Methane on Mars II workshop

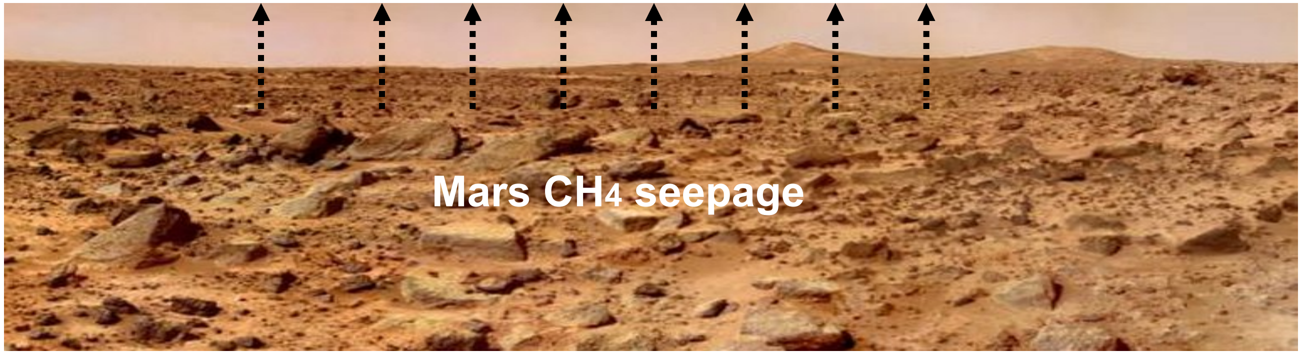
“Gas seepage”

Giuseppe Etiope

(*Seepage WG: G.Etiope, P. Beckett, J. Blank, P. Chen, R. Klusman, D. Oehler, L. Shen)*

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

<u>= **gas seepage,** a process well known on Earth, should exist on Mars.</u>



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]

Icarus 224 (2013) 276–285

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]

NO VOLCANOES

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 2nd 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)

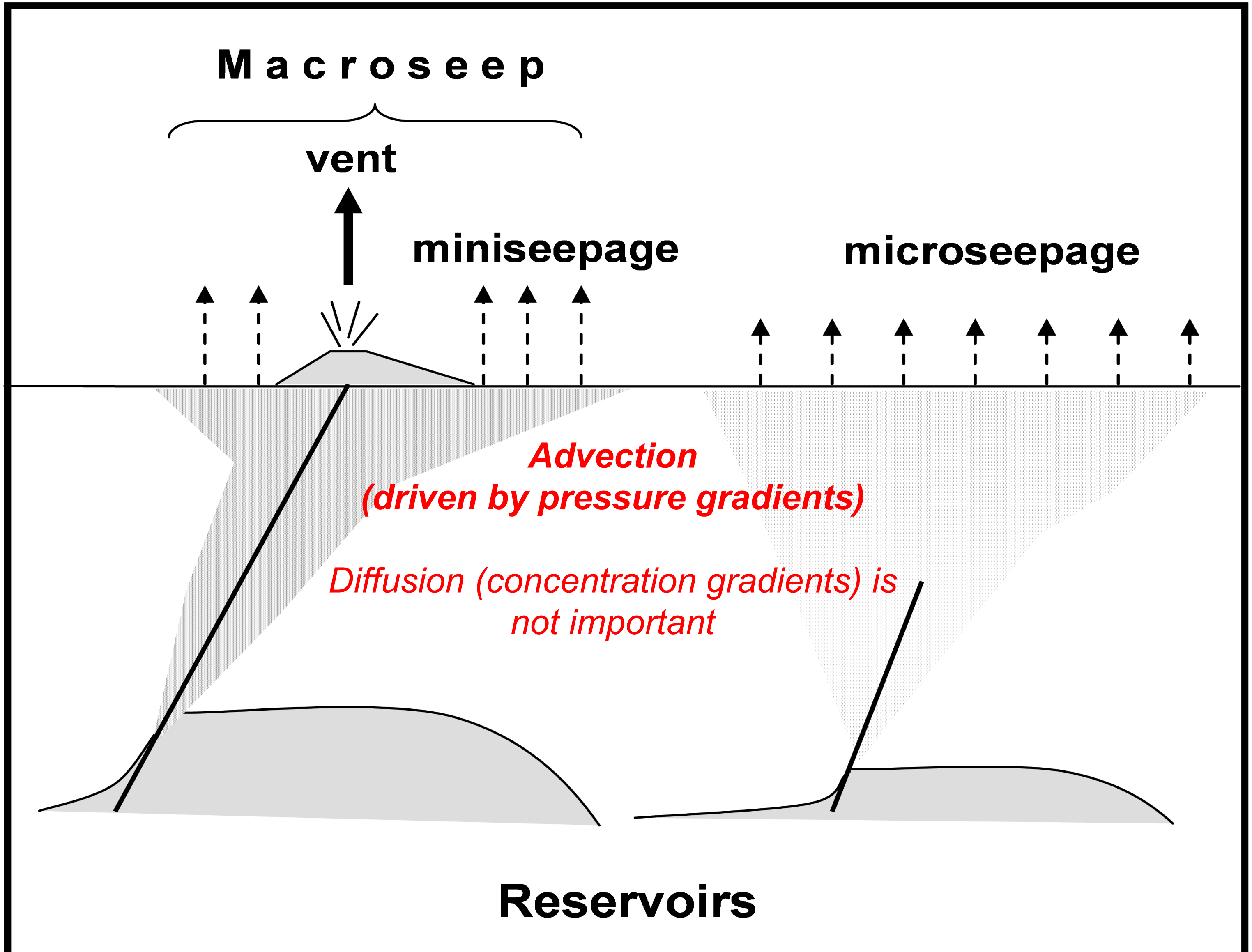
Proposed deliverable

- 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



Gas seeps and "eternal" fires

Release from 1 to 1000 ton CH_4 per year

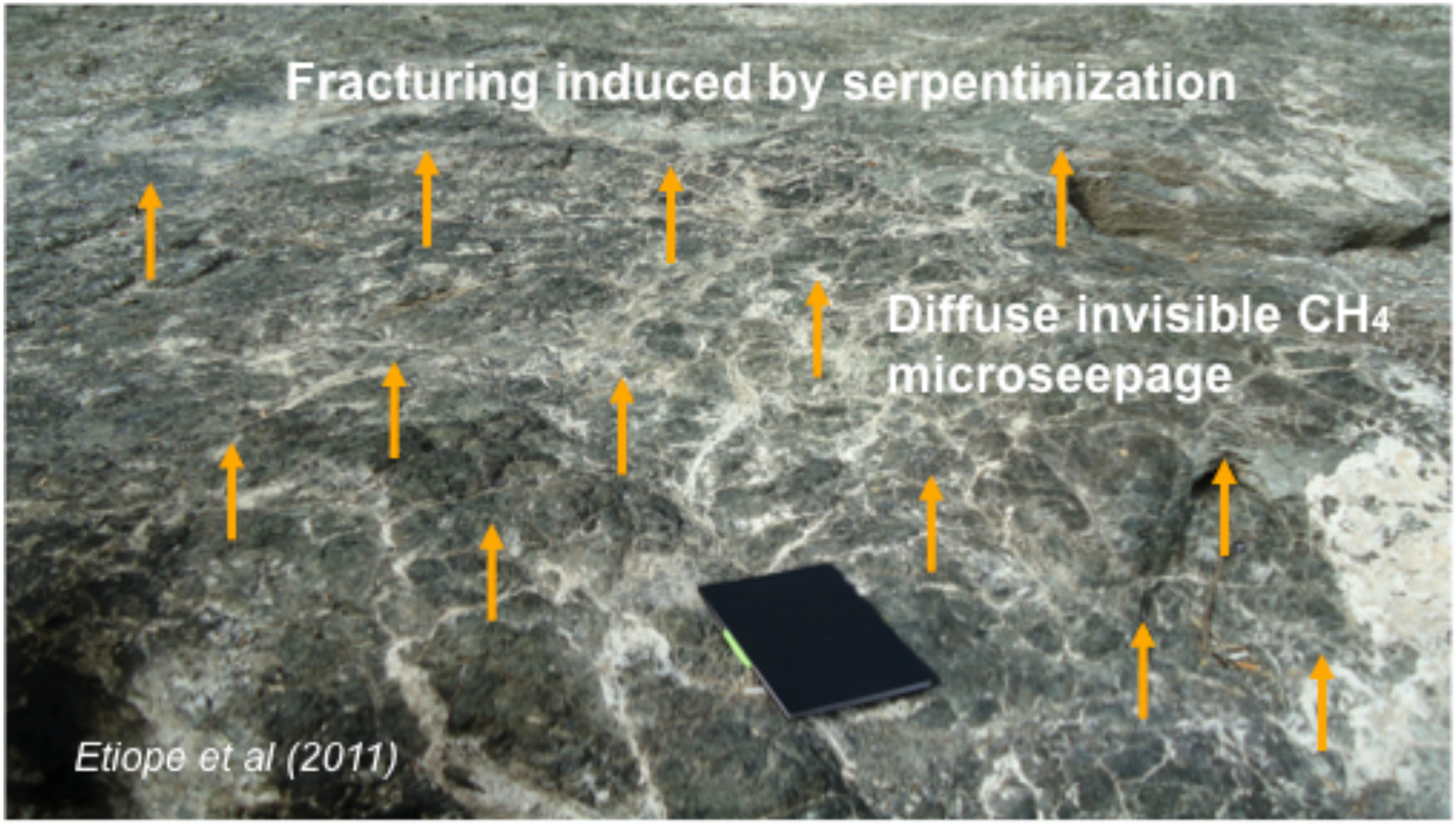
Mud volcanoes

Release from 1 to 500 ton CH_4 per year

Sedimentary volcanism, 3-phase system : gas-water-sediment

MICROSEEPAGE IN OLIVINE-RICH ROCKS (PERIDOTITES)

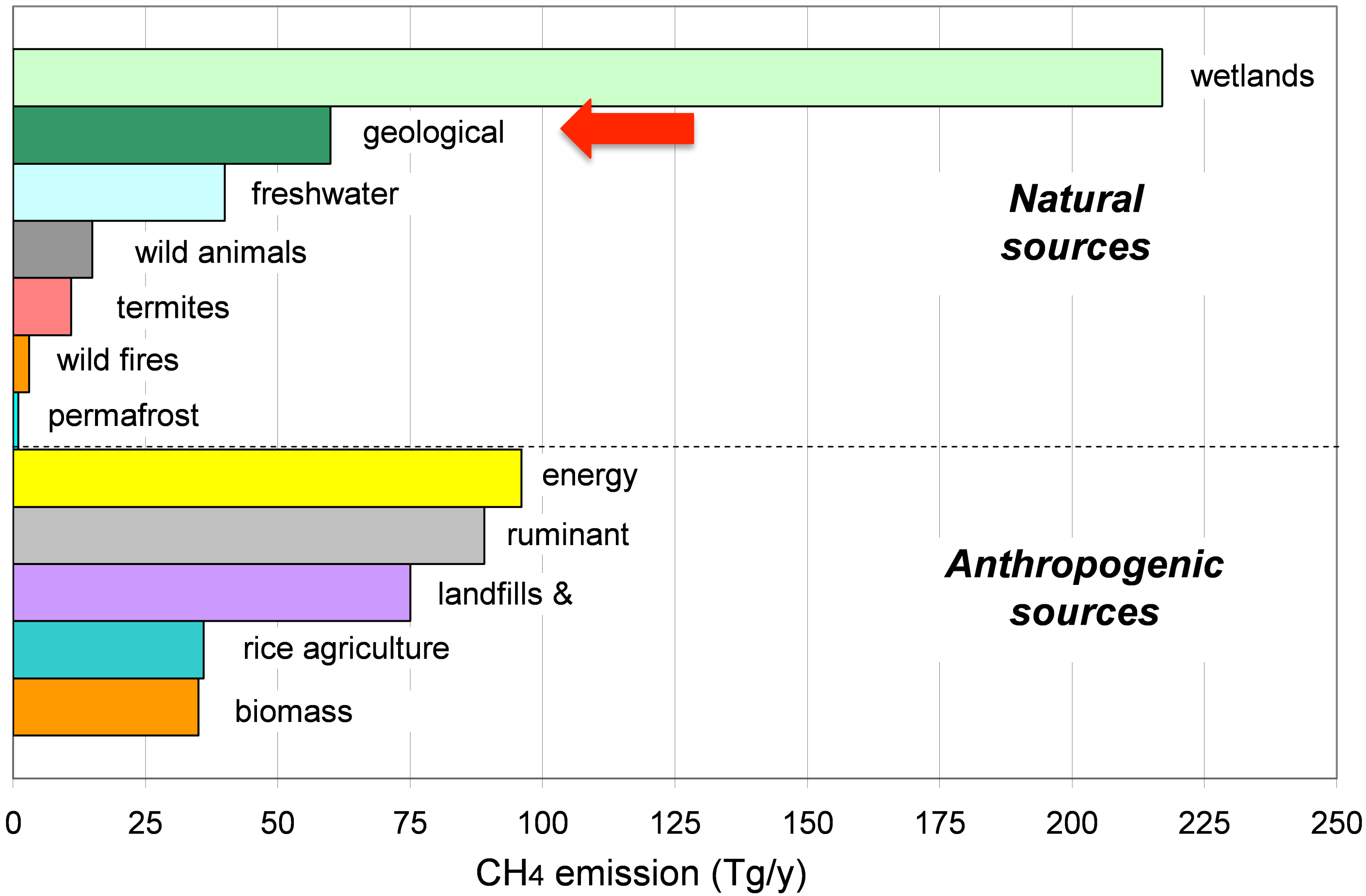
from 1 to 10^3 mg m^{-2} day^{-1}

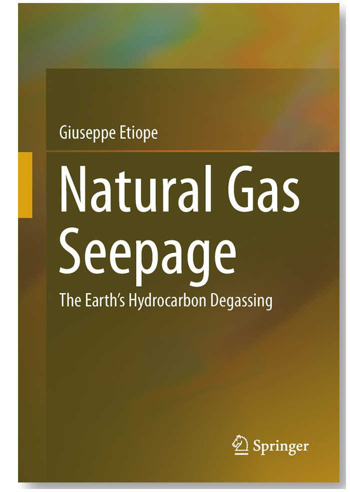


Geological emissions in the global CH_4 budget

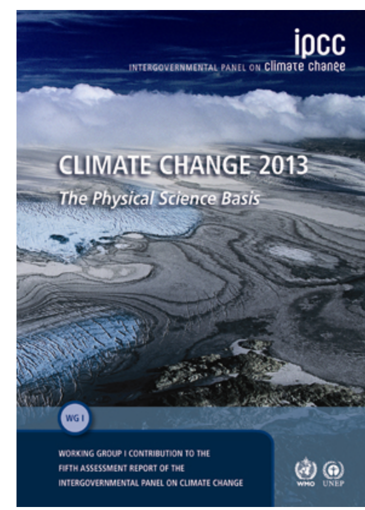
2^{nd} natural CH_4 source
10% of total CH_4 source

Etiope and Ciccioli 2009 (Science)
Etiope, 2012 (Nature Geosci.)





(Etiope, 2015)

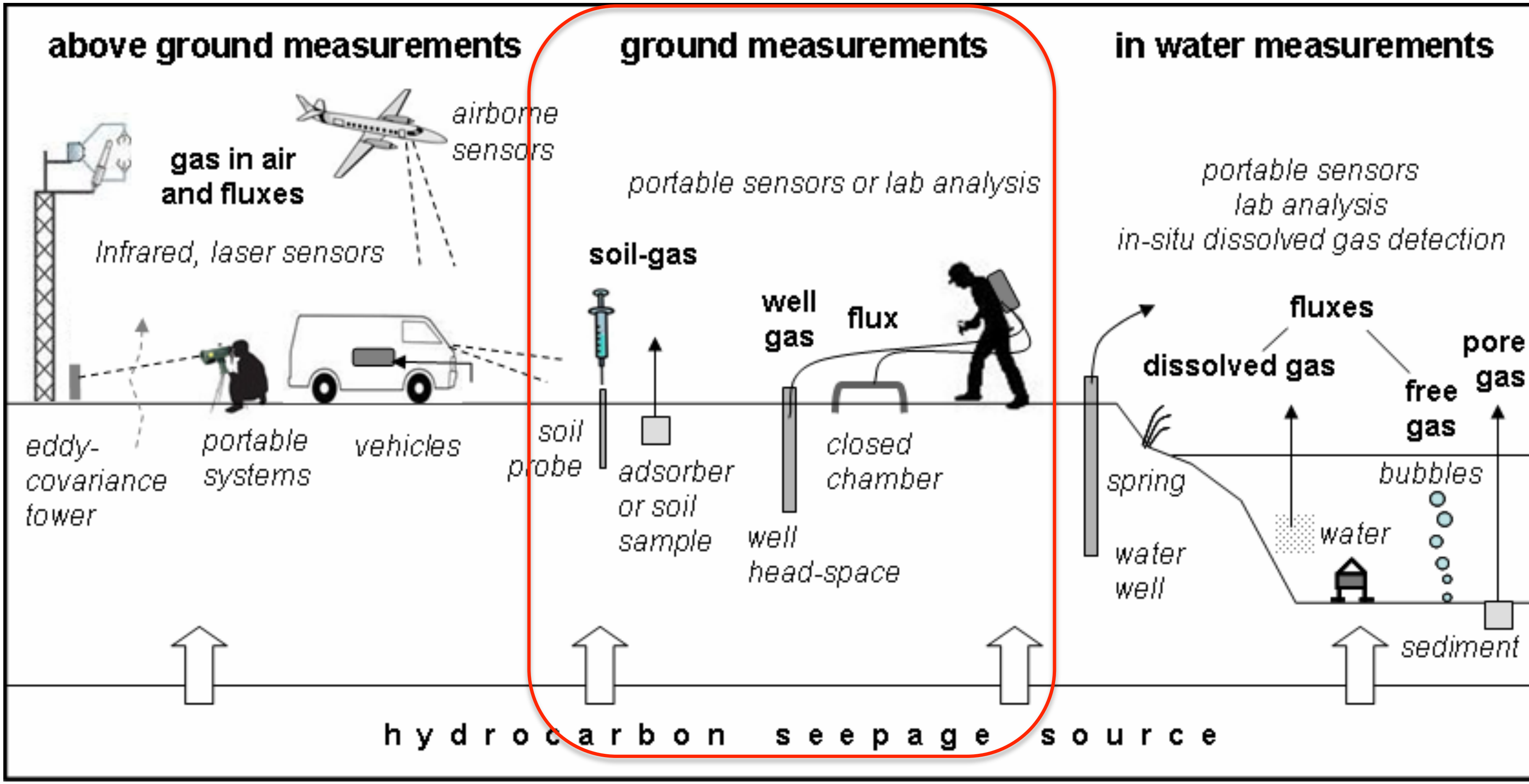


(IPCC, 2013)

How to detect and measure gas seepage

Effective only for significant seepage

Effective also for very low seepage



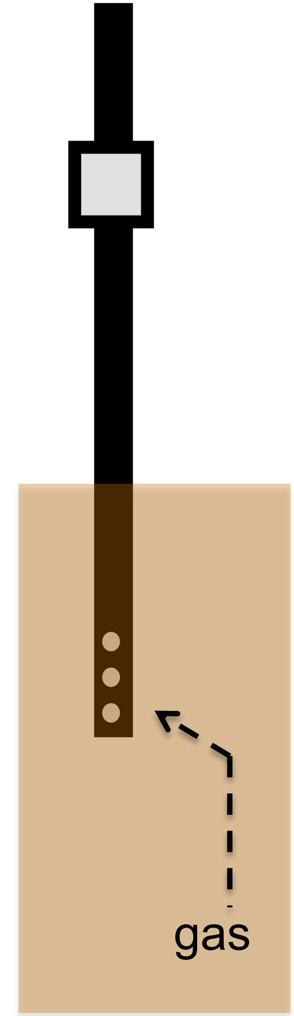
approach to be adopted for Mars

Etiope (2015)

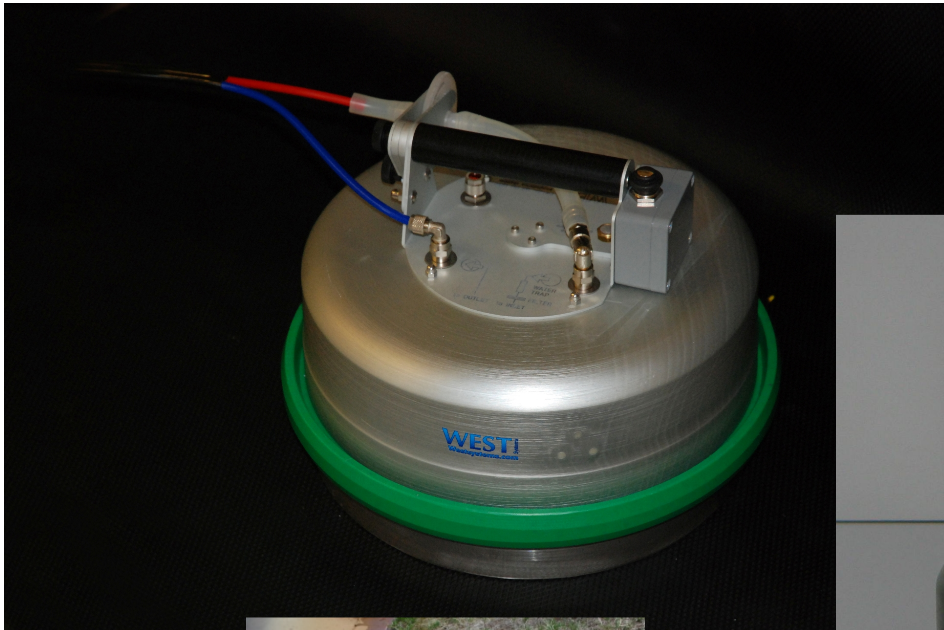
Shallow drilling into the soil

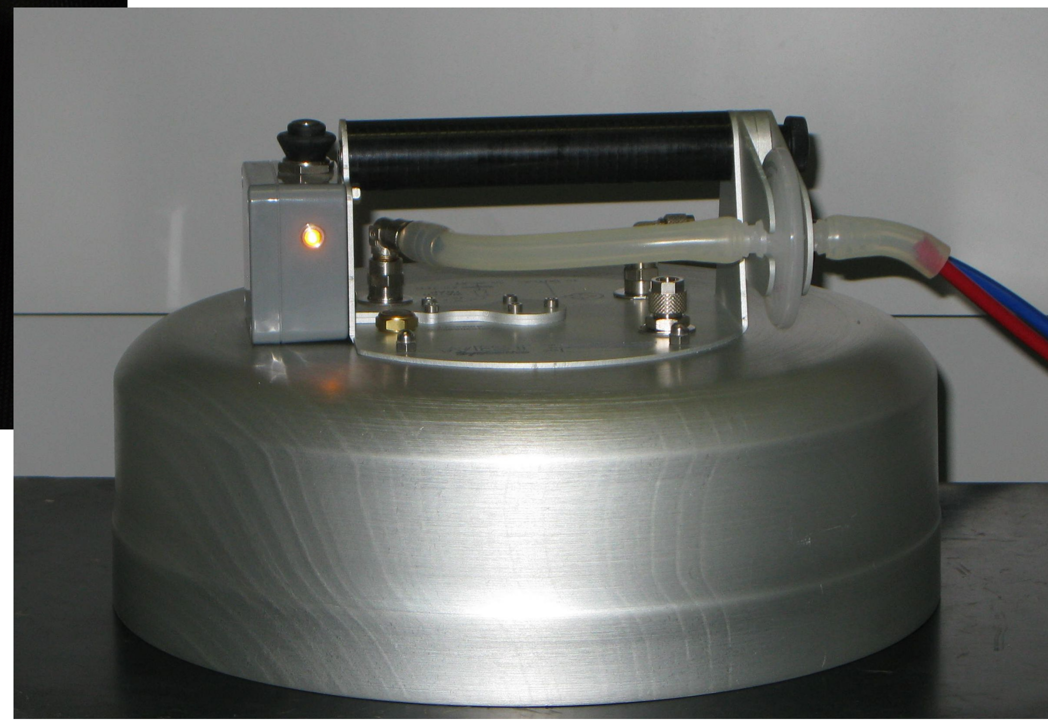
soil-gas probes

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.

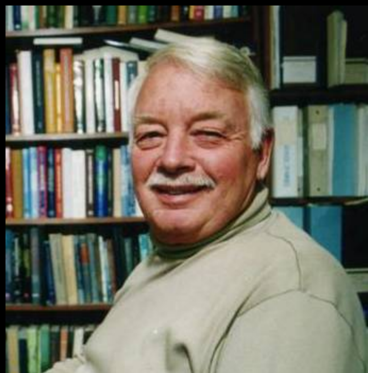
Gas flux Q is expressed in terms of mg m^{-2} day^{-1} by the eq.:

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

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).

Photo: Charlotte Sigsgaard

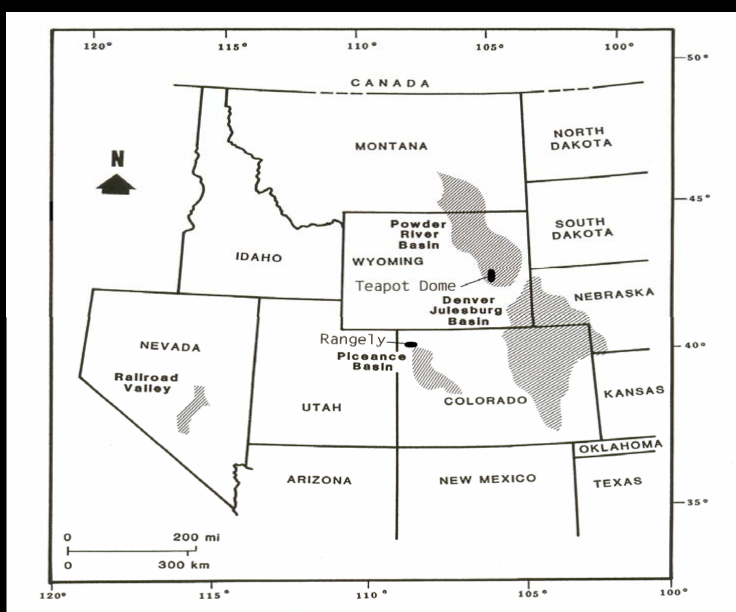
First applications in geology



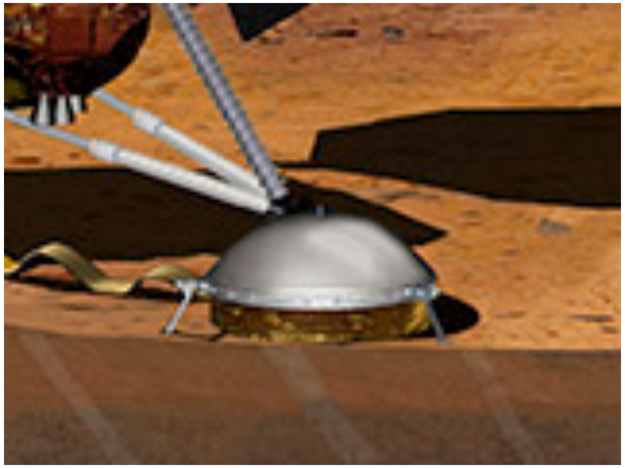
Prof. Ronald Klusman

US Colorado School of Mines

Klusman et al 2000. J. Geoph. Res. 105D, 24,661-24,670
Klusman et al 2000. Geothermics 29, 637-670
Klusman 2003. Applied Geochem., 18, 1825-1838.
Klusman 2006. Applied Geochem., 21, 1498-1521.

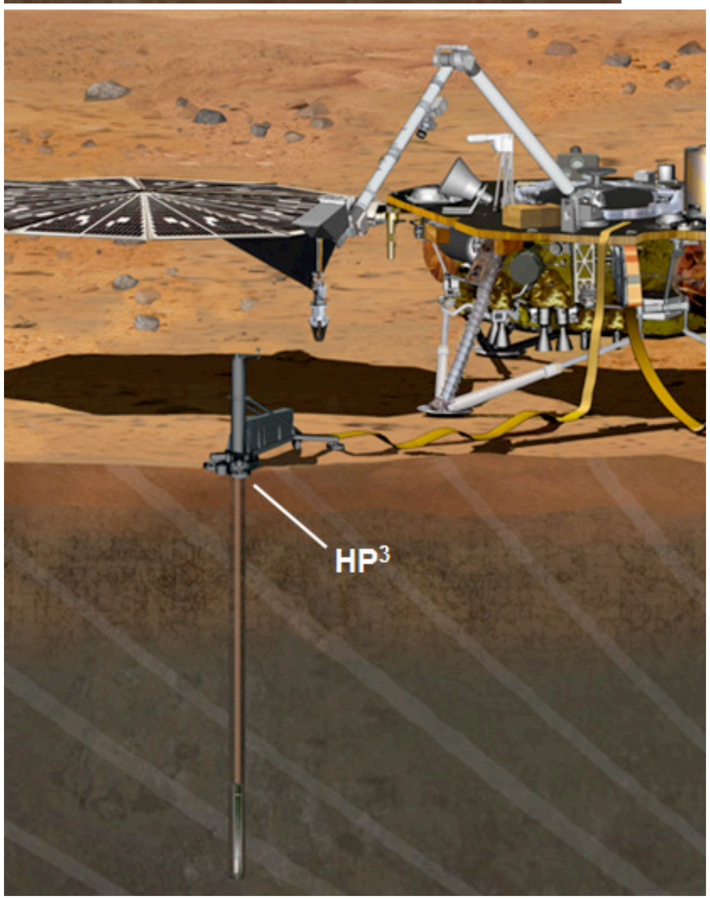


INSIGHT mission *(2018, NASA)*
landing site: Elysium Planitia



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

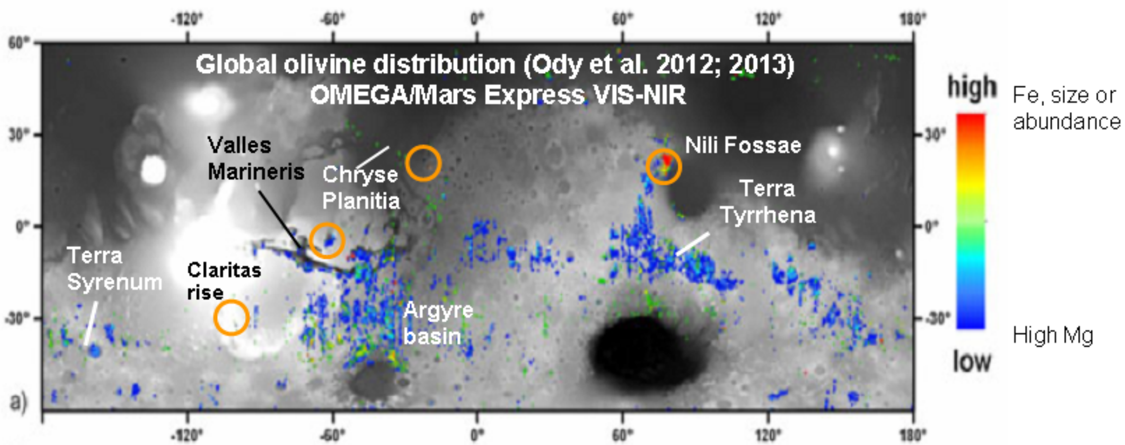
where on Mars are the best chances of finding methane?

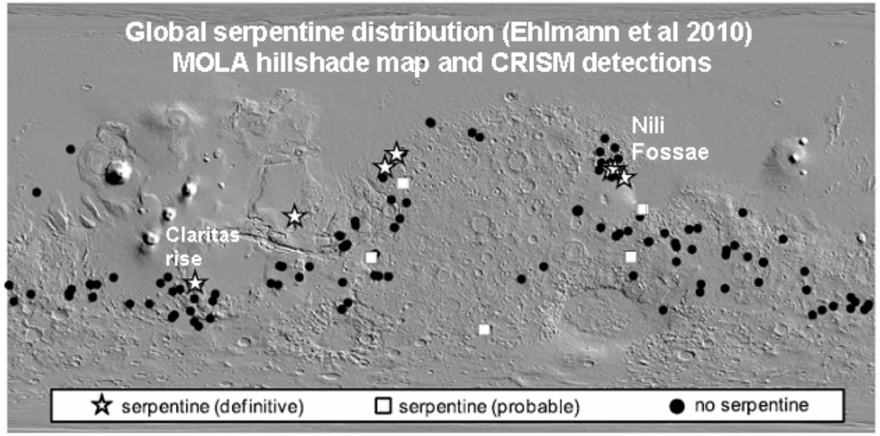
Analog seepage sites

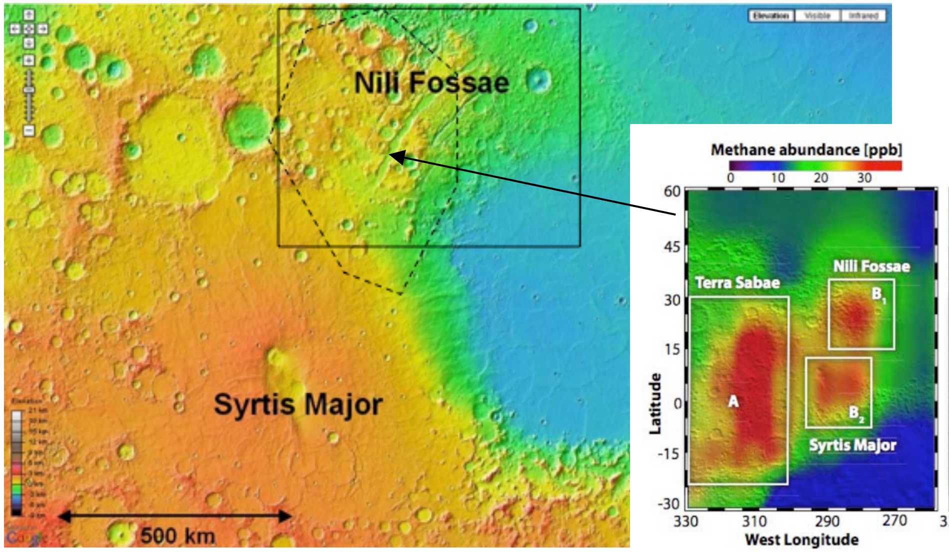
faulted/fractured ultramafic/serpentinized rocks
faulted/fractured sedimentary basins (mud volcanoes, mounds)

Olivine-rich and serpentinized areas on Mars

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

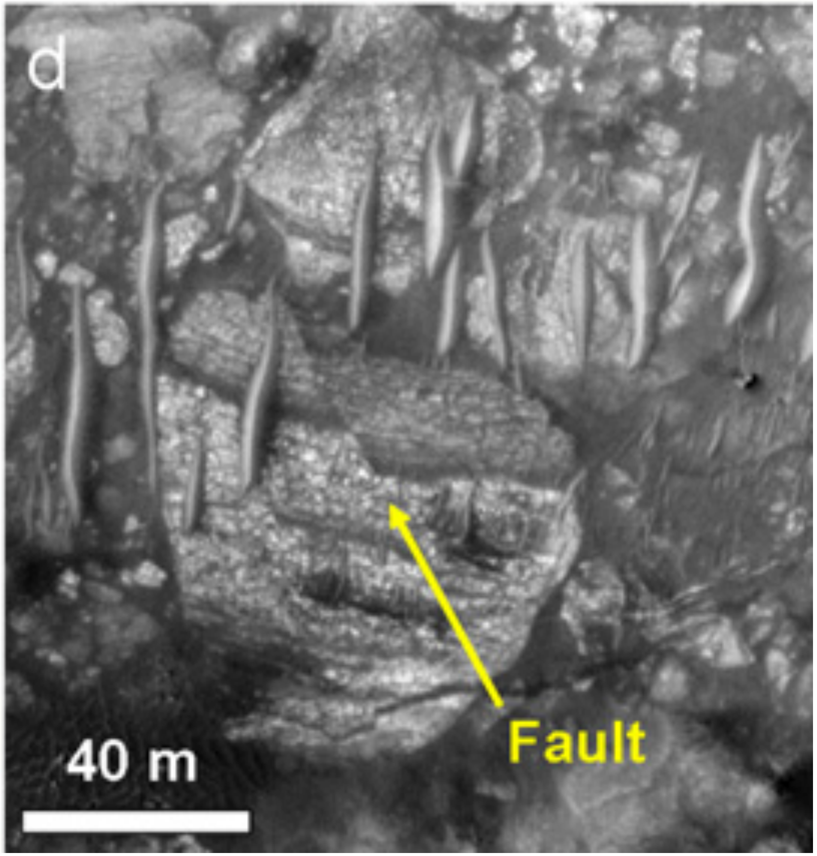




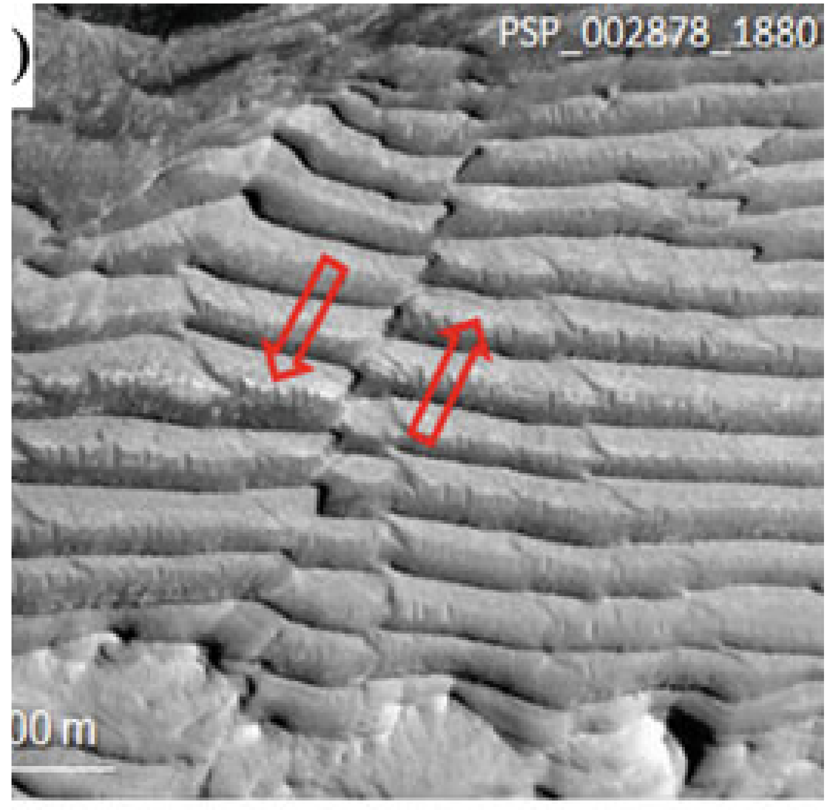


30,000 km^2 olivine-rich outcrop (*Hoefen et al 2003*)

FAULTS



Fault at Nili Fossae, from PSP_006923_1995 (19.381N, 76.421E)
Wray and Ehlmann (2011)



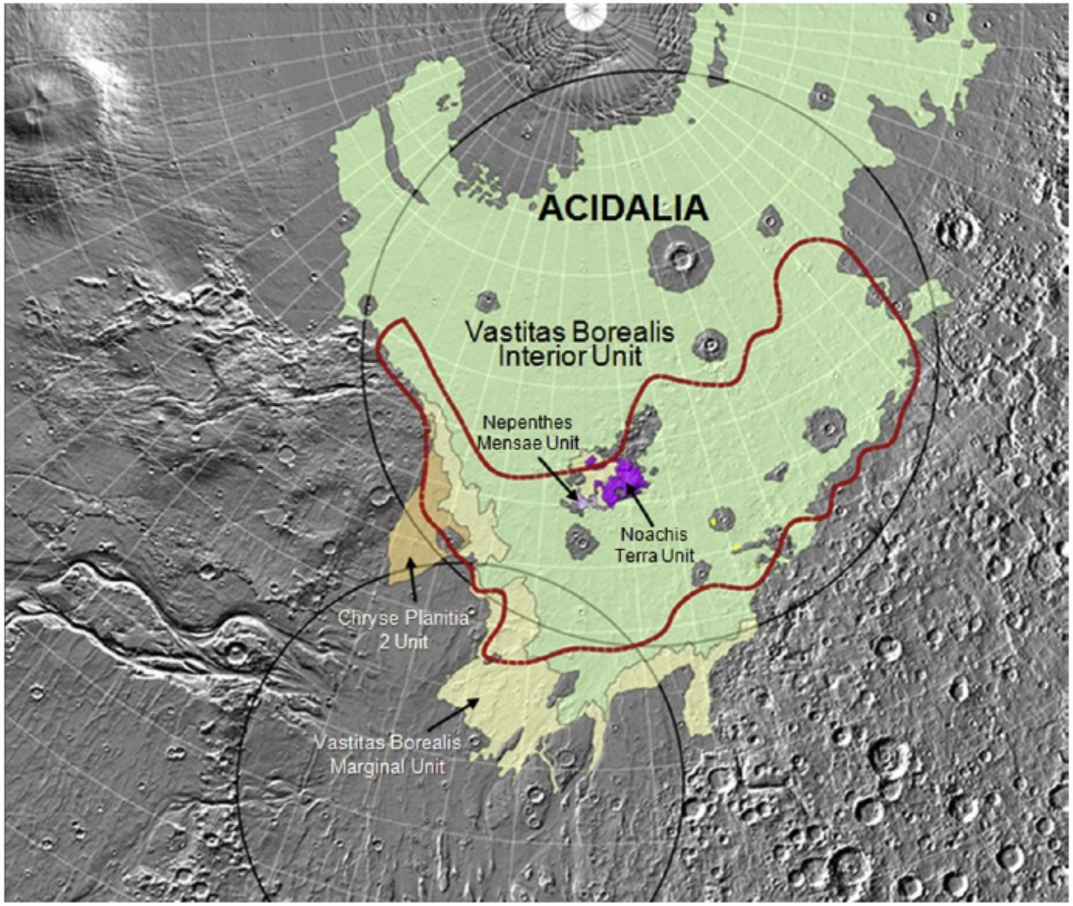
Arabia Terra
(*Etiope et al. 2011*)

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*)

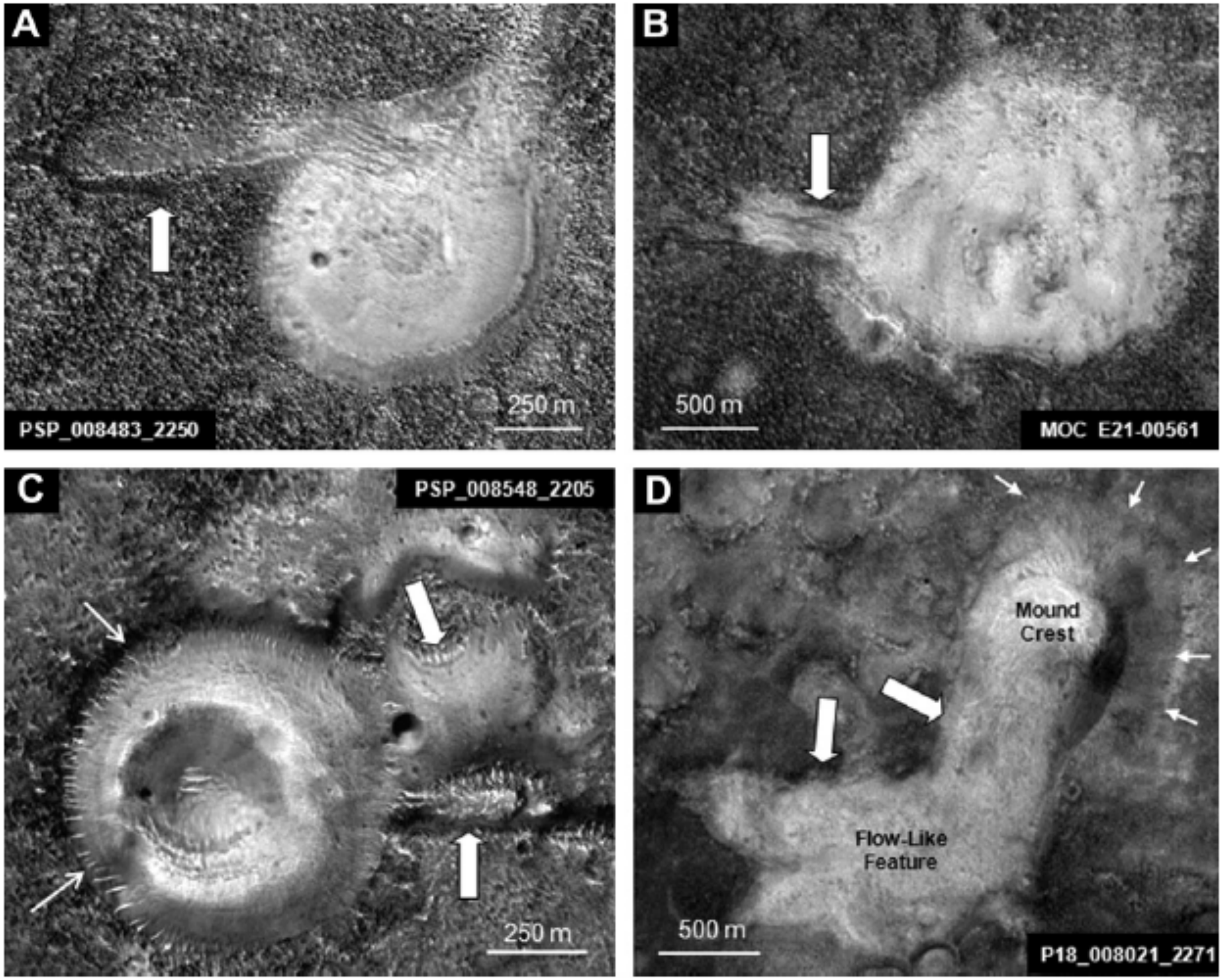
>40000 estimated

(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

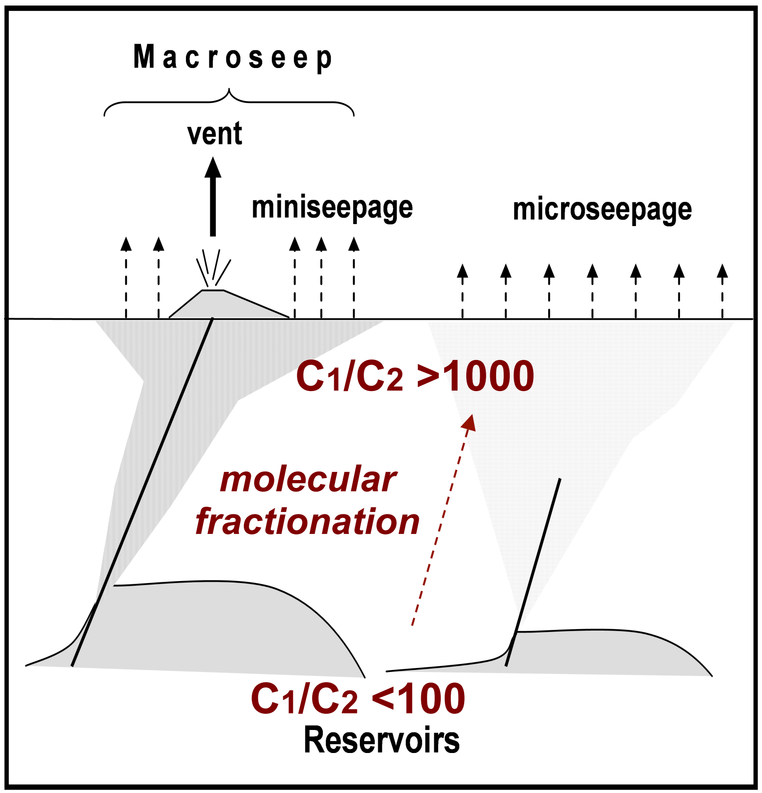
(expected to be measured in the ExoMars 2016 mission)

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)

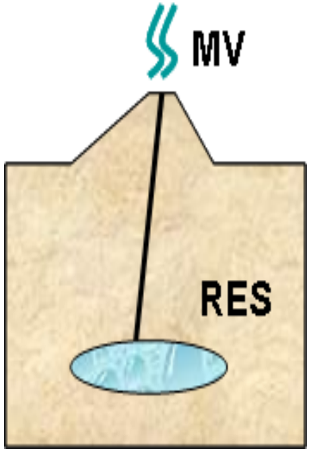


During gas migration, due to molecular adsorption on solid grains of mud/ sediments seeping gas becomes dryer (more CH_4, less C_{2+}) than reservoir gas.

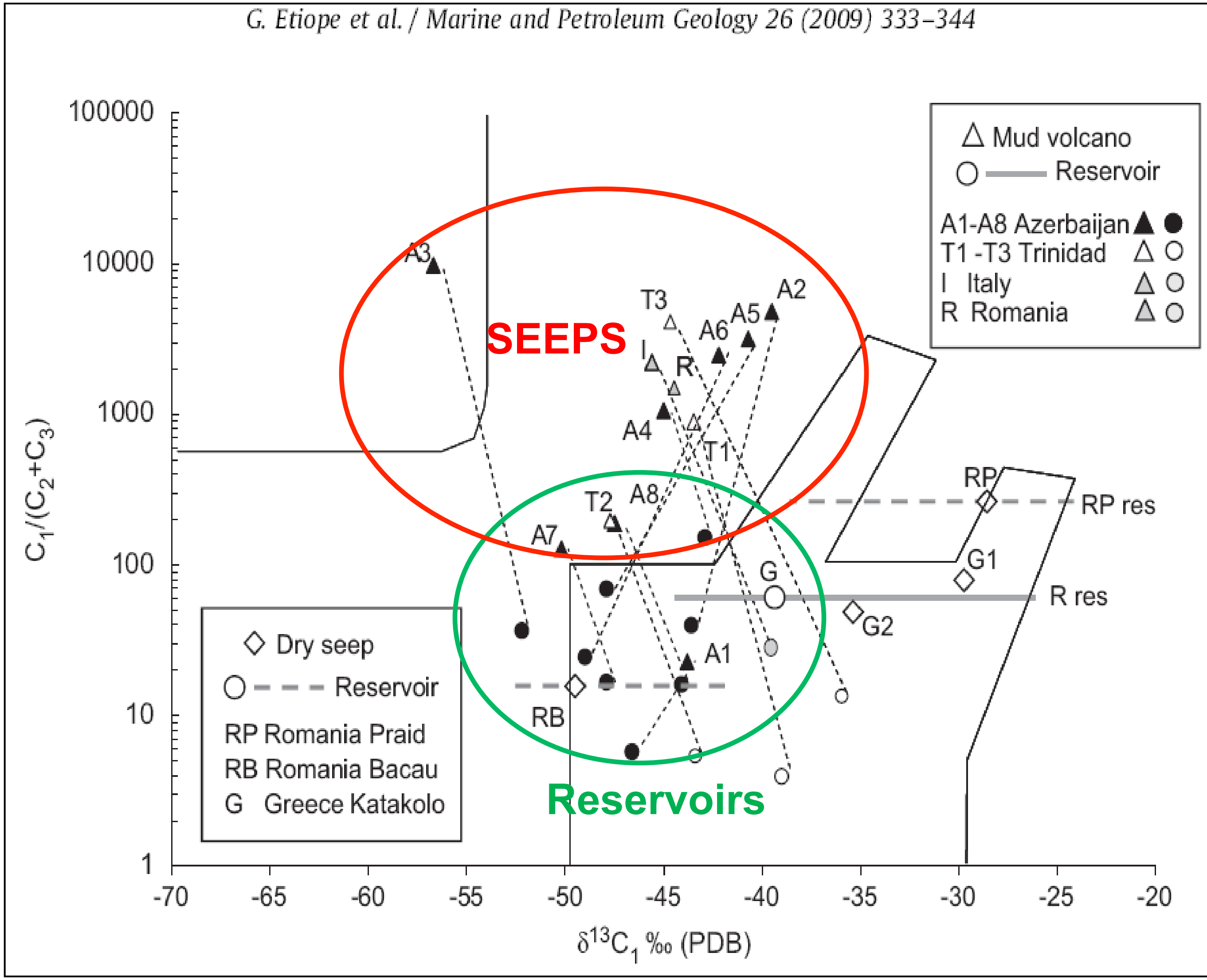
Molecular fractionation is inversely proportional to the flux or velocity of gas

Gas migration from reservoir to surface seeps:

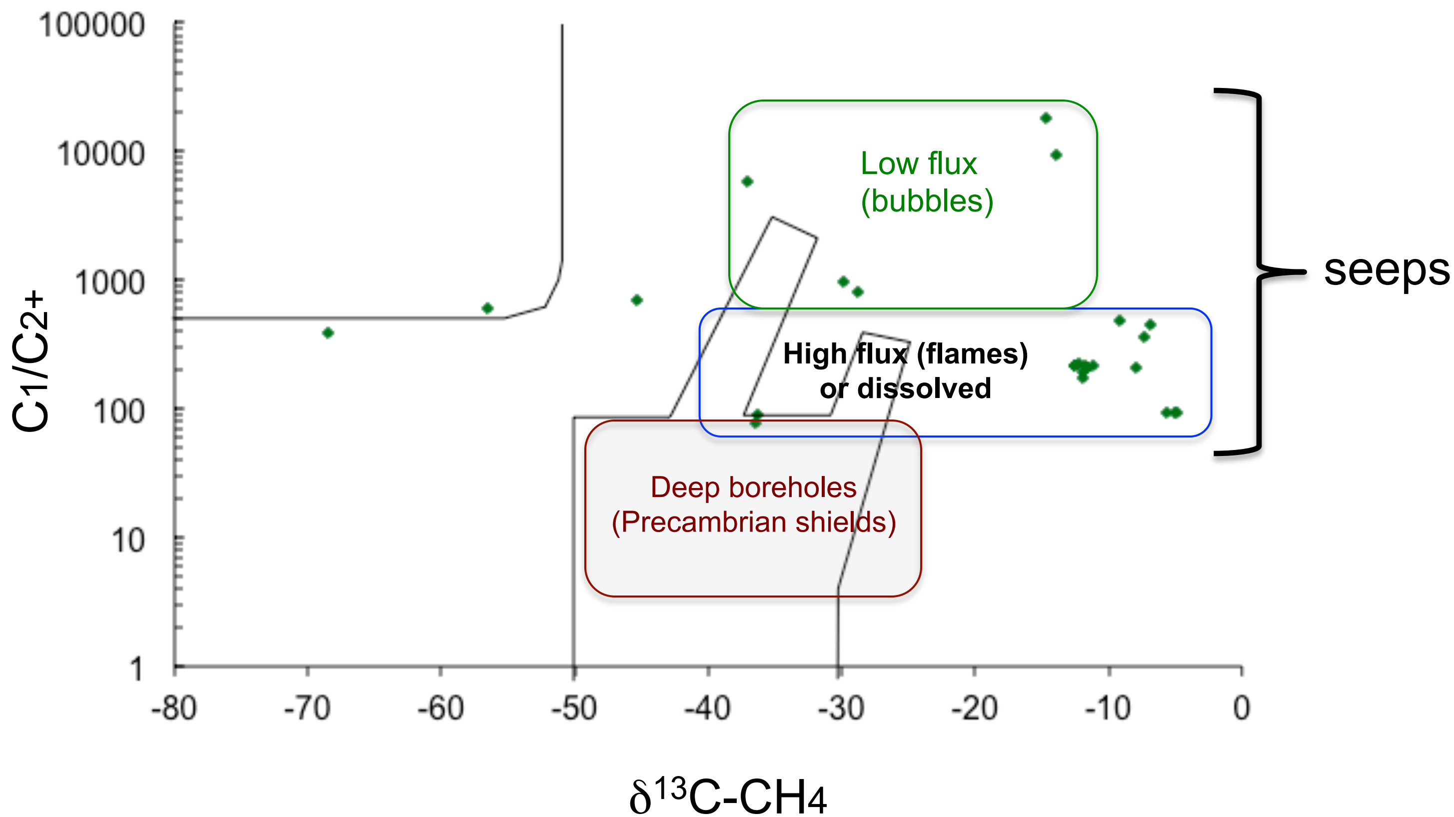
Loss of C2+ hydrocarbons due to molecular fractionation



Analysis of seeps over corresponding reservoirs



ABIOTIC GAS
seeps (continental serpentinization sites)
vs
deep boreholes (Precambrian shields)



OTHER EXAMPLES OF ABIOTIC and GEOTHERMAL GAS

McCollom & Seewald (2007)

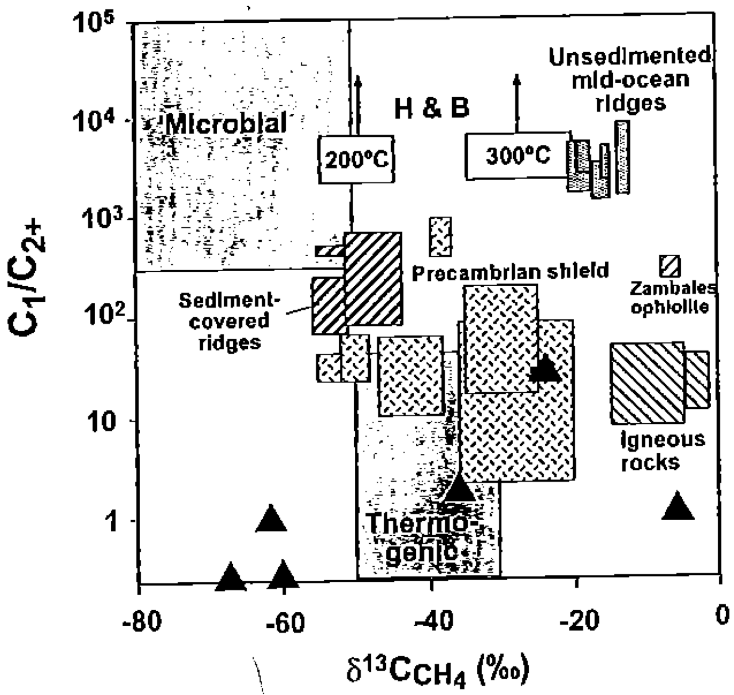


Figure 19. Carbon isotopic composition of methane and C_1/C_{2+} ratios for volatile hydrocarbons in high-temperature fluids from mid-ocean ridge hydrothermal systems. Shown in gray is the range of values observed for typical microbial and thermogenic hydrocarbon gases. Also shown for comparison are 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[43] (C_1/C_{2+} values are minimums because C_{2+} 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)

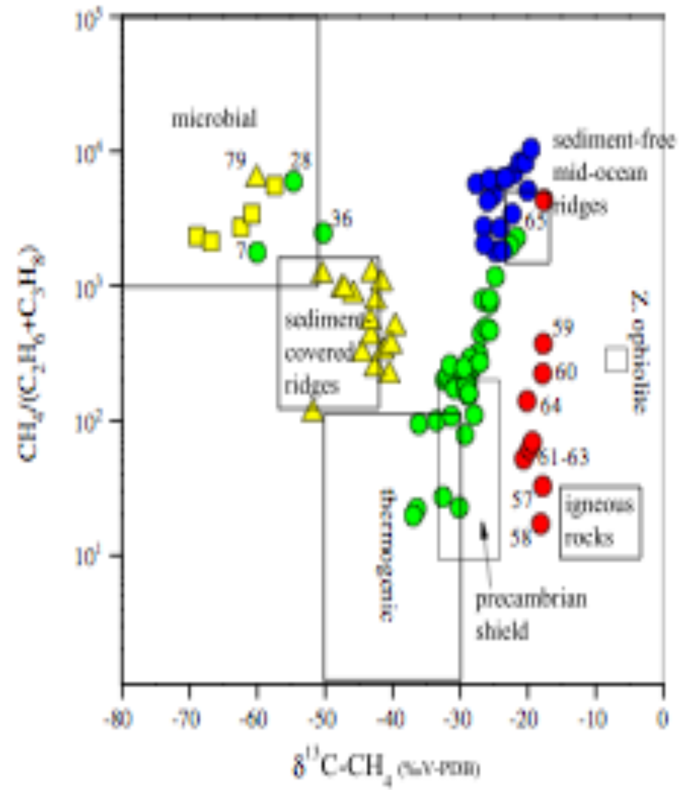
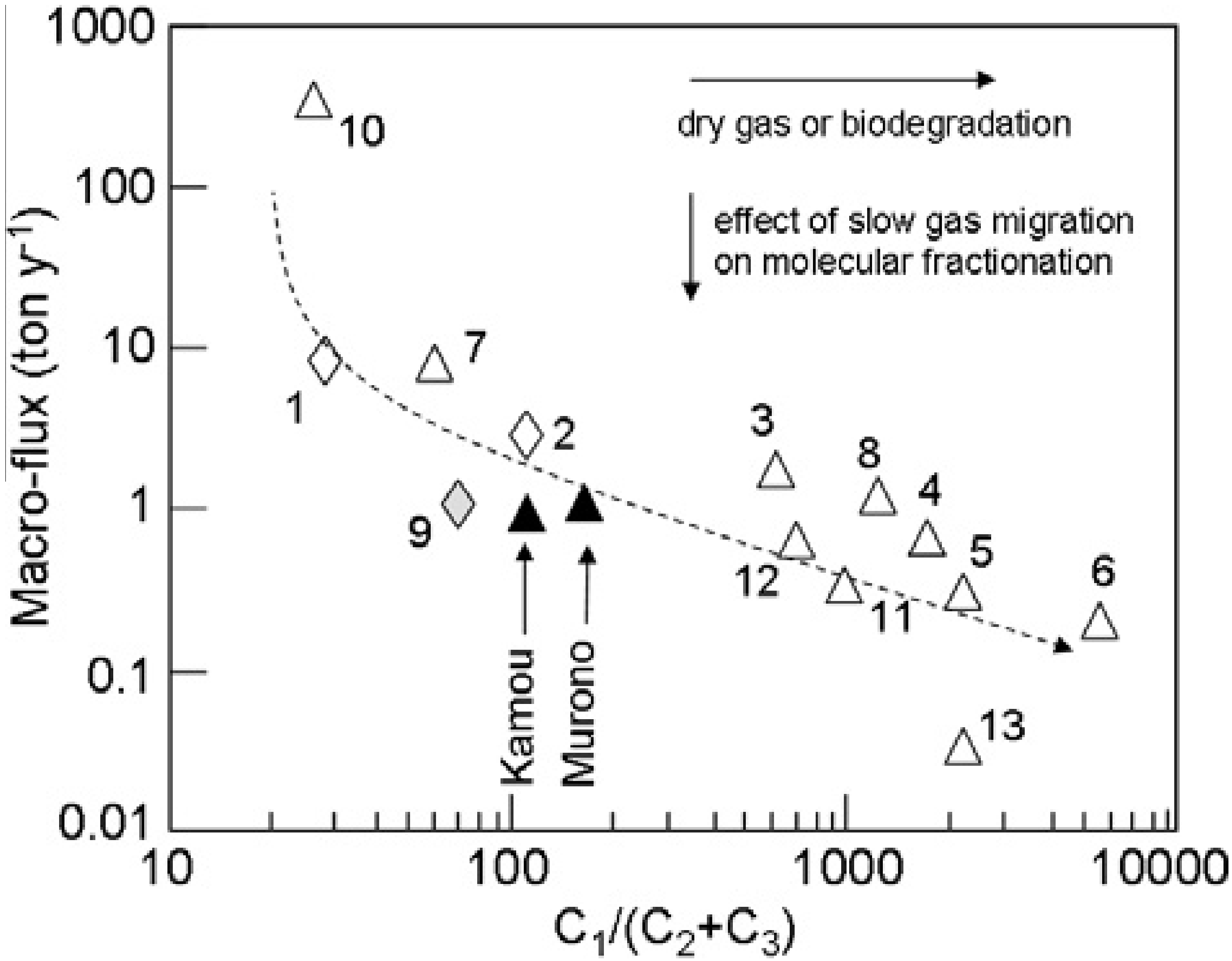


Fig. 3. $CH_4/(C_2H_6+C_3H_8)$ vs. $\delta^{13}C$-CH_4 diagram for the Italian gas discharges. Values for gases of biogenic origin (microbial and thermogenic) and from unsedimented mid-oceanic ridges, sediment-covered ridges and igneous rocks are reported (McCollom and Seewald, 2007, and references therein) for comparison. Green circle: gases from the Tyrrhenian 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



Etiope et al (2011)

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

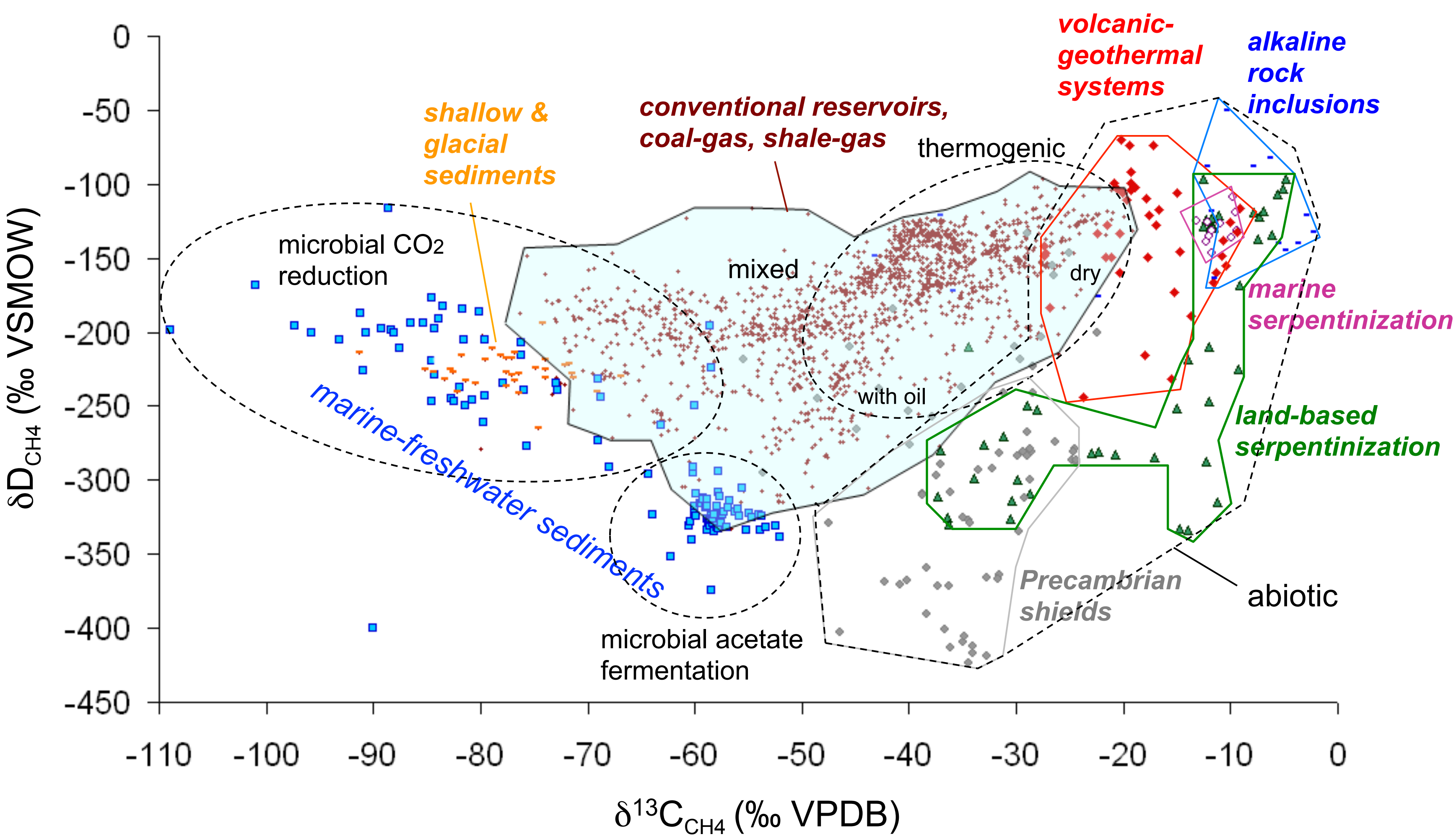
(a) microbial gas
(b) abiotic gas molecularly fractionated
(c) abiotic gas generated at very low T (no enough energy for polymerization of CH_4 molecules to form C_{2+})

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 $\delta^{2}H-CH_4$

Updated (2015) CH_4 isotopic-genetic plot



G. Etiope (2016), Encyclopedia of Geochemistry, Springer

Potential C–H isotopic signatures of CH_4 on Mars

Martian C feedstock: - atmospheric fractionated CO_2 ($\delta^{13}C$: +46 ‰; *Webster et al 2013*)
- atmospheric unfractionated CO_2 ($\delta^{13}C$ -20‰ to 0‰; *Niles et al., 2010*)
- magmatic CO_2 (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 CO_2

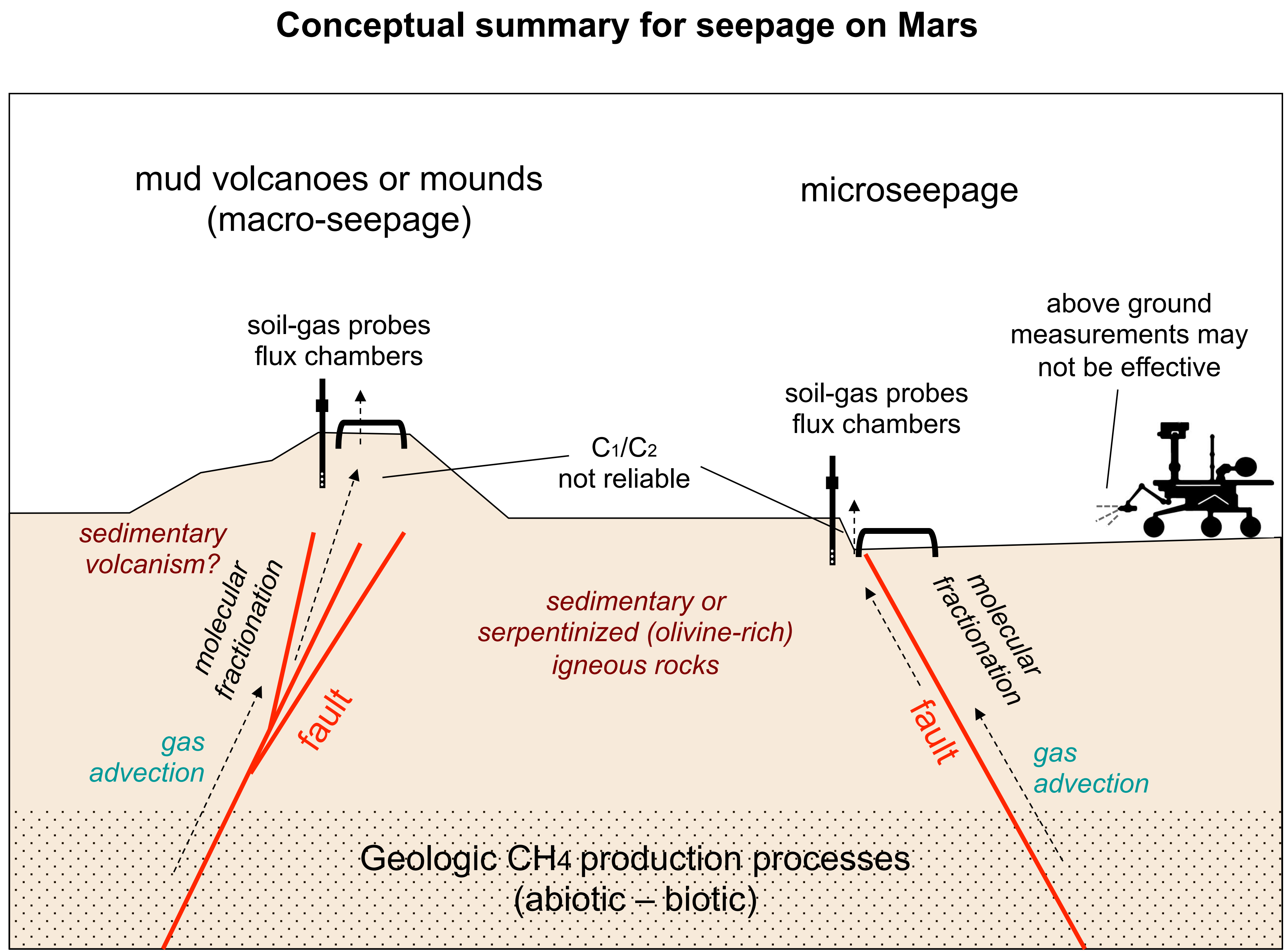
Martian H feedstock: - atmospheric H_2
- H in minerals (meteorites)

} extrem. enriched in deuterium δ^2H up to +4000‰ *Leshin, 2000; Sugiura and Hoshino, 2000* due to atmospheric escape fractionation processes

- subsurface waters ???
- magma: low δ^2H; initial δ^2H similar to Earth; *Boctor et al., 2003; Lunine et al., 2003*
- igneous rocks: olivine, δ^2H: -60 to -280 ‰ *Gillet et al. 2002*

A wide range of δ^2H could be measured for martian CH_4, far outside terrestrial variations

Martian δ^2H–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
above ground
measurements may
not be effective
soil-gas probes
flux chambers
C_1/C_2
not reliable
sedimentary
volcanism?
molecular
fractionation
sedimentary or
serpentinized (olivine-rich)
igneous rocks
molecular
fractionation
fault
fault
gas
advection
gas
advection
Geologic CH_4 production processes
(abiotic – biotic)