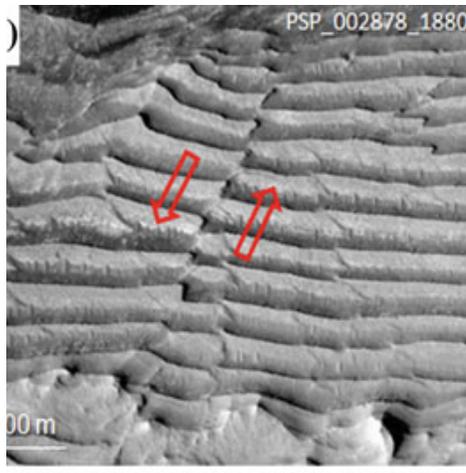


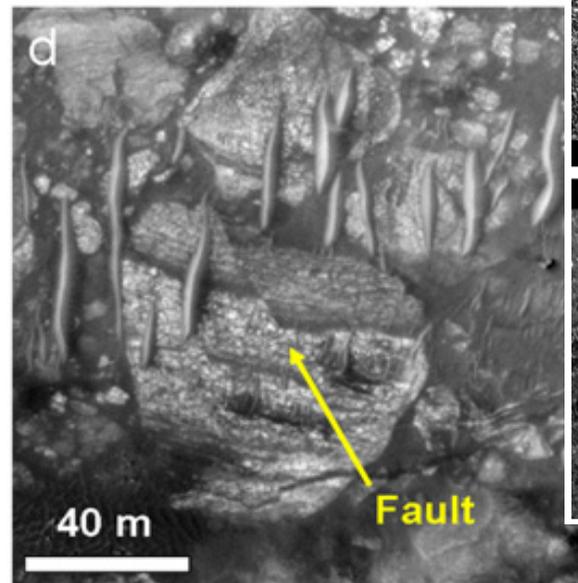
# Potential CH<sub>4</sub> seepage on Mars

**Giuseppe Etiope**

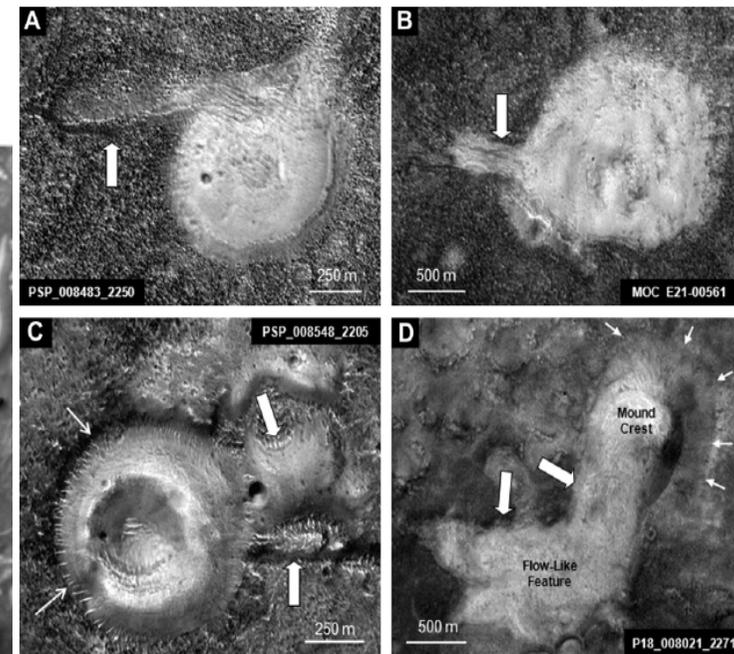
[giuseppe.etiope@ingv.it](mailto:giuseppe.etiope@ingv.it)



Arabia Terra  
(*Etiope et al. 2011*)



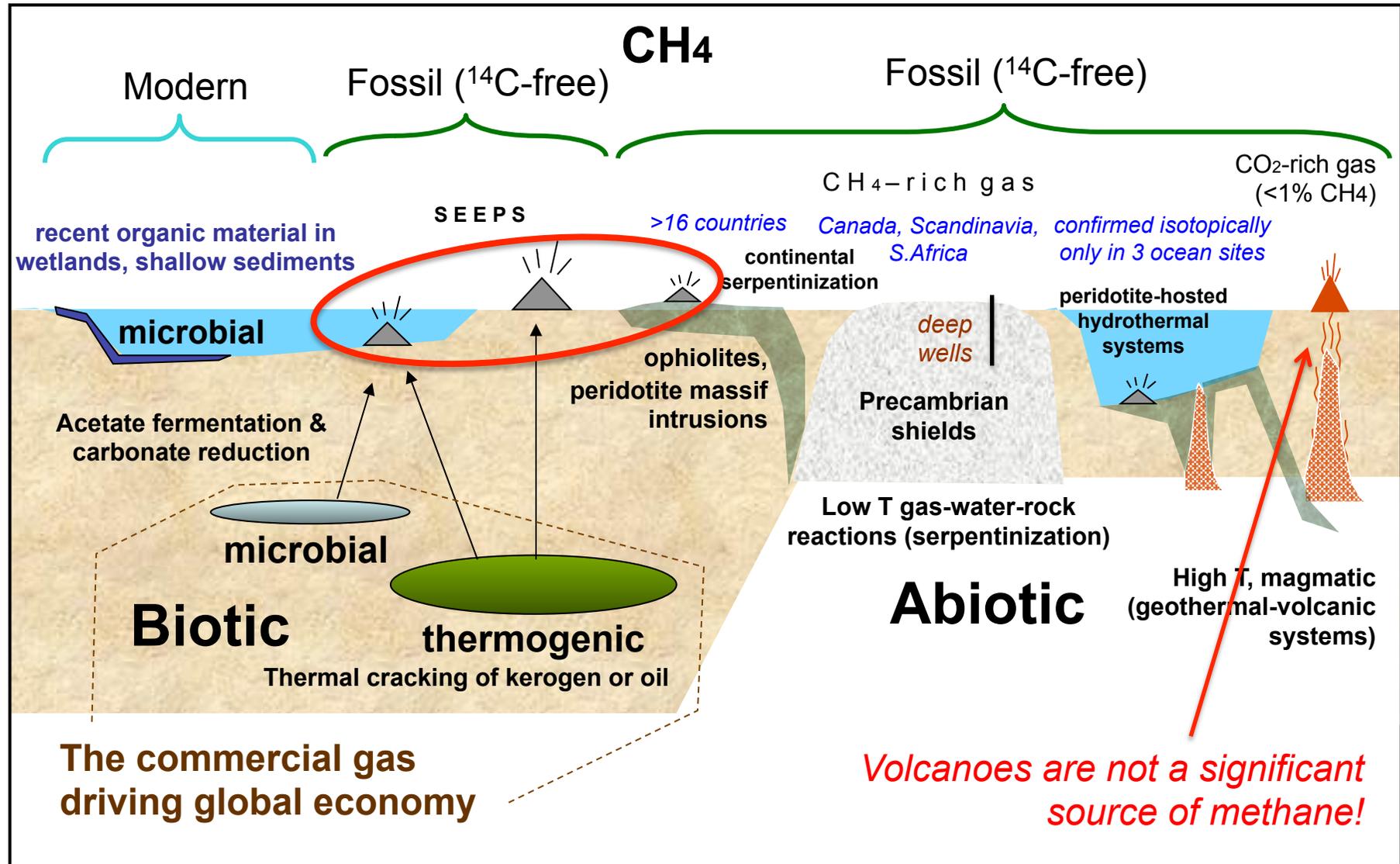
Nili Fossae  
(*Wray and Ehlmann, 2011*)



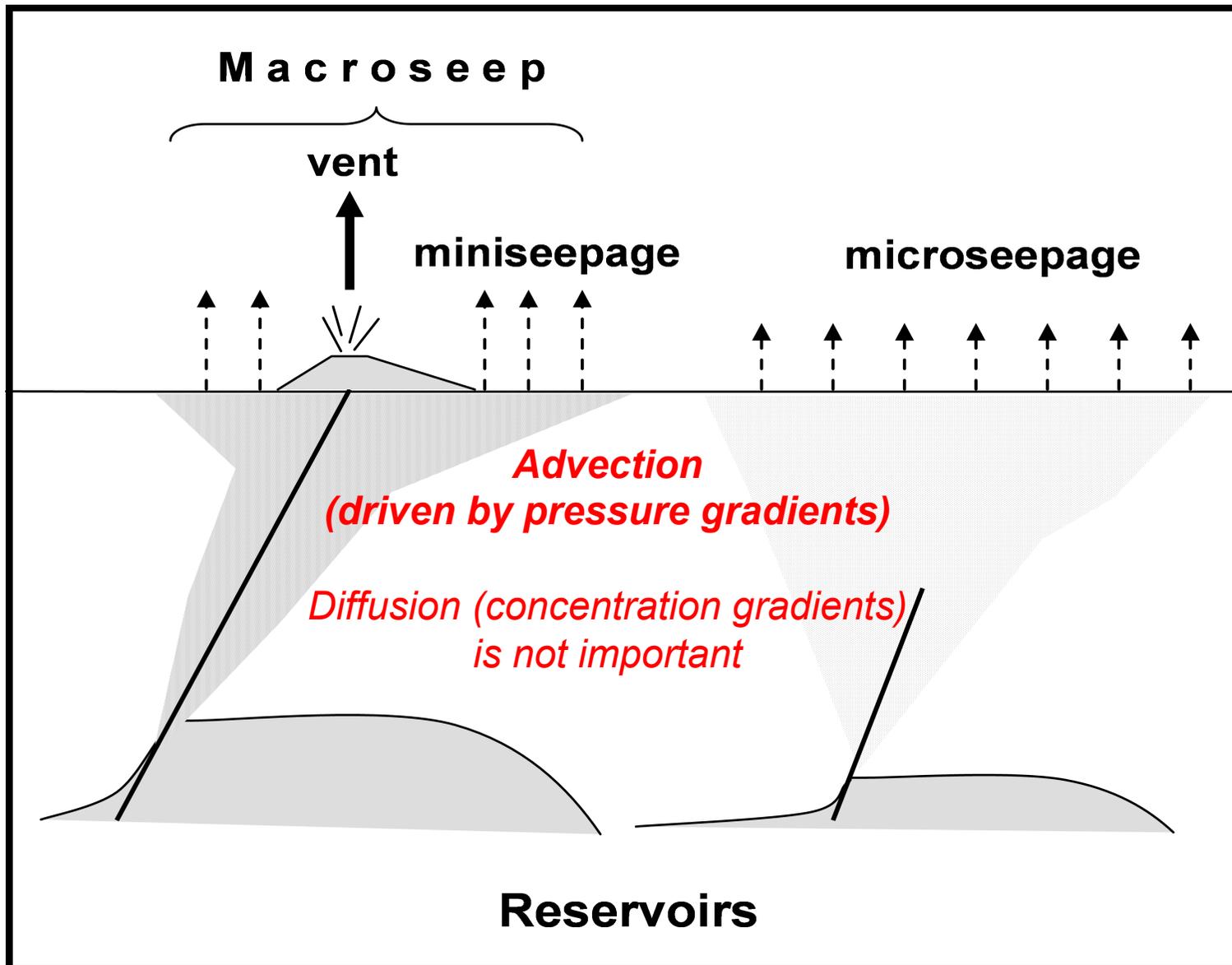
Acidalia Planitia  
(*Oehler and Allen, 2010; Etiope et al. 2011*)

**SEEPAGE ON EARTH**

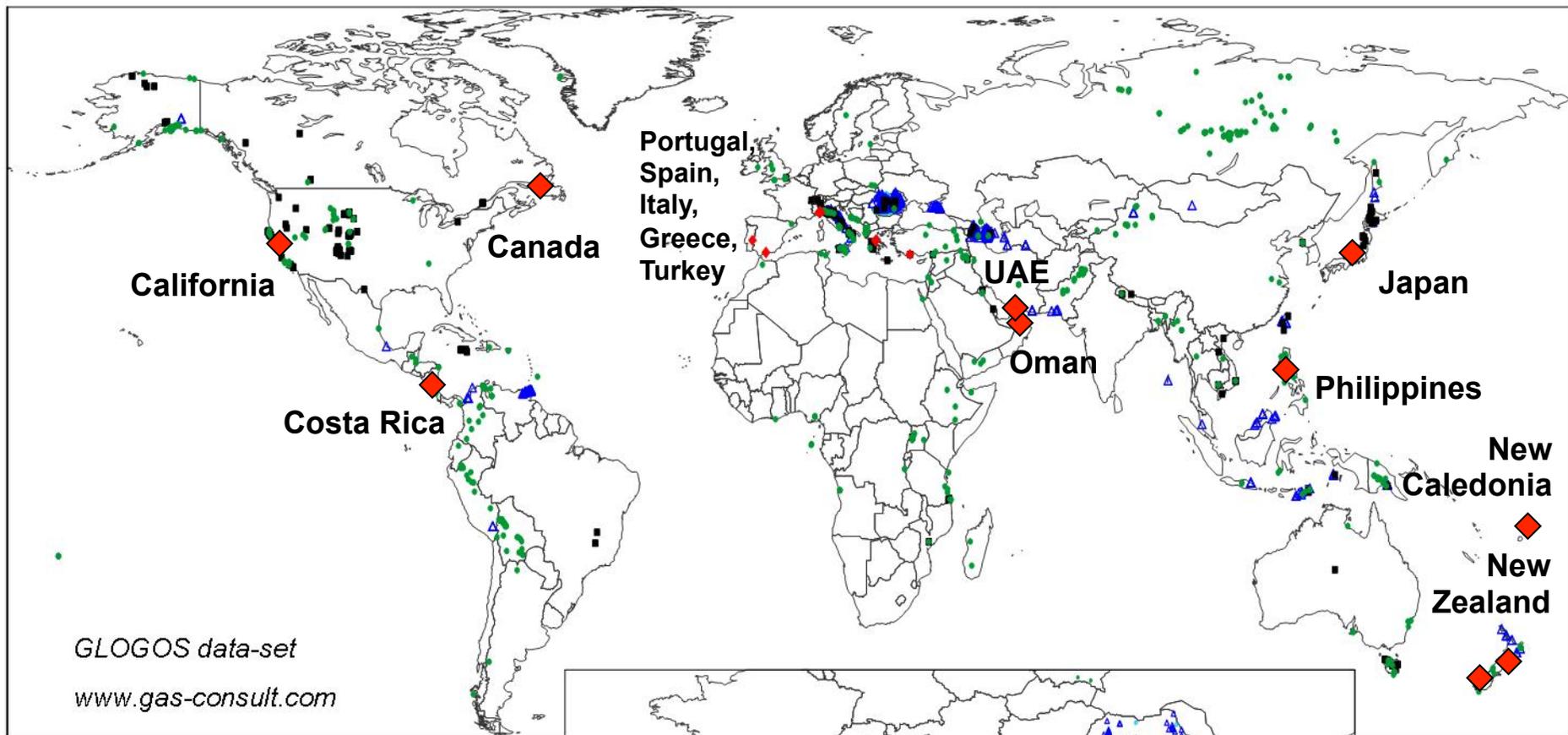
# Methane origin on Earth



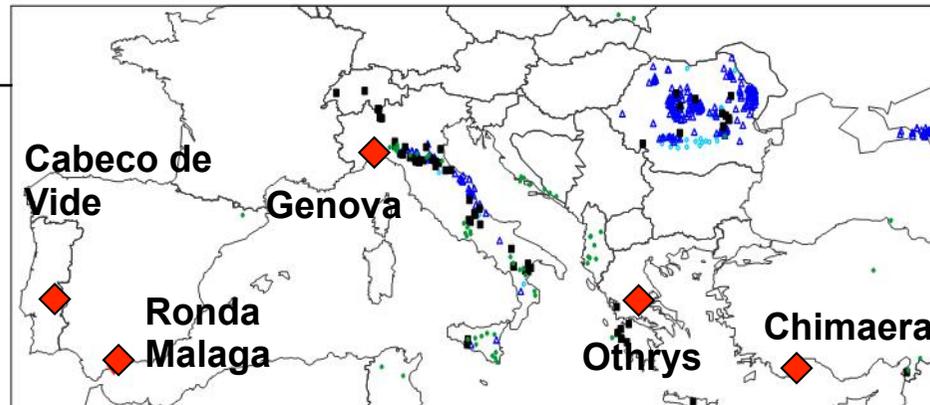
**Gas seepage can be visible or invisible,  
focused or diffuse over large areas**



# 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 CH<sub>4</sub> per year



# Eternal fires and Zoroastrianism



Azerbaijan (*Yanardag*)

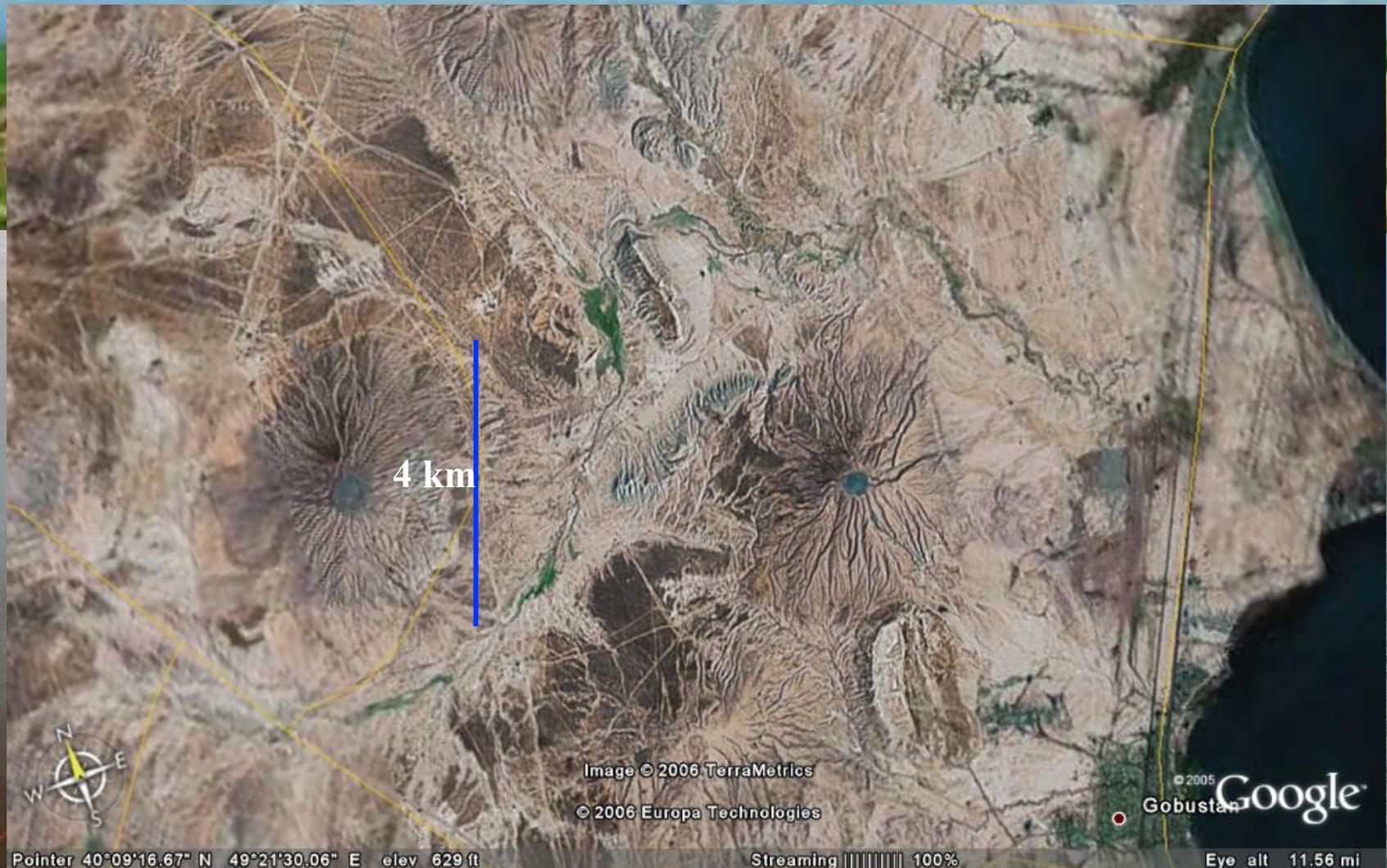
# Mud volcanoes

Release from 1 to 500 ton CH<sub>4</sub> per year

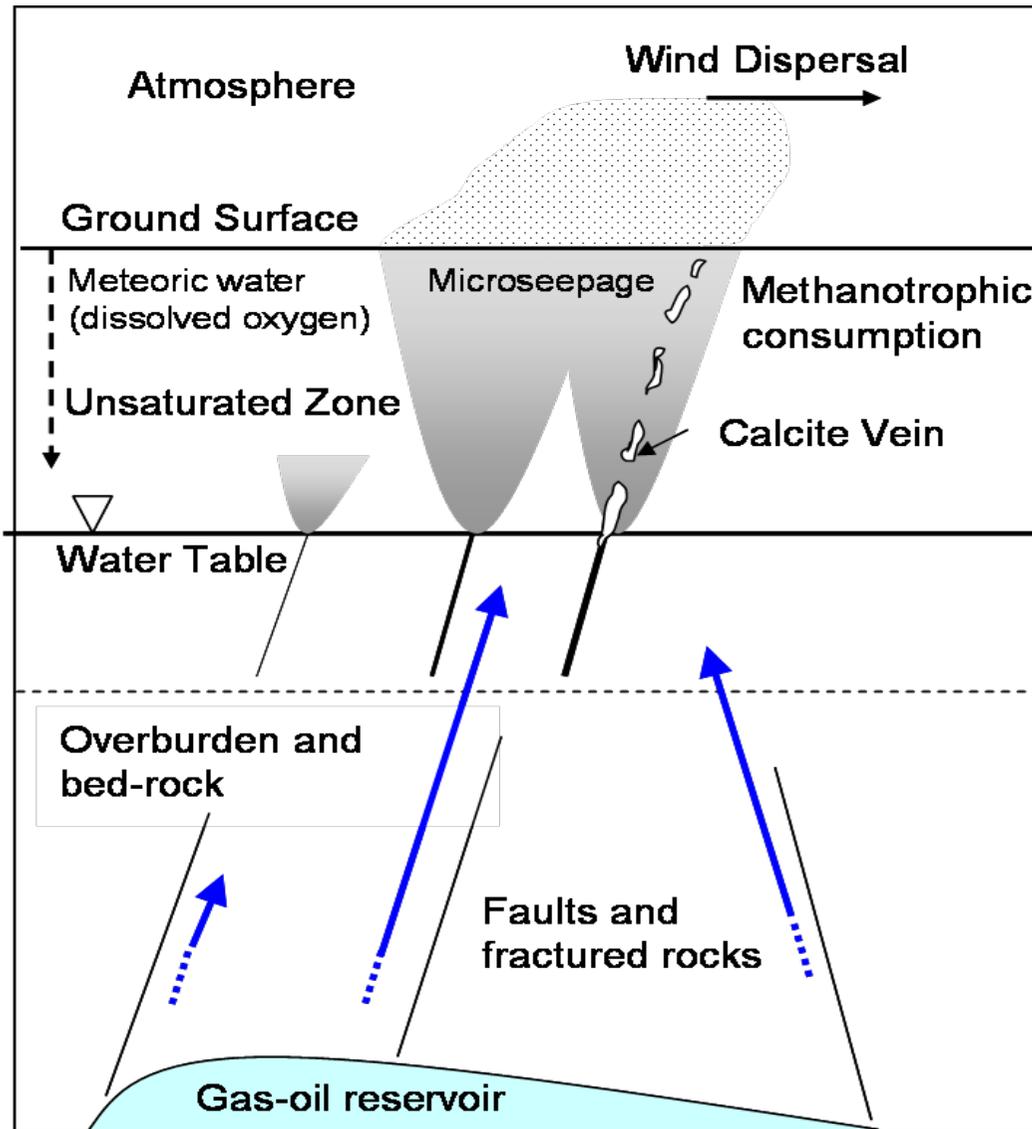


**Sedimentary volcanism, 3-phase system : gas-water-sediment**

# Mud volcanoes – Azerbaijan



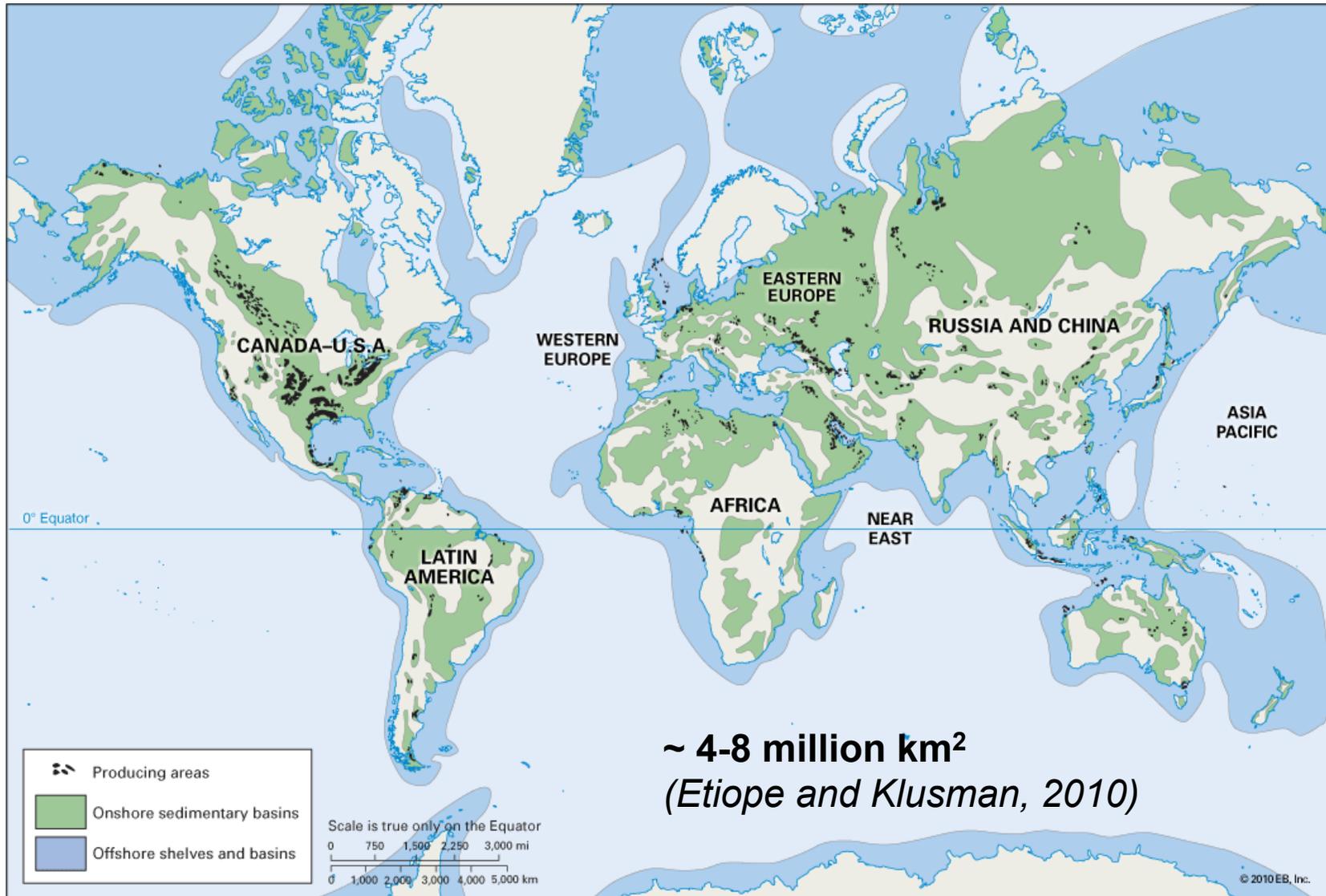
# MICROSEEPAGE



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).

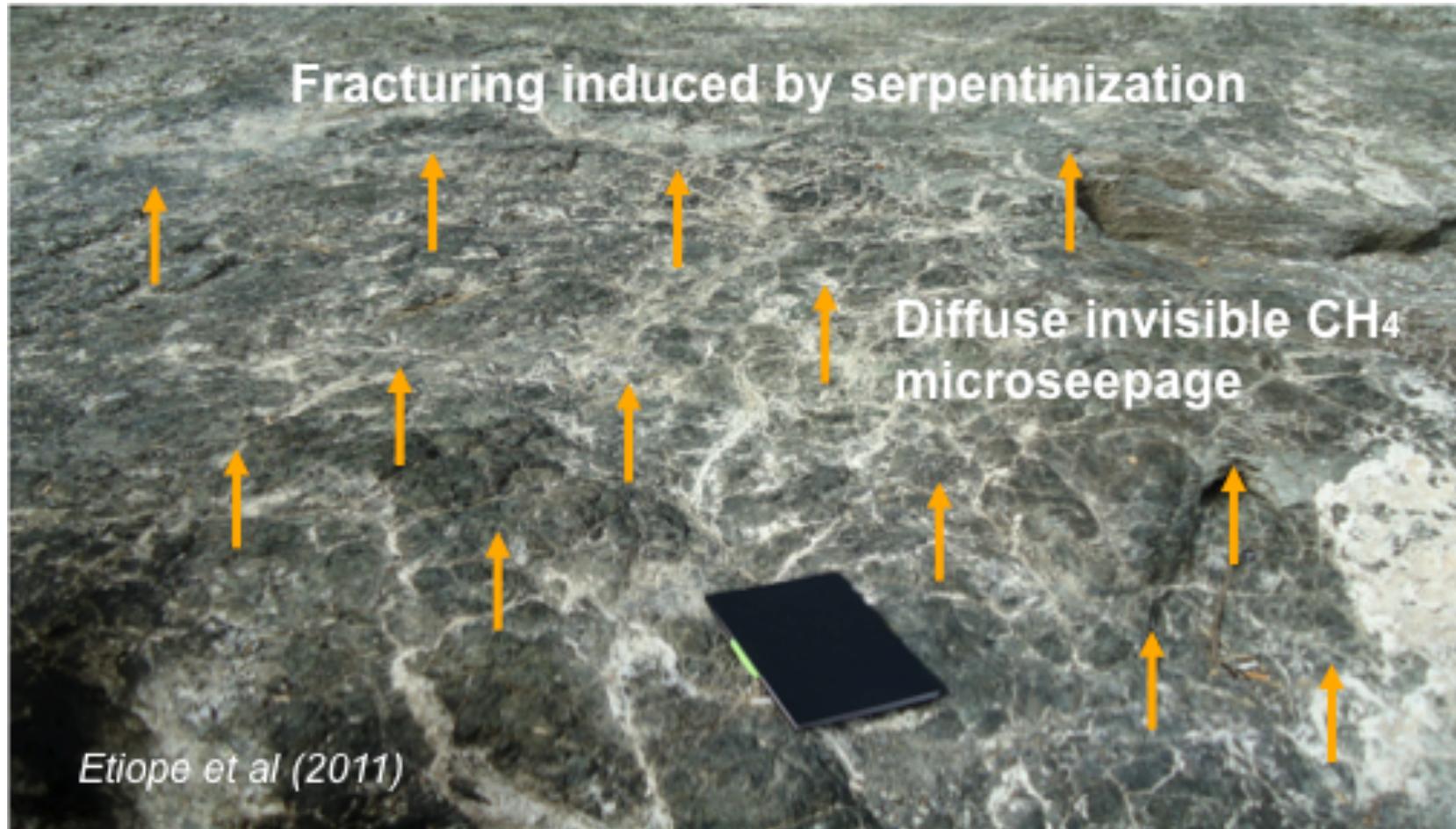
# Microseepage in sedimentary basins

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

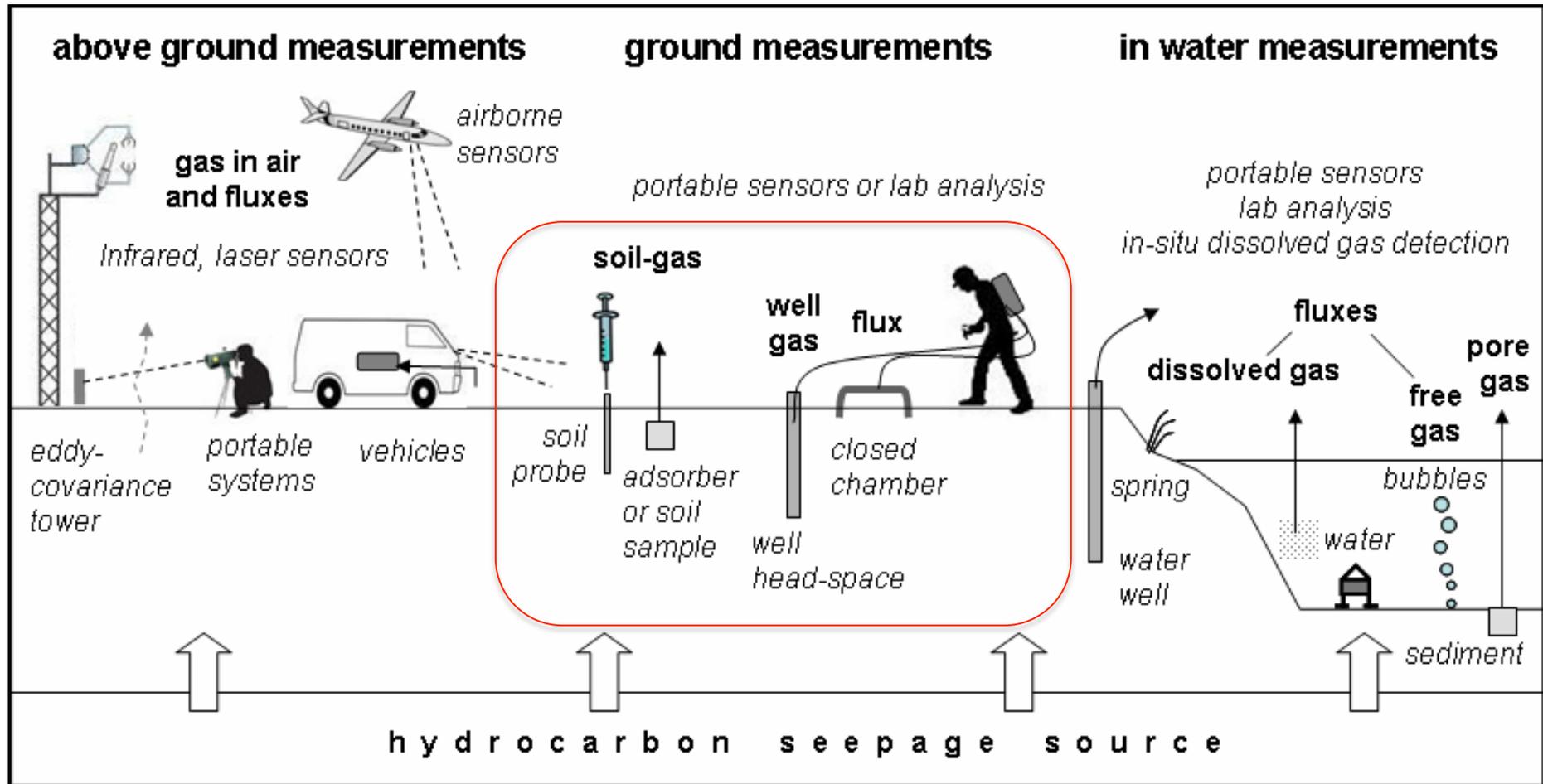


# MICROSEEPAGE IN OLIVINE-RICH ROCKS (PERIDOTITES)

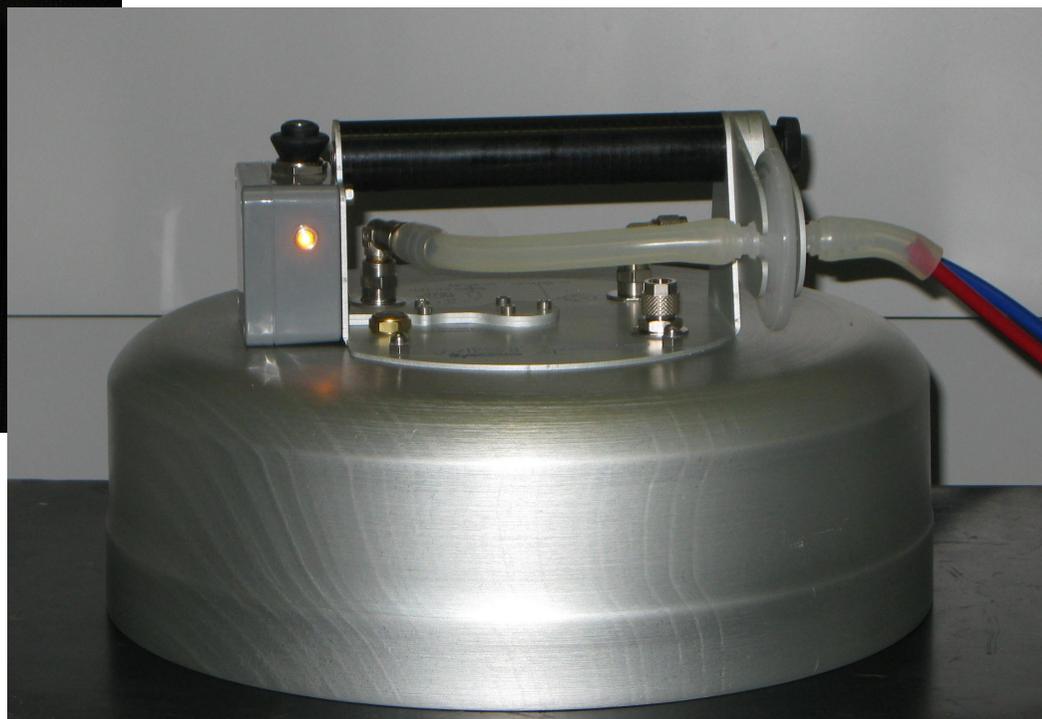
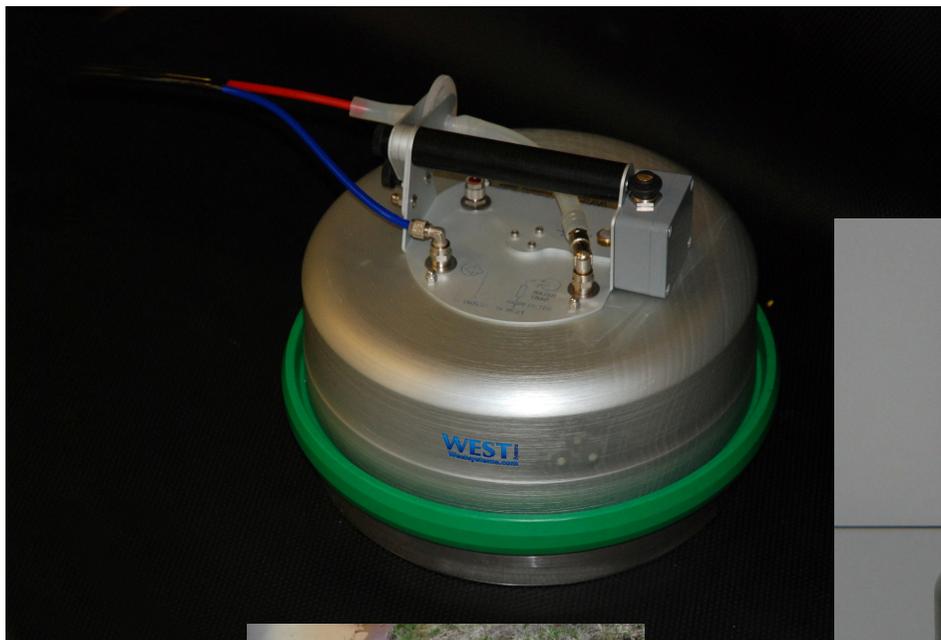
from 1 to  $10^3$  mg m<sup>-2</sup> day<sup>-1</sup>



# 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.:

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

$V_{\text{FC}}$  ( $\text{m}^3$ ) chamber volume

$A_{\text{FC}}$  ( $\text{m}^2$ ) chamber area

$c_1 - c_2$  ( $\text{mg}/\text{m}^3$ ) methane concentrations at times  $t_1 - t_2$  (days).



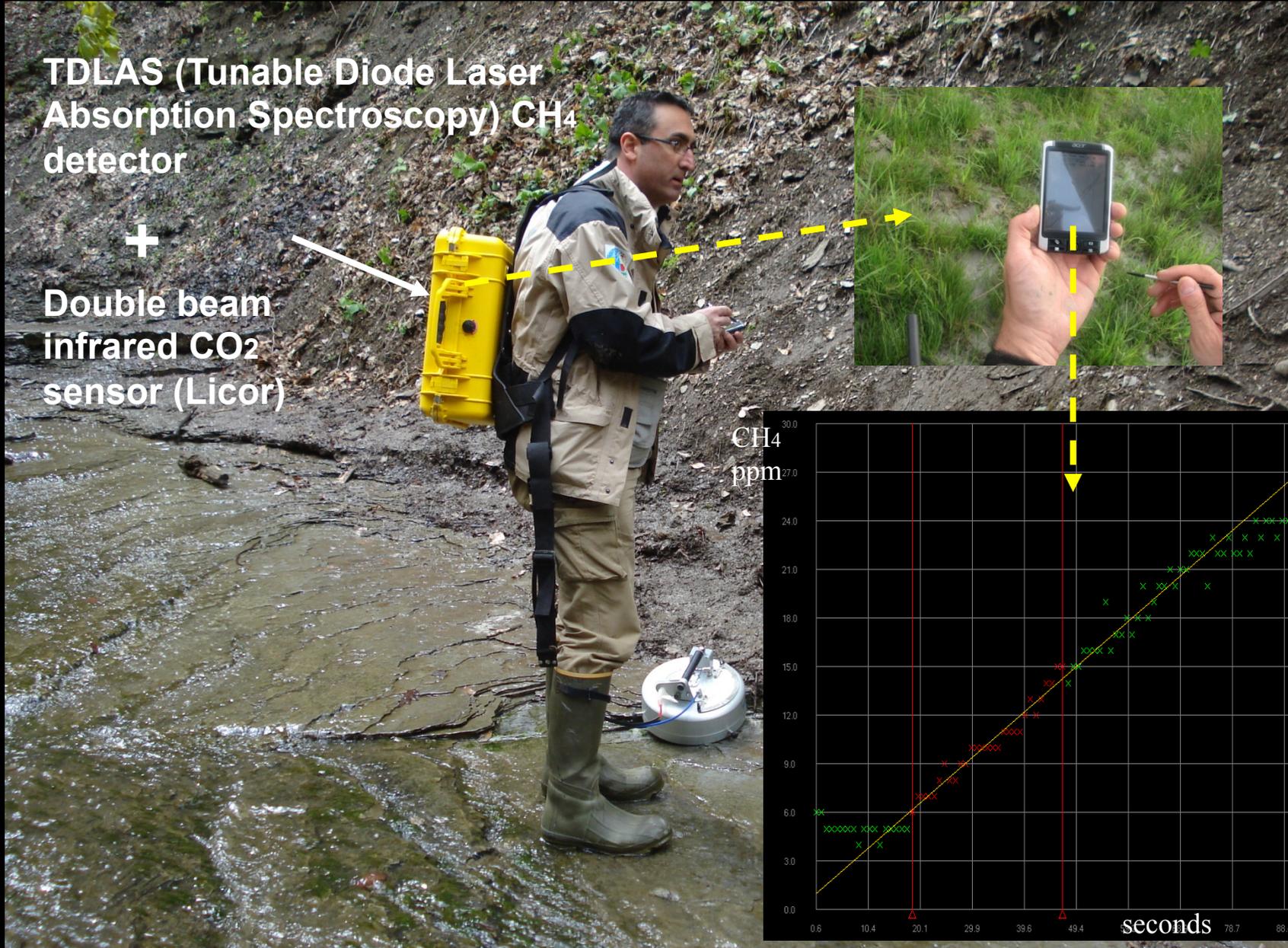
Photo: Charlotte Sigsgaard

# GAS DETECTION AND FLUX MEASUREMENTS WITH A NEW GENERATION OF SENSORS

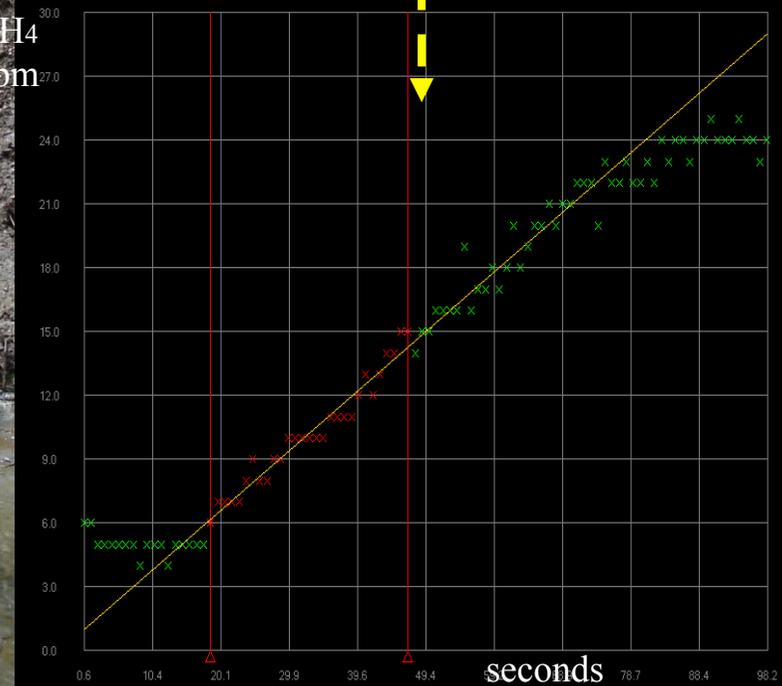
TDLAS (Tunable Diode Laser Absorption Spectroscopy) CH<sub>4</sub> detector

+

Double beam infrared CO<sub>2</sub> sensor (Licor)

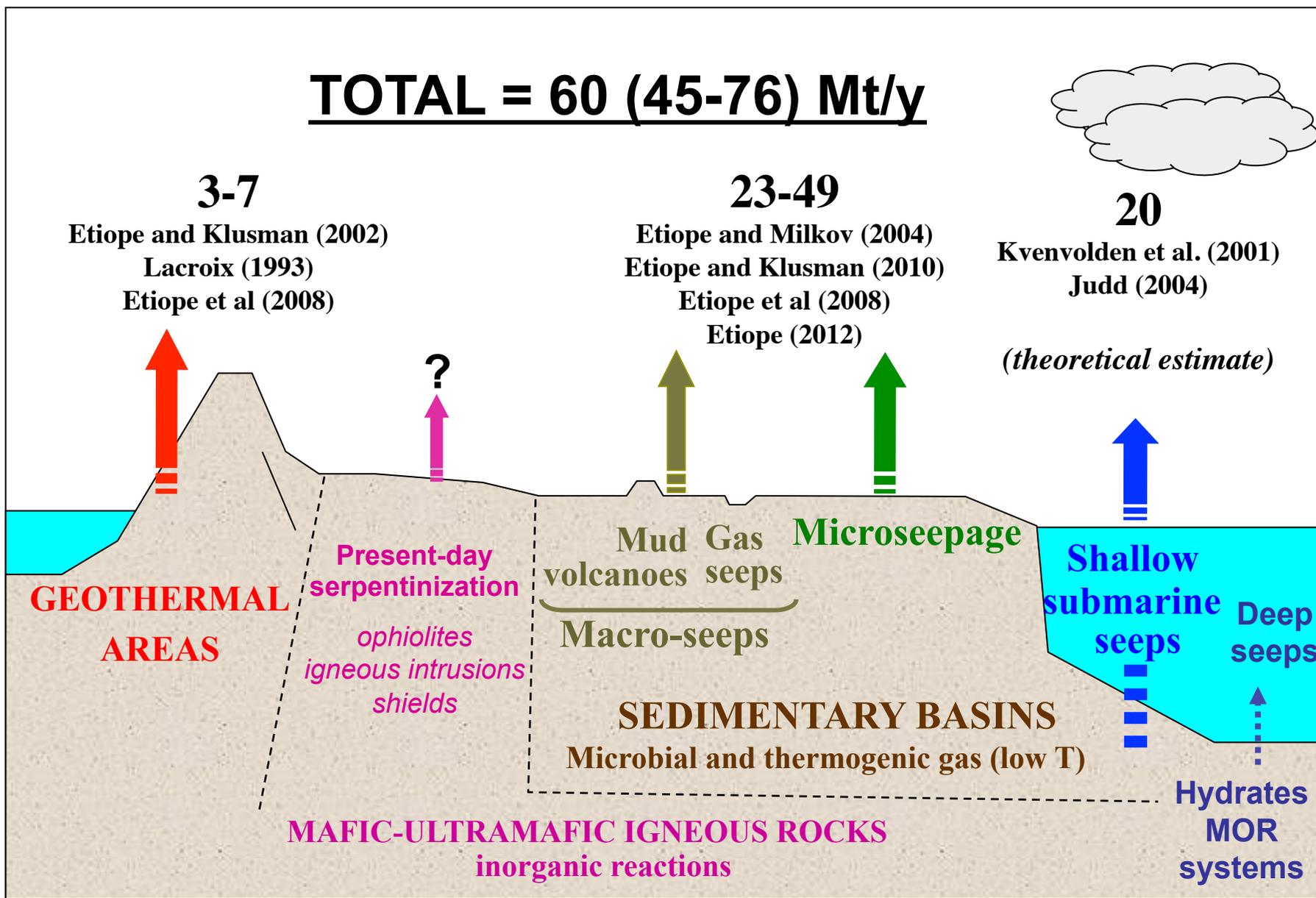


CH<sub>4</sub>  
ppm



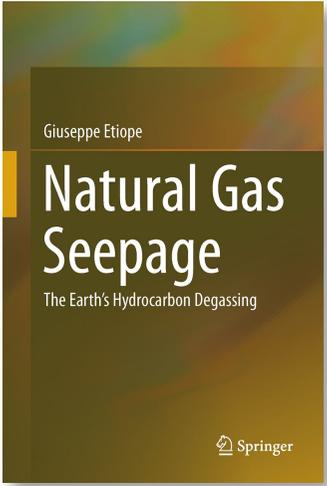
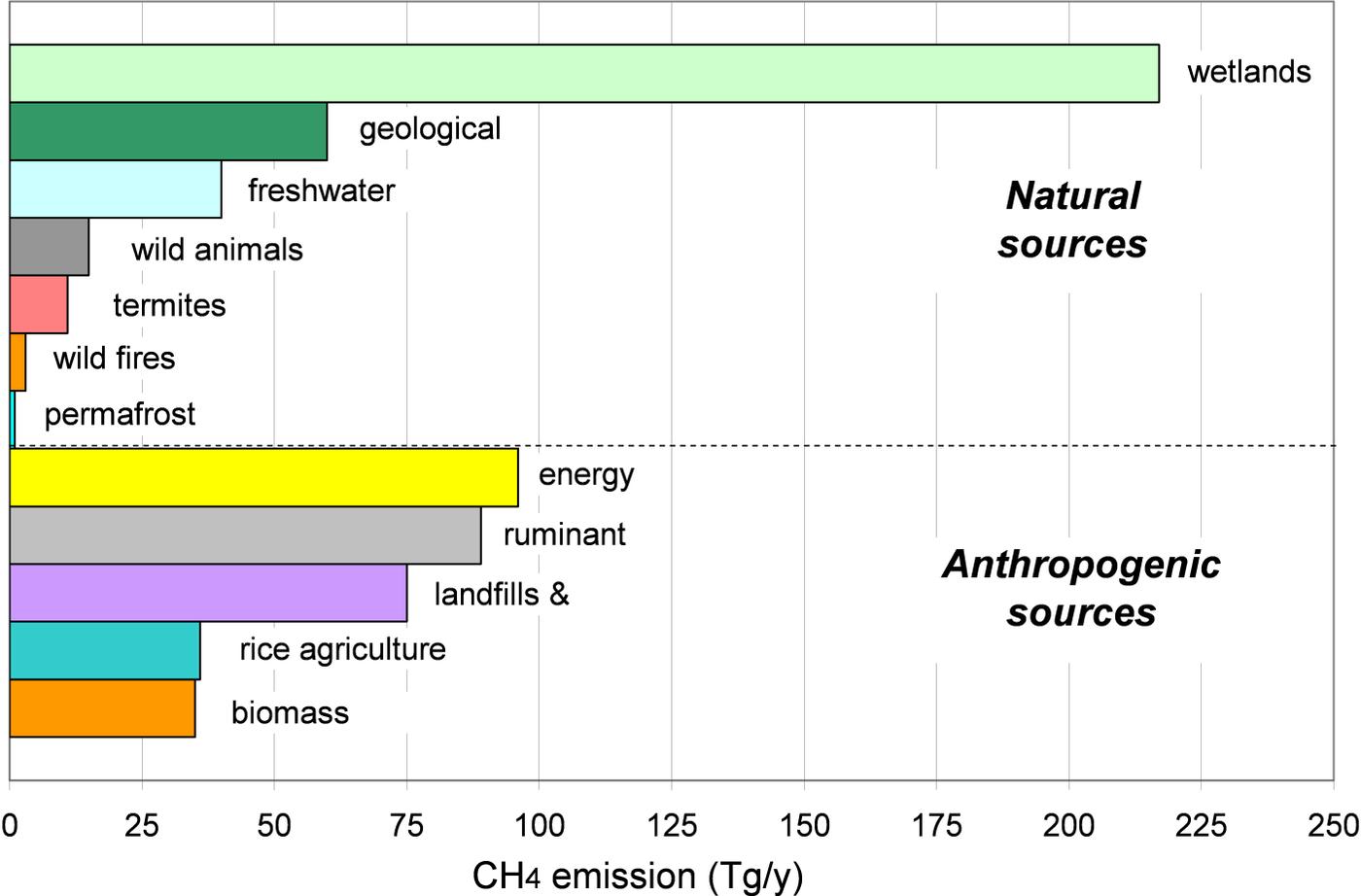
# GEOLOGIC METHANE EMISSIONS

**TOTAL = 60 (45-76) Mt/y**

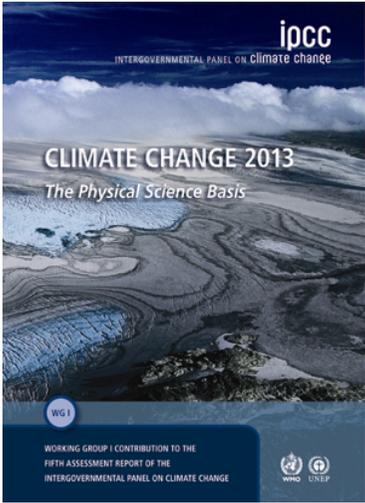


**Geological CH<sub>4</sub>**  
**2<sup>nd</sup> natural CH<sub>4</sub> source**  
**10% of total CH<sub>4</sub> source**

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



*(Etioppe, 2015)*



*(IPCC, 2013)*

# POTENTIAL SEEPAGE ON MARS

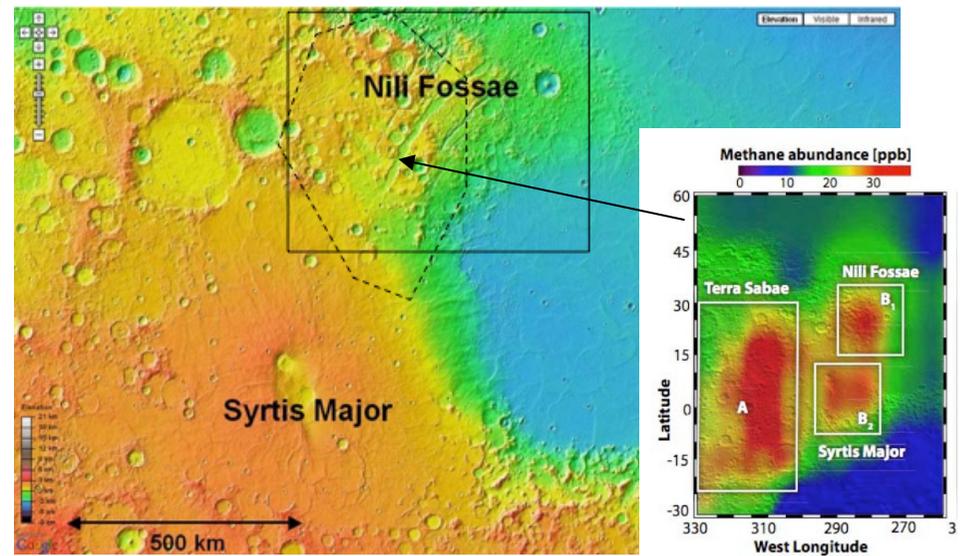
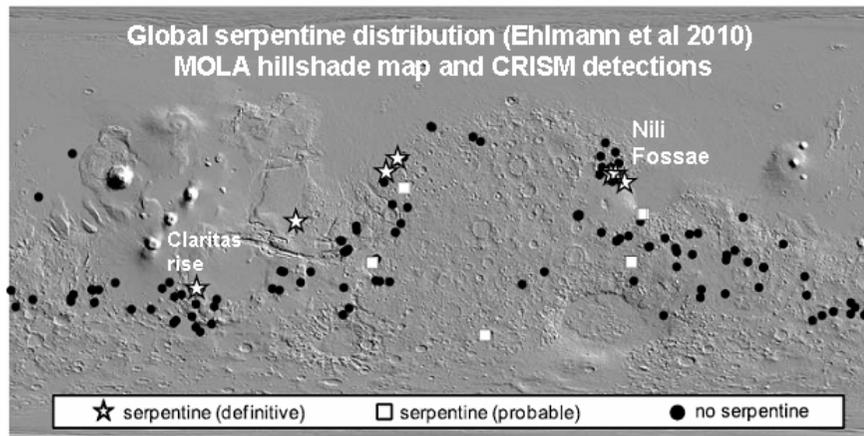
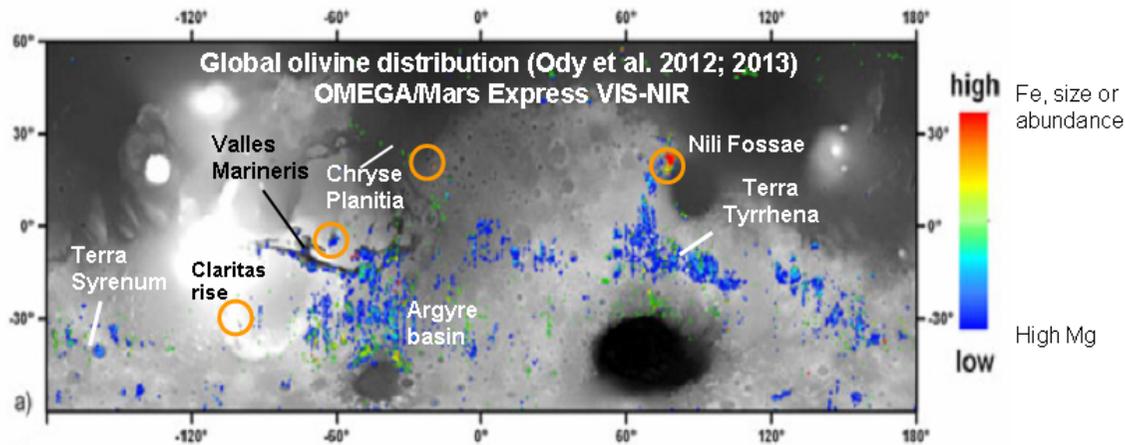
where are the best chances of finding methane?

**Analog seepage sites**

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

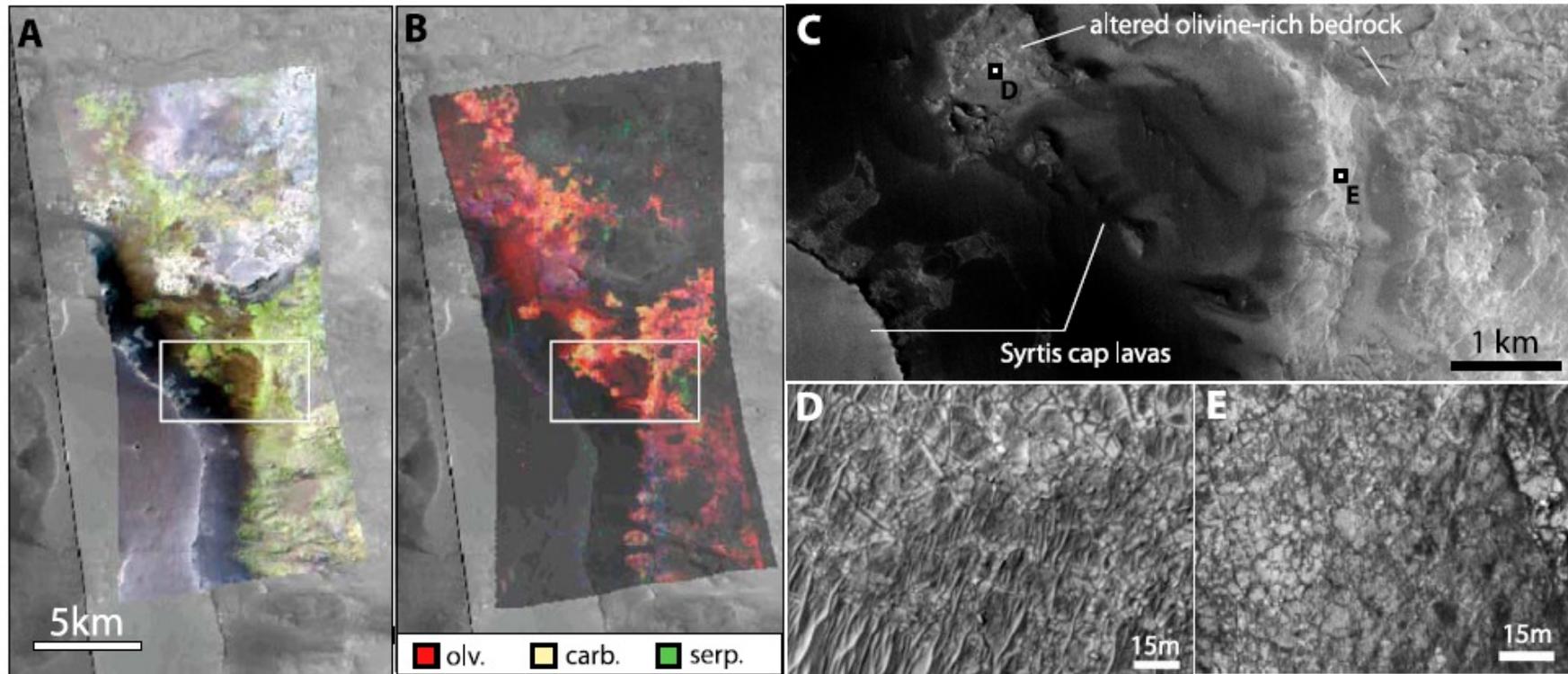
# Olivine-rich and serpentinized areas on Mars

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



30,000 km<sup>2</sup> olivine-rich outcrop (Hoefen et al 2003)

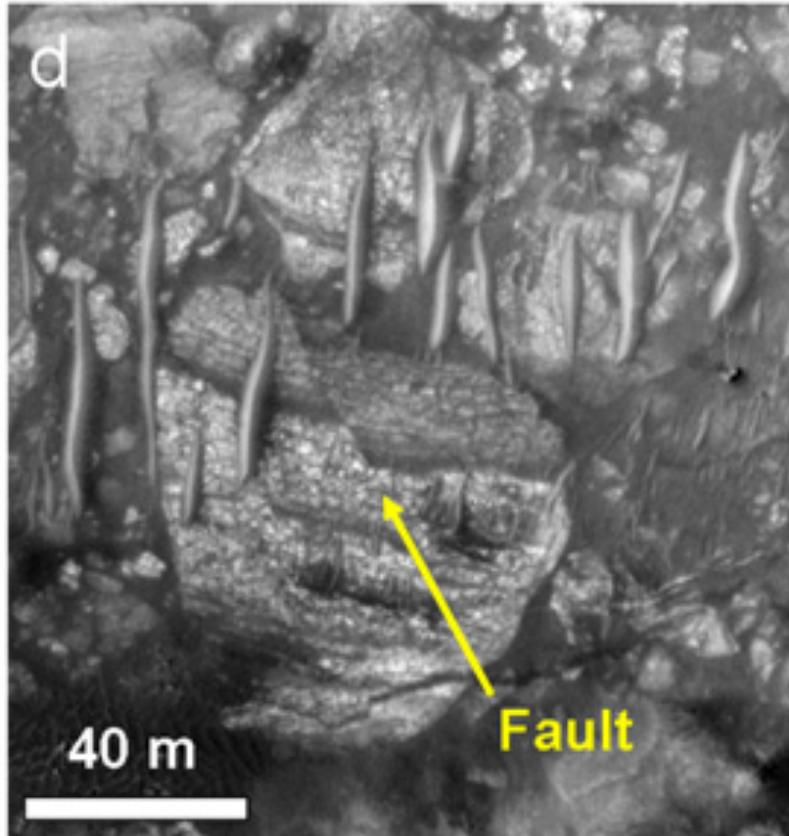
# Nili Fossae



*Ehlmann et al (2010)*

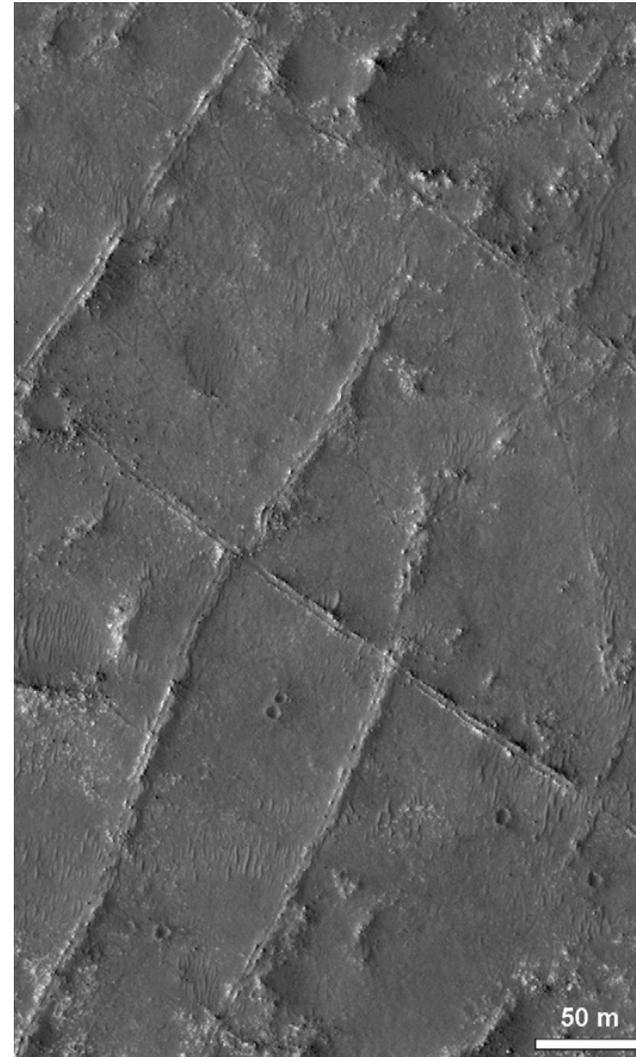
North of the Noachian-Hesperian contact (17.3°N, 77.2°E), erosion exposes a >150 km<sup>2</sup> olivine-rich, highly fractured outcrop, partially altered to serpentine

## Nili Fossae



Fault at Nili Fossae, from  
PSP\_006923\_1995 (19.381N, 76.421E)

*Wray and Ehlmann (2011)*



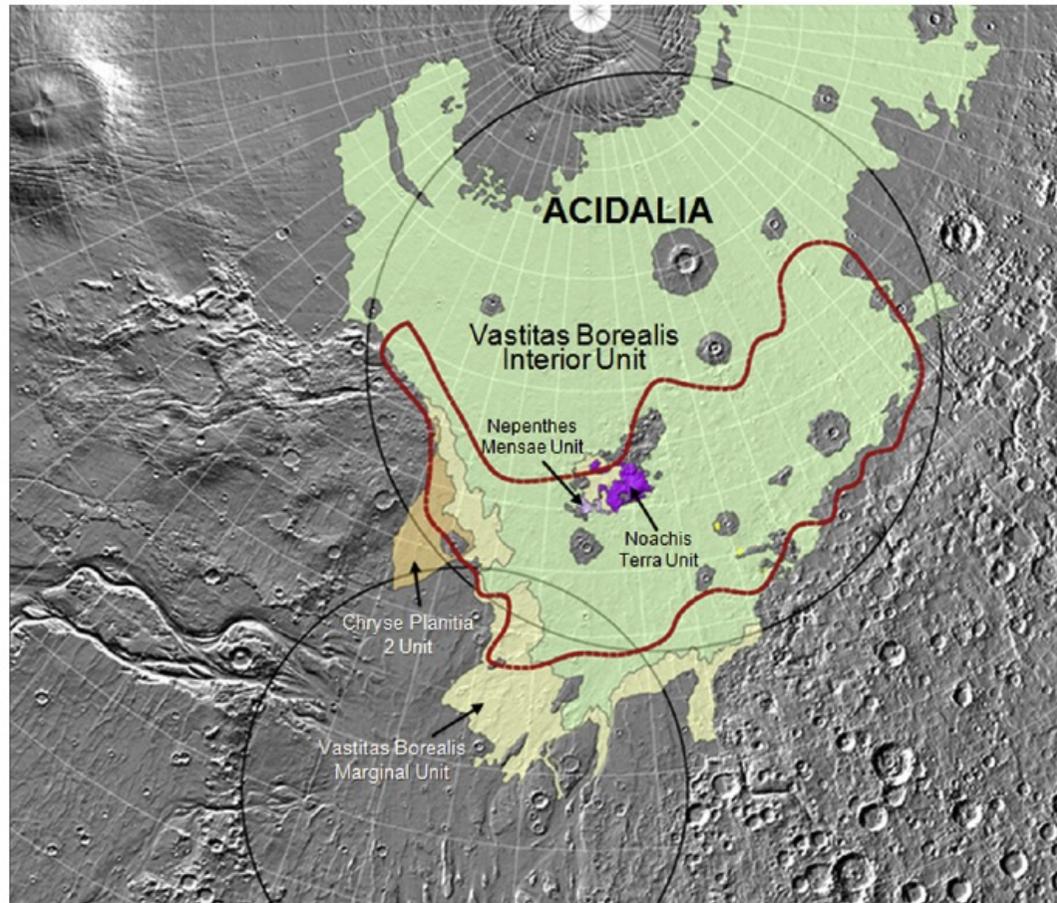
Fluid-precipitation filled fractures on the floor of  
Jezero crater, eastern Nili Fossae

## Potential mud volcano-like seeps

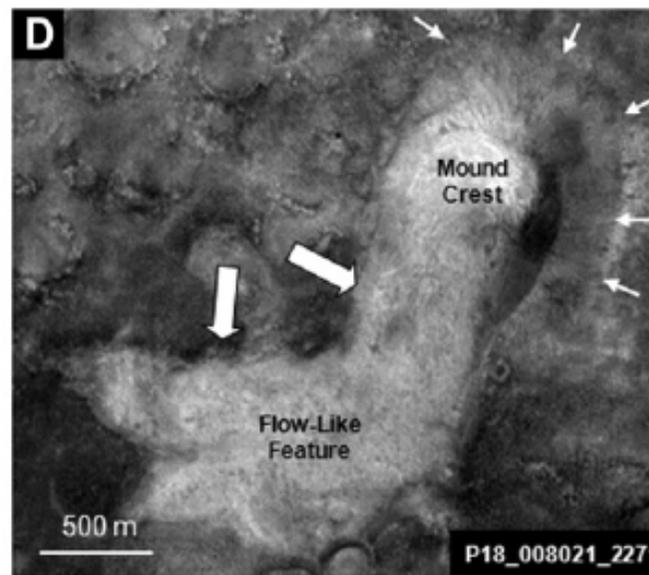
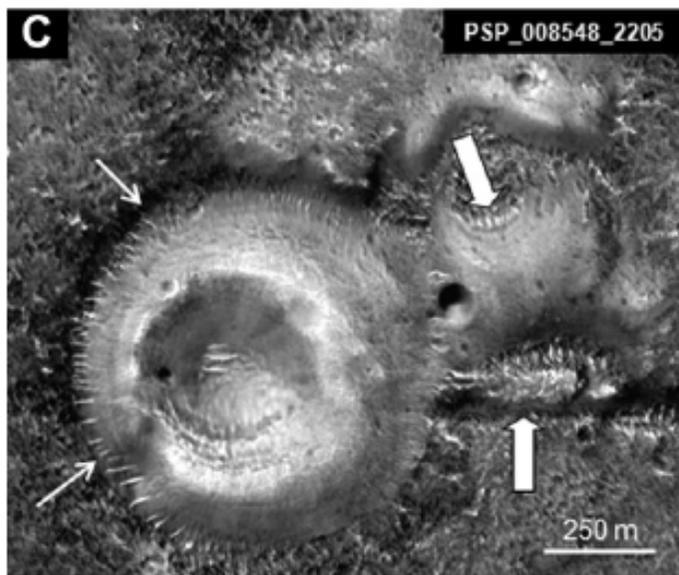
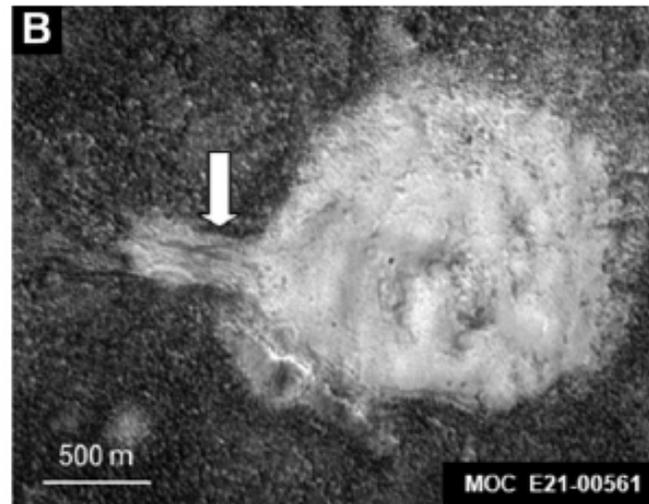
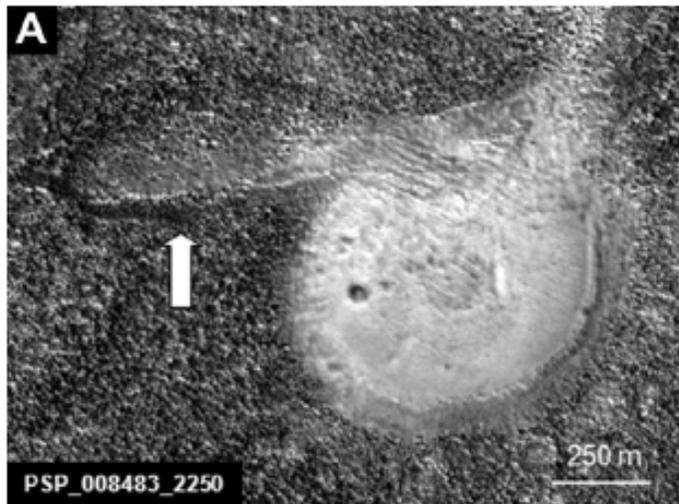
Candidate mud volcanoes reported from Utopia, Isidis, northern Borealis, Scandia, Chryse–Acidalia region (*Davis and Tanaka, 1995; Tanaka, 1997, 2005; Tanaka et al., 2000, 2003, 2008; Farrand et al., 2005; Kite et al., 2007; Rodríguez et al., 2007; Skinner and Tanaka, 2007; Allen et al., 2009; Oehler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

>40000 estimated

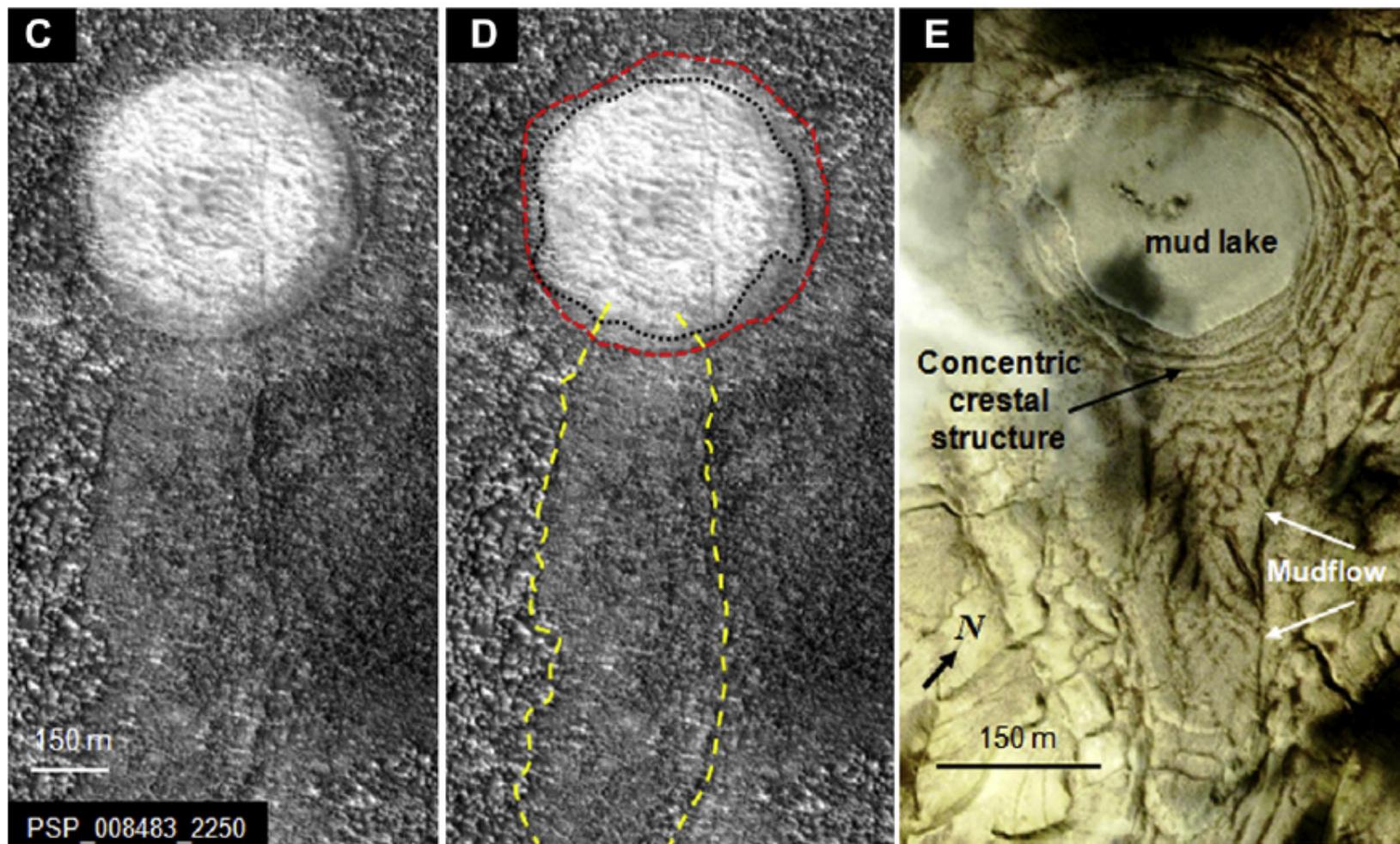
(18000 mapped)  
in Acidalia Planitia  
(*Oehler and Allen, 2010*)



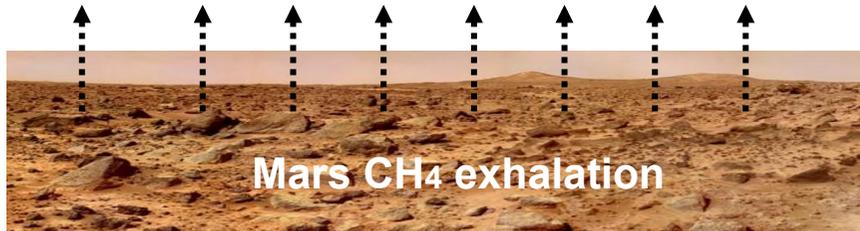
**Potential mud volcano-like seeps** Acidalia Planitia  
(*Oehler and Allen, 2010; Etiopo, Oehler, Allen 2011*)



**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 CH<sub>4</sub> LEVEL (and the Mumma's plume)



the CH<sub>4</sub> plume on Mars reflects an episodic emission of ~19,000 t CH<sub>4</sub> yr<sup>-1</sup> (Mischna et al., 2011) or ~150,000 t CH<sub>4</sub> yr<sup>-1</sup> (Lefevre and Forget, 2009)

equivalent to a diffuse microseepage of ~10-100 mg m<sup>-2</sup>d<sup>-1</sup> from an area of 500 to 5000 km<sup>2</sup>

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

If a global Martian CH<sub>4</sub> source of around 100-300 t yr<sup>-1</sup> 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

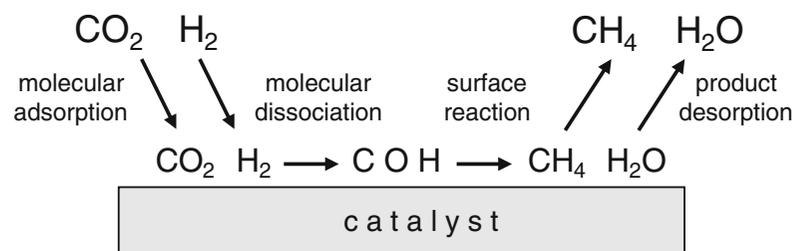
## SABATIER REACTION



*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  $\text{CO}_2$  hydrogenation with geological quantities of ruthenium: a possible abiotic  $\text{CH}_4$  source in chromitite-rich serpentinized rocks

G. ETIOPE<sup>1,2</sup> AND A. IONESCU<sup>2</sup>

**Abiotic  $\text{CH}_4$  can be rapidly produced at low T ( $< 100^\circ\text{C}$ )**

Fast production of considerable amounts of  $\text{CH}_4$  via Sabatier reaction at 90, 50 and  $25^\circ\text{C}$ , 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 CH<sub>4</sub> 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.

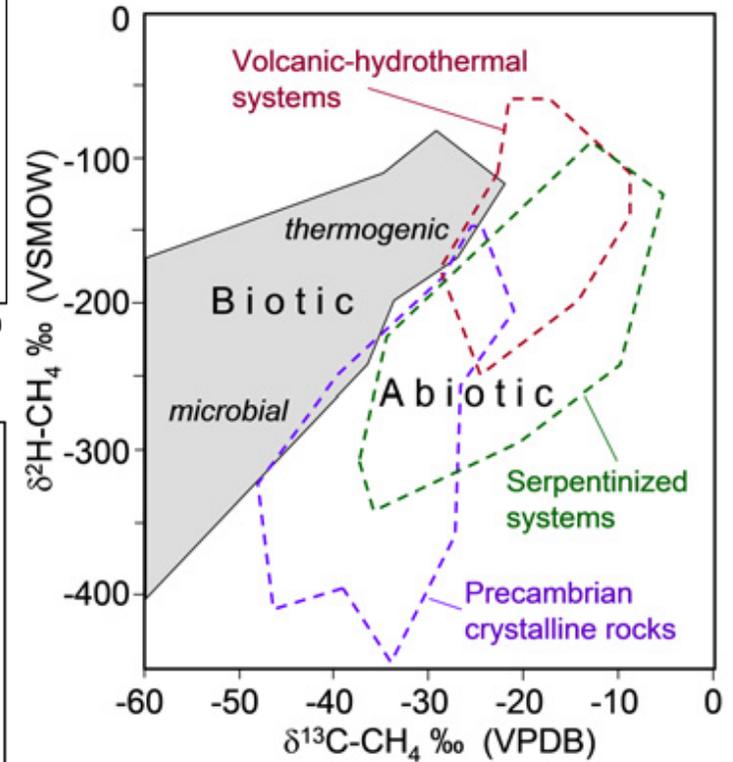
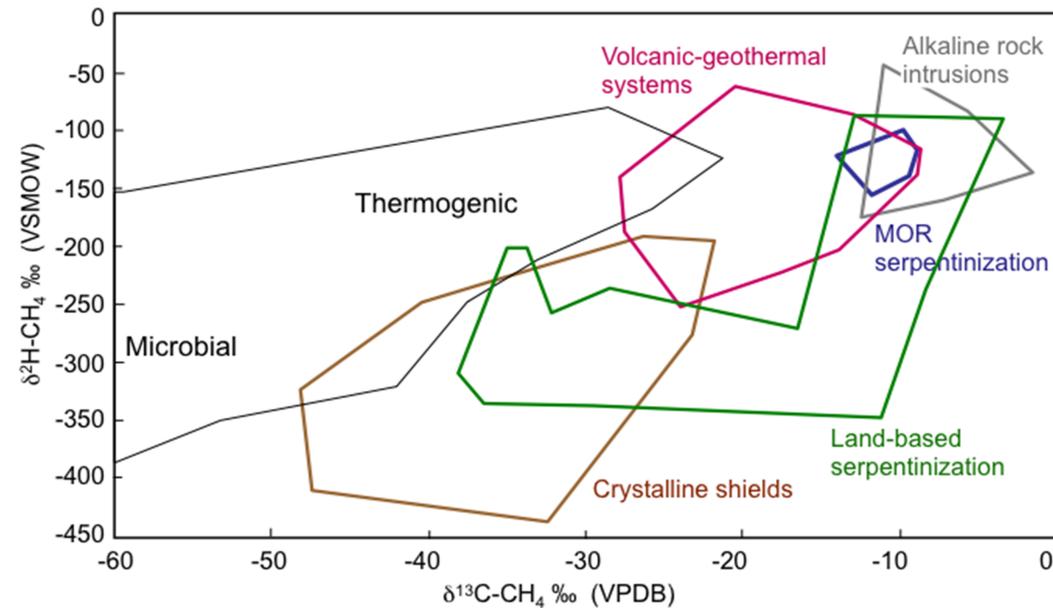
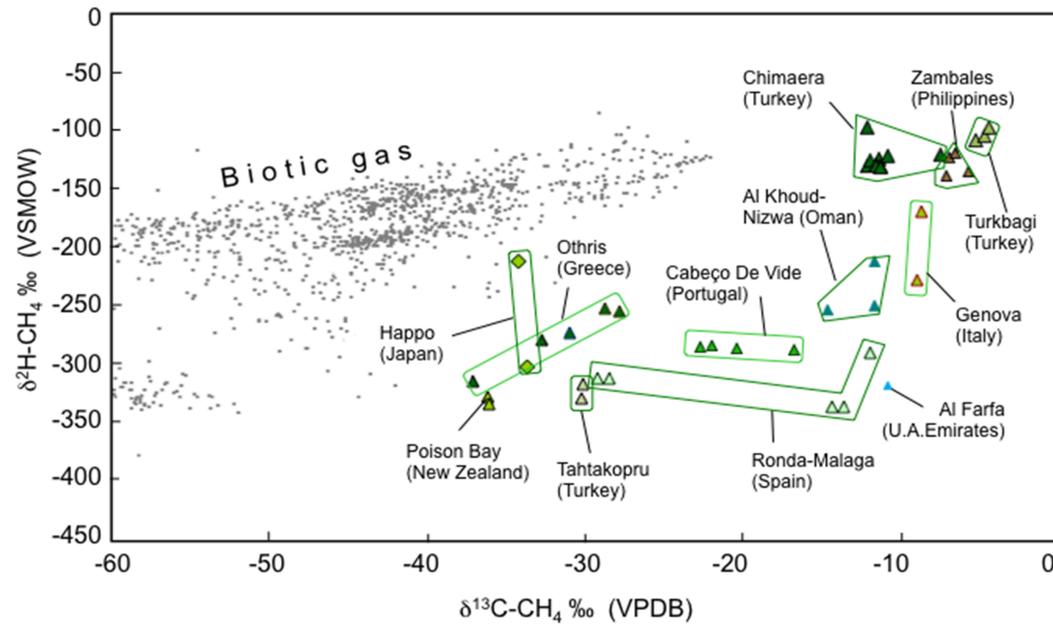
Such a concentration is within the typical range observed in terrestrial chromitites, including those in methane-bearing ultramafic rocks

**no need of hydrothermal or magmatic systems to generate abiotic CH<sub>4</sub> on Mars**

# **CH<sub>4</sub> ISOTOPIC COMPOSITION ON EARTH**

# Abiotic vs biotic methane

well distinguished by C and H isotopic ratios



*Etioppe and Schoell (2014)*  
*Etioppe (2015)*

# **CH<sub>4</sub> ISOTOPIC COMPOSITION ON MARS?**

# Potential C–H isotopic signatures of abiotic CH<sub>4</sub> on Mars

- Martian C feedstock:**
- atmospheric fractionated CO<sub>2</sub> ( $\delta^{13}\text{C}$ : +46 ‰; [Webster et al 2013](#))
  - atmospheric unfractionated CO<sub>2</sub> ( $\delta^{13}\text{C}$  -20‰ to 0‰; [Niles et al., 2010](#))
  - magmatic CO<sub>2</sub> (Zagami meteorites,  $\delta^{13}\text{C}$ : -10 to -20‰)

$\delta^{13}\text{C}$ -CH<sub>4</sub> can be similar to that observed on Earth only if it derives from unfractionated CO<sub>2</sub>

- Martian H feedstock:**
- atmospheric H<sub>2</sub>
  - 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 CH<sub>4</sub>, far outside terrestrial variations

Martian  $\delta^2\text{H}$ -CH<sub>4</sub> 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, CH<sub>4</sub> 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 H<sub>2</sub>, CO<sub>2</sub> and platinum group elements (Ru) are available

Geologic CH<sub>4</sub> 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

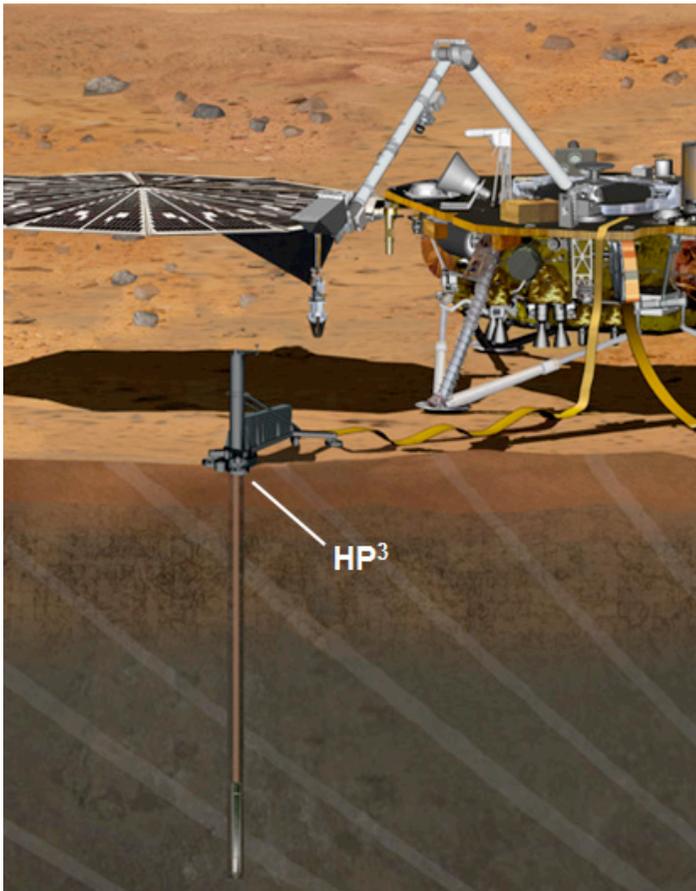


*INSIGHT landing site:  
Elysium Planitia*



### **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**