The occurrence of CH$_4$ in the Martian atmosphere may imply active geologic sources, i.e. gas emission structures in the Martian soil and subsoil = gas seepage, a process well known on Earth, should exist on Mars.
The concept of “gas seepage” on Mars

How does seepage concept translate to the Mars context?

wrongly considered, erroneously associated to volcanic emission only, in:

Icarus 178 (2005) 487-492
A sensitive search for SO$_2$ in the martian atmosphere: Implications for seepage and origin of methane

Krasnopolsky V.A.

First systematic and geologic-geochemical discussions in:

Planetary and Space Science 59 (2011) 182–195
Methane emissions from Earth’s degassing: Implications for Mars
G. Etiope $^{a,*}$, D.Z. Oehler $^{b}$, C.C. Allen $^{b}$

Low temperature production and exhalation of methane from serpentinized rocks on Earth: A potential analog for methane production on Mars
Giuseppe Etiope $^{a,b,*}$, Bethany L. Ehlmann $^{c,d}$, Martin Schoell $^{e}$
Outcomes of the 1st workshop

Gas seepage introduced:  - basic concepts and observational data on Earth
  - potential seepage on Mars

Gas seepage on Mars:

- can be evidenced by specific surface manifestations (macro-seepage structures) over faults and fractured rocks, as observed on Earth (circular depressions, polygonal fractures, mounds, mud volcanoes).

- can be in the form of invisible diffuse exhalation from the ground (microseepage)

- can be detected only through specific procedures/methods: measurements in the atmosphere, a few cm above the ground (as performed by Curiosity) may not be effective in revealing any seepage (trivial CH$_4$ recorded by Curiosity cannot be accepted as evidence of lack of subsoil processes generating methane)

- surface gas geochemical techniques, similar to those that allowed the discovery of seepage and subsoil hydrocarbon reservoirs on Earth, must be considered (soil-gas, accumulation chambers, surface mineralogical alterations).

Take home message

Geologic CH$_4$ on Mars should be searched, preferably above or near faults or at apparent mud volcanoes, in the regions with olivine bearing or sedimentary rocks, ideally by drilling into the soil, or using accumulation chambers on the ground.
Objectives of the 2\textsuperscript{nd} workshop

More detailed discussions on…..

1. **Macro and microseepage on Earth**
   - typical soil-gas concentrations and flux values,
   - detection methods, indirect methods (soil-gas, closed-chamber, drilling, instrumental requirements. What can be applied on Mars?)

2. **Potential seepage structures and manifestations on Mars**
   - recognition by high-resolution images (e.g. HiRISE, CaSSIS, land-based cameras)

3. **Seepage proxies**: carbonate cement, secondary alterations of minerals…….

4. **Meaning of methane/ethane ratio in seeping gas**
   - review of methane genetic mechanisms; post-genetic alterations during seepage,
   - meaning (and ambiguity) of $C_1/C_2$ ratio (expected to be measured by ExoMars 2016)

**Proposed deliverable**

- Report in a format suitable for submission to a peer-reviewed journal
- Integration with the overall results of the workshop, for a comprehensive paper (e.g., EOS)

We can propose the search for gas seepage as one of the guiding scientific goals for Mars exploration in the 2020’s.
What is gas seepage
visible or invisible, focused or diffuse over large areas

**Macroseep**

- vent
- Miniseepage
- Microseepage

**Advection**
*(driven by pressure gradients)*

**Diffusion** *(concentration gradients) is not important*
Gas seeps and “eternal” fires

Release from 1 to 1000 ton CH$_4$ per year
**Mud volcanoes**

Release from 1 to 500 ton CH₄ per year

- Azerbaijan
- Romania
- Italy (Sicily)
- Italy (Po Basin)
- Italy (Po Basin)
- Italy (Adriatic basin)

Sedimentary volcanism, 3-phase system: gas-water-sediment
MICROSEEPAGE IN OLIVINE-RICH ROCKS (PERIDOTITITES)

from 1 to $10^3$ mg m$^{-2}$ day$^{-1}$

Fracturing induced by serpentinization

Diffuse invisible CH$_4$ microseepage

Etiope et al (2011)
Geological emissions in the global CH$_4$ budget

2$^{nd}$ natural CH$_4$ source

10% of total CH$_4$ source

Etiope and Ciccioli 2009 (Science)

Etiope, 2012 (Nature Geosci.)

(Etiope, 2015)

(IPCC, 2013)
How to detect and measure gas seepage

Effective only for significant seepage

Effective also for very low seepage

above ground measurements

gas in air and fluxes
Infrared, laser sensors

portable systems

vehicles

eddy-covariance tower

ground measurements

portable sensors or lab analysis

soil-gas

adsorber or soil sample

well head-space

closed chamber

in water measurements

portable sensors lab analysis

in-situ dissolved gas detection

dissolved gas

free gas

bubbles

water well

water

sediment

Approach to be adopted for Mars

Etiope (2015)
Shallow drilling into the soil

soil-gas probes

Sampling gas in soil-air at depths of 50-100 cm
CLOSED-CHAMBER SYSTEM
for microseepage
Widely used for soil-respiration, gas fluxes from wetlands, rice paddies and permafrost.

Gas flux $Q$ is expressed in terms of mg m$^{-2}$ day$^{-1}$ by the eq.:

$$Q = \frac{V_{FC}}{A_{FC}} \frac{c_2 - c_1}{t_2 - t_1} \left[ \frac{mg}{m^2 * d} \right]$$

$V_{FC}$ (m$^3$) chamber volume  
$A_{FC}$ (m$^2$) chamber area  
$c_1 - c_2$ (mg/m$^3$) methane concentrations at times $t_1 - t_2$ (days).
First applications in geology

Prof. Ronald Klusman
US Colorado School of Mines

INSIGHT mission (2018, NASA)
landing site: Elysium Planitia

SEIS seismometer

A similar arm could be used for positioning a closed-chamber

HP3 (Heat Flow and Physical Properties Probe)

CONNECTING A GAS SENSOR TO THESE PROBES WOULD BE A GREAT OPPORTUNITY TO RELIABLY DETECT METHANE SEEPAGE

Can KISS support the development of such a concept and technology?

(prototype design, development, involvement of robotics companies)
POTENTIAL SEEPAGE ON MARS

where on Mars are the best chances of finding methane?

**Analog seepage sites**
- faulted/fractured ultramafic/serpentinitized rocks
- faulted/fractured sedimentary basins (mud volcanoes, mounds)
Olivine-rich and serpentinized areas on Mars

Serpentine occurs in Mars’ ancient Noachian terrains, Nili Fossae, Syrtis Major, Claritas Rise

30,000 km² olivine-rich outcrop (Hoefen et al 2003)
Faults at Nili Fossae, from PSP_006923_1995 (19.381N, 76.421E) 
Wray and Ehlmann (2011)

Arabia Terra 
(Etiope et al. 2011)
Potential mud volcano-like seeps

Candidate mud volcanoes reported from Utopia, Isidis, northern Borealis, Scandia, Chryse–Acidalia region (Davis and Tanaka, 1995; Tanaka, 1997, 2005; Tanaka et al., 2000, 2003, 2008; Farrand et al., 2005; Kite et al., 2007; Rodríguez et al., 2007; Skinner and Tanaka, 2007; Allen et al., 2009; Oehler and Allen, 2009; Skinner and Mazzini, 2009; McGowan, 2009; McGowan and McGill, 2010)

>40000 estimated

(18000 mapped) in Acidalia Planitia (Oehler and Allen, 2010)
Potential mud volcano-like seeps  Acidalia Planitia

(Oehler and Allen, 2010; Etiope, Oehler, Allen 2011)
INTERPRETING MOLECULAR COMPOSITION OF GAS

THE MEANING OF METHANE/ETHANE RATIOS

(expected to be measured in the ExoMars 2016 mission)

is it a reliable indicator of gas origin?
It is generally assumed that $C_1/C_2$ is a good indicator of methane origin, microbial ($C_1/C_2 > 1000$) or thermogenic or abiotic ($C_1/C_2 < 1000$)

But this is true only if gas is sampled/detected at the point of its origin

(on Mars we may only detect seeping gas)

During gas migration, due to molecular adsorption on solid grains of mud/sediments seeping gas becomes dryer (more $\text{CH}_4$, less $\text{C}_2+$) than reservoir gas.

Molecular fractionation is inversely proportional to the flux or velocity of gas
Gas migration from reservoir to surface seeps: Loss of C2+ hydrocarbons due to molecular fractionation

Analysis of seeps over corresponding reservoirs
ABIOTIC GAS
seeps (continental serpentinization sites)
vs
deep boreholes (Precambrian shields)

\[ \frac{C_1}{C_2^{+}} \]

\[ \delta^{13}\text{C-CH}_4 \]
OTHER EXAMPLES OF ABIOTIC and GEOTHERMAL GAS

McCollom & Seewald (2007)

Figure 19. Carbon isotopic composition of methane and $C_1/C_{2\text{+}}$ ratios for volatile hydrocarbons in high-temperature fluids from mid-ocean ridge hydrothermal systems. Shown in gray is the range of values observed for typical microbial and thermogenic hydrocarbon gases. Also shown for comparison are values for gases proposed to have an abiotic origin in Precambrian shield rocks, igneous rocks, and gases venting from a continental serpentinite (Zambales ophiolite). The fields marked "H & B" are abiotic methane generated in hydrothermal experiments of Horita and Berndt (2012) ($C_1/C_{2\text{+}}$ values are minimums because $C_{2\text{+}}$ compounds were below detection limits). ▲ represent hydrocarbons formed in Fischer–Tropsch synthesis experiments.27,52,54 Adapted with permission from ref 43. Copyright 1999 AAAS (http://www.aaas.org).

Tassi et al (2012)

Fig. 3. $C\text{H}_4/(C_2\text{H}_6 + C_3\text{H}_8)$ vs. $\delta^{13}\text{C-CH}_4$ diagram for the Italian gas discharges. Values for gases of biogenic origin (microbial and thermogenic) and from unsedimented mid-oceanic ridges, sediment-covered ridges and igneous rocks are reported (McCollom and Seewald, 2007, and references therein) for comparison. Green circle: gases from the Tyrrenian domain; blue circle: gases from the geothermal systems of Mt. Amiata, Larderello, Latera, Manziana and Ischia; red circle: gases from Solfatara, Vesuvio, Panarea and Pantelleria volcanic-hydrothermal systems; yellow triangle: gas discharges in the Apenninic domain; yellow square: gases from the Adriatic domain.
Molecular fractionation inversely proportional to gas flux
Therefore.....

1. If both methane and ethane will be detected, then it is likely that gas is abiotic, but we shall assume that

(a) there are not ethanogens on Mars (ethane-producing microbes exist on Earth)

(b) there is no ancient organic matter in deep sedimentary rocks that could be degraded by temperature (i.e. the possibility for thermogenic gas shall be excluded, and we shall explain why)

2. If ethane will not be detected, then we may hypothesize

(a) microbial gas
(b) abiotic gas molecularly fractionated
(c) abiotic gas generated at very low T (no enough energy for polymerization of CH$_4$ molecules to form C$_{2+}$)

In any case, we will have a certain degree of uncertainty on the origin. However, detecting ethane would make the interpretation a bit easier (probable abiotic gas); considering the geological framework and the features of the sampled site (mud volcano, sedimentary basin, basalt and serpentines..etc..) could help.
INTERPRETING ISOTOPIC COMPOSITION OF GAS

The meaning of $\delta^{13}C$-CH$_4$ and $\delta^2H$-CH$_4$
Updated (2015) CH$_4$ isotopic-genetic plot

- Shallow & glacial sediments
- Conventional reservoirs, coal-gas, shale-gas
- Microbial CO$_2$ reduction
- Microbial acetate fermentation
- Thermogenic
- Mixed
- Dry
- Volcanic-geothermal systems
- Alkaline rock inclusions
- Marine serpentinization
- Land-based serpentinization
- Abiotic
- Precambrian shields

G. Etiöpe (2016), Encyclopedia of Geochemistry, Springer
Potential C–H isotopic signatures of CH4 on Mars

**Martian C feedstock:**
- atmospheric fractionated CO2 ($\delta^{13}C$: +46‰; *Webster et al. 2013*)
- atmospheric unfractionated CO2 ($\delta^{13}C$ -20‰ to 0‰; *Niles et al., 2010*)
- magmatic CO2 (Zagami meteorites, $\delta^{13}C$: -10 to -20‰)

$\delta^{13}C$-CH$_4$ can be similar to that observed on Earth only if it derives from unfractionated or magmatic CO2

**Martian H feedstock:**
- atmospheric H$_2$
- H in minerals (meteorites)
- subsurface waters ???
- magma: low $\delta^2$H; initial $\delta^2$H similar to Earth; *Boctor et al., 2003; Lunine et al., 2003*
- igneous rocks: olivine, $\delta^2$H: -60 to -280‰ *Gillet et al. 2002*

A wide range of $\delta^2$H could be measured for martian CH$_4$, far outside terrestrial variations

Martian $\delta^2$H–CH$_4$ values could be within the terrestrial range if the precursor hydrogen derives from primordial, unfractionated, magmatic gas or is similar to that of martian olivine.
Conceptual summary for seepage on Mars

- **mud volcanoes or mounds** (macro-seepage)
- **microseepage**
  - soil-gas probes
  - flux chambers

**Geologic CH₄ production processes** (abiotic – biotic)

- **sedimentary or serpentinized (olivine-rich) igneous rocks**
- **gas advection**
- **molecular fractionation**
- **fault**

Above ground measurements may not be effective.