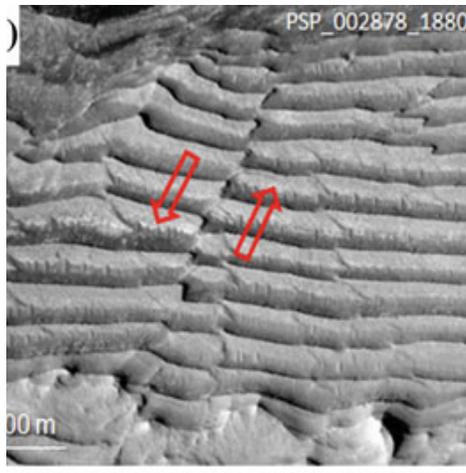


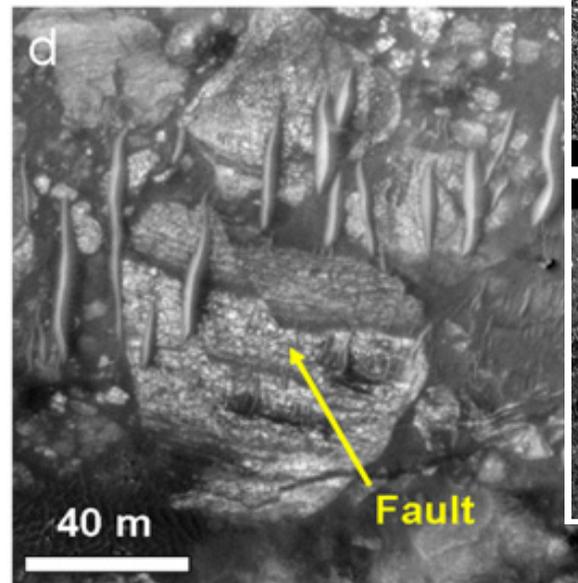
Potential CH₄ seepage on Mars

Giuseppe Etiope

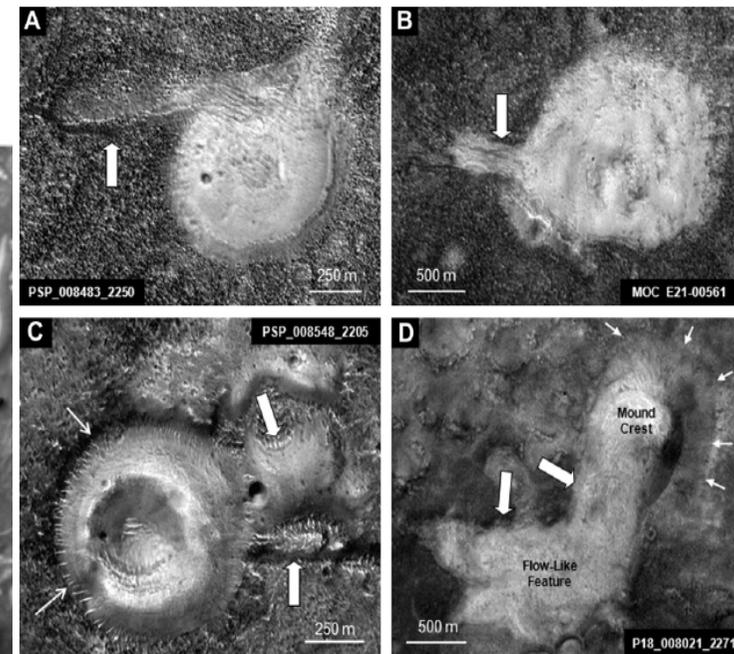
giuseppe.etiope@ingv.it



Arabia Terra
(*Etiope et al. 2011*)



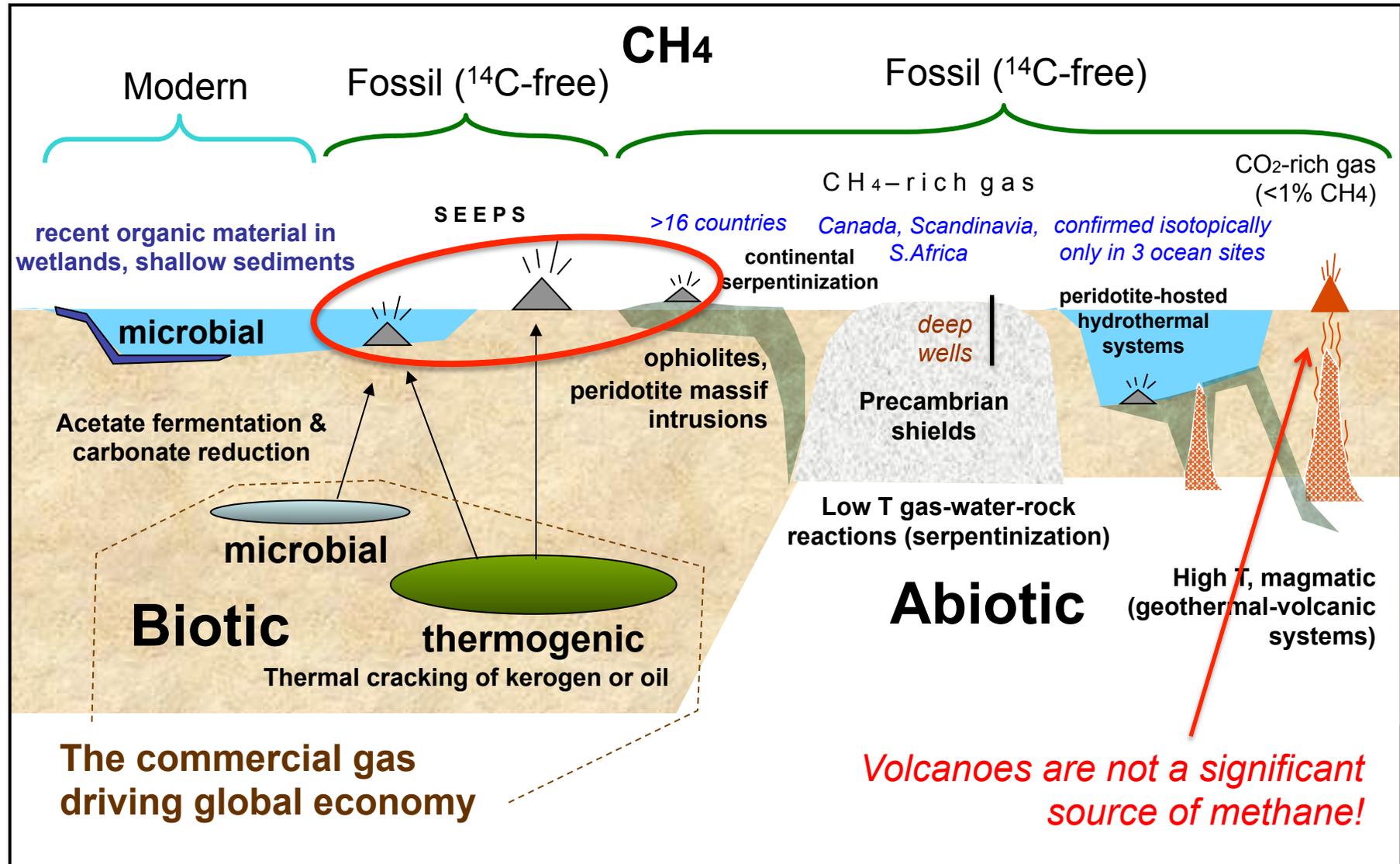
Nili Fossae
(*Wray and Ehlmann, 2011*)



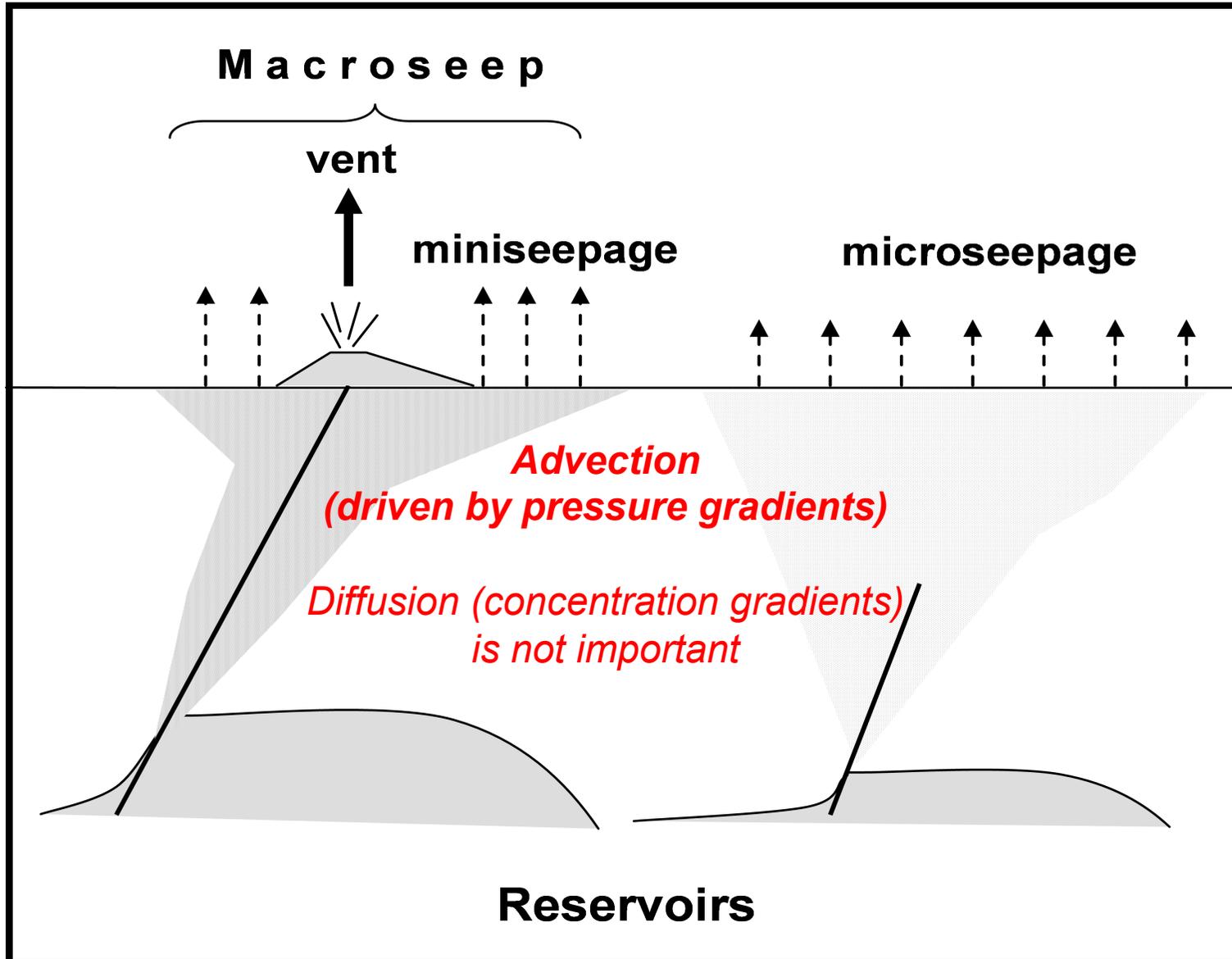
Acidalia Planitia
(*Oehler and Allen, 2010; Etiope et al. 2011*)

SEEPAGE ON EARTH

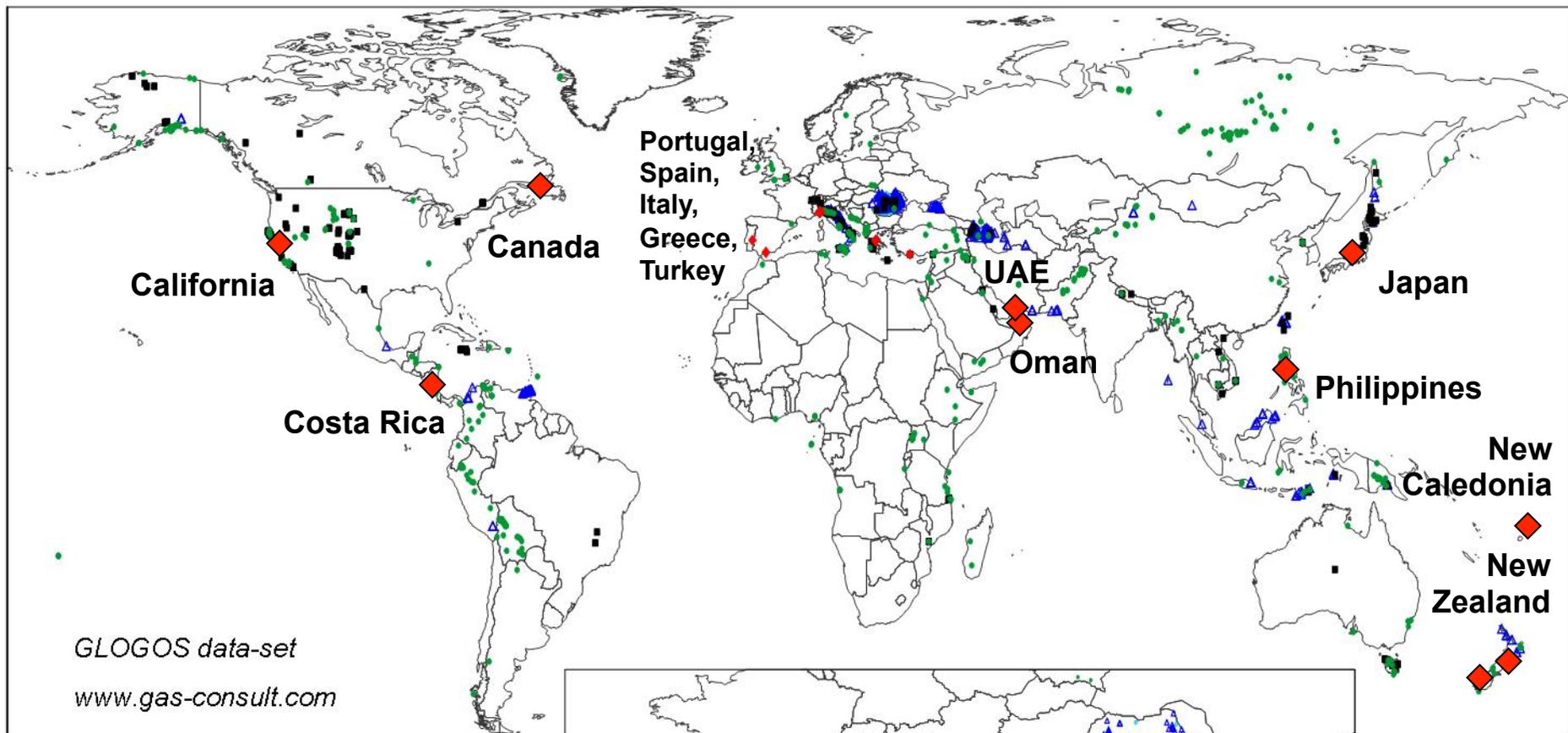
Methane origin on Earth



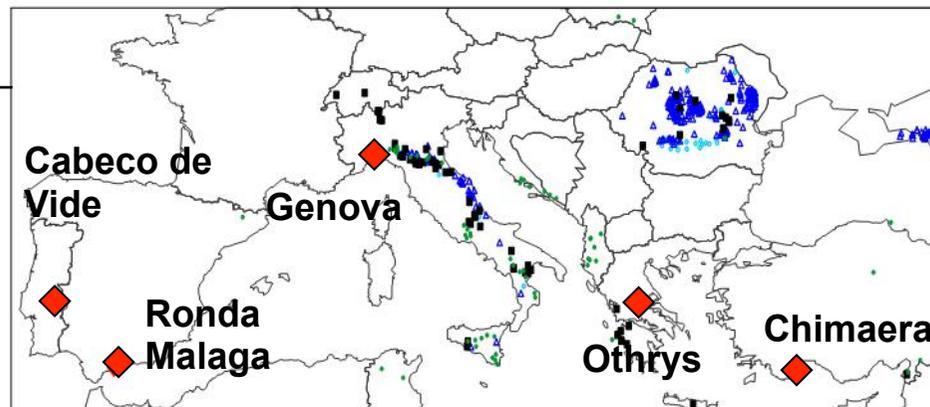
**Gas seepage can be visible or invisible,
focused or diffuse over large areas**



BIOTIC and ABIOTIC METHANE SEEPS



- Oil seep
- Gas seep
- △ Mud volcano
- Gas-bearing spring
- ◆ Seep/spring abiotic gas



Gas seeps and “eternal” fires

Release from 1 to 1000 ton CH₄ per year



Eternal fires and Zoroastrianism



Azerbaijan (*Yanardag*)

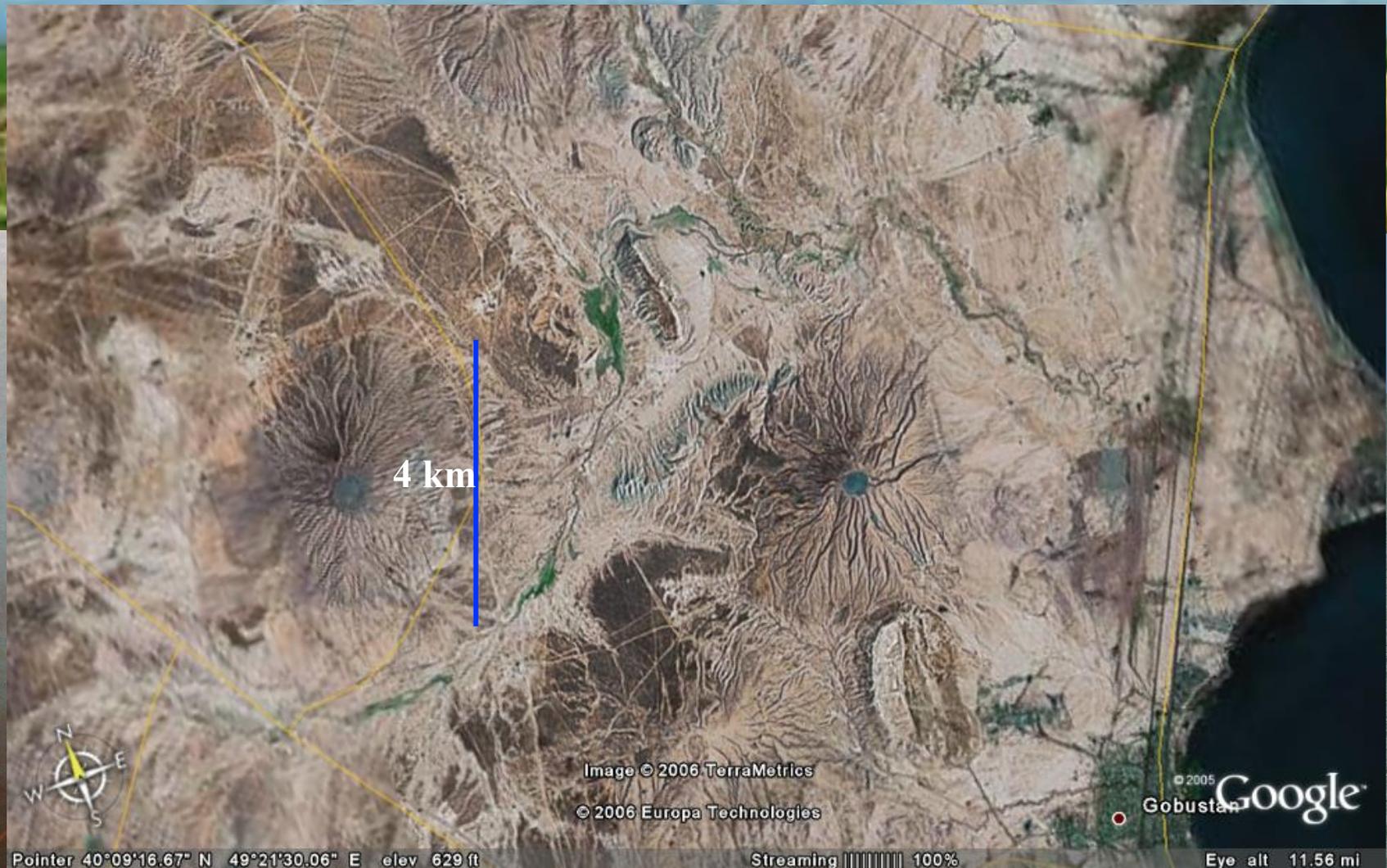
Mud volcanoes

Release from 1 to 500 ton CH₄ per year

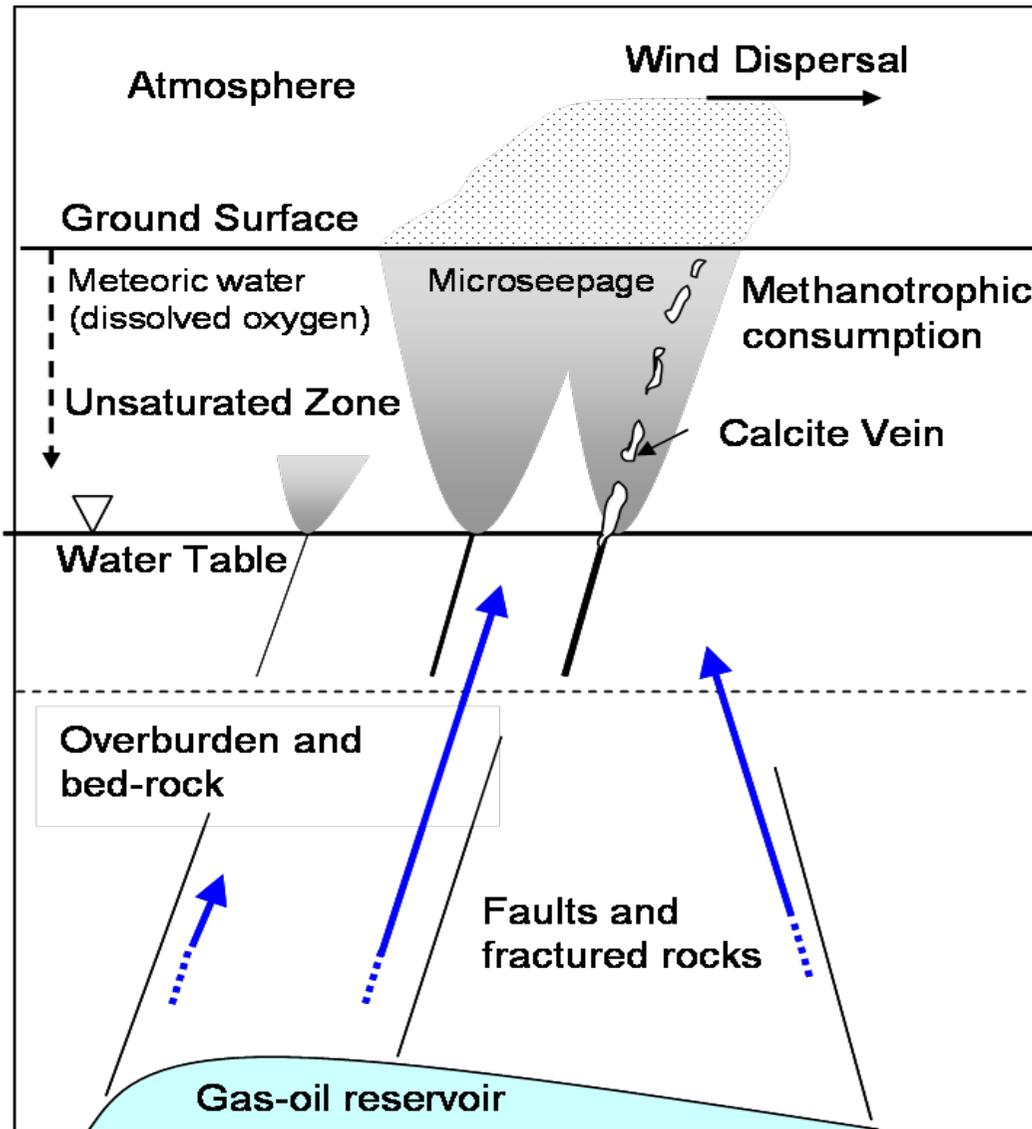


Sedimentary volcanism, 3-phase system : gas-water-sediment

Mud volcanoes – Azerbaijan



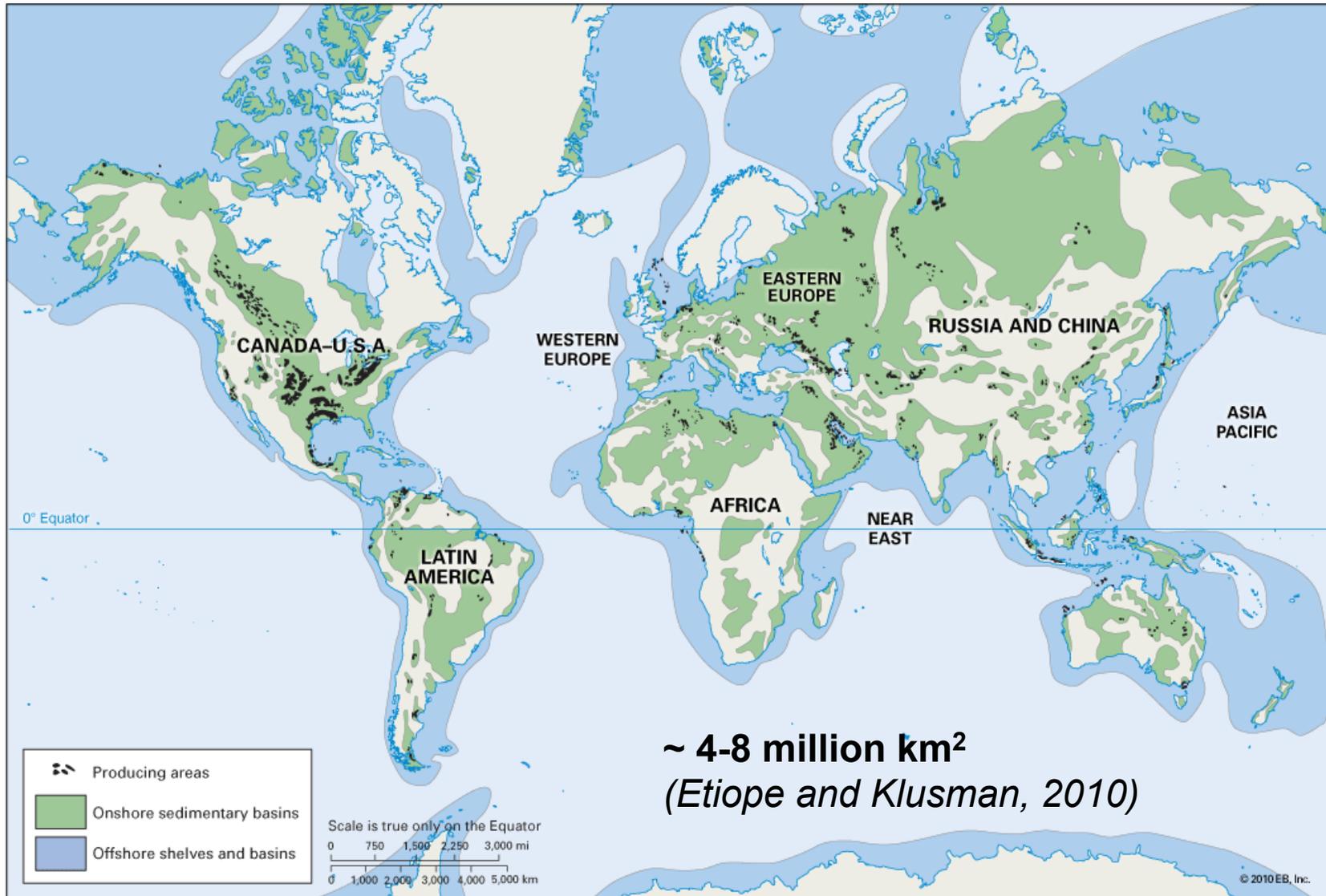
MICROSEEPAGE



Widely used for
petroleum
exploration

*Etioppe and Klusman
(2010)*

Potential microseepage area



Sedimentary basins and petroleum-producing areas of the world
(from *Britannica Online for Kids*. Web. 11 Mar. 2014).

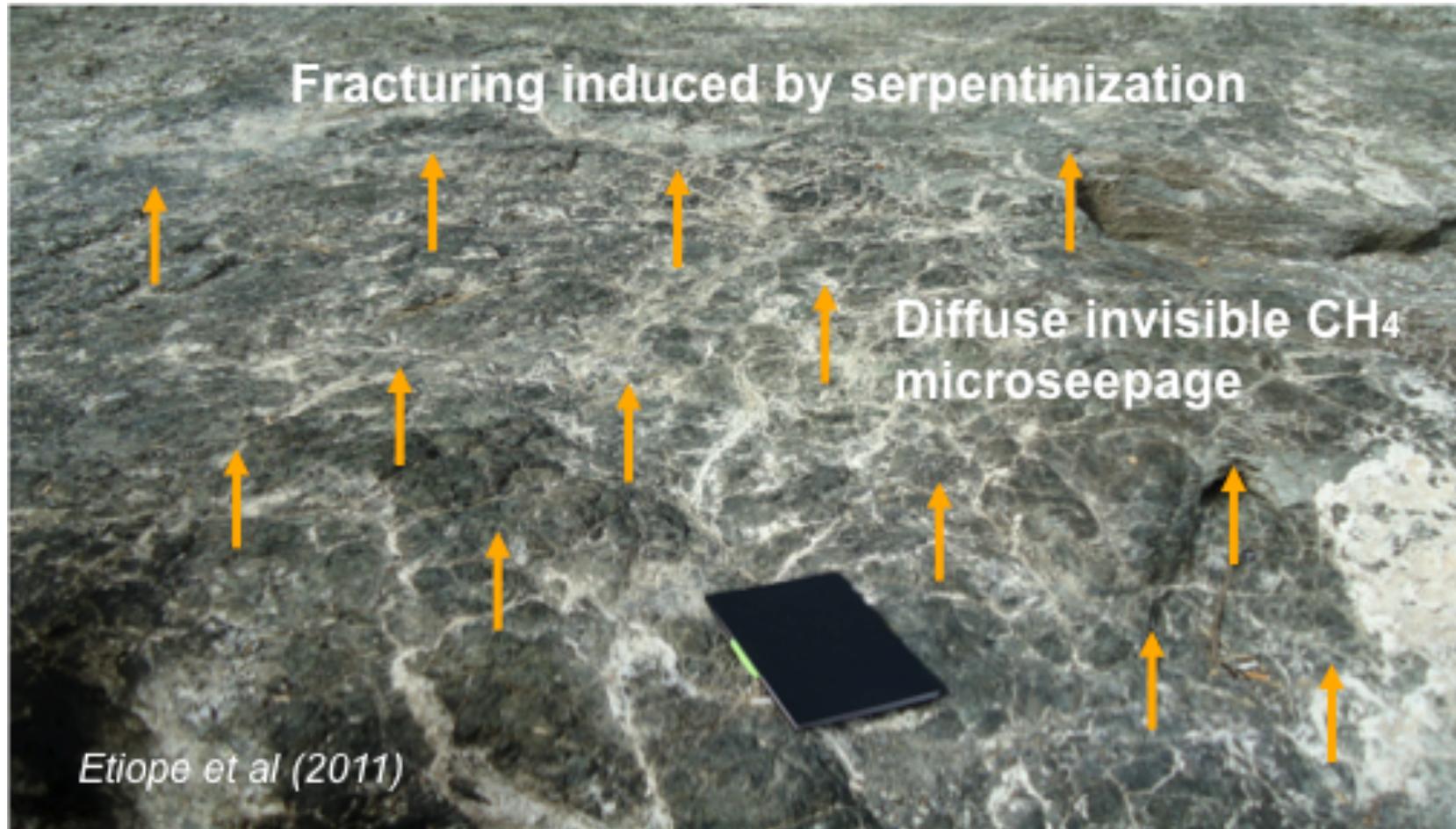
Microseepage in sedimentary basins

Invisible degassing
Positive fluxes of methane
($> 1 \text{ mg m}^{-2} \text{ d}^{-1}$)

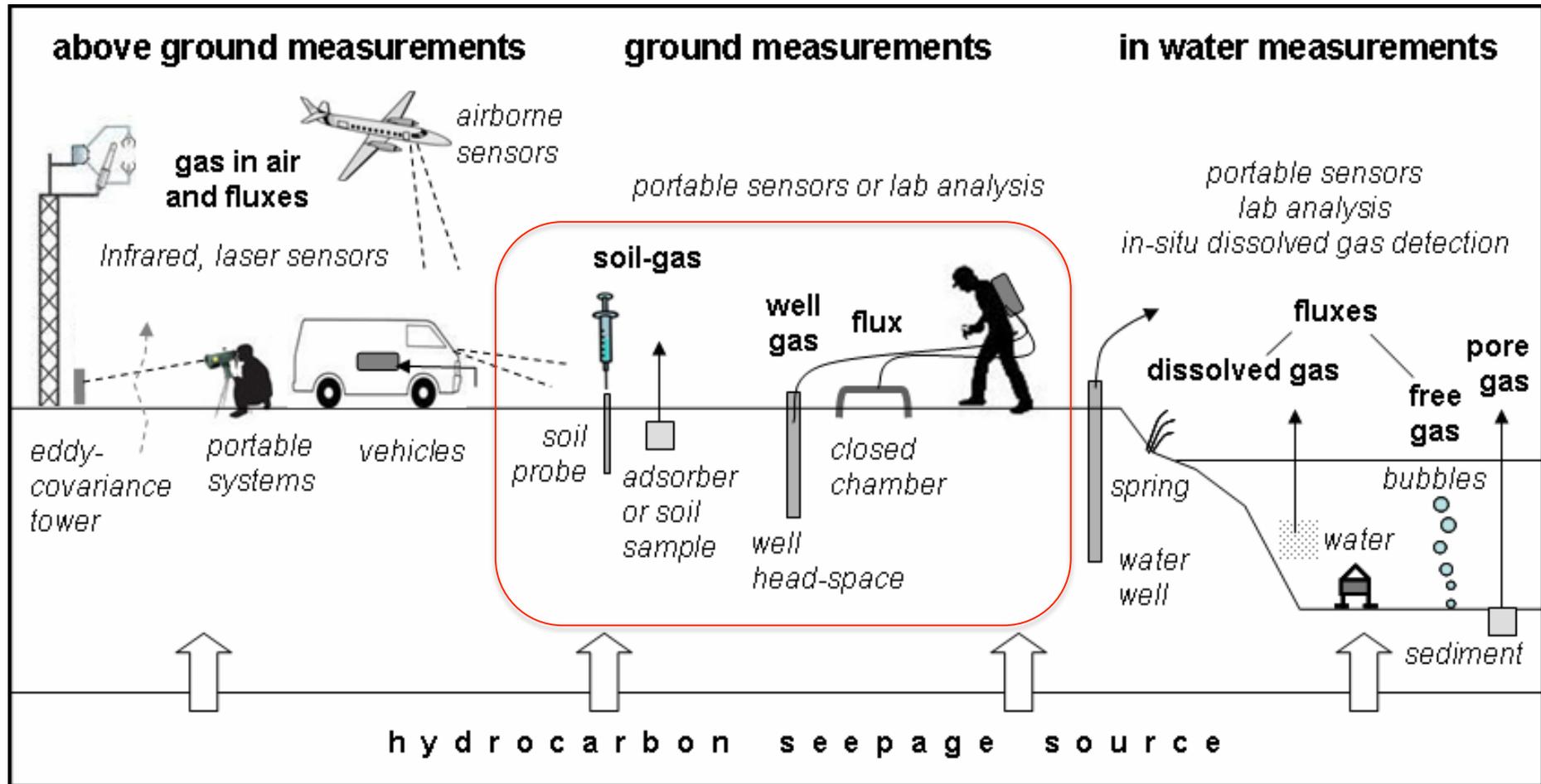


MICROSEEPAGE IN OLIVINE-RICH ROCKS (PERIDOTITES)

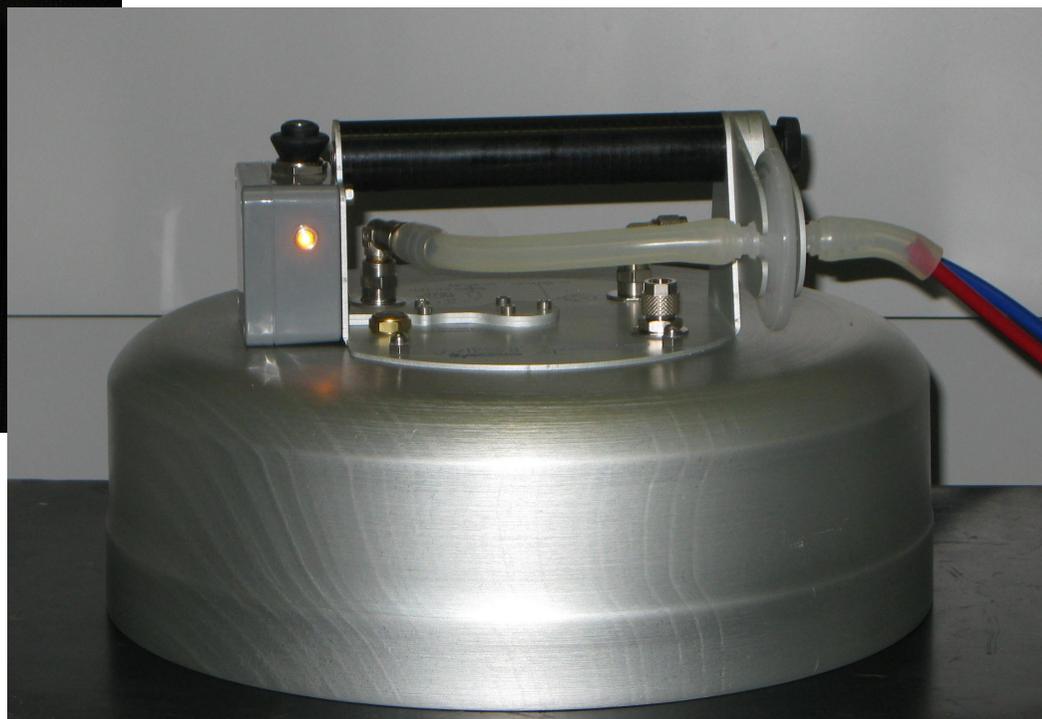
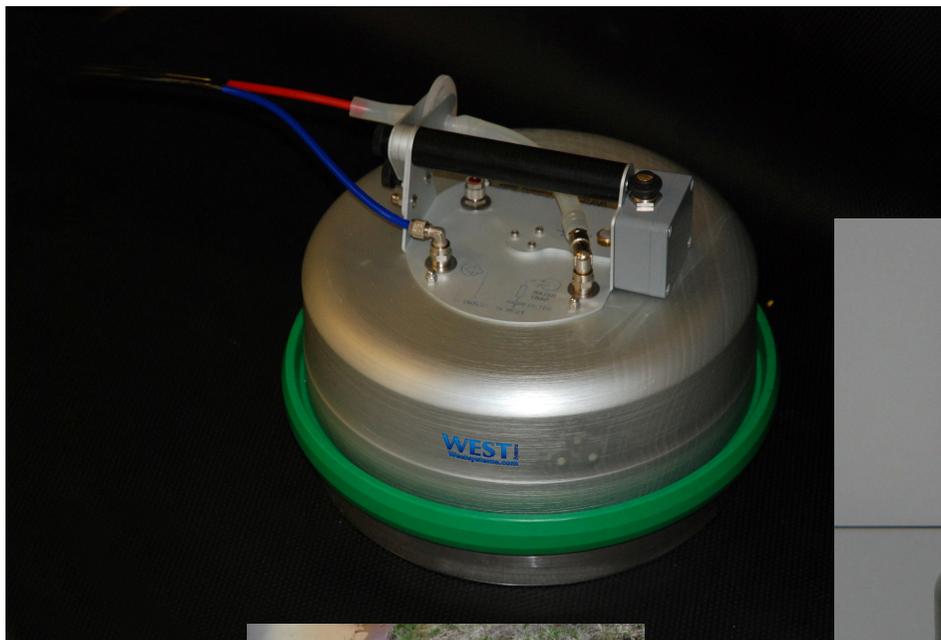
from 1 to 10^3 mg m⁻² day⁻¹



How to detect and measure gas seepage



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 $\text{mg m}^{-2} \text{day}^{-1}$ by the eq.:

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

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).



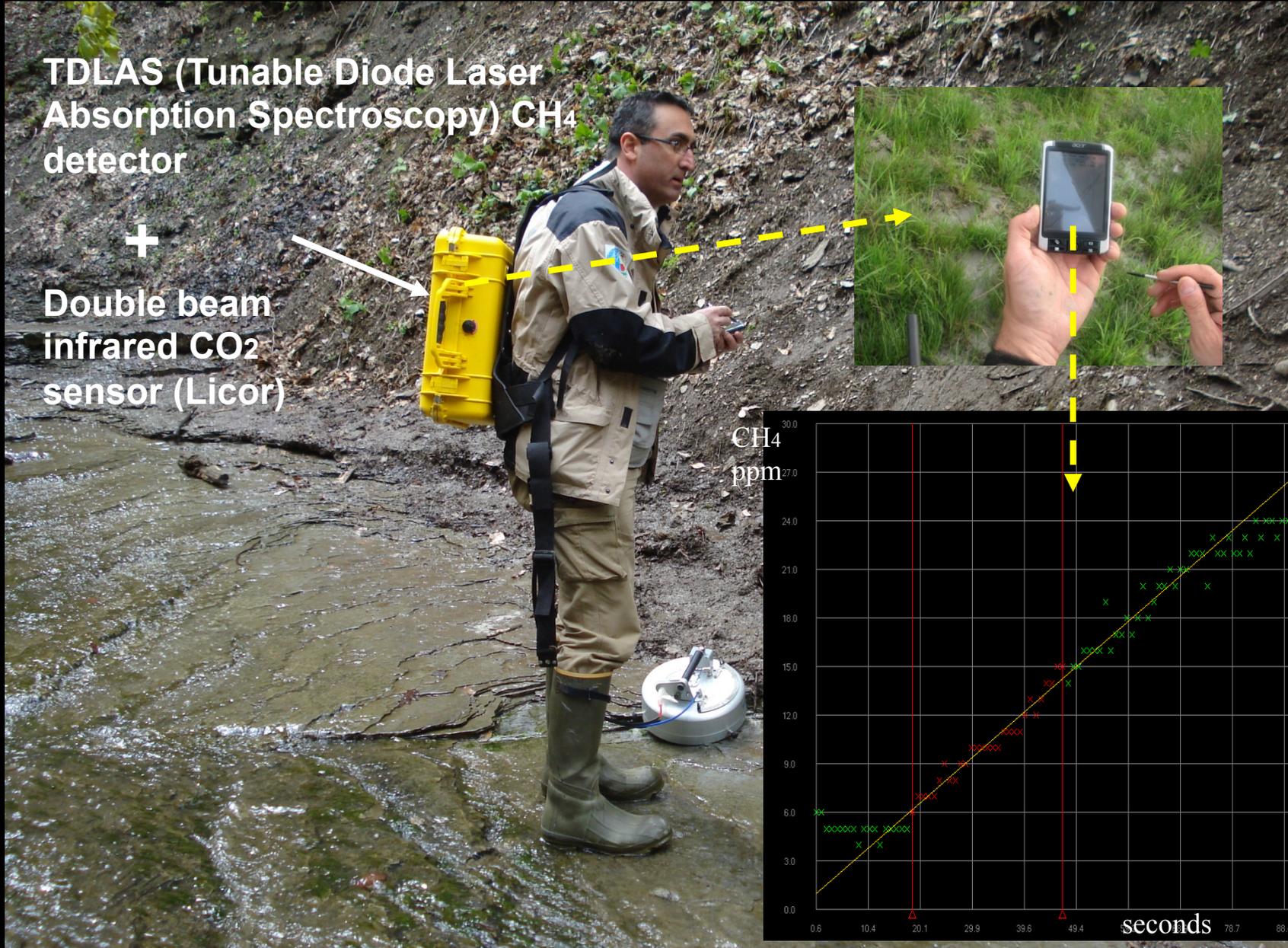
Photo: Charlotte Sigsgaard

GAS DETECTION AND FLUX MEASUREMENTS WITH A NEW GENERATION OF SENSORS

TDLAS (Tunable Diode Laser Absorption Spectroscopy) CH₄ detector

+

Double beam infrared CO₂ sensor (Licor)



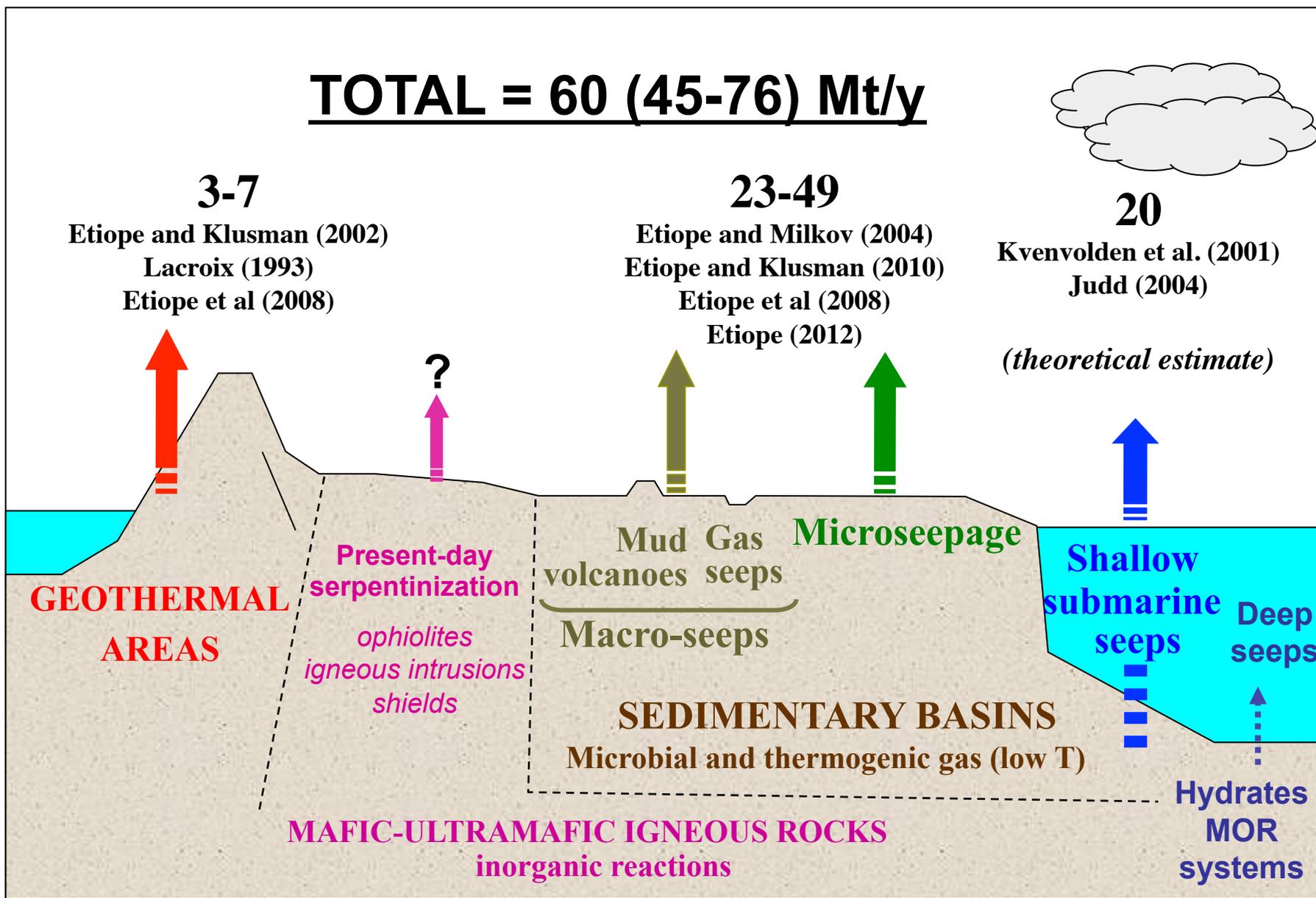
CH₄
ppm

seconds



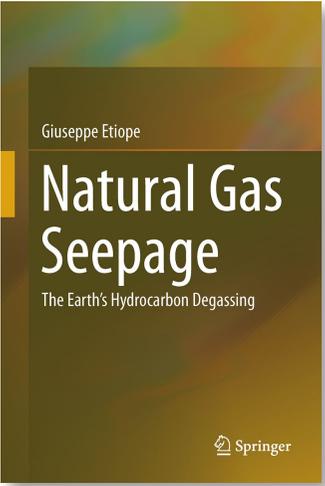
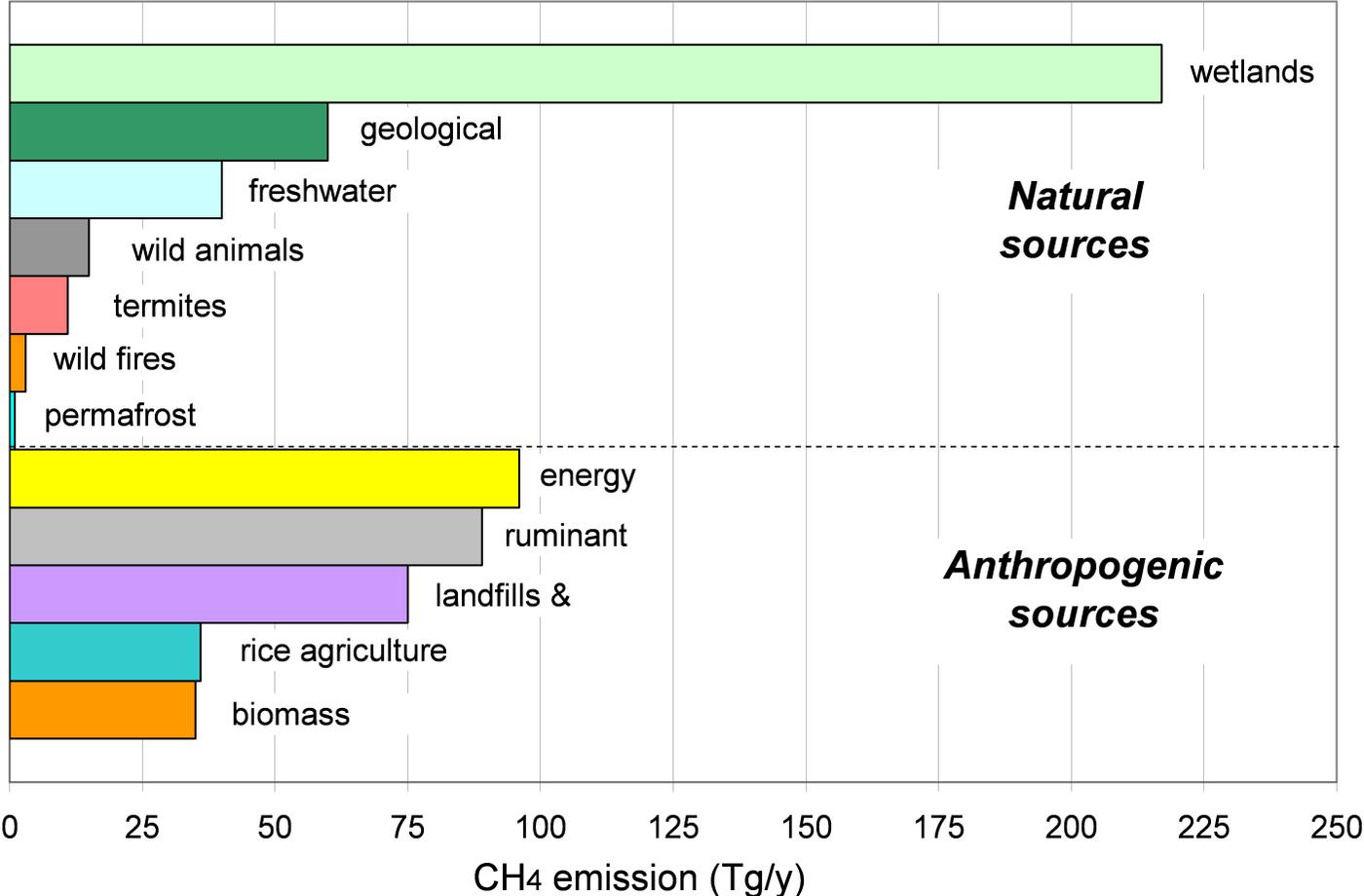
GEOLOGIC METHANE EMISSIONS

TOTAL = 60 (45-76) Mt/y

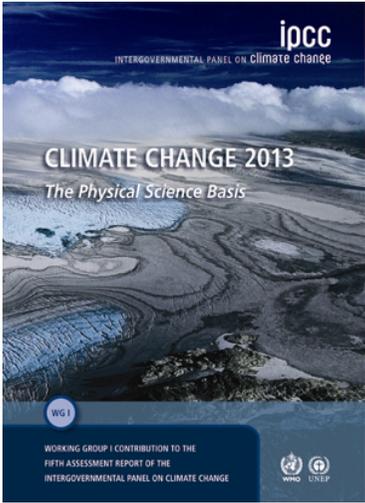


Geological CH₄
2nd natural CH₄ source
10% of total CH₄ source

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



(Etioppe, 2015)



(IPCC, 2013)

POTENTIAL SEEPAGE ON MARS

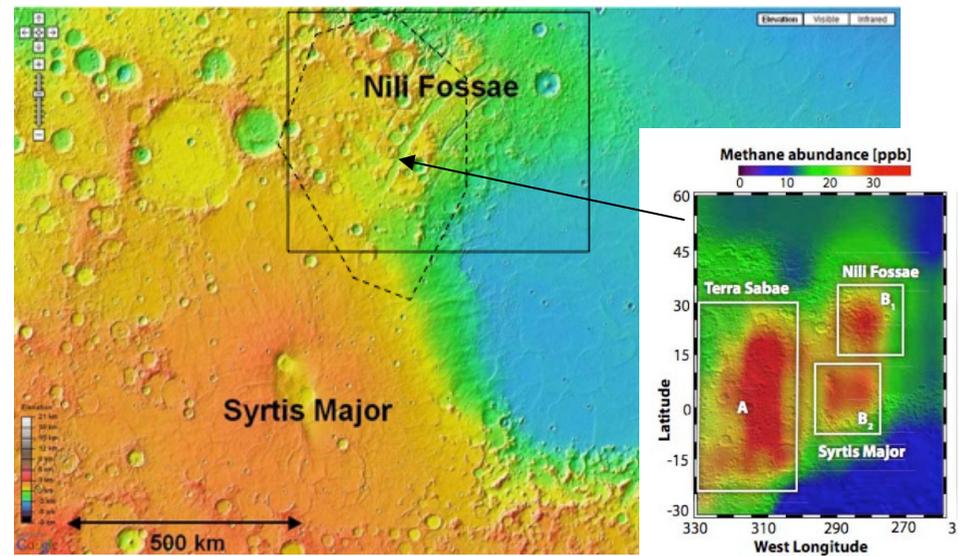
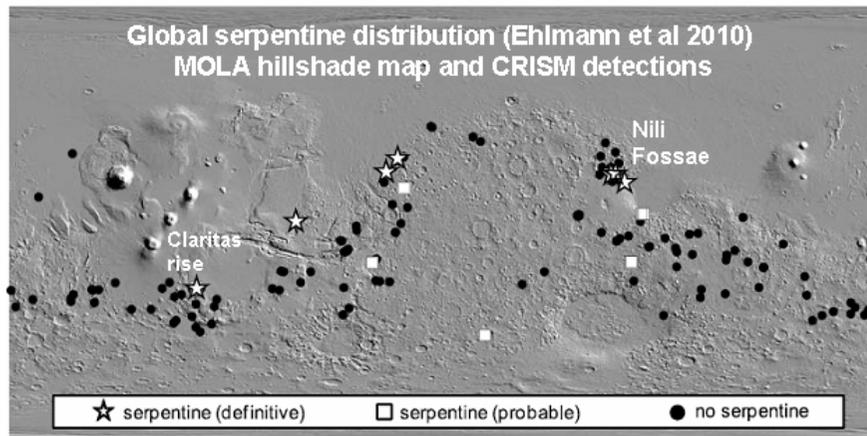
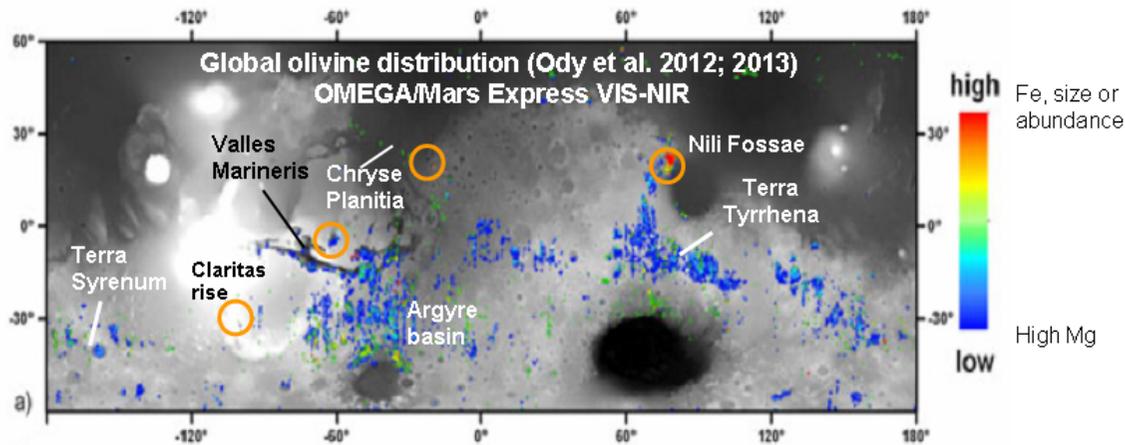
where are the best chances of finding methane?

Analog seepage sites

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

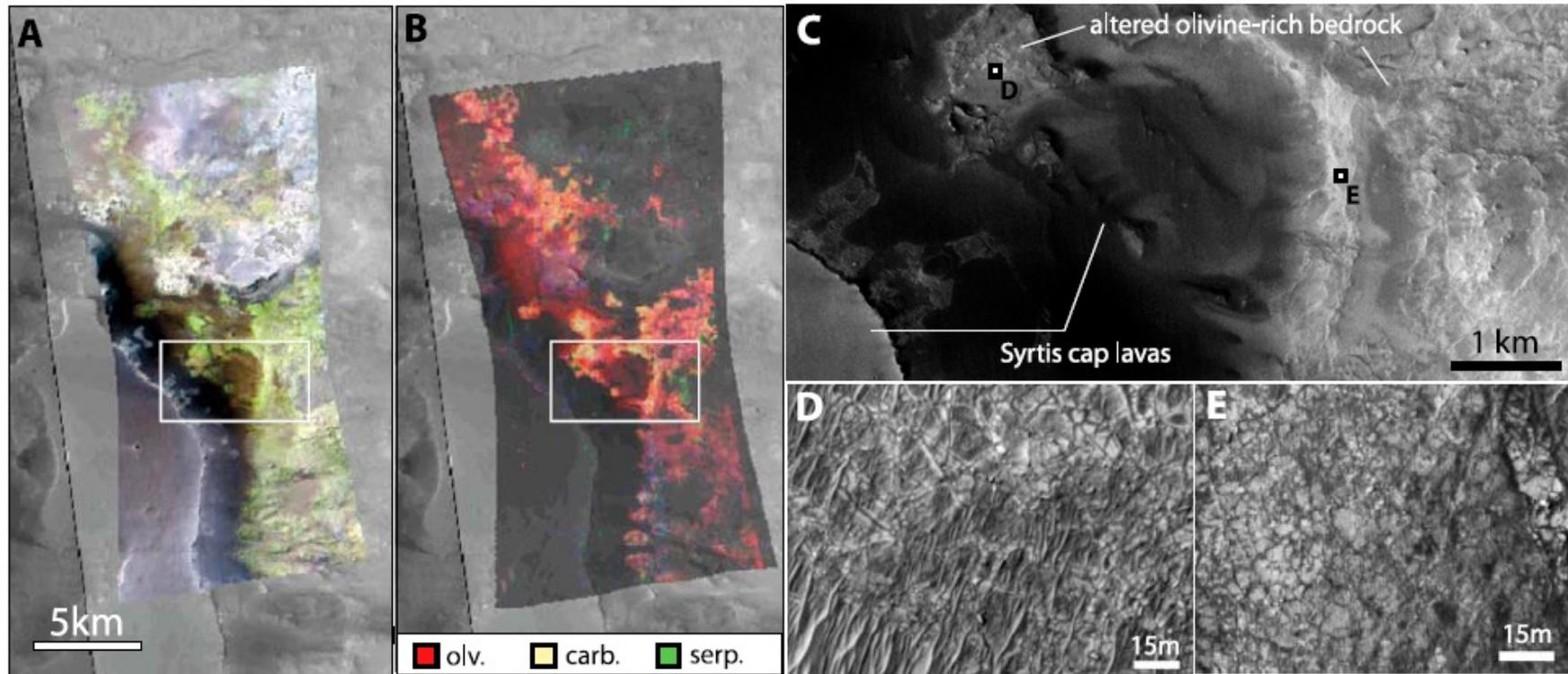
Olivine-rich and serpentinized areas on Mars

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



30,000 km² olivine-rich outcrop (Hoefen et al 2003)

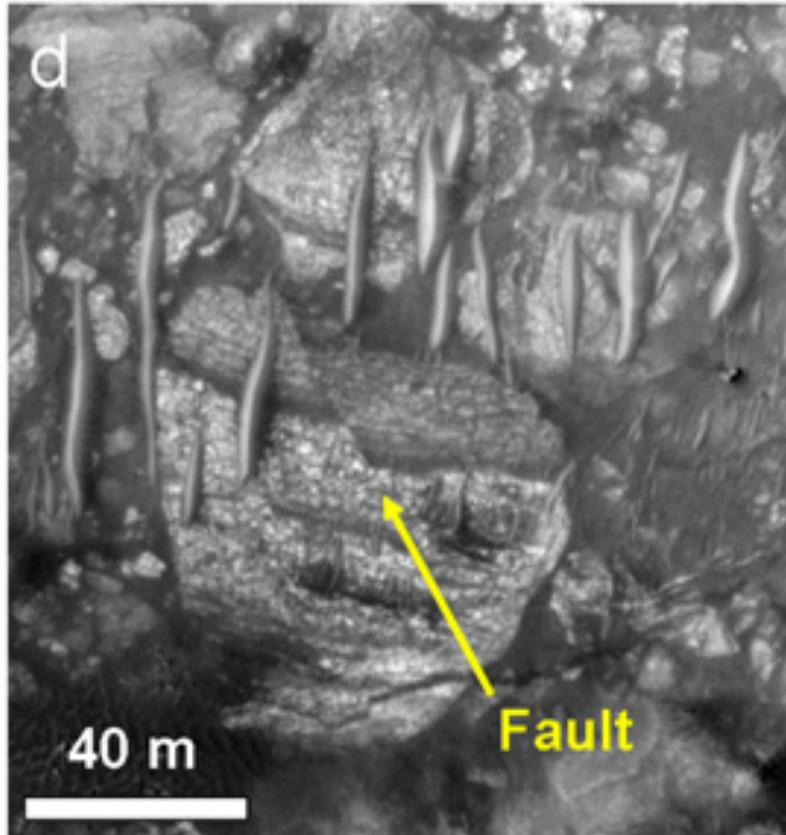
Nili Fossae



Ehlmann et al (2010)

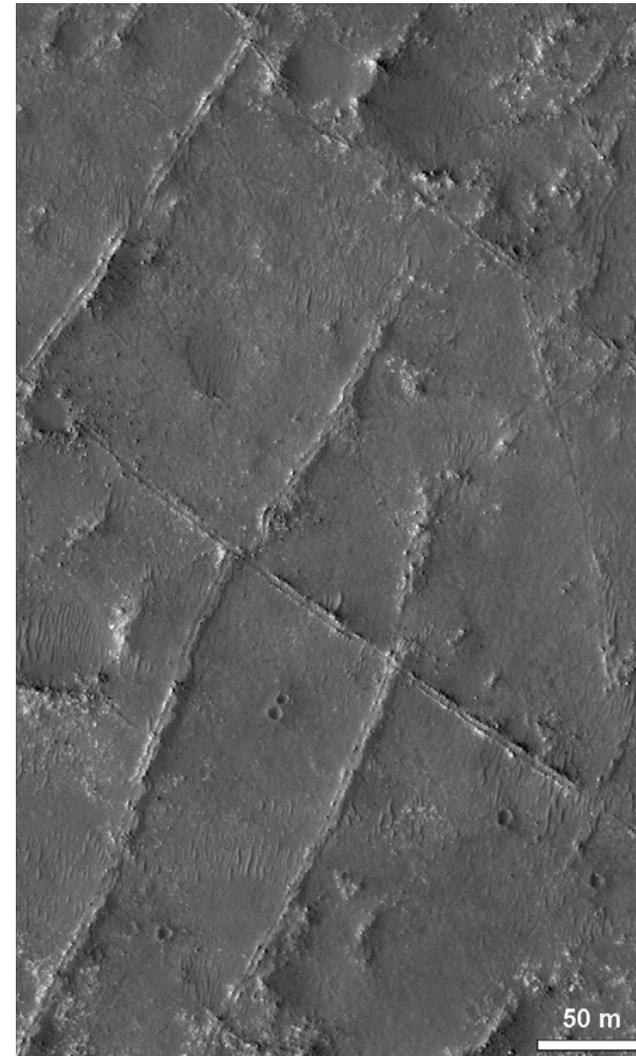
North of the Noachian-Hesperian contact (17.3°N, 77.2°E), erosion exposes a >150 km² olivine-rich, highly fractured outcrop, partially altered to serpentine

Nili Fossae



Fault at Nili Fossae, from
PSP_006923_1995 (19.381N, 76.421E)

Wray and Ehlmann (2011)



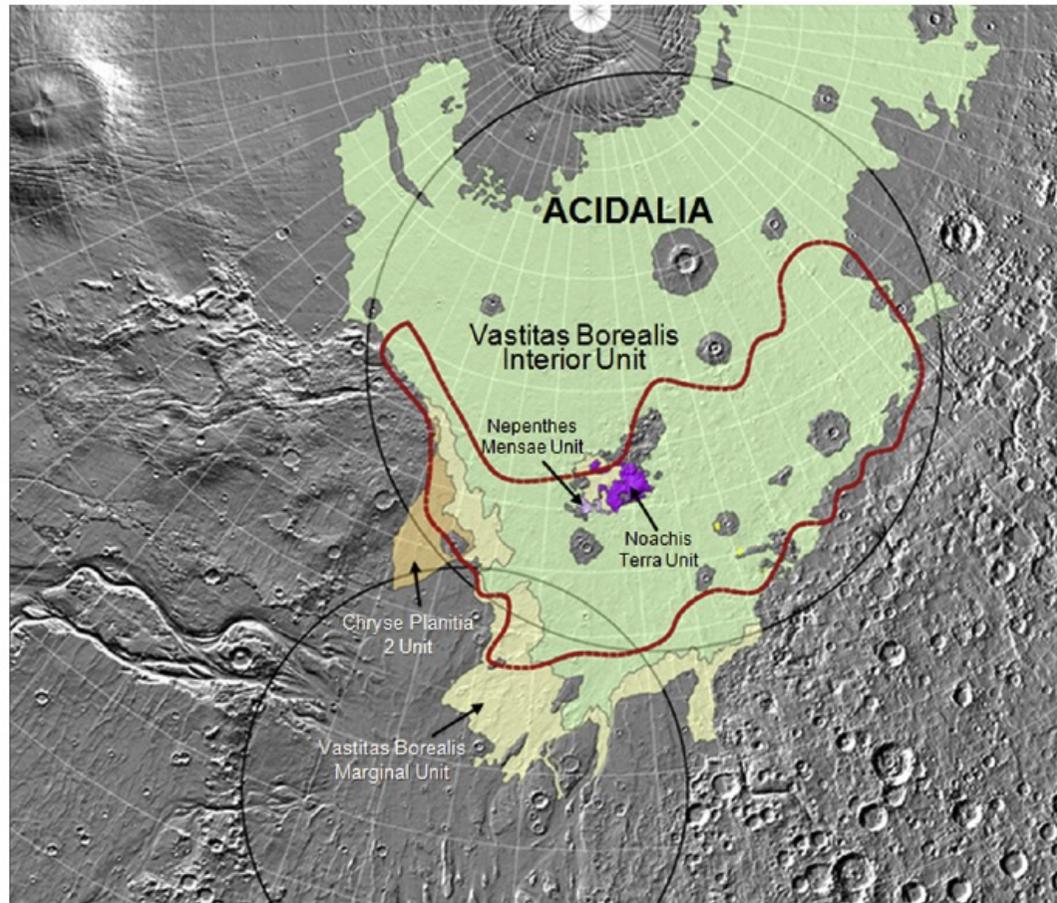
Fluid-precipitation filled fractures on the floor of
Jezero crater, eastern Nili Fossae

Potential mud volcano-like seeps

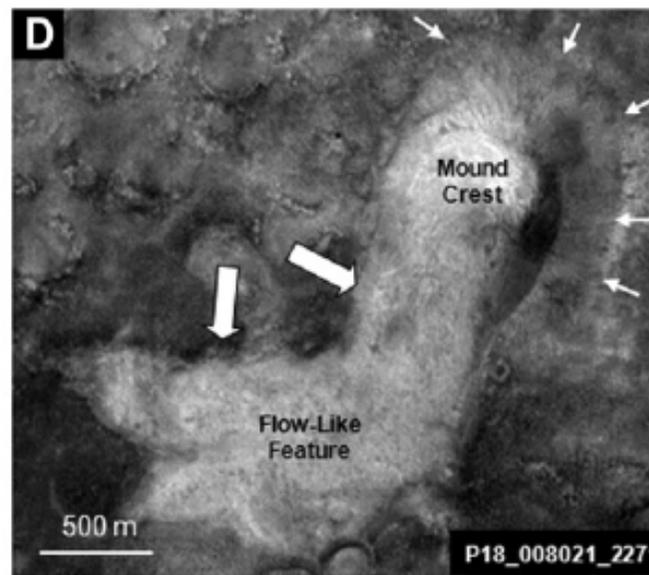
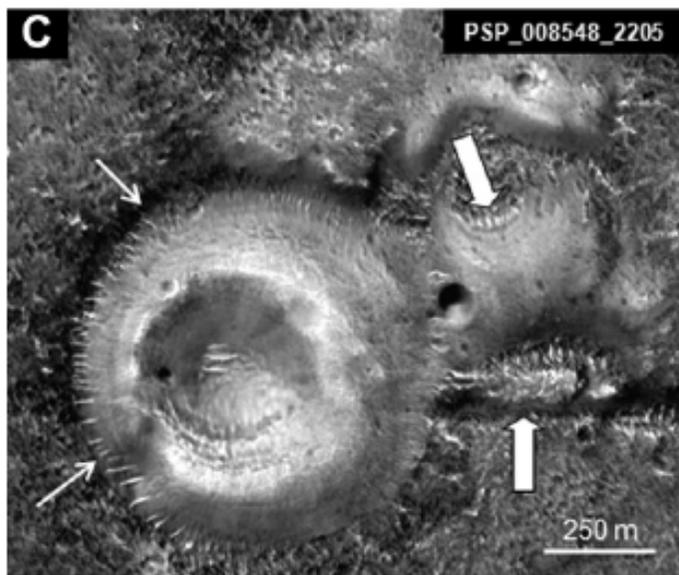
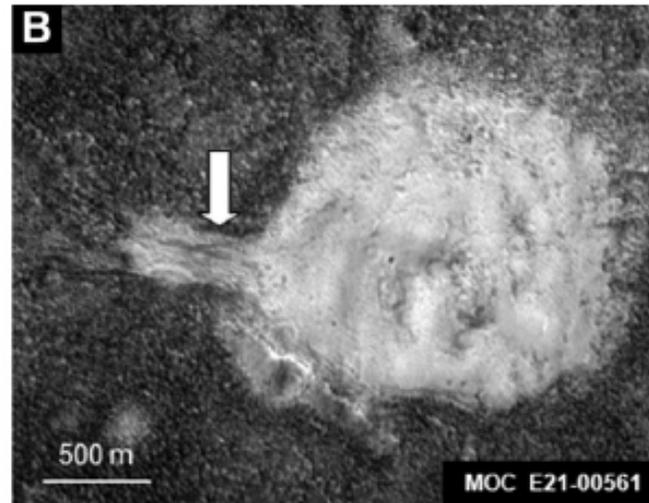
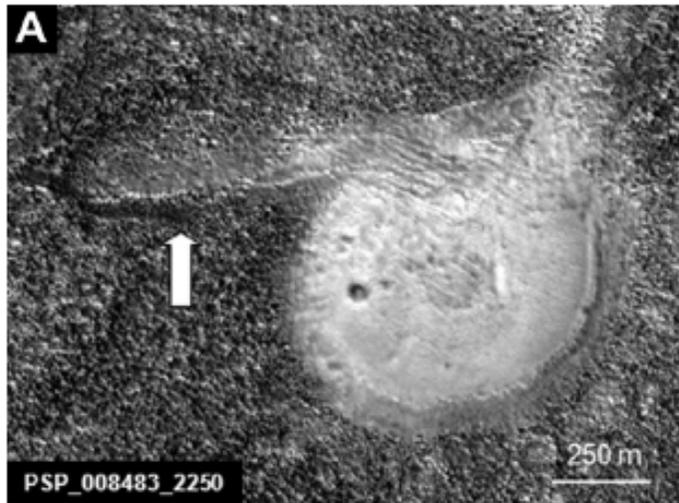
Candidate mud volcanoes reported from Utopia, Isidis, northern Borealis, Scandia, Chryse–Acidalia region (*Davis and Tanaka, 1995; Tanaka, 1997, 2005; Tanaka et al., 2000, 2003, 2008; Farrand et al., 2005; Kite et al., 2007; Rodríguez et al., 2007; Skinner and Tanaka, 2007; Allen et al., 2009; Oehler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

>40000 estimated

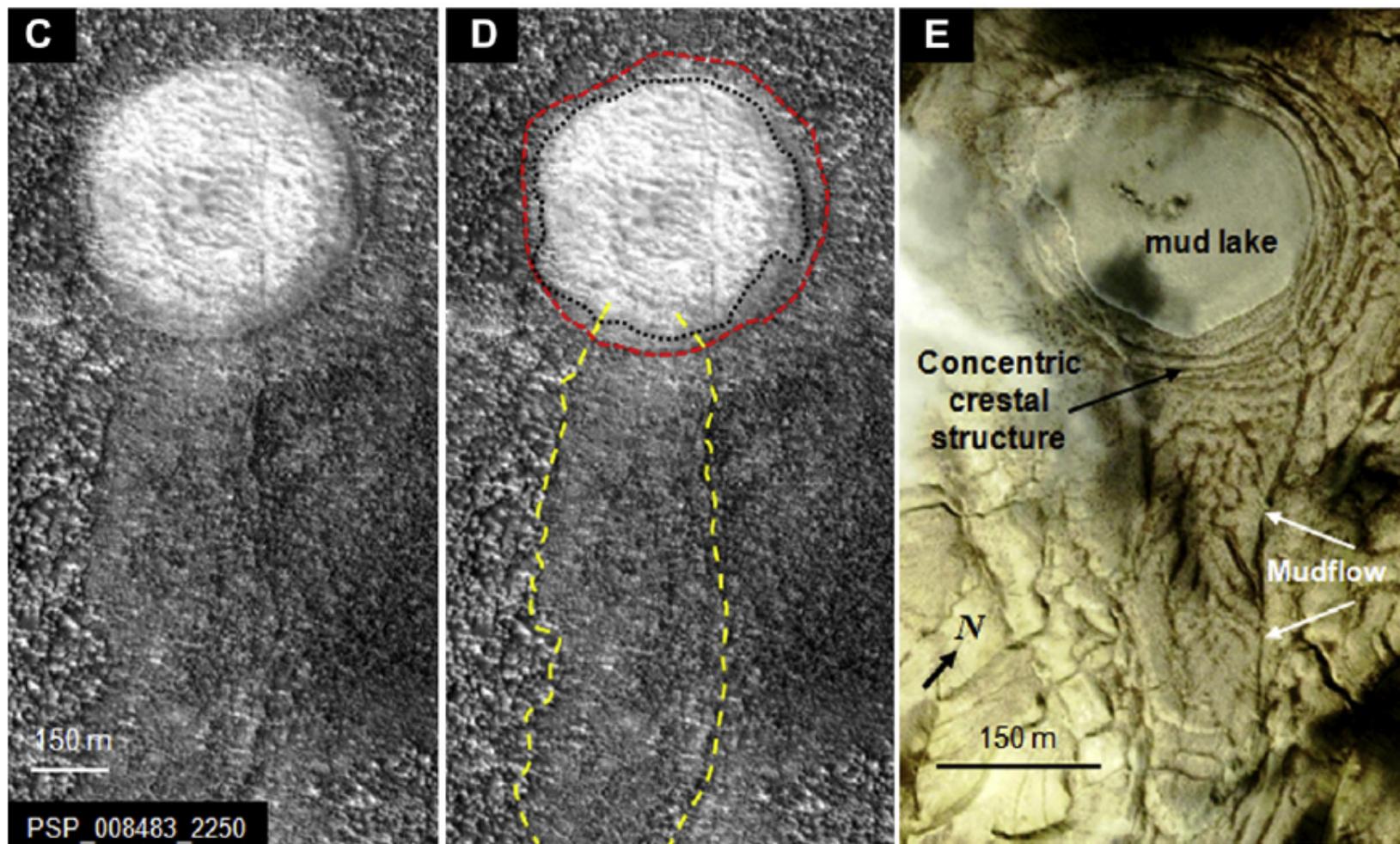
(18000 mapped)
in Acidalia Planitia
(*Oehler and Allen, 2010*)



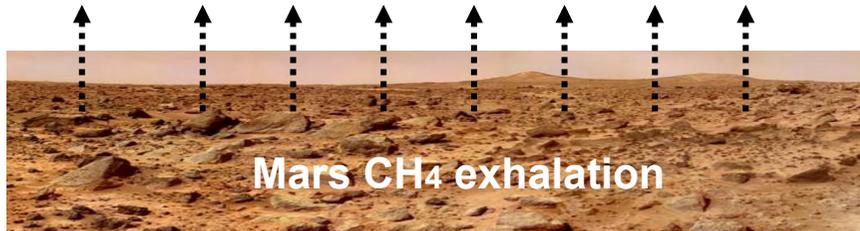
Potential mud volcano-like seeps Acidalia Planitia
(*Oehler and Allen, 2010; Etiopo, Oehler, Allen 2011*)



Potential mud volcano-like seeps Acidalia Planitia (*Oehler and Allen, 2010; Etiopie et al. 2011*)



A FEW MARTIAN SEEPS or WEAK MICROSEEPAGE CAN SUSTAIN THE ATMOSPHERIC CH₄ LEVEL (and the Mumma's plume)



the CH₄ plume on Mars reflects an episodic emission of ~19,000 t CH₄ yr⁻¹ (Mischna et al., 2011) or ~150,000 t CH₄ yr⁻¹ (Lefevre and Forget, 2009)

equivalent to a diffuse microseepage of ~10-100 mg m⁻²d⁻¹ from an area of 500 to 5000 km²

If the whole 30000 km² olivine outcrop at the Nili Fossae (Hoefen et al., 2003) is assumed to exhale, a microseepage of 2 mg m⁻²d⁻¹ (the lowest level detected in terrestrial peridotites) would be sufficient to support the plume

If a global Martian CH₄ source of around 100-300 t yr⁻¹ is required to maintain the 10 ppb atmospheric level (Atreya et al, 2007), one large mud volcano or a few small mud volcanoes, or just a very weak microseepage, sparse in different zones of Mars, would be sufficient.

Etioppe, Oehler, Allen (2011)
Etioppe, Ehlmann, Schoell (2013)

**A NOTE ON ABIOTIC
METHANE PRODUCED AT
LOW TEMPERATURES**

Low T abiotic methane

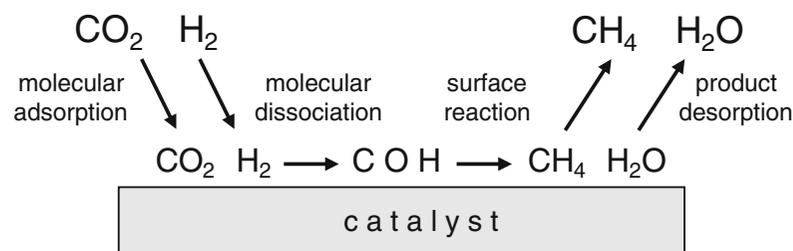
SABATIER REACTION



The simplest way to form abiotic methane

A fundamental reaction for life origin ($\text{H}_2\text{-CH}_4 = \text{energy sources for microbes}$), the transition from inorganic to organic chemistry (Russell et al. 2010)

So far considered to take place at $T > 200^\circ\text{C}$



Geofluids (2014)

Low-temperature catalytic CO_2 hydrogenation with geological quantities of ruthenium: a possible abiotic CH_4 source in chromitite-rich serpentinized rocks

G. ETIOPE^{1,2} AND A. IONESCU²

Abiotic CH_4 can be rapidly produced at low T ($< 100^\circ\text{C}$)

Fast production of considerable amounts of CH_4 via Sabatier reaction at 90, 50 and 25°C , using small concentrations of ruthenium (Ru) equivalent to natural amounts in chromitites

inorganic to organic transition at $T < 100^\circ\text{C}$

no need to invoke hydrothermal systems for life origin

Ruthenium exists on Mars....

...so CH₄ may originate at T<100°C

Ruthenium (PGE, Platinum Group Elements) and other siderophile elements, associated to chromium minerals, can be particularly enriched in martian mantle rocks (*Jones et al., 2003*).

About 16 ppb of Ru were detected in the Chassigny meteorite (*Jones et al., 2003*), belonging to the SNC (Shergotty, Nakhla, Chassigny) meteorites, which are derived from martian mantle.

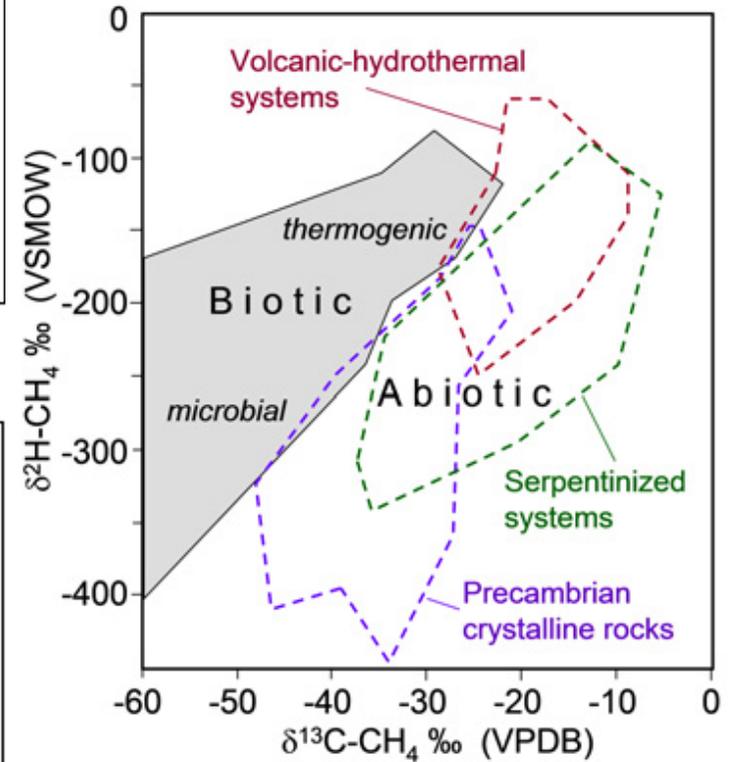
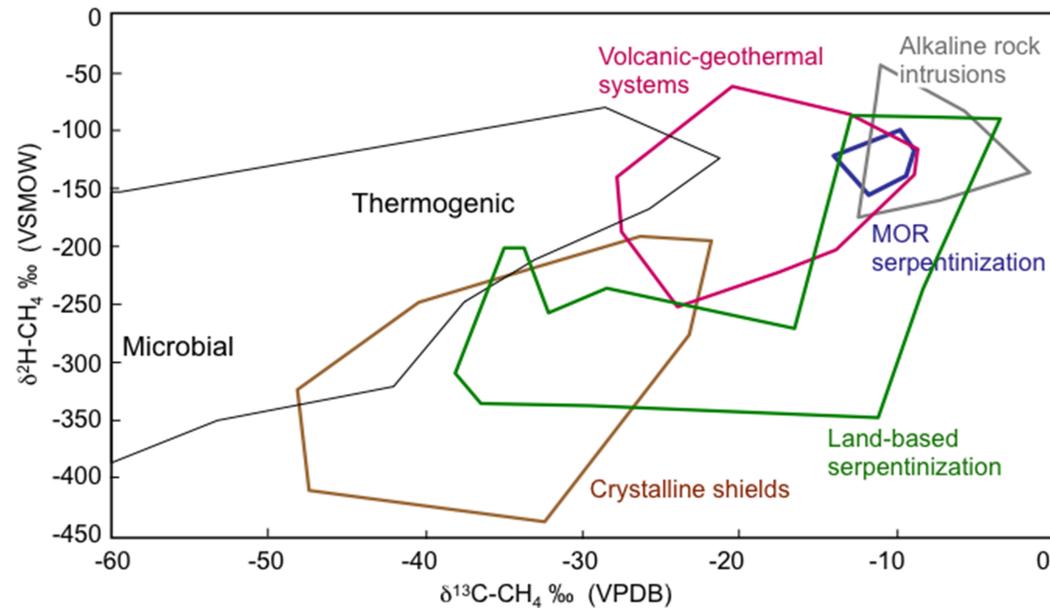
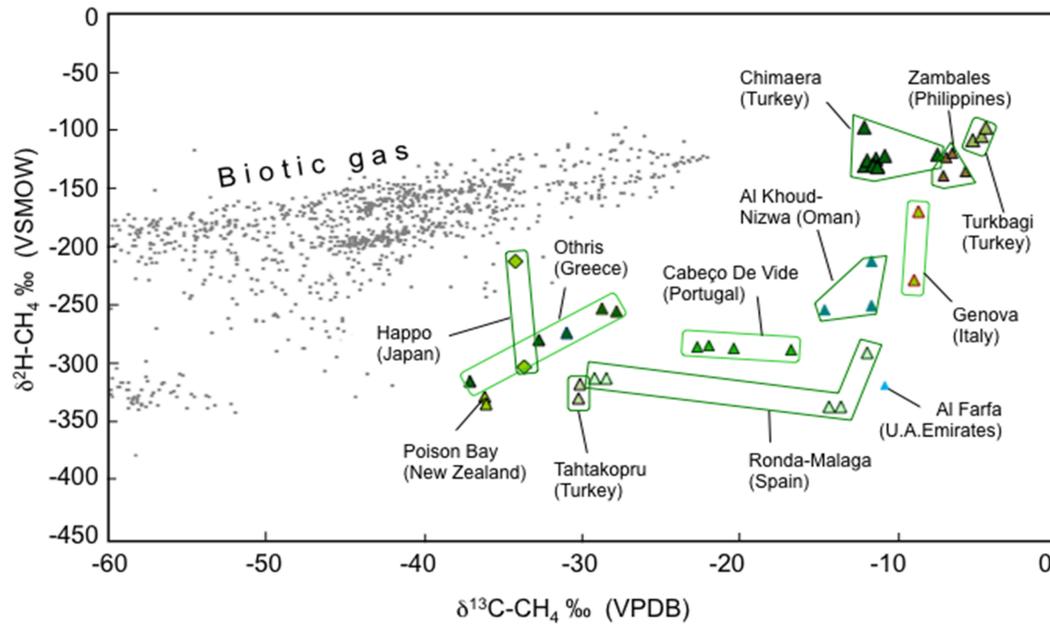
Such a concentration is within the typical range observed in terrestrial chromitites, including those in methane-bearing ultramafic rocks

no need of hydrothermal or magmatic systems to generate abiotic CH₄ on Mars

CH₄ ISOTOPIC COMPOSITION ON EARTH

Abiotic vs biotic methane

well distinguished by C and H isotopic ratios



Etioppe and Schoell (2014)
Etioppe (2015)

CH₄ ISOTOPIC COMPOSITION ON MARS?

Potential C–H isotopic signatures of abiotic CH₄ on Mars

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

$\delta^{13}\text{C}$ -CH₄ can be similar to that observed on Earth only if it derives from unfractionated CO₂

- Martian H feedstock:**
- atmospheric H₂
 - H in minerals (meteorites)
 - subsurface waters ???
 - magma : low $\delta^2\text{H}$; initial $\delta^2\text{H}$ similar to Earth; [Boctor et al., 2003](#); [Lunine et al., 2003](#)
 - igneous rocks: olivine, $\delta^2\text{H}$: -60 to -280 ‰ [Gillet et al. 2002](#)
- extrem. enriched in deuterium $\delta^2\text{H}$ up to +4000‰
[Leshin, 2000](#); [Sugiura and Hoshino, 2000](#)
due to atmospheric escape fractionation processes

A wide range of $\delta^2\text{H}$ could be measured for martian CH₄, far outside terrestrial variations

Martian $\delta^2\text{H}$ -CH₄ 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.

Main messages

Observations of terrestrial gas seepage, in sedimentary basins and serpentinized rocks, can be used to infer forms and magnitude of potential seepage on Mars

Low microseepage, sparse in different zones of Mars, would be sufficient to sustain methane observed in the atmosphere

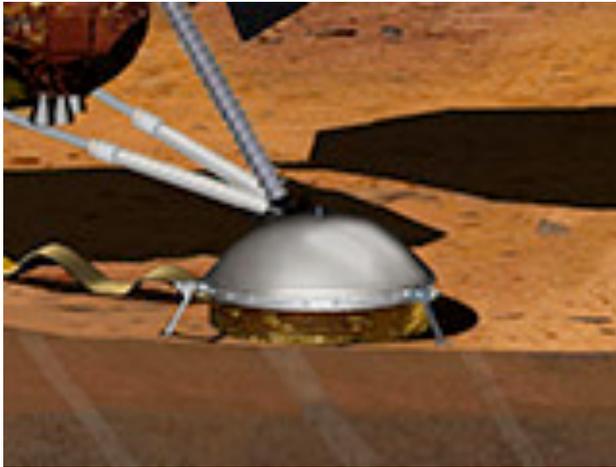
BUT, as on Earth, CH₄ microseeping on Mars cannot be detected a few cm above the soil, because of winds and dilution of the leaking gas

Abiotic methane can be generated at very low T by Sabatier reaction
ANYWHERE H₂, CO₂ and platinum group elements (Ru) are available

Geologic CH₄ on Mars should be searched in the regions with olivine-bearing rocks, preferably above or near faults or at apparent mud volcanoes, ideally by **drilling** into the soil, or using **accumulation chambers** on the ground

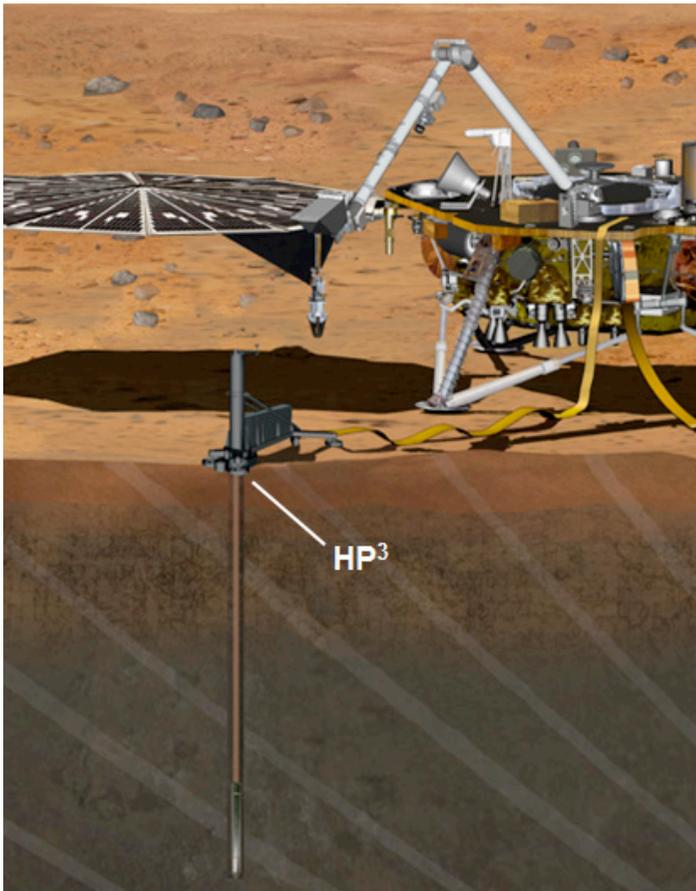


*INSIGHT landing site:
Elysium Planitia*



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**