Chapter 7
Seepage in Serpentinised Peridotites and on Mars

Thus far, this book has mainly addressed the classical seepage of natural gas of biotic (microbial and thermogenic) origin in sedimentary rocks. However, it is also known that methane and other light hydrocarbons can be abiotically produced (i.e., by chemical reactions that do not directly involve organic matter). Abiotic production may occur over a wide range of temperatures and pressures and within a variety of geological systems. Two main classes of abiotic CH_4 generation processes can be distinguished, magmatic and gas-water-rock interactions. For details, the reader is referred to the review of Etiope and Sherwood Lollar (2013). Here, it is important to keep in mind that while magmatic or mantle-derived CH_4 is abiotic, not all abiotic CH_4 is mantle derived. Magmatic and high temperature hydrothermal processes in volcanic and geothermal systems produce a gas mixture that is mainly composed of carbon dioxide (CO_2), while abiotic methane is a very minor component. Indeed, field observations suggest that the majority of abiotic gas on Earth's surface is produced by low-temperature, gas–water–rock reactions. Of particular interest are the Fischer-Tropsch Type (FTT) reactions, the mechanism most widely invoked for explaining large quantities of abiotic CH_4 seeping to the surface. In the sub-chapters that follow, only CH_4-rich abiotic gas seeping to the surface is considered. Such seepage generally occurs in serpentinised ultramafic rocks (peridotites). Serpentinisation (the hydration of olivine and pyroxene minerals, which leads to the formation of H_2 and the subsequent production of CH_4 through FTT synthesis) is considered a fundamental step in the origin of life, representing the primordial passage from inorganic to organic chemistry (Russell et al. 2010). Serpentinisation can also be a source of methane in atypical petroleum systems where hydrocarbon reservoirs are formed by or are adjacent to igneous rocks (Sect. 7.1.2), and a potential source of methane on other planets, such as Mars (Sect. 7.2).

G. Etiope, *Natural Gas Seepage*, DOI 10.1007/978-3-319-14601-0_7

7.1 Seeps and Springs in Active Serpentinisation Systems

7.1.1 Where Abiotic Methane Is Seeping

Abiotic methane seeps have been discovered in an increasing number of countries, beginning from the 1980s with the pioneering work of Abrajano et al. (1988) and Lyon et al. (1990) who reported unusual gas, with large concentrations of CH_4 and H_2, issuing from ultramafic rocks in the Philippines (the Los Fuegos Eternos of Zambales) and New Zealand (Poison Bay). Similar gas was then reported in Oman (Fritz et al. 1992; in the Semail ophiolite springs) and in Turkey (Hosgormez et al. 2008; Etiope et al. 2011b; in Chimaera fires; Fig. 7.1). Recent isotopic analyses have also indicated a dominant abiotic origin for methane seeping from serpentinised

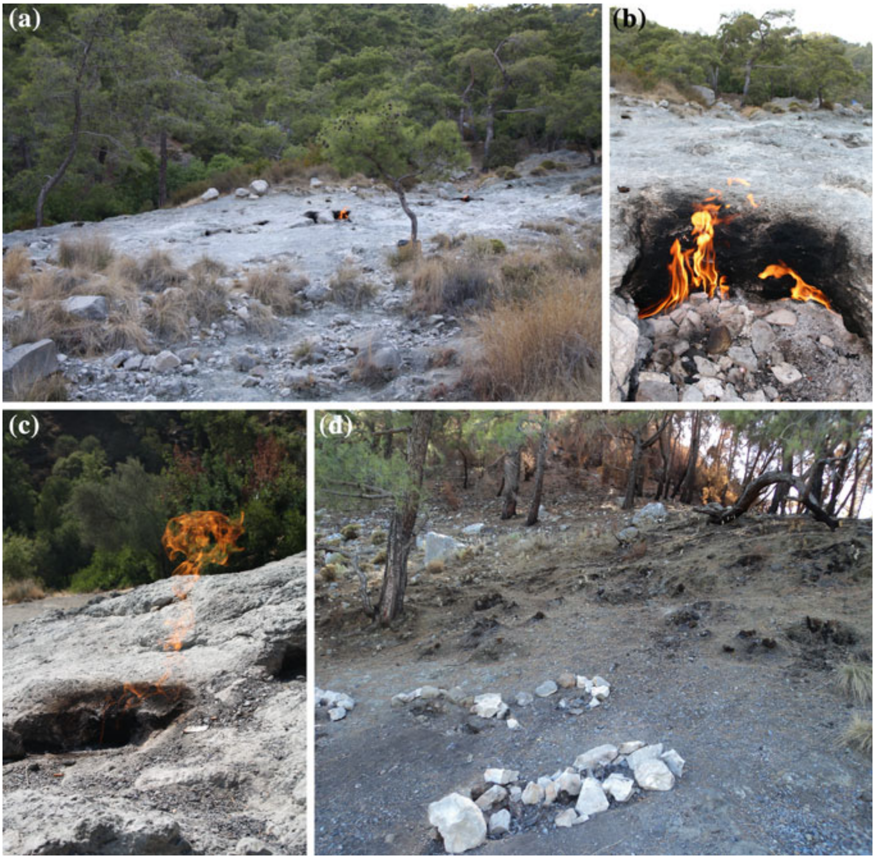

Fig. 7.1 The burning gas seep of Chimaera, near Cirali (Turkey). **a** A general view of the peridotite outcrop with the natural flames; **b**–**c** two perennial flames from fractured ground; **d** a second seepage site, with burned trees, on the Olympos Mountain a few hundreds meters north of Chimaera

peridotites in Italy (Boschetti et al. 2013; the Genova hyperalkaline springs, Fig. 7.2d), Greece (Etiope et al. 2013b; the Othrys ophiolite), Portugal (Etiope et al. 2013c; the Cabeço de Vide springs), Japan (Suda et al. 2014; the Hakuba-Happo springs), Spain (Etiope et al. 2014; the Ronda peridotites; Fig. 7.2b–c), the United Arab Emirates (Etiope et al. 2015; Fig. 7.2a), and again in Turkey (Yuce et al. 2014; Amik Basin) and New Zealand (Pawson et al. 2014; Dun Mountain ophiolite). Gas in similar serpentinised rocks has also been reported in Serbia (Milenic et al. 2009; the Zlatibor ophiolite), Norway (Okland et al. 2012; the Leka ophiolite), Canada (Szponar et al. 2013; the Tablelands), California (Morrill et al. 2013; The Cedars springs), New Caledonia (Monnin et al. 2014; Prony Bay), and Costa Rica (Sanchez-Murillo et al. 2014; the Santa Elena ophiolite). However, the isotopic data required

Fig. 7.2 Gas-bearing springs **a** in the United Arab Emirates (Al Farfar; photo by J. Judas), **b–c** in the Ronda peridotite massif, Spain (Del Puerto Spring with bubble plumes; photos by I. Vadillo), and **d** near Genova, Italy (the bubbling vent at Acquasanta; photo by M. Whiticar)

Table 7.1 A list of land-based serpentinisation sites where methane seepage (or transport by hyperalkaline waters) has been documented (updated December, 2014)

Country	Site	Setting	References
Methane C–H isotopes determined			
Greece	Othrys Mt. (Archani, Ekkara)	Ophiolite	Etiope et al. (2013b)
Italy	Voltri-Genova (e.g., Acquasanta)	Ophiolite	Boschetti et al. (2013)
Japan	Hakuba-Happo	Orogenic massif	Suda et al. (2014)
New Zealand	Poison Bay	Ophiolite	Lyon et al. (1990)
New Zealand	Red Hills, Dun Mountain	Ophiolite	Pawson et al. (2014)
Oman	Semail (e.g., Al Khaoud, Nizwa)	Ophiolite	Fritz et al. (1992), Boulart et al. (2013)
Philippines	Zambales (Los Fuegos Eternos)	Ophiolite	Abrajano et al. (1988)
Portugal	Cabeço de Vide	Igneous intrusion	Etiope et al. (2013c)
Spain	Ronda peridotites	Orogenic massif	Etiope et al. (2014)
Turkey	Chimaera	Ophiolite	Etiope et al. (2011b)
Turkey	Amik Basin (Kurtbagi, Tahtakopru)	Ophiolite	Yuce et al. (2014)
U.A.Emirates	Al Farfar	Ophiolite	Etiope et al. (2015)
Incomplete or missing C–H isotope analyses			
Canada	Tablelands	Ophiolite	Szponar et al. (2013)
Costa Rica	Santa Elena	Ophiolite	Sanchez-Murillo et al. (2014)
New Caledonia	Prony Bay Fiordland	Ophiolite	Monnin et al. (2014)
Norway	Leka	Ophiolite	Okland et al. (2012)
Philippines	Zambales (Manleluag)	Ophiolite	Meyer-Dombard et al. (2013)
Philippines	Palawan (Brooke's Point)	Ophiolite	Meyer-Dombard et al. (2013)
Serbia	Zlatibor	Ophiolite	Milenic et al. (2009)
US—California	The Cedars	Ophiolite	Morrill et al. (2013)

for CH_4 origin assessments are missing or incomplete (for some of these studies only the stable carbon isotopic composition of CH_4 is available). The list of known methane-bearing serpentinisation seeps and springs, updated for 2014, is reported in Table 7.1. Geographic distribution of those for which the abiotic origin of CH_4 is suspected at least on the basis of the C and H isotopic composition, is shown in Chap. 2, Fig. 2.8.

Land-based peridotites generally belong to an ophiolite (mantle rock obducted on continents), an orogenic peridotite massif, or a batolith intrusion. Abiotic gas can reach the surface while dissolved in groundwater (with concentrations on the order of 0.1–10 mg CH_4/L in springs or in shallow groundwater boreholes), or as a free phase in gas seeps (up to 87 vol.%) and microseepage in the soil (see below). Groundwater is typically of meteoric origin, of the calcium hydroxide (Ca^{2+}–OH^{-}) hydrochemical type and hyperalkaline, with a $pH > 9$; these are specific features of active serpentinisation systems resulting from the liberation of OH^{-} and Ca^{2+} during the hydration of olivine and pyroxenes. The hydrochemistry details of these serpentinisation waters have been reported, for example, in Barnes and O'Neil (1969), Bruni et al. (2002), and Marques et al. (2008). Emissions of abiotic gas related to serpentinisation have also been discovered at a few deep-sea hydrothermal sites located in the Mid-Atlantic Ridge (the Lost City, Logatchev, Rainbow, Ashadze), the Central Indian Ridge (Kairei), and the Mariana Forearc (Charlou et al. 2002; Proskurowski et al. 2008; Schrenk et al. 2013), although the complete C and H isotopic composition of CH_4, at the time this chapter was written, is only available for the Lost City and Logatchev. Abiotic methane is also known to occur in deep boreholes within Precambrian crystalline shields (e.g., Sherwood Lollar et al. 1993) although seepage to the surface has, thus far, not been reported.

In practice, most abiotic methane seeps have been observed on land in correspondence with serpentinised ultramafic rocks along the Alpine-Himalayan orogenic belt (Jurassic-Cretaceous), the Western Pacific and Cordilleran ophiolite belts (Paleozoic-Tertiary), and the Paleozoic plutons. The following chapters refer to the methane observed in these environments, not to gas located in high temperature deep-sea serpentinisation settings for which the reader may refer to the review paper of Schrenk et al. (2013).

7.1.2 How Abiotic Methane in Land-Based Serpentinisation Systems Is Formed

Abiotic methane formation was first recognized in the laboratory in 1913 when Paul Sabatier received the Nobel Prize for discovering that methane can be generated by reacting CO_2 and H_2 with metal catalysts. In 1925, Franz Fischer and Hans Tropsch succeeded in synthesizing more complex hydrocarbons using CO and H_2. The Sabatier reaction, also known as "hydrogenation of CO_2", and the Fischer-Tropsch reaction (with CO) are today cumulatively termed *Fischer-Tropsch Type* (FTT) reactions.

The origin of abiotic gas in serpentinisation systems is generally attributed to these FTT reactions, involving H_2 and a carbon-bearing compound (CO_2, CO, HCOOH), as discussed in a wide array of scientific literature (Etiope and Sherwood Lollar 2013; McCollom 2013, and references therein). A general form of the FTT reaction is the following:

$$nCO + (2n + 1)H_2 \rightarrow C_nH_{(2n+2)} + nH_2O \qquad (7.1)$$

or for CO_2, in aqueous solutions:

$$CO_2(aq) + (2 + m/2n)H_2(aq) = (1/n)C_nH_m + 2H_2O \qquad (7.2)$$

and in the gas-phase:

$$CO_2 + 4H_2 = CH_4 + 2H_2O \qquad (7.3)$$

The last reaction is also known as the Sabatier reaction. H_2 is directly produced via serpentinisation, peridotite (olivine and pyroxene) hydration driven by seawater (in submarine environment) or meteoric water (on land) (e.g., McCollom and Seewald 2007; Schrenk et al. 2013). An alternative mechanism for CH_4 production could be the one occurring via the hydration of olivine in the presence of CO_2, without the initial mediation of H_2; such a process is theoretically possible (Oze and Sharma 2005; Etiope et al. 2013b; Suda et al. 2014) but not easily identifiable (Whiticar and Etiope 2014a) and has not, to date, been demonstrated in the laboratory.

The abiotic synthesis of methane following serpentinisation is considered to be a fundamental step in the prebiotic chemistry and origin of living matter (Russell et al. 2010). Serpentinisation during the Archean may have provided the necessary reducing and high-pH conditions and the relatively low temperatures appropriate for supporting early life. Methane, in particular, was an effective energy source (electron donor) for the development of biomolecules and microrganisms on early Earth. Whether this occurred in ocean floor hydrothermal systems or in continental rocks is an open question.

FTT reactions take place on the surface of a metal (catalyst), lowering the activation energy needed for the reaction (Fig. 7.3); the higher the temperature, the easier methane production.

Many metals (Fe, Ni, Co, and Cr) are known to effectively catalyse the reaction at high temperatures, generally above 200 °C (e.g., Horita and Berndt 1999; Taran et al. 2007; McCollom 2013). FTT reactions are very sluggish in aqueous solutions. As a result, high temperatures are even more important for water saturated rocks. Nevertheless, land-based serpentinisation rock systems are characterised by relatively low temperatures, generally below 100 °C (Bruni et al. 2002; Etiope et al.

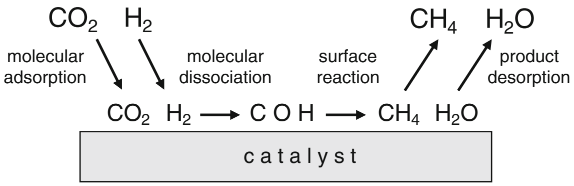

Fig. 7.3 Sketch of methane production via Sabatier reaction, between CO_2 and H_2, catalysed on a metal surface

2013b; Suda et al. 2014; Monnin et al. 2014). The thickness of ophiolite nappes, for example, is generally on the order of a few km, up to 4–5 km, and low geothermal gradients, typical of these areas, suggest maximum temperatures at the deepest ultramafic rock sectors of 100–120 °C. The maximum temperature, at the base of the 3-km deep Tekirova ophiolite in Turkey (where the Chimaera seep is located), is 80 °C (Etiope et al. 2011b). FTT reactions and methane production at such low temperatures are not obvious. Therefore, the following series of questions arise:

(a) Was methane produced at higher temperatures (>200 °C) when peridotites were still influenced by ocean hydrothermal conditions (and the gas was preserved after peridotite obduction or emplacement in the orogen)?
(b) Was methane produced at higher temperatures (>200 °C) during the early stages of peridotite emplacement on land, for example, near the high-temperature "metamorphic sole" (the shear zone) at the base of the ophiolite?
(c) If methane was, instead, formed after the peridotites were emplaced on the continent, at present-day temperatures, did the FTT reaction take place in dry rock or in an aqueous solution?
(d) And, if so, what catalyst was capable of supporting the reaction at temperatures <100 °C?

At present, conclusive answers cannot be determined, although some reasoning is outlined below.

Some land-based peridotites, in ophiolites, orogenic massifs, or intrusions, may conserve the residual gases formed or those that were present during hydrothermal conditions for mantle extrusion on the ocean floor. Such gases such as helium and methane of magmatic origin and methane from high temperature, water-rock-interactions, today, may be found in certain fluid inclusions within the minerals of continental peridotites or within the surrounding mafic rocks (e.g., Sachan et al. 2007). Gas in these inclusions are, in fact, well protected and may survive inside peridotite during obduction or orogenic tectonisation and fracturing. Gas dispersed in peridotite fractures on the ocean floor hardly remained; and it is difficult to imagine that the large amounts of gas observed today in land-based peridotites derived from fluid inclusions alone, or are, in any way, the same gas formed in ancient oceanic hydrothermal systems. A more plausible explanation is that the abundant methane today observed in seeps was formed during the initial stages of ophiolite formation when the "metamorphic sole" (the shear zone at the base of the ophiolite above the sedimentary crust) was still "warm". Detailed studies on ophiolite cooling following obduction are necessary for evaluating such a possibility. However, if such is the case, methane would not be genetically related to low temperature (<100 °C) serpentinisation and the hydrogen identified in many land-based peridotites.

If, instead, methane was formed during present-day low temperature conditions, we need to understand how low-temperature FTT reactions can occur. Below 100 °C, FTT reactions in aqueous solutions are extremely sluggish. Some scholars have assumed, however, that CH_4 is formed in the hyperalkaline waters observed on the seafloor or in onshore springs. Analyses of the radiocarbon contained in CH_4

(^{14}C-CH_4) have indicated that, generally, the carbon is older than 50,000 years (percent of modern carbon ~0; Abrajano et al. 1990; Etiope and Schoell 2014; Whiticar and Etiope 2014b; Etiope et al. 2014), while carbon in the hyperalkaline waters is typically a few thousand years old (e.g., Marques et al. 2008; Whiticar and Etiope 2014b). As a result, methane was formed from carbon that is not related to that occurring in the waters. Furthermore, for high pH, CO_3^{2-} is the only available carbon source dissolved in the water, and the aqueous reaction would be (e.g., Mottl et al. 2004):

$$4H + CO_3^{2-} = CH_4 + H_2O + 2OH^- \tag{7.4}$$

The problem, experts of catalysis say, is that CO_3^{2-} does not significantly react with H_2 on metals, especially at low temperatures. The easiest way to produce CH_4 at temperatures below 100 °C is through the Sabatier reaction in a dry system (reaction 7.3). CH_4 could derive from the H_2 and fossil, ^{14}C-free CO_2 that originate in different, separate systems. H_2 would come from serpentinisation in peridotites. Fossil CO_2 may derive from limestone, any C-bearing rock, mantle or even ancient (older than 50,000 years) atmospheric air. The source rock of abiotic methane would then be a rock that offers the best conditions for FTT reactions, i.e. abundant catalysts (metals) and the mixing of H_2 and CO_2. What are these "magic" rocks and catalysts that allow low temperature CO_2 hydrogenation?

The only catalysts known to be effective below 100 °C, at least on laboratory time scales, are rhodium (Rh) (Jacquemin et al. 2010) and ruthenium (Ru) (Thampi et al. 1987). Rhodium is extremely rare and dispersed in parts-per-billion concentrations within ultramafic rocks. Ruthenium is rare in submarine hydrothermal systems (Pasava et al. 2007) but within the chromitites of many continental ophiolites and igneous complexes it is a dominant Platinum Group Element (PGE), reaching parts-per-million concentration levels (e.g., Economou-Eliopoulos 1996). Ru is mainly found in the form of sulphur minerals such as laurite (RuS_2) or ruthenian pentlandite ($(Ni,Fe)_8RuS_8$), or as Ru-Ir-Os alloys or oxides (RuO_2) (Garuti and Zaccarini 1997). All these Ru forms are found in either stratiform or podiform chromitites with Ru concentrations typically in the range of 0.1–1 ppm (relative to mass chromitite) and up to several ppm in Cr-rich veins (e.g., Page and Talkington 1984; Bacuta et al. 1990). In ophiolite sequences, Ru-enrichments are preferentially located within tectonite and Moho transition zones, particularly in crustal dunite (Prichard and Brough 2009; Mosier et al. 2012). As a result, there is a surprising coincidence between the location of Ru-rich chromitites and the presence of methane. Most of the land-based serpentinisation seeps documented thus far are adjacent to chromite mines or located above ultramafic rocks hosting Ru-enriched chromitites. Examples include the Chimaera fires in Turkey, located near the ancient chrome mines of Cirali (Juteau 1968), the Semail ophiolite in Oman (Page et al. 1982), the Othrys ophiolite in Greece (Garuti et al. 1999), the Zambales in the Philippines (Bacuta et al. 1990), Newfoundland in Canada (Page and Talkington 1984), and the Cabeço de Vide in Portugal (Dias et al. 2006). Deep boreholes, providing abiotic gas from crystalline Precambrian rocks at Sudbury in Canada (Sherwood Lollar et al. 2008), are located in one of the richest Ru mines in North America (Ames and Farrow 2007). Furthermore, large amounts of methane leading to explosions have been reported in what is likely the world's largest Ru mine complex, Bushveld, located in South Africa (Cook 1998). Recent laboratory experiments have demonstrated that abiotic methane can actually be produced by the Sabatier reaction at temperatures below 100 °C (even at room temperature, 20–25 °C) using ruthenium at concentrations equivalent to those occurring in chromitites in ophiolites or in igneous complexes (Etiope and Ionescu 2014). Therefore, Ru-enriched chromitites are good candidates for inorganic source rocks in land-based serpentinisation systems. Alternatively, we may assume that traditional and more abundant catalysts, Fe, Ni, and Cr are also effective on longer, geological time scales, although this cannot be experimentally confirmed in the laboratory.

In summary, it seems that the most logical answers to the questions above are as follows:

(a) Methane could be produced at high temperatures (>200 °C) during the early stage of ophiolite emplacement near the metamorphic sole, but not under seafloor hydrothermal conditions; and methane is not related to low T serpentinisation and hydrogen.
(b) Methane could be produced at low temperatures (<100–150 °C) and on geological time scales with the support of traditional catalysts (Fe, Ni, and Cr), but this process could not be demonstrated in human time-scale laboratory experiments.
(c) Methane could be produced more rapidly at low temperatures (<100 °C) with the support of ruthenium-based catalysts in chromitites, as already demonstrated in the laboratory.

If these inorganic source rocks occur within or adjacent to a Total Petroleum System (see the definition provided in the Introduction), it is possible that portions of the generated abiotic gas may migrate and mix with biotic natural gas in sedimentary rocks. Since serpentinisation produces microfracturing and increases the permeability of peridotite, these igneous rocks can also directly act as hydrocarbon reservoirs in atypical and deep petroleum systems (Farooqui et al. 2009; Schutter 2003). Serpentinised rocks, for example, form reservoirs for oilfields in Texas and Cuba (Smith et al. 2005). Petroleum pools have also been suggested to incorporate trace metals from reservoir igneous rocks (Szatmari et al. 2011), implying the exchange of material between hydrocarbon fluids and the hosting minerals. The occurrence of minor amounts of abiotic gas in commercial fields has been suggested in China, for example, in the Songliao Basin (Dai et al. 2005; Ni et al. 2009) and in the United States (Jenden et al. 1993). Until the early 1990s, commercial accumulations of abiotic CH_4 have not been identified by the petroleum industry and far less than 1 % of the CH_4 in most oil and gas fields is abiotic (Jenden et al. 1993). However, as shown in Sect. 7.1.3, abiotic methane may have a carbon isotopic composition that overlaps that of biotic gas, and minor amounts of abiotic gas mixed with biotic gas may not be recognised using C and H isotopes. In addition, as suggested by recent laboratory experiments (Etiope and Ionescu 2014), low temperature FTT reactions can produce CH_4 with a large C isotope fractionation between CO_2 and CH_4, leading to relatively “light” (^{13}C-depleted) CH_4, resembling microbial gas. As a result, the origins of gas, within atypical petroleum systems characterised by igneous rocks, should be re-examined using modern geochemical interpretative techniques (Etiope and Sherwood Lollar 2013).

7.1.3 How to Distinguish Abiotic and Biotic Methane

As described in Chap. 1, combining stable carbon and hydrogen isotopes of CH_4 is the first, basic step for determining the origin of methane. Until a few years ago and based on a limited amount of data, the isotopic composition of abiotic gas was considered to be typically enriched in ^{13}C, when $\delta^{13}C$ values are above −25 ‰. Today, a wide set of data is available that allows us to draw a new isotopic picture of abiotic methane. The $\delta^{13}C$ of methane in land-based serpentinised ultramafic rocks can have values of up to −37 ‰, while the methane from Precambrian shields can be even lighter (Etiope and Sherwood Lollar 2013). Figure 7.4a provides an updated diagram of $\delta^{13}C$ versus $\delta^{2}H$ for the methane released from land-based serpentinisation seeps or springs. Figure 7.4b compares this methane with that found in the following four types of geological settings: Precambrian crystalline shields, Mid-Ocean Ridge serpentinisation, inclusions in intrusive alkaline rocks, and volcanic and geothermal fluids. The isotopic distinction between biotic and abiotic is quite clear. The diagram, however, is only the first step for determining the abiotic origin of gas and cannot be revealed if the methane is completely abiotic or mixed with some biotic components. Additional interpretative tools are necessary and may include the use of noble gases (helium isotopes), Schulz-Flory distribution tests, the molecular and isotopic composition of associated gases (other hydrocarbons and CO_2), and methane vs. ethane mixing plots (Etiope and Sherwood Lollar 2013). In any case, knowledge of the geological context is an essential precondition for final interpretations.

Figure 7.4a–b indicates that methane seeping from land-based serpentinisation sites may have a wide range of C and H isotopic composition. The result is likely due to the variety in the isotopic composition of the carbon feedstocks involved in the production of CH_4 (CO_2 or other C-bearing molecules that may derive from the mantle, limestone, the atmosphere, or metasedimentary rocks), the temperature of the CH_4 generation mechanism, isotopic fractionations in the presence of H_2O (especially for $\delta^{2}H_{CH4}$), and the degree of the reaction itself (Etiope and Ionescu 2014).

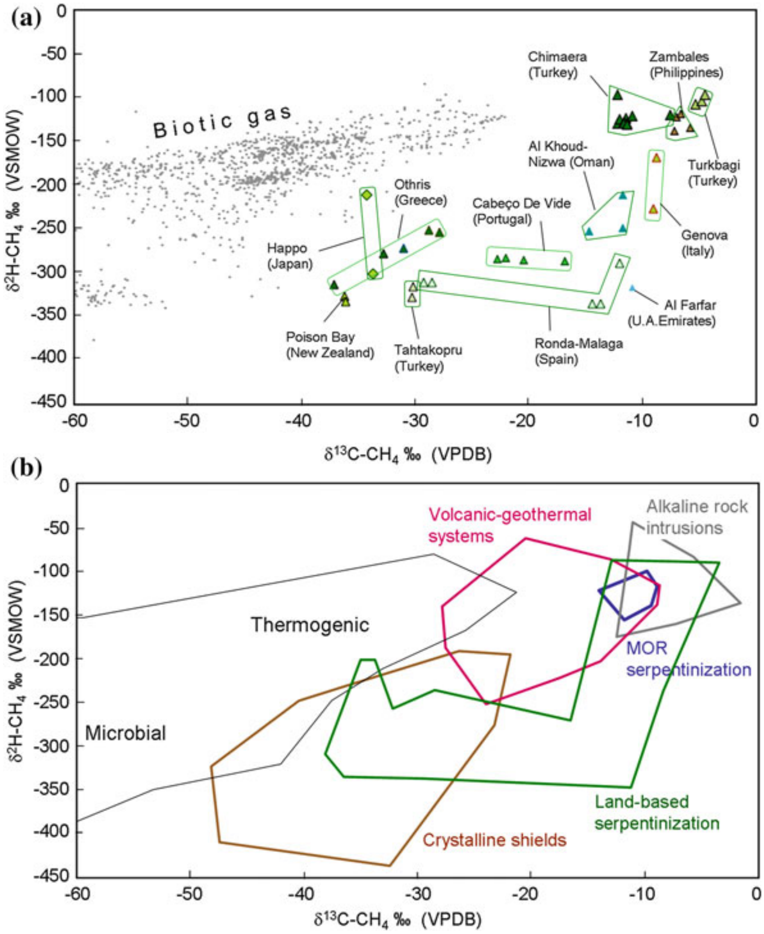

Fig. 7.4 **a** The C and H isotopic diagram for methane discharged in seeps and springs in land-based serpentinised peridotites, as listed in Table 7.1. **b** An isotopic diagram distinguishing fields relative to the abiotic methane shown in (**a**) from other abiotic methane documented in Mid-Ocean Ridges (MOR) (i.e., the Lost City and Logatchev), Precambrian crystalline shields (South Africa, Canada, and Scandinavia), volcanic-hydrothermal systems (e.g., the East Pacific Rise, the southwestern Indian Ridge, Socorro, and Milos), and inclusions in intrusive alkaline rocks (Lovozero, Khibina, and Illimaussaq). Biotic (thermogenic and microbial) data refer to a global dataset of gases in petroleum fields (also see Etiope et al. 2013a; Etiope and Schoell 2014). Diagrams were updated according to Etiope and Sherwood Lollar (2013), Etiope et al. (2013c), and Etiope and Schoell (2014); with additions from Etiope et al. (2014; Spain), Yuce et al. (2014; Turkey, Tahtakopru and Kurtbagi in the Amik Basin) and Etiope et al. (2015; the United Arab Emirates)

7.1.4 Seepage to the Surface

While the exact origin of abiotic methane is sometimes difficult to understand, the story is less cryptic as far as gas seepage is concerned. As revealed by gas flux data acquired at various sites in Italy, Turkey, Greece, and Spain, the relationship between seeps or springs and local geology is quite clear. Abiotic gas seeps or spring sites all have the following characteristics in common:

(a) the seep or spring is typically located in correspondence with a fault or at the intersection of more faults;
(b) the faults are in tectonic contact between ultramafic rocks and carbonate-rich rocks (limestones, flysch, metasedimentary rocks);
(c) gas miniseepage (see the definition in Chap. 2) is frequently observed surrounding visible seeps or springs; and
(d) microseepage also exists along faults, even far from macro-seeps and springs.

The amount of methane detected in land-based serpentinisation seeps and water springs is considerable. CH_4 concentrations in these waters range from 0.01 to 14 mg/L (normal water in equilibrium with the atmosphere has 0.00003 mg CH_4/L). With water flow rates on the order of one litre per second (as for the springs in Greece and Italy), the total amount of CH_4 transported to the surface by a single spring outlet can reach hundreds of kilograms per year. Dry seeps, without water discharge, have CH_4 concentrations of approximately 20 vol.% (as for the seeps in New Zealand) to ~50 vol.% (as for the Zambales seeps located in the Philippines), and up to ~90 vol.% (as for the Chimaera seep in Turkey). Gas flux has been measured at the Chimaera seep and surrounding hyperalkaline and bubbling springs in Greece, Italy, and Spain.

Chimaera, near Çiraly in the Antalya Gulf, is likely the largest terrestrial abiotic gas seep on Earth. Gas burns in at least 20 large flames that are up to half a meter in height (Fig. 7.1a–c). Gas escapes from visible vents in rock fractures and in the form of invisible seepage throughout peridotite outcrops, approximately 5,000 m^2 wide, along the flank of the Olympos Mountain. Based on closed-chamber measurements (see Chap. 4) at least 190 tonnes of CH_4 are released to the atmosphere each year from this main macro-seep (Etiope et al. 2011b). Additional emissions of gas, likely on the same order of magnitude of the Chimaera seep site, occur in a second peridotite outcrop recently discovered on the top of the mountain (Etiope and Schoell 2014). Here, there are two actively burning gas vents and numerous burned trees over an area of at least 2,000 m^2. As suggested by the surrounding burned soil, the trees were likely killed by episodic combustion of gas from the ground (Fig. 7.1d). The total gas flux from the two seepage sites is certainly higher than that of any other land-based serpentinisation seep or spring.

Additionally, methane microseepage, with fluxes up to 1,040 mg $m^{-2}day^{-1}$, was measured along a fault approximately 3 km from the Chimaera seep site at another peridotite outcrop along Çirali Beach (Etiope et al. 2011b). Radiocarbon (^{14}C) analyses of CH_4 demonstrated that the carbon of Chimaera methane is older than 50,000 years (the percent of modern carbon is ~ 0; Etiope and Schoell 2014). Considering that "eternal flames" have been active for at least two millennia (they were documented by Pliny the Elder in *Naturalis Historia, <79 AD*), the continuous release of hundreds of tonnes of gas per year must be driven by high pressure gradients. The result is only possible if a pressurised gas accumulation exists, by analogy with observations of thermogenic gas seeps. Simple calculations suggest that the total amount of methane emitted thus far would be on the order of 400 Mm^3. Thus, the initial amount of methane stored in the reservoir (the ultimate reserve) could have been on the order of thousands of millions of cubic meters, similar to a conventional biotic gas field. Therefore, it is difficult to imagine that this gas formed during hydrothermal serpentinisation on the ocean floor and has been preserved throughout ophiolite obduction.

At the hyperalkaline water springs in Italy (the Voltri ophiolite, near Genova; Boschetti et al. 2013), Greece (the Othrys ophiolite; Etiope et al. 2013b), and Spain (the Ronda peridotite massif, between Ronda and Malaga; Etiope et al. 2014), gas is transported to the surface both by water and by autonomous gas-phase seepage, either as bubble plumes in water pools or as miniseepage and microseepage from the ground (see the definitions in Chap. 2). Methane fluxes from individual bubble trains, with bubbles having diameters of approximately 1 cm, are on the order of 1–2 kg/day. Methane miniseepage surrounding the springs is on the order of several hundreds of mg CH_4 m^{-2} day^{-1}. Microseepage, measured even at distances of approximately 100 m from the bubble-spring site, generally has fluxes on the order of tens of mg CH_4 m^{-2} day^{-1}. Springs, bubble streams, and microseepage locations in all areas appear to be strictly controlled by faults. Interesting to note is that gas microseepage can be measured even in the absence of organic soil, directly from peridotite outcrops that are apparently unfractured and homogeneous (Etiope et al. 2013a). Given the significant fluxes and rapid pressure build-up in closed-chambers, gas movement in rock is mainly due to advection driven by pressure gradients (Darcy's law), rather than diffusion which is controlled by concentration gradients (Fick's law) (see Chap. 3). Exhalation must take place through pervasive microfractures in rocks. In general, the small-scale permeability of partially serpentinised peridotites is comparable to the permeability of shaley materials. However, olivine hydration generates large volume changes and, thus, high local strains and stresses with episodic cracking (Macdonald and Fyfe 1985). Micro-scale fractures are pervasive throughout peridotite outcrops and are often mineralised by carbonates. As a result of tectonic overthrusting above sedimentary Mesozoic and Cenozoic sequences, ophiolite outcrops can also be characterised by larger joints and faults. Serpentinisation-related microfractures and tectonic fractures are, therefore, important escape pathways for the methane generated inside ultramafic rocks.

7.1.5 Is Abiotic Gas Seepage Important for the Atmospheric Methane Budget?

Section 6.4 discusses global emissions of geological methane to the atmosphere, including microbial and thermogenic gas from all types of seeps, onshore and offshore, in sedimentary basins, and gases of mixed origin, biotic and abiotic, in geothermal systems. Today, as stated in the latest IPCC assessment report, total geological CH_4 emissions are approximately 54 Mt CH_4/y (60 Mt CH_4/y are suggested in Chap. 6) and represent the second natural source of atmospheric methane after wetlands (Ciais et al. 2013). Also of note is that this emission estimate does not include abiotic gas seepage from serpentinised ultramafic rocks. Nevertheless, as widely reported above, such abiotic gas seepage is not rare and in some places is quite considerable. Can it be a significant additional global component of the geologically derived atmospheric budget of methane? At present, no sufficient data exists to fully answer this question. Specific studies and a wider dataset of flux measurements are necessary to better evaluate emission factors and, above all, to estimate at least the order of magnitude of the global area where this type of abiotic gas seepage exists. Today, we know that abiotic methane (also mixed with biotic gas) reaches the Earth's surface from seeps in at least 16 countries (see Table 7.1). Hyperalkaline springs, where methane is yet to be documented, although very likely to occur, are also found in Bosnia and Cyprus. Rather than visible gas emissions from spring sites, invisible seepage, miniseepage, and microseepage, which may extend over wide areas, are likely more important for global methane emissions to the atmosphere. That this invisible seepage is also widespread in other ophiolitic or ultramafic rocks massifs, where hyperalkaline springs and seeps do not exist, cannot be excluded. For example, abiotic microseepage may occur throughout serpentine soils, a special type of soil derived from ultramafic rock bedrock and characterised by unusual plant associations adapted to extreme soil conditions, such as low calcium-to-magnesium ratios, a lack of nutrients such as nitrogen, potassium, and phosphorous, and high concentrations of nickel and chromium (e.g., Proctor and Woodell 1975). These types of ultramafic rock soils occupy approximately 1 % of the global land surface (i.e., $\sim 148{,}000\ \text{km}^2$; Garnier et al. 2009) but at least 3 % of the Earth's surface is made up of serpentinised peridotite (Guillot and Hattori 2013). Presently, any estimate or guess of the portion of this area that actually hosts microseepages of abiotic gas produced in underlying peridotites, as well as the attribution of an average microseepage flux in this portion, are highly speculative and inappropriate. However, the argument deserves to be studied.

An interesting link exists between such a potential methane emission and carbon dioxide consumption. Due to their capacity for the conversion of CO_2 gas into solid carbonate minerals, peridotite outcrops are, in fact, also potential sinks of atmospheric CO_2. For example, CO_2 uptake by the near surface carbonation of mantle peridotite during weathering consumes $\sim 10^3$ tons per km^3 per year in Oman (Kelemen and Matter 2008) and, by pumping greenhouse gas within peridotites, has been proposed to exploit this process for artificially storing atmospheric CO_2.

Studying how much of the injected CO_2 could react with H_2 and produce CH_4 (a greenhouse gas much more powerful than CO_2) would be an interesting endeavour.

7.2 Potential Methane Seepage on Mars

7.2.1 Looking for Methane on Mars

The information acquired in studies of gas seepage on Earth represents a fundamental reference for the recognition and understanding of possible gas seepage on other planets known to have methane within their atmospheres or the ground. One of the most studied planets in this respect is Mars. Serpentinised ultramafic rocks and hydrated silicates also exist on Mars (Mustard et al. 2008; Ehlmann et al. 2010) and have been considered a plausible source of methane (Oze and Shama 2005; Atreya et al. 2007; Etiope et al. 2013a). The possible existence of methane on Mars has enormous implications because, as for Earth, methane could, in theory, have originated from microbes or could have been an energy source for some microbial organisms or even for prebiotic mechanisms germane to the origin of life. In these cases, methane could be a proxy for life on Mars.

At the time of writing this chapter, the presence of methane on Mars is still being debated because previous reports of methane in the atmosphere are not unequivocal. The first telescopic measurements reporting 10–20 ppb of methane in the martian atmosphere (Mumma et al. 2003; Formisano et al. 2004; Krasnopolsky et al. 2004) suggested the existence of an active gas source. The CH_4 plume observed in the martian region called Northern Summer 2003, indicates emissions from the ground of 19,000 tons CH_4 year^{-1} (Mumma et al. 2009) or 150,000 tons CH_4 year^{-1} (Lefevre and Forget 2009), and possibly up to 570,000 tons CH_4 year^{-1} (Chizek et al. 2010). Although possibly a coincidence, elevated CH_4 concentrations have been detected in correspondence with olivine-bearing rocks, frequently serpentinised, in the martian regions of Syrtis Major, Terra Sirenum, and Nili Fossae (Hoefen et al. 2003; Ehlmann et al. 2010).

The occurrence of CH_4 on Mars has, however, been questioned because atmospheric photochemistry and transport models make short-lived methane plumes implausible and because ground-based observations of methane are heavily affected by telluric interference (Zahnle et al. 2011). In addition, plumes of methane have not been reported since the original report in 2009. However, the Curiosity lander seems to have recently found traces of methane, up to 7.2 ppbv, near the martian surface (Webster et al. 2014), although the location of the measurement (the Gale Crater) is not a favourable place for abiotic methane production due to the lack, at least on the surface, of serpentinised rocks. In any case, the special nature of the processes generating and transporting methane to the surface (i.e. seepage) may not allow detection in the atmosphere 1 m above the ground, a notion supported by observations of low flux seepage in serpentinised rocks on Earth, where amounts of methane decline rapidly with distance above the surface.

Macro-seeps, like Chimaera in Turkey or Los Fuegos Eternos in the Philippines, are improbable on Mars, as they require considerable amounts of gas and pressurised reservoirs; at least on Earth, Chimaera seep represents a rare phenomenon. Rather, microseepage would be an easier and a more plausible degassing scenario on Mars, whereby minor amounts of dispersed gas can diffusely and slowly migrate to the surface. A diffuse flux of 100–1,000 mg m^{-2} day^{-1} from an area of 500–5,000 km^2 would be sufficient to support the martian CH_4 emissions estimated by Mumma et al. (2009) and Lefevre and Forget (2009). If the entire 30,000 km^2 of the olivine-rich outcrop at Nili Fossae (Hoefen et al. 2003) is assumed to exhale, then a microseepage of 15 mg m^{-2} day^{-1} (i.e. 4–5 times lower than the minimum detected in the ophiolites in Turkey) could account for the observed martian CH_4 plume observed by Mumma et al. (2009). Models of CH_4 release on Mars indeed suggest that the Northern Summer 2003 plume was formed by a broad source rather than a point emission (Mischna et al. 2011). Microseepage can either be 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 underground gas pressure gradients, migration mechanisms, and changes in exogenic (atmospheric) factors (Etiope and Klusman 2010). The crux of the query is that low levels of microseepage may not be detected by measurements in air. On Earth, in most cases, methane microseepage cannot be detected a few cm above the soil due to winds and large dilutions of small amounts of leaking CH_4. For example, for proof of geological abiotic CH_4 on Mars, attempts to measure such gas should be concentrated in regions with olivine-bearing rocks (e.g., Syrtis Major, Terra Sirenum Nili Fossae, Claritas Fossae; Fig. 7.5) ideally by drilling deep into the soil, or using accumulation chambers on the ground,

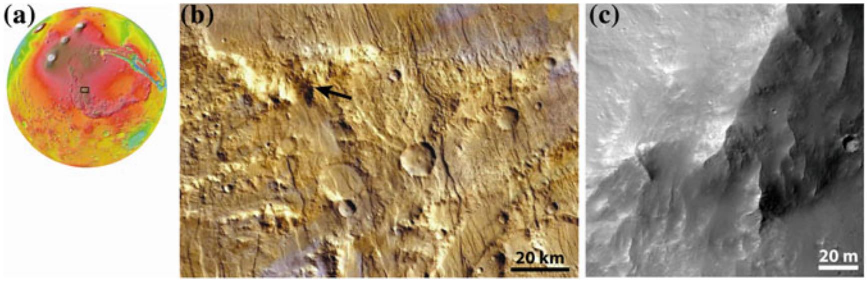

Fig. 7.5 Serpentine occurs in Mars' ancient Noachian terrains, in, for example, the Claritas Fossae highlands on the southern end of Mars' Tharsis Region (26.8 s, 101.2 W). **a** A Mars Orbiter Laser Altimeter (MOLA) topographic map of a location in the Claritas Rise. **b** A high resolution stereo camera color image of the fractured, ancient terrain. **c** Serpentine occurs in the select rock outcrops pictured here in High Resolution Imaging Science Experiment (HiRISE) data and originally detected using visible/near infrared imaging spectrometer data (Ehlmann et al. 2010). Images kindly provided by B. Ehlmann (Caltech/JPL)

preferably above or near tectonic faults. Without these tests, we cannot infer that methanogenic processes related to serpentinisation do not exist on Mars.

7.2.2 A Theoretical Martian Seepage

The potential surface release of methane produced in the martian subsurface depends on the physical properties of the substrate, including water occurrence, permeability, porosity, and pressure and thermal gradients, all of which can affect advection and diffusion migration processes, as discussed in Chap. 3. In general, martian terrains seem to have good gas-transport properties. Vapour–ice deposition models for ice distribution predict that the upper tens to hundreds of meters of Mars' subsurface exchange with the atmosphere, and large-scale aquifer models predict fluid migration through pores at several kilometers in depth (Mellon et al. 1997; Grimm and Painter 2009). Due to repeated meteorite impacts and fracturing during the cooling of lavas, the martian crust is also known to be fractured on multiple scales. As mentioned above, additional fracturing can be due to serpentinisation. Therefore, olivine-bearing rocks may have a relatively high secondary permeability which could enhance the potential for microseepage to the surface.

In such fractured rocks, gas advection, the most important mechanism of gas migration in the subsoil on Earth, can occur in two forms depending on the presence of water, as described in Chap. 3. In dry porous or fractured media, gas flows through interstitial or fissure spaces (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 equatorial and mid-latitudes on the surface of Mars today, water is typically only stable in the vapour phase (Haberle et al. 2001). However, near-surface salts and thin-film type weathering point to small amounts of liquid water on the surface within the geological recent past (Arvidson et al. 2010). The availability of subsurface water remains a subject of active research, though it is generally believed that subsurface liquid water was available in the past, causing chemical alterations (Ehlmann et al. 2010). Radar investigations have not revealed any present subsurface aquifer, although the modern seepage of brines indicates the potential for episodic subsurface water occurrence in some places on Mars (McEwen et al. 2011). Liquid water could exist today as a brine at depths shallower than 4 km (Oze and Sharma 2005). Subsurface ice may act as a barrier for the advection of gases to the surface; however, evidence for seasonal melting/sublimation offers a mechanism whereby gases of any origin could be trapped by ice-filled pore spaces can occasionally be released. Therefore, the most common 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 on the order of 10^0–10^3 m/day for highly permeable, fractured rocks whose fracture aperture or voids are on the order of several mm (see Chap. 3). A simple, first-order estimation of a gas-advection model suggests that methane fluxes on the order of several mg m^{-2} day^{-1}, similar to the microseepage observed in terrestrial peridotites (as described above), could occur in martian rocks (Etiope et al. 2013a). Overall, serpentinised ultramafic rocks on Mars are likely to have both the necessary chemical constituents for methane production and the fractures that would allow seepage of gas to the atmosphere, similar to serpentinised ultramafic rocks on Earth.

However, in addition to serpentinised ultramafic rocks, methane seepage on Mars could also take place in other regions of the planet characterised by extensive faults and fractures, or regions with particular morphological structures (Fig. 7.6), such as the mounds in the Acidalia Planitia, which have been compared to terrestrial, methane-seeping mud volcanoes (Oehler and Allen 2010; Etiope et al. 2011a), possible ancient springs in Arabia Terra associated with faults and dipping

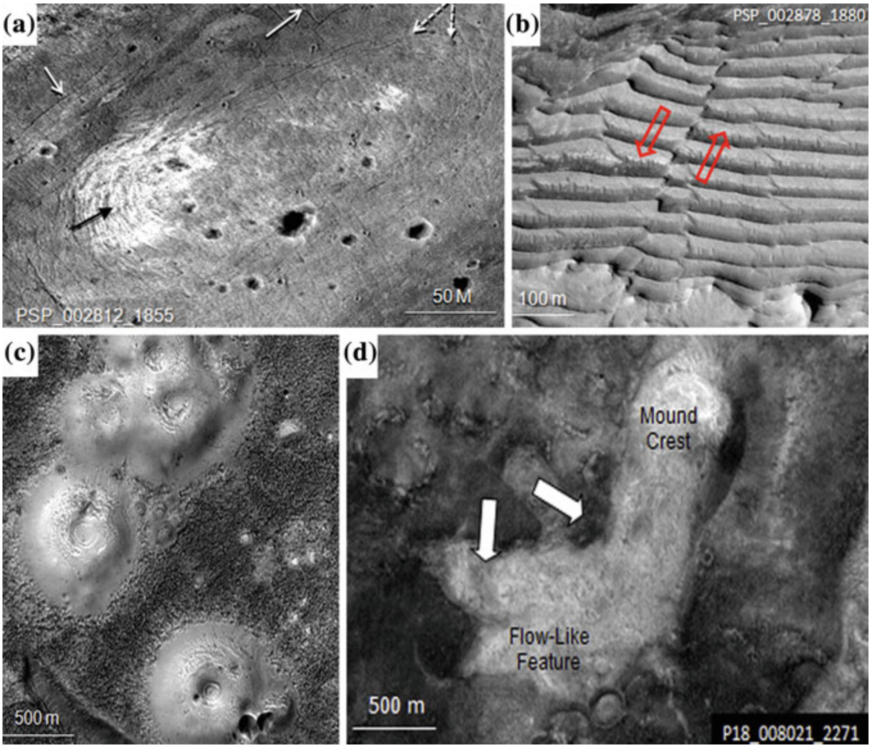

Fig. 7.6 Potential seepage structures on Mars. **a** An elliptical tonal anomaly in Arabia Terra, interpreted as an ancient spring mound (Allen and Oehler, 2008). *Solid white arrows* point to linear fractures; *dashed arrows* point to circumferential faults associated with elliptical features; the *black arrow* points to possible terracing. **b** Faulted sediments in Arabia Terra. As indicated by the warping of layered sediments on either side of the fault, arrows indicate the direction of relative movement across the fault. **c** The mounds in Acidalia Planitia, interpreted as relicts of mud volcanoes. **d** The flow-like extension (*arrow*) of the high-albedo material of the mound. HiRISE images prepared by D. Oehler (NASA/JPL/University of Arizona)

beds (Allen and Oehler 2008), and large-scale polygonal fractures (often called, “giant polygons”) in Chryse and Acidalia.

The latter martian polygonal fractures, in particular, appear to be similar to fluid-bearing polygonal faults discovered on Earth thanks to 3D seismic images (e.g., Goulty 2008; Oehler and Allen 2012; Allen et al. 2013). The development of large scale fracture systems could provide both a source of subsurface fluids and migration pathways for those fluids. These polygonal fractures are additionally often associated with mud volcanoes and methane seepage Similarly, the martian “giant polygons” are frequently associated with mounds that have been compared to terrestrial mud volcanoes. Therefore, areas on Mars having both the “giant polygons” and the associated mounds could be important sites for future searches for methane occurrences and evidence of past life (Oehler and Allen 2012).

References

Abrajano TA, Sturchio NC, Bohlke JK, Lyon GL, Poreda RJ, Stevens CM (1988) Methane-hydrogen gas seeps, Zambales Ophiolite, Philippines: deep or shallow origin? Chem Geol 71:211–222

Abrajano TA, Sturchio NC, Kennedy BM, Lyon GL, Muehlenbachs K, Bohlke JK (1990) Geochemistry of reduced gas related to serpentinization of the Zambales Ophiolite, Philippines. Appl Geochem 5:625–630

Allen CC, Oehler DZ (2008) A case for ancient springs in Arabia Terra, Mars. Astrobiology 8:1093–1112

Allen CC, Oehler D, Etiope G, van Rensbergen P, Baciu C, Feyzullayev A, Martinelli G, Tanaka K, Van Rooij D (2013) Fluid expulsion in terrestrial sedimentary basins: a process providing potential analogs for giant polygons and mounds in the martian lowlands. Icarus 224:424–432

Ames DE, Farrow CEG (2007) Metallogeny of the sudbury mining camp, Ontario. In: Goodfellow, WD (ed) Mineral deposits of Canada: a synthesis of major deposit-types, district metallogeny, the evolution of geological provinces, and exploration methods. Geological Association of Canada, Mineral Deposits Division, pp 329–350, Special Publication No. 5

Arvidson RE, Ruff SW, Morris RV, Ming DW, Crumpler LS, Yen AS, Squyres SW, Sullivan RJ, Bell III JF et al (2010) Spirit mars rover mission: overview and selected results from the northern home plate winter haven to the side of Scamander crater. J Geophys Res 115:E00F03. http://dx.doi.org/10.1029/2008JE003183

Atreya SK, Mahaffy PR, Wong A-S (2007) Methane and related trace species on Mars: origin, loss, implications for life, and habitability. Planet Space Sci 55:358–369

Bacuta GC, Kay RW, Gibbs AK, Bruce RL (1990) Platinum-group element abundance and distribution in chromite deposits of the Acoje Block, Zambales ophiolite complex, Philippines. J Geochem Explor 37:113–143

Barnes I, O’Neil JR (1969) The relationship between fluids in some fresh Alpine-type ultramafics and possible modern serpentinization, Western United States. Geol Soc Am Bull 80:1947–1960

Boschetti T, Etiope G, Toscani L (2013) Abiotic methane in hyperalkaline springs of Genova, Italy. Procedia Earth Planet Sci 7:248–251

Boulart C, Chavagnac V, Monnin C, Delacour A, Ceuleneer G, Hoareau G (2013) Differences in gas venting from ultramafic-hosted warm springs: the example of Oman and Voltri ophiolites. Ofioliti 38:143–156

Bruni J, Canepa M, Cipolli F, Marini L, Ottonello G, Vetuschi Zuccolini M (2002) Irreversible water–rock mass transfer accompanying the generation of the neutral, Mg–HCO_3 and high-pH, Ca–OH spring waters of the Genova province, Italy. App Geochem 17:455–474

Charlou JL, Donval JP, Fouquet Y, Jean-Baptiste P, Holm N (2002) Geochemistry of high H2 and CH4 vent fluids issuing from ultramafic rocks at the Rainbow hydrothermal field (36°14′N, MAR). Chem Geol 191:345–359

Chizek MR, Murphy JR, Kahre MA, Haberle RM, Marzo GA (2010) A shortlived trace gas in the martian atmosphere: a general circulation model of the likelihood of methane. Lunar Planet Sci 41 Abstract 1527

Ciais P, Sabine C, Bala G, Bopp L, Brovkin V, Canadell J, Chhabra A, DeFries R, Galloway J, Heimann M, Jones C, Le Quéré C, Myneni RB, Piao S, Thornton P (2013) Carbon and other biogeochemical cycles. In:Stocker TF et al (eds) Climate change 2013: the physical science basis. contribution of working group i to the fifth assessment report of IPCC, Cambridge Univ Press, Cambridge, UK and New York, NY, USA

Cook AP (1998). Occurrence, emission and ignition of combustible strata gases in Witwatersrand gold mines and Bushveld platinum mines, and means of ameliorating related ignition and explosion hazards, part 1: literature and technical review. Safety in mines research advisory committee, GAP 504 (report)

Dai J, Yang S, Chen H, Shen X (2005) Geochemistry and occurrence of inorganic gas accumulations in Chinese sedimentary basins. Org Geochem 36:1664–1688

Dias PA, Leal Gomes C, Castelo Branco JM, Pinto Z (2006) Paragenetic positioning of PGE in mafic and ultramafic rocks of Cabeço de Vide—alter do Chão Igneous Complex. Book of abstracts, VII Congresso Nacional de Geologia, pp 1007–1010

Economou-Eliopoulos M (1996) Platinum-group element distribution in chromite ores from ophiolite complexes: implications for their exploration. Ore Geol Rev 11:363–381

Ehlmann BL, Mustard JF, Murchie SL (2010) Geologic setting of serpentine deposits on Mars. Geophys Res Lett 37:L06201. http://dx.doi.org/10.1029/2010GL042596

Etiope G, Ionescu A (2014) Low-temperature catalytic CO_2 hydrogenation with geological quantities of ruthenium: a possible abiotic CH_4 source in chromitite-rich serpentinized rocks. Geofluids. doi: 10.1111/gfl.12106 (first published online)

Etiope G, Klusman RW (2010) Microseepage in drylands: flux and implications in the global atmospheric source/sink budget of methane. Global Planet Change 72:265–274

Etiope G, Schoell M (2014) Abiotic gas: atypical but not rare. Elements 10:291–296

Etiope G, Sherwood Lollar B (2013) Abiotic methane on Earth. Rev Geophys 51:276–299

Etiope G, Ehlmann B, Schoell M (2013a) Low temperature production and exhalation of methane from serpentinized rocks on Earth: a potential analog for methane production on Mars. Icarus 224:276–285

Etiope G, Oehler DZ, Allen CC (2011a) Methane emissions from Earth's degassing: Implications for Mars. Planet Space Sci 59:182–195

Etiope G, Schoell M, Hosgormez H (2011b) Abiotic methane flux from the Chimaera seep and Tekirova ophiolites (Turkey): understanding gas exhalation from low temperature serpentinization and implications for Mars. Earth Planet Sci Lett 310:96–104

Etiope G, Tsikouras B, Kordella S, Ifandi E, Christodoulou D, Papatheodorou G (2013b) Methane flux and origin in the Othrys ophiolite hyperalkaline springs, Greece. Chem Geol 347:161–174

Etiope G, Vance S, Christensen LE, Marques JM, Ribeiro da Costa I (2013c) Methane in serpentinized ultramafic rocks in mainland Portugal. Mar Pet Geol 45:12–16

Etiope G, Vadillo I, Whiticar MJ, Marques JM, Carreira P, Tiago I, Benavente J, Jiménez P, Urresti B (2014) Methane seepage at hyperalkaline springs in the Ronda peridotite massif (Spain). AGU 2014 Fall Meeting Abstracts

Etiope G, Judas J, Whiticar MJ (2015) First detection of abiotic methane in the eastern United Arab Emirates ophiolite aquifer. Arab J Geosci (in press)

Farooqui MY, Hou H, Li G, Machin N, Neville T, Pal A, Shrivastva C, Wang Y, Yang F, Yin C, Zhao J, Yang Z (2009) Evaluating volcanic reservoirs. Oilfield Rev 21:36–47

Formisano V, Atreya S, Encrenaz T, Ignatiev N, Giuranna M (2004) Detection of methane in the atmosphere of Mars. Science 306:1758–1761

Fritz P, Clark ID, Fontes J-C, Whiticar MJ, Faber E (1992) Deuterium and ^{13}C evidence for low temperature production of hydrogen and methane in a highly alkaline groundwater environment in Oman. In: Kharaka YK, Maest AS (eds), Proceedings of 7th int symp water–rock interaction: low temperature environments, vol 1. Balkema, Rotterdam, pp 793–796

Garnier J, Quantin C, Guimaraes E, Garg VK, Martins ES, Becquer T (2009) Understanding the genesis of ultramafic soils and catena dynamics in Niquelandia, Brazil. Geoderma 151:204–214

Garuti G, Zaccarini F (1997) In situ alteration of platinum-group minerals at low temperature: evidence from serpentinized and weathered chromitite of the Vourinos complex, Greece. Can Miner 35:611–626

Garuti G, Zaccarini F, Economou-Eliopoulos M (1999) Paragenesis and composition of laurite from chromitites of Othrys (Greece): implications for Os-Ru fractionation in ophiolitic upper mantle of the Balkan peninsula. Min Deposit 34:312–319

Geminale A, Formisano V, Giuranna M (2008) Methane in martian atmosphere: average spatial, diurnal, and seasonal behaviour. Planet Space Sci 56:1194–1203

Goulty NR (2008) Geomechanics of polygonal fault systems: a review. Petrol Geosci 14:389–397

Grimm RE, Painter SL (2009) On secular evolution of groundwater on Mars. Geophys Res Lett 36:L24803

Guillot S, Hattori K (2013) Serpentinites: essential roles in geodynamics, arc volcanism, sustainable development, and the origin of life. Elements 9:95–98

Haberle RM, McKay CP, Schaeffer J, Cabrol NA, Grin EA, Zent AP, Quinn R (2001) On the possibility of liquid water on present-day Mars. J Geophys Res 106(E10):23317–23326

Hoefen TM, Clark RN, Bandfield JL, Smith MD, Pearl JC, Christensen PR (2003) Discovery of olivine in the Nili Fossae region of Mars. Science 302:627–630

Horita J, Berndt ME (1999) Abiogenic methane formation and isotopic fractionation under hydrothermal conditions. Science 285:1055–1057

Hosgormez H, Etiope G, Yalçın MN (2008) New evidence for a mixed inorganic and organic origin of the Olympic Chimaera fire (Turkey): a large onshore seepage of abiogenic gas. Geofluids 8:263–275

Jacquemin M, Beuls A, Ruiz P (2010) Catalytic production of methane from CO_2 and H_2 at low temperature: insight on the reaction mechanism. Catal Today 157:462–466

Jenden PD, Hilton DR, Kaplan IR, Craig H (1993) Abiogenic hydrocarbons and mantle helium in oil and gas fields. In: Howell D (ed) Future of energy gases, USGS Professional paper, vol 1570, pp 31–35

Juteau T (1968) Commentaire de la carte geologique des ophiolites de la region de Kumluca (Taurus lycien, Turquie meridionale): cadre structural, modes de gisement et description des principaux fades du cortege ophiolitique. MTA Bull 70:70–91

Kelemen PB, Matter JM (2008) In situ carbonation of peridotite for CO_2 storage. Proc Nat Acad Sci USA 105(17):295–17,300

Krasnopolsky VA, Maillard JP, Owen TC (2004) First detection of methane in the martian atmosphere: evidence for life? Icarus 172:537–547

Lefevre F, Forget F (2009) Observed variations of methane on Mars unexplained by known chemistry and physics. Nature 460:720–723

Lyon G, Giggenbach WF, Lupton JF (1990) Composition and origin of the hydrogen rich gas seep, Fiordland, New Zealand. EOS Trans V51D(10):1717

Macdonald AH, Fyfe WS (1985) Rate of serpentinization in seafloor environments. Tectonophysics 116:123–135

Marques JM, Carreira PM, Carvalho MR, Matias MJ, Goff FE, Basto MJ, Graça RC, Aires-Barros L, Rocha L (2008) Origins of high pH mineral waters from ultramafic rocks, Central Portugal. App Geochem 23:3278–3289

McCollom TM (2013) Laboratory simulations of abiotic hydrocarbon formation in Earth's deep subsurface. Rev Min Geochem 75:467–494

McCollom TM, Seewald JS (2007) Abiotic synthesis of organic compounds in deep-sea hydrothermal environments. Chem Rev 107:382–401

McEwen AS, Ojha L, Dundas CM, Mattson SS, Byrne S, Wray JJ, Cull SC, Murchie SL, Thomas N, Gulick VC (2011) Seasonal flows on warm martian slopes. Science 333:740–743

Mellon MT, Jakosky BM, Postawko SE (1997) The persistence of equatorial ground ice on Mars. J Geophys Res 102:19357–19369

Meyer-Dombard DR, Woycheese KM, Cardace D, Arcilla C (2013) Geochemistry of Microbial Environments in Serpentinizing Springs of the Philippines. AOGS 2013, Brisbane. Abstract # IG19-D2-PM2-P-007

Milenic D, Dragisic V, Vrvic M, Milankovic D, Vranjes A (2009) Hyperalkaline mineral waters of Zlatibr ultramafic massif in Western Serbia, Europe. Abstract proceedings of the AWRA International Water Congress—Watershed Management for Water systems, Seattle, USA

Mischna MA, Allen M, Richardson MI, Newman CE, Toigo AD (2011) Atmospheric modelling of Mars methane surface releases. Planet Space Sci 59:227–237

Monnin C, Chavagnac V, Boulart C, Ménez B, Gérard M, Gérard E, Quéméneur M, Erauso G, Postec A, Guentas-Dombrowski L, Payri C, Pelletier B (2014) The low temperature hyperalkaline hydrothermal system of the Prony bay (New Caledonia). Biogeosciences Discuss 11:6221–6267

Morrill PL, Gijs Kuenen J, Johnson OJ, Suzuki S, Rietze A, Sessions AL, Fogel ML, Nealson KH (2013) Geochemistry and geobiology of a present-day serpentinization site in California: the Cedars. Geochim Cosmochim Acta 109:222–240

Mosier DL, Singer DA, Moring BC, Galloway JP (2012) Podiform chromite Deposits—database and grade and tonnage models. U.S. Geological Survey Scientific Investigations, Report, pp 2012–5157

Mottl MJ, Wheat C, Frier P (2004) Decarbonateion, serpentinization, abgiogenic methane, and extreme pH beneath the Mariana Forearc. AGU Fall Meeting 2004, abstract V13A-1441

Mumma MJ, Novak RE, DiSanti MA, Bonev BP (2003) A sensitive search for methane on Mars. Am Astron Soc Bull 35:937–938

Mumma MJ, Villanueva G, Novak RE, Hewagama T, Bonev BP, DiSanti MA, Mandell AM, Smith MD (2009) Strong release of methane on Mars in Northern summer 2003. Science 323:1041–1045

Mustard JF, Murchie LS, Pelkey SM et al (2008) Hydrated silicate minerals on Mars observed by the Mars Reconnaissance Orbiter CRISM instrument. Nature 454:305–309

Ni Y, Dai J, Zhou Q, Luo X, Hu A, Yang C (2009) Geochemical characteristics of abiogenic gas and its percentage in Xujiaweizi Fault Depression, Songliao Basin, NE China. Petrol Explor Dev 36:35–45

Oehler DZ, Allen CC (2010) Evidence for pervasive mud volcanism in Acidalia Planitia, Mars. Icarus 208:636–657

Oehler DZ, Allen CC (2012) Giant polygons and mounds in the lowlands of Mars: signatures of an ancient ocean? Astrobiology 12:601–615

Okland I, Huang S, Dahle H, Thorseth IH, Pedersen RB (2012) Low temperature alteration of serpentinized ultramafic rock and implications for microbial life. Chem Geol 318–319:75–87

Oze C, Sharma M (2005) Have olivine, will gas: serpentinization and the abiogenic production of methane on Mars. Geophys Res Lett 32:L10203. doi:10.1029/2005GL022691

Page NJ, Talkington RW (1984) Palladium, platinum, rhodium, ruthenium and iridium in peridotites and chromitites from ophiolite complexes in Newfoundland. Can Miner 22:137–149

Page NJ, Pallister JS, Brown MA, Smewing JD, Haffty J (1982) Palladium, platinum, rhodium, iridium and ruthenium in chromite-rich rocks from the Samail ophiolite, Oman. Can Miner 20:537–548

Pašava J, Vymazalová A, Petersen S (2007) PGE fractionation in seafloor hydrothermal systems: examples from mafic- and ultramafic-hosted hydrothermal fields at the slow spreading Mid Atlantic Ridge. Min Deposita 42:423–431

Pawson JF, Oze C, Etiope G, Horton TW (2014) Discovery of new methane-bearing hyperalkaline springs in the serpentinized Dun Mountain Ophiolite, New Zealand. AGU 2014 Fall Meeting Abstracts

Prichard HM, Brough CP (2009) Potential of ophiolite complexes to host PGE deposits. In: Chusi L, Ripley EM (eds) New developments in magmatic Ni-Cu and PGE Deposits. Geological Publishing House, Beijing, pp 277–290

Proctor J, Woodell SRJ (1975) The ecology of serpentine soils. Adv Ecol Res 9:255–365

Proskurowski G, Lilley MD, Seewald JS, Früh-Green GL, Olson EJ, Lupton JE, Sylva SP, Kelley DS (2008) Abiogenic hydrocarbon production at lost city hydrothermal field. Science 319:604–607

Russell MJ, Hall AJ, Martin W (2010) Serpentinization as a source of energy at the origin of life. Geobiology 8:355–371

Sachan HK, Mukherjee BK, Bodnar RJ (2007) Preservation of methane generated during serpentinization of upper mantle rocks: evidence from fluid inclusions in the Nidar ophiolite, Indus Suture Zone, Ladakh (India). Earth Planet Sci Lett 257:47–59

Sanchez-Murillo R, Gazel E, Schwarzenbach E, Crespo-Medina M, Schrenk MO, Boll J, Gill BC (2014) Geochemical evidence for active tropical serpentinization in the Santa Elena Ophiolite, Costa Rica: an analog of a humid early Earth? Geochem Geophys Geosyst 15:1783–1800

Schrenk MO, Brazelton WJ, Lang S (2013) Serpentinization, carbon and deep life. Rev Min Geochem 75:575–606

Schutter SR (2003) Occurrences of hydrocarbons in and around igneous rocks. In: Hydrocarbons in crystalline rocks. Geol Soc London, Spec Pub 214:35–68

Sherwood Lollar B, Frape SK, Weise SM, Fritz P, Macko SA, Welhan JA (1993) Abiogenic methanogenesis in crystalline rocks. Geochim Cosmochim Acta 57:5087–5097

Sherwood Lollar B, Lacrampe-Couloume G, Voglesonger K, Onstott TC, Pratt LM, Slater GF (2008) Isotopic signatures of CH_4 and higher hydrocarbon gases from precambrian shield sites: a model for abiogenic polymerization of hydrocarbons. Geochim Cosmochim Acta 72:4778–4795

Smith NJP, Sheperd TJ, Styles MT, Williams GM (2005) Hydrogen exploration: a review of global hydrogen accumulations and implications for prospective areas in NW Europe. In: Doré´ AG, Vining BA (eds) Petroleum geology: North-West Europe and global perspectives, Proceedings of 6th petroleum geology conference, 349–358

Suda K, Ueno Y, Yoshizaki M, Nakamura H, Kurokawa K, Nishiyama E, Yoshino K, Hongoh Y, Kawachi K, Omori S, Yamada K, Yoshida N, Maruyama S (2014) Origin of methane in serpentinite-hosted hydrothermal systems: the CH_4–H_2–H_2O hydrogen isotope systematics of the Hakuba Happo hot spring. Earth Planet Sci Lett 386:112–125

Szatmari P, da Fonseca TCO, Miekeley NF (2011) Mantle-like trace element composition of petroleum—contributions from serpentinizing peridotites. In: Closson D (ed) Tectonics, InTech, 3:332–358

Szponar N, Brazelton WJ, Schrenk MO, Bower DM, Steele A, Morrill PL (2013) Geochemistry of a continental site of serpentinization in the Tablelands ophiolite, gros morne national park: a Mars analogue. Icarus 224:286–296

Taran YA, Kliger GA, Sevastyanov VS (2007) Carbon isotope effects in the open-system Fischer-Tropsch synthesis. Geochim Cosmochim Acta 71:4474–4487

Thampi KR, Kiwi J, Grätzel M (1987) Methanation and photo-methanation of carbon dioxide at room temperature and atmospheric pressure. Nature 327:506–508

Webster CR, Mahaffy PR, Atreya SK plus 26 others and the MSL Science Team (2014) Mars methane detection and variability at Gale crate. Science doi:10.1126/science.1261713

Whiticar MJ, Etiope G (2014a) Hydrogen isotope fractionation in land-based serpentinization systems. In:Suda et al. (eds) Comment on "Origin of methane in serpentinite-hosted hydrothermal systems: the CH_4–H_2–H_2O hydrogen isotope systematics of the Hakuba Happo hot spring". Earth Planet Sci Lett 386 (2014) 112–125, Earth Planet Sci Lett 401:373–375

Whiticar MJ, Etiope G (2014b) Methane in land-based serpentinized peridotites: new discoveries and isotope surprises. AGU 2014 Fall Meeting Abstracts

Yuce G, Italiano F, D'Alessandro W, Yalcin TH, Yasin DU, Gulbay AH, Ozyurt NN, Rojay B, Karabacak V, Bellomo S, Brusca L, Yang T, Fu CC, Lai CW, Ozacar A, Walia V (2014) Origin and interactions of fluids circulating over the Amik Basin (Hatay-Turkey) and relationships with the hydrologic, geologic and tectonic settings. Chem Geol 388:23–39

Zahnle K, Freedman RS, Catling DC (2011) Is there methane on Mars? Icarus 212:493–503