). Abiotic hydrocarbons also occur within deep igneous and metasedimentary rocks (e.g., Sherwood Lollar et al., 2008) and, partially, within sedimentary basins (e.g., Jenden et al., 1993; Ni et al., 2009). However, to date the surface seepage of these gases has not been documented.

Abiotic hydrocarbons issuing from serpentinized ultramafic rocks (generally including gabbro and different types of peridotites, such as dunite, harzburgite and lherzolite) are mainly related to water-rock
interactions including low temperature olivine hydrolysis (Barnes et al., 1978; Fruh-Green et al., 2004); diatomic hydrogen ($H_2$) is produced through Mg-rich or forsteritic olivine via Fe$^{2+}$ oxidation and magnetite ($Fe_3O_4$) formation (e.g., McCollom and Bach, 2009; Oze and Sharma, 2005). Then, $H_2$ may react with $CO_2$ or CO producing $CH_4$ and heavier alkanes (abiotic methanogenesis) through mechanisms not exactly specified, and that may include Fischer–Tropsch Type reactions (FTT). The specific reaction with $CO_2$, producing only $CH_4$ ($CO_2 + 4H_2 = CH_4 + 2H_2O$) is the Sabatier reaction or methanation. Experimentally, FTT synthesis has been widely reported under hydrothermal conditions, at temperatures above 200 °C and high pressures, using natural catalysts (e.g., Foustoukos and Sfyried, 2004; McCollom and Seewald, 2006; Taran et al., 2010). Only recently has the production of $CH_4$ by olivine hydration at 30–70 °C been documented (Neubek et al., 2011). Methanation at room temperatures (<50 °C) and atmospheric pressure, starting from $H_2$ and $CO_2$ mixtures, has however been long proven with different catalysts (Jacquemin et al., 2010; Thampi et al., 1987). We can conclude, then, that low temperature FTT or methanation reactions may occur naturally under geologic conditions, expanding the environments on Mars has been recently questioned by some authors (e.g., Zahnle et al., 2010), a $CH_4$ plume was apparently found corresponding to serpentinized olivine-bearing rocks in the Martian regions of Syrtis Major and Nili Fossae (Ehlmann et al., 2010; Mumma et al., 2009). Terrestrial ophiolites which contain serpentinized ultra-mafic rocks may then represent "analogue" to Martian sites to study the actual production rates and fluxes of abiotic gases from low temperature serpentinization. However, $CH_4$ fluxes and exhalation modality (i.e., diffuse, pervasive throughout wide areas or confined within fractures, intermittent or continuous) on terrestrial onshore ophiolites, have never been investigated.

Here we present the first systematic measurements of methane flux ever done on terrestrial ophiolites. We investigated the ophiolitic outcrops of the Tekirova Unit in Turkey (Cirali, Antalya) which host what is probably the biggest onshore abiotic gas seep on Earth, "Chimaera" (de Boer et al., 2007; Hosgormez, 2007; Hosgormez et al., 2008). The macro-seep of Chimaera is composed by tens of large flames that are released from fractures within the area of the outcropping ophiolite. Previous studies have suggested that the gas, mainly composed of $CH_4$ and $H_2$, has at least 50% of abiotic $CH_4$ mixed with a thermogenic component (Hosgormez et al., 2008). A magmatic origin for the gas (de Boer et al., 2007) is unlikely since there is no evidence for intrusive igneous bodies in the sedimentary sequence below the ophiolitic block and deep temperatures are quite low (<80 °C at 3 km; Demirel and Gunay, 2000). Moreover there are no significant mantle signals in regard to carbon dioxide or nitrogen (Hosgormez et al., 2008). A minor mantle contribution suggested by the helium isotopic ratio (R/Ra: 0.41; Hosgormez et al., 2008) can be attributed to traces of remnant magmatic He in the ultramafic mantle rocks, as found in other ophiolitic sequences (e.g., Sano et al., 1993).

Instead, deep boreholes have revealed the presence, under the ophiolites, of mature Mesozoic and Paleozoic organic rich and bituminous source rocks up to depths of 6 km (Demirel and Gunay, 2000). The detailed account of gas released to the atmosphere has not yet been established. However, based only on the size of the flames (Hosgormez et al., 2008), a minimum total emission on the order of 50 t of $CH_4$ per yr has been estimated.

The objectives of this work were to better determine the amount of the abiotic component, to assess the amount and distribution of gas released into the atmosphere, and to verify the occurrence of gas exhalation from ophiolites outside the visible seepage manifestation of Chimaera. Molecular and isotopic compositions of $CH_4$, $C_2$, $C_3$, alkanes, $CO_2$, and $N_2$ were combined with source rock maturity data and thermogenic gas formation modelling. $CH_4$–$H_2$ isotope geothermometers were used to estimate the gas formation temperature. The flux of $CH_4$ and $CO_2$ was directly measured by closed-chamber system from both focused vents (macro-seepage) and diffuse, invisible ground exhalation: this includes miniseepage (a pervasive, medium–high gas flux, typically hundreds to thousands of mg m$^{-2}$ d$^{-1}$, generally surrounding the macro-seeps) and microseepage (lower $CH_4$ fluxes from soil, typically units up to hundreds of mg m$^{-2}$ d$^{-1}$, more distant from seeps or independent of seep occurrence; Etiope et al., 2011a). Finally, assuming the possibility that the observed ophiolitic degassing may also occur in the serpentinized rocks on Mars, we speculate on its significance for methane apparently detected in the Martian atmosphere.

2. Seep geology

The Chimaera seep (or Yanartaş, "flaming rock") is a famous archaeological site in the western Taurus region (Cirali, Antalya Gulf, Turkey; Fig. 1) that belongs to the Olimpos Beydağları Millik Park, which hosts a ruined temple to Hephaestus, the Greek god of fire (2nd century BC, Hellenistic period). The name “Chimaera” refers to the legendary monstrous female fire-breathing creature killed by Bellerophon (Homer, 2004). The existence of fires issuing from the ground dates back at least two millennia, as was even reported by Pliny the Elder in his Historia Naturalis. Today, gas is emitted from at least 50 main vents from fractures located within a 5000 m² wide ophiolitic outcrop. At least 20 vents burn continuously, producing flames up to a half metre in height. There are no water discharges, so all fractures emit only gas. No hot springs are known in the region. The ophiolites belong to the Tekirova Unit (Upper Cretaceous) which is part of the Neotethyan ophiolite complex exposed across the circum-Mediterranean region (Aldanmaz et al., 2009). Tekirova ophiolite at Cirali is an assemblage of ultra-mafic rocks, with a thickness of about 3 km (Bağcı et al., 2006), composed of peridotite and gabbro, and include serpentinized harzburgites with minor lherzolite, podiform dunites and chromitites, with a degree of serpentization ranging from ~30 to 65% (Aldanmaz et al., 2009; Juteau, 1968). Cirali–Tekirova ophiolite is particularly enriched of chrome, which has been widely mined in the past (Fig. 1). The ophiolitic unit has also incorporated organic-rich limestone belonging to the Paleozoic–Mesozoic basement. Below and adjacent to the ophiolitic block, the sedimentary sequence reaches a depth of at least 6 km, and it hosts three main source rocks with hydrocarbons generation potential (Demirel and Gunay, 2000; Hosgormez, 2007): Sapandere bituminous shale (Orдовик–Silurian, Type I and II organic matter), Beydağları limestone (lower Mesozoic, Type II, maturity of 0.4–1% Ro), and Pamucakyayla siltstones and coal (Carboniferous, Type III, 0.9–1% Ro). Further geological and petrographic details are reported by Bağcı et al. (2006), Juteau (1968), Hosgormez (2007), and Hosgormez et al. (2008).

3. Methods

Routine sampling and analytical methods were utilised for the gas released from a vent, as described in Etiope et al. (2011a). Gas vent samples were analysed for $C_1$–$C_5$ hydrocarbons, $He$, $H_2$, $Ar$, $O_2$, $CO_2$, $N_2$ (Carle AGC 100–400 TCD-FID GC; accuracy 2%), and isotopic compositions $\delta^{13}C$ of C$_1$ to C$_5$ alkanes, $\delta^{13}C_{DCH_4}$, $\delta^{12}C_{DOC}$, $\delta^{13}C_{DOC}$ (Finnigan Delta Plus XL mass spectrometer, precision ±0.1% for $^{13}C$ and ±2% for $^{12}C$) at Isotech Laboratories Inc. (Illinois, USA). $CH_4$ and $CO_2$ fluxes from the ground were measured with a closed-chamber system equipped with portable sensors and wireless data communication to a palm-top computer (West Systems srl, Italy); the gas fluxes are automatically calculated through a linear regression of the gas concentration build-up in the chamber. Maximum accumulation time of 15 min allowed detecting fluxes down to 10 mg $CH_4$ m$^{-2}$ d$^{-1}$ with a reproducibility better than 5% (Etiope et al., 2011a). Measurements were performed in 28 vents (macro-seeps) and in 27 points with
diffuse seepage (miniseepage) that were homogeneously distributed over 9800 m² in and around the ophiolitic outcrop (Fig. A2 in the Supplementary material). Additional 25 measurements were obtained far away from the seep, up to a distance of 3 km, in order to verify the occurrence of diffuse microseepage. Five measurements were obtained over faulted ophiolitic outcrops at Çirali Beach (Fig. 1and Supplementary material). To assess the origin of the methane fluxes detected here, air samples from the closed-chamber were collected with a syringe, stored in 12 cm³ evacuated glass vials, and analysed for the δ^{13}C/δ^{12}C ratio of CH₄ at the Stable Isotope Facility of University of California Davis, using a SerCon Cryoprep TGII trace gas concentration system interfaced to a PDZ Europa 20–20 isotope ratio mass spectrometer (Sercon Ltd., Cheshire, UK). Two laboratory standards (CH₄ gas diluted in helium) were used and calibrated against NIST 8560. Accuracy is ±1‰ and repeatability has a standard deviation of 0.22.

The methane output in burning vents was estimated using fire dynamics models of gas flux vs. flame size (Delichatsios, 1990; Hosgormez et al., 2008). Such a method provides an estimate of the order of magnitude of the gas emission, attributing at least a range of possible flux for each flame (details are in the Supplementary material). Total output from Chimaera macro-seepage was derived by summing the output from burning vents and the output from the main 50 non-burning emission points. The total output from miniseepage was estimated using a “natural neighbour” spatial interpolation between individual gas measurements. ‘Natural neighbour’ was tested in other seepage cases (Etiope et al., 2011a; Spulber et al., 2010) and it provides the best interpolation for irregularly spaced points avoiding the assignment of flux values to sectors that were not actually sampled. Flux values were expressed in “mg m⁻² d⁻¹” for CH₄ and “gm⁻² d⁻¹” for CO₂ in analogy with previous works on thermogenic gas seepage and biologic fluxes from soils.

4. Results and discussion

4.1. Gas origin

4.1.1. Abiotic vs thermogenic gas

Our new molecular and isotopic composition analyses confirmed the previous data acquired in 2008 (Hosgormez et al., 2008; Tables 1 and 2). The gas was determined to be mainly composed of CH₄ (~87 vol.%) and H₂ (~10 vol.%), with minor concentrations of N₂ (~2 vol.%), CO₂ (<0.1 vol.%), and C₂–C₆ alkanes (in total ~0.5 vol.%). The δ^{13}C and δD of CH₄ were approximately −12‰ and −129‰, respectively. In the δ^{15}Cvs.

Table 1
Molecular composition of Chimaera gas (vol.%).

<table>
<thead>
<tr>
<th>Sample</th>
<th>N₂</th>
<th>CO₂</th>
<th>H₂</th>
<th>CH₄</th>
<th>C₂</th>
<th>C₁</th>
<th>i-C₄</th>
<th>n-C₄</th>
<th>i-C₅</th>
<th>n-C₅</th>
<th>C₆+</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH2010</td>
<td>1.96</td>
<td>0.08</td>
<td>9.86</td>
<td>87.51</td>
<td>0.30</td>
<td>0.10</td>
<td>0.027</td>
<td>0.053</td>
<td>0.030</td>
<td>0.026</td>
<td>0.032</td>
</tr>
<tr>
<td>K01</td>
<td>4.91</td>
<td>0.07</td>
<td>7.46</td>
<td>86.94</td>
<td>0.31</td>
<td>0.10</td>
<td>0.031</td>
<td>0.035</td>
<td>0.034</td>
<td>0.056</td>
<td></td>
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<tr>
<td>K02</td>
<td>2.15</td>
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<td>9.43</td>
<td>87.78</td>
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<td>0.10</td>
<td>0.03</td>
<td>0.038</td>
<td>0.035</td>
<td>0.061</td>
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</tr>
<tr>
<td>K03</td>
<td>2.09</td>
<td>0.01</td>
<td>10.24</td>
<td>87.03</td>
<td>0.29</td>
<td>0.10</td>
<td>0.029</td>
<td>0.059</td>
<td>0.037</td>
<td>0.035</td>
<td>0.073</td>
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<td>0.01</td>
<td>10.04</td>
<td>86.81</td>
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<td>0.10</td>
<td>0.03</td>
<td>0.058</td>
<td>0.035</td>
<td>0.032</td>
<td>0.057</td>
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<td>0.02</td>
<td>11.30</td>
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<tr>
<td>K06</td>
<td>3.53</td>
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<td>10.40</td>
<td>86.50</td>
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<tr>
<td>GS9914</td>
<td>6.32</td>
<td>0.04</td>
<td>92.76</td>
<td>0.43</td>
<td>0.11</td>
<td>0.06</td>
<td>0.03</td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>GS9915</td>
<td>21.24</td>
<td>0.05</td>
<td>77.87</td>
<td>0.28</td>
<td>0.09</td>
<td>0.05</td>
<td>0.03</td>
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<tr>
<td>GS9916</td>
<td>34.2</td>
<td>0.07</td>
<td>65.24</td>
<td>0.17</td>
<td>0.13</td>
<td>0.07</td>
<td>0.02</td>
<td></td>
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<tr>
<td>GS9917</td>
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<td>93.22</td>
<td>0.15</td>
<td>0.13</td>
<td>0.06</td>
<td>0.03</td>
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<td>GS9918</td>
<td>14.49</td>
<td>0.16</td>
<td>84.66</td>
<td>0.30</td>
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<td>0.06</td>
<td>0.03</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Note. “K” data are from Hosgormez et al. (2008); “GS” data are from Hosgormez (2007), not corrected for air contamination. Blank spaces mean “not analysed.”
### Table 2: Isotopic composition of Chimaera gas.

<table>
<thead>
<tr>
<th>Sample</th>
<th>δ13C1</th>
<th>δD</th>
<th>δ13C2</th>
<th>δ13C3</th>
<th>δ13C4</th>
<th>δ13C5</th>
<th>δ15N</th>
<th>R/Ra</th>
</tr>
</thead>
<tbody>
<tr>
<td>K01</td>
<td>−15.1</td>
<td>−191.1</td>
<td>−7.88</td>
<td>−24.25</td>
<td>−25.54</td>
<td>−21.68</td>
<td>−21.71</td>
<td>−25.16</td>
</tr>
<tr>
<td>K02</td>
<td>−122.5</td>
<td>−11.74</td>
<td>−25.56</td>
<td>−26.34</td>
<td>−26.04</td>
<td>−21.68</td>
<td>−21.71</td>
<td>−25.16</td>
</tr>
<tr>
<td>K06</td>
<td>−19.6</td>
<td>−127.2</td>
<td>−11.9</td>
<td>−22.9</td>
<td>−23.7</td>
<td>−21.68</td>
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<tr>
<td>GS9914</td>
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<td>−11.6</td>
<td>−23.3</td>
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<td>−21.68</td>
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<td>−23.0</td>
<td>−23.5</td>
<td>−21.68</td>
<td>−21.71</td>
<td>−25.16</td>
</tr>
</tbody>
</table>

Note. δ13C, δD, VPDB; δ13N, VSMOW; R/Ra = (13C/12C)sample/(13C/12C)atmosphere; Ra = 1.39 × 10−4. “K” and “GS” as in Table 1.
Blank spaces mean “not analysed.”

### Figure 2: The methane δ13C vs. δD plot. Chimaera data are compared with biotic (from a global data-set owned by the authors) and abiotic gas (East Pacific Rise — EPR: Welhan and Craig, 1983; Socorro, Mexico: Taran et al., 2010; Lost City: Proskurowski et al., 2008; Lovozero and Khibiny Eudialyte, Russia: Potter et al., 2004; Songliao, China: Ni et al., 2009; Zambales, Philippines: Abrajano et al., 1988; Oman: Fritz et al., 1992; Kloof, Witwatersrand Basin, South Africa: Sherwood Lollar et al., 2006; and Poison Bay, New Zealand: Lyon et al., 1996).
thermogenic and abiotic endmembers indicate that the Chimaera gas has a thermogenic component of approximately 10–20% (Fig. 6). In this respect Chimaera would be similar to Khibiny urtite, which represents mixed gas at the Khibiny intrusion margin (Beeskow et al., 2006). Notwithstanding the uncertainties of the thermogenic and abiotic endmembers, it is clear that the Chimaera gas has a dominant abiotic origin. A subordinate thermogenic component can explain, however, the low isotopic values of C2+ alkanes, and is consistent with the presence of small amounts of thermogenic CO2 and N2.

4.1.2. The abiotic gas component
Apart from the minor thermogenic component, Chimaera is quite similar to other serpentinization gases reported in the literature (e.g., Abrajano et al., 1988; Bradley and Summons, 2010; Sano et al., 1993).

Fig. 3. Plot of $^{13}$C sequence of C1–C5 alkanes of Chimaera compared with other abiotic (red lines) and thermogenic (blue lines) gases. Lost City: Proskurowski et al. (2008); Lovozero and Khibiny: Potter et al. (2004); Songliao: Ni et al. (2009); Avalon, San Joaquin and low pressure pyrolysis: Chung et al. (1988); Murchison meteorite: Yuen et al. (1984).

Fig. 4. He isotopic ratios vs. $\delta^{13}$C02, assuming the course of CO2 is mixing between mantle-derived CO2 and CO2-derived from either organic or inorganic sedimentary material (the mixing curves are based on end-member values from Sano and Marty, 1995). Carbon dioxide isotope zonation after Hogormez et al. (2008) and Jenden et al. (1993). AO, aerobic hydrocarbon oxidation; KD, kerogen decarboxylation; AC, alteration of marine carbonates; BSM, biodegradation and secondary methanogenesis. Zambales, Oman and Socorro data are from the same references in Fig. 2.

Fig. 5. (a) Ethane vs. propane maturity plot (vitrinite reflectance, % Ro) of the Paleozoic–Mesozoic source rocks. Dashed horizontal lines define the maturity measured from borehole samples (Demirel and Guinay, 2000), and related isotopic C2 composition. Initial isotope values of marine (Types I and II) and terrestrial (Type III) kerogen are taken as $-27\%, -28\%$, and $-23.5\%$, respectively. (b) Thermogenic gas formation modelling from default Type I, II and III kerogen (calculated using Geochem Corp. GOR Isotopes software 1.94; heating rate of 5 °C per million yr).
where abiotic CH$_4$ is assumed to derive from FTT synthesis or Sabatier reaction (methanation of CO$_2$, i.e., CO$_2$ + 4H$_2$ $\rightarrow$ CH$_4$ + 2H$_2$O), although the presence of some mantle C in the CH$_4$ cannot be excluded a priori. The deuterium/hydrogen isotopic ratio of H$_2$ suggests however a quite low serpentinitization temperature; $\delta$D$_{H_2}$ = $-720$‰, is lower than that measured in other H$_2$-rich seeps ($-590$‰ of Zambales in the Philippines, Abrajano et al., 1988; $-699$‰ of Oman, Neal and Stanger, 1983; $-605$ to $-689$‰ of Lost City; Proskurowski et al., 2006). For Chimaera gas, the CH$_4$/H$_2$ fractionation factor 1000ln $\alpha$ is 1135 (following the standard notation used by Horibe and Craig, 1995 or Proskurowski et al., 2006). Assuming isotopic equilibrium between hydrogen and methane and insignificant subsequent isotopic exchange, and applying the CH$_4$/H$_2$ geothermometers by Bottinga (1969) and Horibe and Craig (1995) results in an isotope formation temperature of $\leq 50$ °C (Fig. 7), similar to that of the Oman seeps (Neal and Stanger, 1983). This is consistent with the low temperatures occurring in the Tekirova Unit ($\leq 80$ °C at 3 km, the maximum depth of the Çirali–Tekirova ophiolitic block; Bağcı et al., 2006; Demirel and Günay, 2000). The abiotic synthesis of methane is therefore proceeding at these low temperatures. This conclusion seems to be supported by recent laboratory experiments of Neubeck et al. (2011), who found a production rate of about 1.7 kg of CH$_4$ per tonne of olivine per yr, at only 30 °C.

Presently it is not clear whether CH$_4$ was actually originated by FTT or Sabatier reactions, but we can note that all ingredients necessary for such syntheses are available. Apart from the minor thermogenic component discussed above, CO$_2$ seems to be largely available either from the limestones, incorporated in the ophiolitic formation and adjacent in tectonic contact (see Fig. 1), or from serpentinitization reactions (some CO$_2$ is produced during the brucite–magnesite–hydromagnesite transformation). Calcite veins, quite diffuse in the ophiolite fractures, have a carbon isotopic ratio $\delta^{13}$C = $-11.2$‰ (VPDB), which may result from precipitation of mixed CO$_2$ (thermogenic and inorganic dissolved from the limestones). The isotopic value, however, also resembles that of CH$_4$ (Table 2) suggesting that some CO$_2$ forming calcite may derive from CH$_4$ oxidation.

Lastly, it is worth noting that the Tekirova ophiolite is particularly enriched in chromium minerals, which are potent FTT catalysts (e.g., Foustoukos and Seyfried, 2004); chromite mines, largely exploited in the past, are numerous throughout the Çirali area (Juteau, 1968 and Fig. 1). Specific mineralogical analyses of the Chimaera peridotite, including compositional and isotopic analyses of eventual fluid inclusions, would be required to better define the specific reactions during the serpentinitization and subsequent CO$_2$-reduction processes.

4.2. Gas flux

4.2.1. Macro-seep and miniseepage flux

At least 50 vents were counted, of which 20 were burning. The burning vents were actually composed by one or more flames and a surrounding non-burning zone where methane flux was detected by the closed-chamber. So, 50 non-burning points (30 independent of flames and 20 around the flames) plus 20 flames were considered in total. Methane flux measured in 28 non-burning points of different size was found to be on the order of $10^{-10}$–$10^6$ mg m$^{-2}$ d$^{-1}$ (macro-seepage), equivalent to a range of 0.05 to 2.2 t yr$^{-1}$. Summing the individual emissions from these vents gives a total output of 15 t yr$^{-1}$. Proportionally, the other 22 non-burning points (which have sizes similar to the measured ones) would give a total CH$_4$ output of about 12 t yr$^{-1}$. Total non-burning vents would then emit around 27 t yr$^{-1}$. The gas emission represented by the flames (determined as described in the Supplementary material) was estimated in the range of 32–75 t yr$^{-1}$. Total emission from macro-seepage...
(50 non-burning points plus 20 flames) is then about 60–100 t yr$^{-1}$. These values are similar to those measured in thermogenic gas seeps linked to deep and pressurised hydrocarbon reservoirs (e.g., see Table 4 in Etiope, 2009 and references therein).

Gas is then pervasively released throughout the ophiolitic outcrop (miniseepage), with fluxes found to range from 32 to 95,000 mg CH$_4$ m$^{-2}$ d$^{-1}$. It was interesting to note that gas exhalation, with rapid accumulation of methane in the chamber, occurred even in correspondence with exposed rock which is apparently unfractured and homogeneous; this phenomenon was confirmed in additional 20 points where the chamber was positioned on the rock for a few seconds, without flux calculations (Fig. A2, Supplementary material). Possibly the exhalation is taking place through diffuse and pervasive microfractures in the rock. The overall CH$_4$ seepage distribution is visualised in Fig. 8. CO$_2$ fluxes were generally lower (~10 g m$^{-2}$ d$^{-1}$) over exposed rocky ground, and higher (up to 65 g m$^{-2}$ d$^{-1}$) where soil layers covered ophiolitic rocks (Table A1 in Supplementary material), suggesting a contribution from biological soil respiration. In the biggest vents the volumetric ratios between the CH$_4$ flux and the CO$_2$ flux were similar to the compositional CH$_4$/CO$_2$ volume ratio (order of $10^3$); such a coherence, observed also in thermogenic seeps (e.g., Etiope et al., 2011a), indicates that the measurements at the vents are reasonably faithful. By using a generally lower (~150 g CH$_4$ m$^{-2}$ d$^{-1}$) for Chimaera methane output (macro-seepage plus miniseepage) is then estimated at ~90 t yr$^{-1}$. The total Chimaera methane output (macro-seepage plus miniseepage) is then ~150–190 t yr$^{-1}$ (~27,000 l of total gas per hour). This is comparable to the emissions measured in large and active thermogenic gas seeps and mud volcanoes in Italy, Romania, and Azerbaijan (Etiope, 2009), and it is higher than those from large (km-scale) magmatic volcanoes or geothermal manifestations (Etiope et al., 2007). For example, CH$_4$ emissions from Mt. Etna and from most Icelandic volcanoes are lower than 100 t yr$^{-1}$. The Semial ophiolite seeps in Oman and the Los Fuegos Eternos of Zambales in the Philippines are apparently smaller than Chimaera; however, the gas flux should still be rigorously investigated (Abrajano, personal communication; Neal and Stanger, 1983).

4.2.2. Abiotic microseepage outside the Chimaera ophiolite outcrop

Outside the Chimaera seep site, methane exhalation decreased to values of 40, 87, and 35 mg CH$_4$ m$^{-2}$ d$^{-1}$ up to 100 m from the seep, then fell below the detection limit (10 mg m$^{-2}$ d$^{-1}$). Positive methane fluxes were found to appear again approximately 3 km from Chimaera, along Cirali Beach (Fig. 1), in relation to an outcrop of ophiolites that were heavily fractured around a main fault zone. Five measurements provided 68, 82, 280, 344, and 1040 mg CH$_4$ m$^{-2}$ d$^{-1}$.

Similar flux values have been extensively reported for microseepage of thermogenic gas in various sedimentary basins (Etiope and Kusman, 2010). The isotopic analyses of CH$_4$ in the chamber, performed at two points (Cirali 4 and 5), displayed evidence for the release of $^{13}$C$_1$ enriched gas: beginning with an atmospheric value of ~47‰, $^{13}$C$_1$ values increased to ~41.2‰ after 10 min of chamber exposure, to ~36.6‰ after 15 min at the first point, and to ~29.9‰ after 15 min at the second point (Fig. 9). Assuming there is no isotopic fractionation artefact in the chamber, as shown for a similar closed-chamber method by Thielemann et al. (2000), a two-endmember mixing model would fit the seepage profile for gas with 90% of CH$_4$ and $^{13}$C$_1$ of ~15‰, a value very similar to that of Chimaera gas. This is the first documented case of invisible exhalation of abiotic CH$_4$ over ophiolites.

5. Implications for Mars

The future missions on Mars planned by NASA (National Aeronautics and Space Administration) and ESA (European Space Agency), such as the 2012 Mars Science Laboratory (MSL), the 2013 Mars Atmospheric and Volatile Evolution (MAVEN) orbiter and the 2016 ExoMars/Trace Gas orbiter, hopefully will clarify the doubts about the occurrence and variability of methane in the Martian atmosphere. If significant atmospheric methane were to be confirmed, it will be essential to verify whether the gas is actually related to serpentinization of ultramafic rocks, as presently proposed (Atreya et al., 2007; Oze and Sharma, 2005) and whether these serpentinized rocks may release enough methane to account for the atmospheric observations. Since ophiolites with low temperature and present-day serpentinization, such as those of Chimaera, are considered an important analogue for methane generation in the serpentinized ultra-mafic rocks on Mars (Blank et al., 2009; Szporar et al., 2010), we may speculate on the significance the gas fluxes we have measured have for the Martian atmosphere. It should be emphasised that the analogy refers to the serpentinized rocks and not to the fact that ophiolites are the product of tectonic thrusting, which is not the case for the hydrated silicate terrains on Mars.

An atmospheric CH$_4$ plume was apparently detected in the Northern Summer of 2003 over Syrtis Major and Nil Fossae regions (Mumma et al., 2009), which actually host serpentinized olivine-bearing rocks (Ehlmann et al., 2010; Hoefen et al., 2003). It was estimated that the plume reflects an episodic emission of ~19,000 t CH$_4$ yr$^{-1}$ (Mumma et al., 2009) or ~150,000 t CH$_4$ yr$^{-1}$ (Lefevre and Forget, 2009). If confirmed, such fluxes could be supplied by one hundred to one thousand macro-seeps like Chimaera. We believe however that the occurrence of such a large number of Chimaera-like seeps on Mars is quite improbable, as Chimaera represents, at least on Earth, a rare (probably unique) phenomenon. An
easier and more probable degassing scenario would be that of diffuse microseepage, as we detected over the ophiolites along the Çıralı beach: 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 Martian CH\(_4\) plume. If the entire 30,000 km\(^2\) olivine outcrop at the Nili Fossae (Hoefen et al., 2003) is assumed to exhale, then a microseepage <15 mg m\(^{-2}\) d\(^{-1}\) (4–5 times lower than the minimum detected at Çıralı) would be enough. Just one seep like Chimaera or a very weak microseepage sparse in different areas on Mars, would be sufficient to account for the global Martian CH\(_4\) source of 100–300 yr\(^{-1}\) which is required to maintain the 10–30 ppb atmospheric level (Atreya et al., 2007). Recent modelling of CH\(_4\) release on Mars actually suggested that the Northern Summer 2003 gas plume was formed by a broad source rather than a point emission (Mischna et al., 2011). The abiotic ophiolitic microseepage opens a new perspective for assessing the CH\(_4\) sources on Mars. Microseepage would be a simple degassing pathway in the Martian rocks, since: (a) it does not require the special focused gas flows and pressure gradients necessary for sustaining large seeps and active mud volcanoes (so it could occur on Mars even if macro-seeps were lacking or inactive); (b) it does not need liquid water: the gas migration mechanism would be basically related to single-phase gas advection (Brown, 2000; Etope and Martinelli, 2002); (c) it can then be either episodic (as required by the Martian model of Mischna et al., 2011) or quasi-permanent, depending on the underground gas pressure gradients and migration mechanisms (Brown, 2000); (d) it may be independent of the occurrence of gas hydrates or it may result from melting hydrates which eventually stored abiotic gas (on Earth, seepage of thermogenic gas was also found over deep permafrost; e.g. Yakushev and Chuvilin, 2000). A specific model of the possible microseepage migration mechanism in the ultra-mafic rocks of Mars should be developed. In any case, if the terrestrial ophiolite degassing can be applied to Mars, the search for the origin of Martian CH\(_4\), whether biotic or abiotic, should not necessarily be focused on “point” sources, since weak and diffuse microseepage throughout relatively large areas can be a primary degassing pathway. Other onshore ophiolitic sites with present-day serpentinization, (e.g., Blank et al., 2009; Spzonar et al., 2010) should however be investigated to verify the occurrence and extent of abiotic gas microseepage.

In view of the controversy that emerged on the existence of methane on Mars (Zahnle et al., 2011) we may consider our model of microseepage in serpentinized ultramafic rocks as support for the reality of CH\(_4\) on Mars that has been reported to be closely associated with ultramafic hydrates mineral complexes (Mumma et al., 2009).

6. Conclusions

The gas released from the Chimaera seep in the serpentinized Tekirova ophiolites has a dominant (80–90%) abiotic methane component. High concentrations of H\(_2\) (\(-10%\) v/v), low d\(_{\text{D,2}}\) (\(-720\)), and seepage through altered ophiolitic rocks are all suggestive of syntheses related to low temperature (certainly \(<100^\circ\)C) serpentinization, similar to those invoked for the abiotic gas of Zambales, in the Philippines, and Oman (Abrajano et al., 1988; Fritz et al., 1992). Chimaera produces one of the most deuterium-depleted hydrogen found in natural gas (Neal and Stanger, 1983; Sherwood Lollar et al., 2007).

With fluxes of at least 150 to 190 t of CH\(_4\) per yr, Chimaera is probably the largest abiotic gas seeps on land. By considering the long-lasting activity of the seep (>2 millennia), the continuous release of this amount of gas should be driven by high pressure gradients, possible only if pressurised gas accumulation exists (in analogy with what observed in thermogenic gas seeps), otherwise low temperature abiogenic synthesis must be very fast and effective in continuously producing an amount of gas equivalent to that released to the atmosphere. Such a possibility could be investigated by laboratory experiments on low temperature synthesis, as those preliminarily reported by Neubeck et al. (2011), especially if based on chromium catalysis (as those of Foustoukos and Seyfried, 2004). Over the same ophiolitic formation, 3 km away from Chimaera, we also detected an invisible microseepage of abiotic CH\(_4\) with fluxes from 0.07 to 1 g m\(^{-2}\) d\(^{-1}\). Until now, though theoretically postulated (Etope et al., 2011b), the existence of invisible microseepage of abiotic gas from ophiolites was not documented on Earth; so far microseepage was only known for biotic (thermogenic or microbial) natural gas in petroleum sedimentary basins (Brown, 2000; Etope and Klusman, 2010). The large emission of abiotic methane by Chimaera macro-seepage and the pervasive microseepage far from the macro-seep site indicate a considerable gas generation potential of ophiolites with low temperature serpentinization. If similar fluxes would occur in the serpentinized ultra-mafic rocks on Mars, they would be more than enough to sustain the methane levels apparently detected in the atmosphere of the red planet.

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