Methane emissions from Earth's degassing:
a reference for Mars

Giuseppe ETIOPE
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Istituto Nazionale di Geofisica e Vulcanologia, Roma

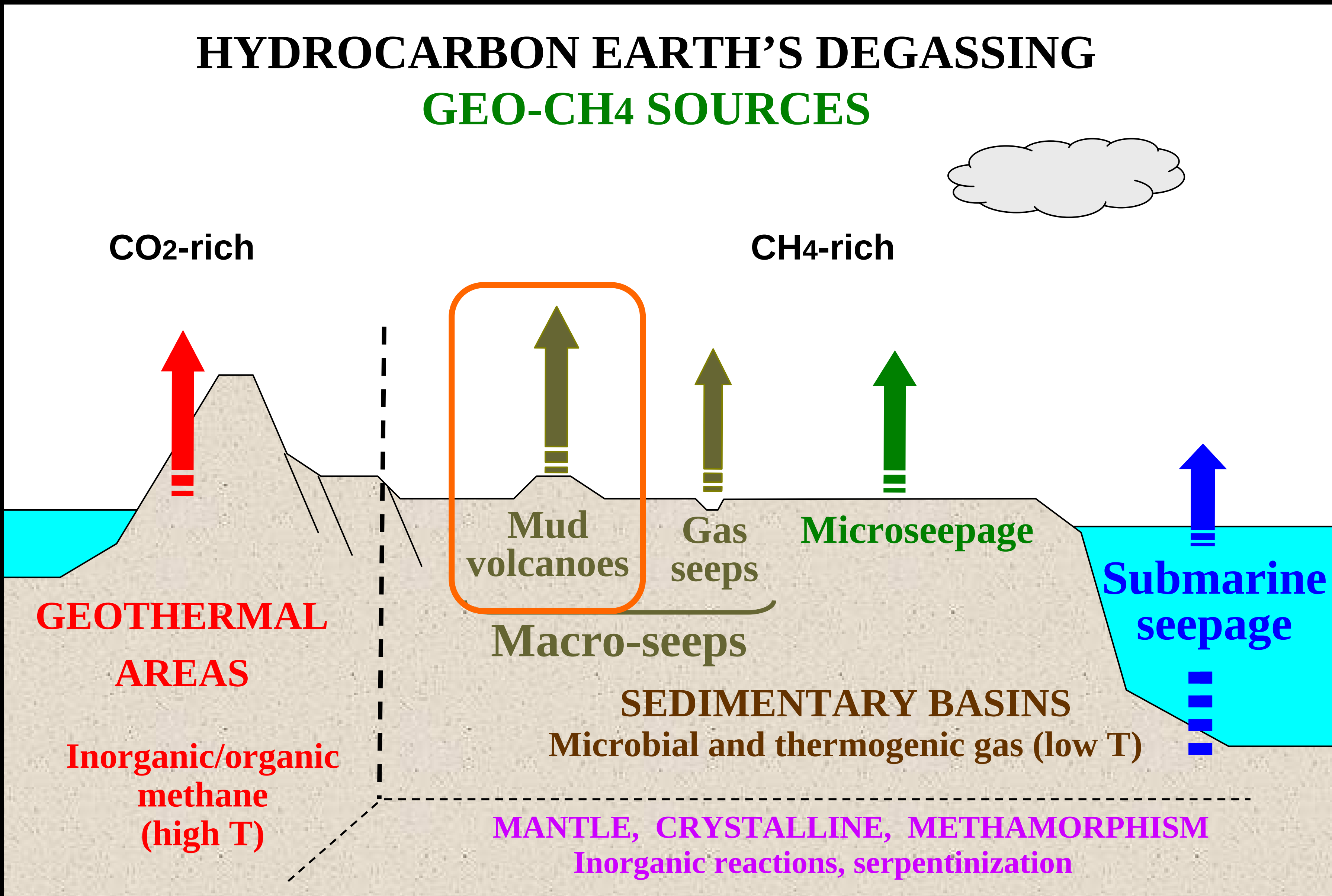
1. **Classification** of geological CH_4 emissions

2. **Gas fluxes**: emission factors and global emission

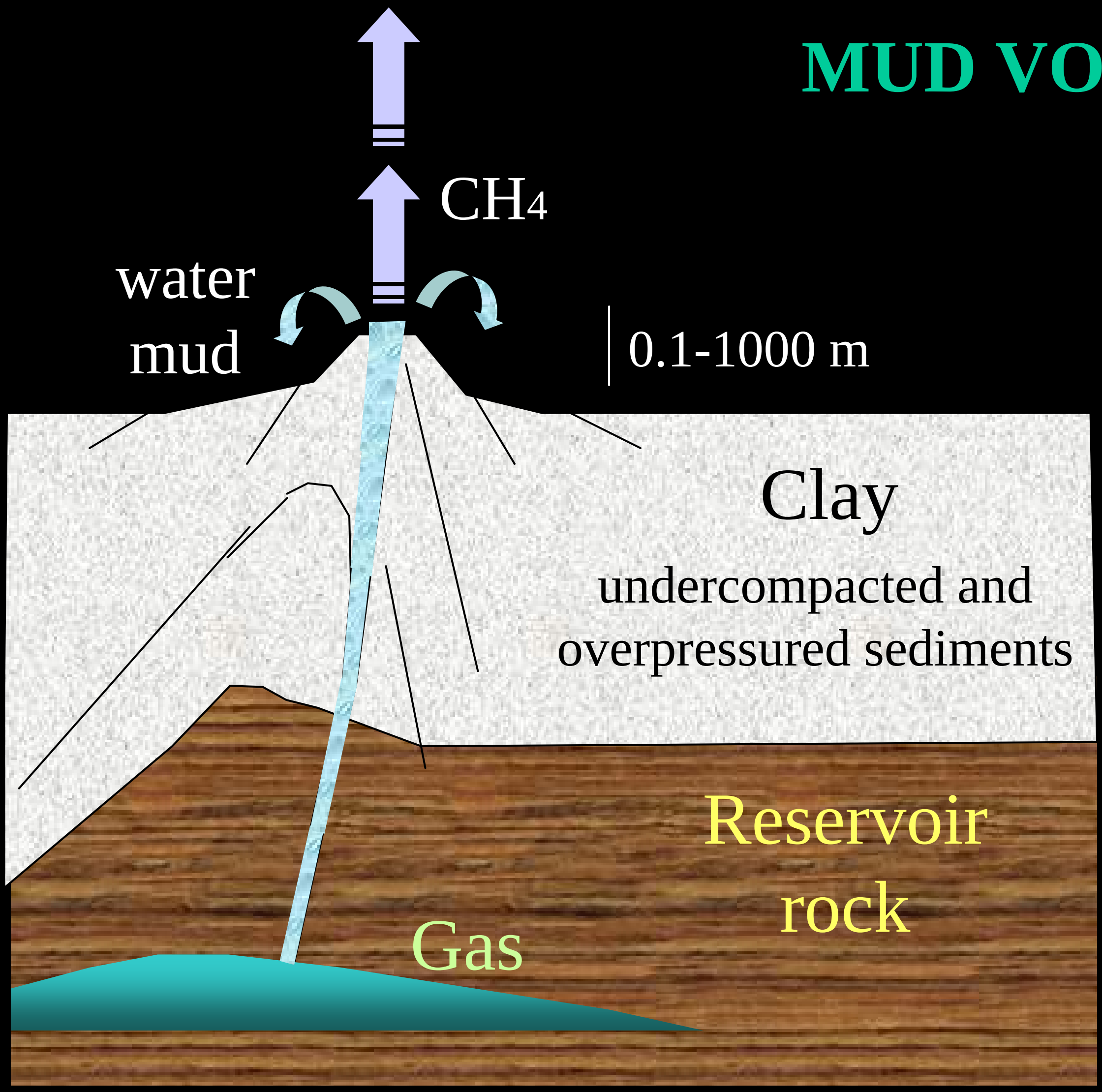
3. **Gas origin**: global perspective, problems, some rarities….

4. Considerations for unravelling CH_4 origin on Mars

1. Classification of geological CH_4 emissions



MACRO-SEEPS
MUD VOLCANO



Gas release to the atmosphere

Gas migration along faults

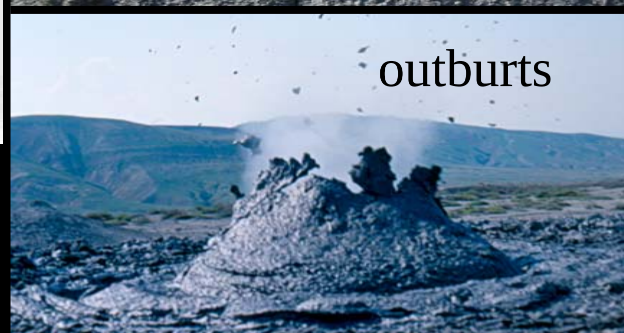
Pressurised gas from hydrocarbon reservoir

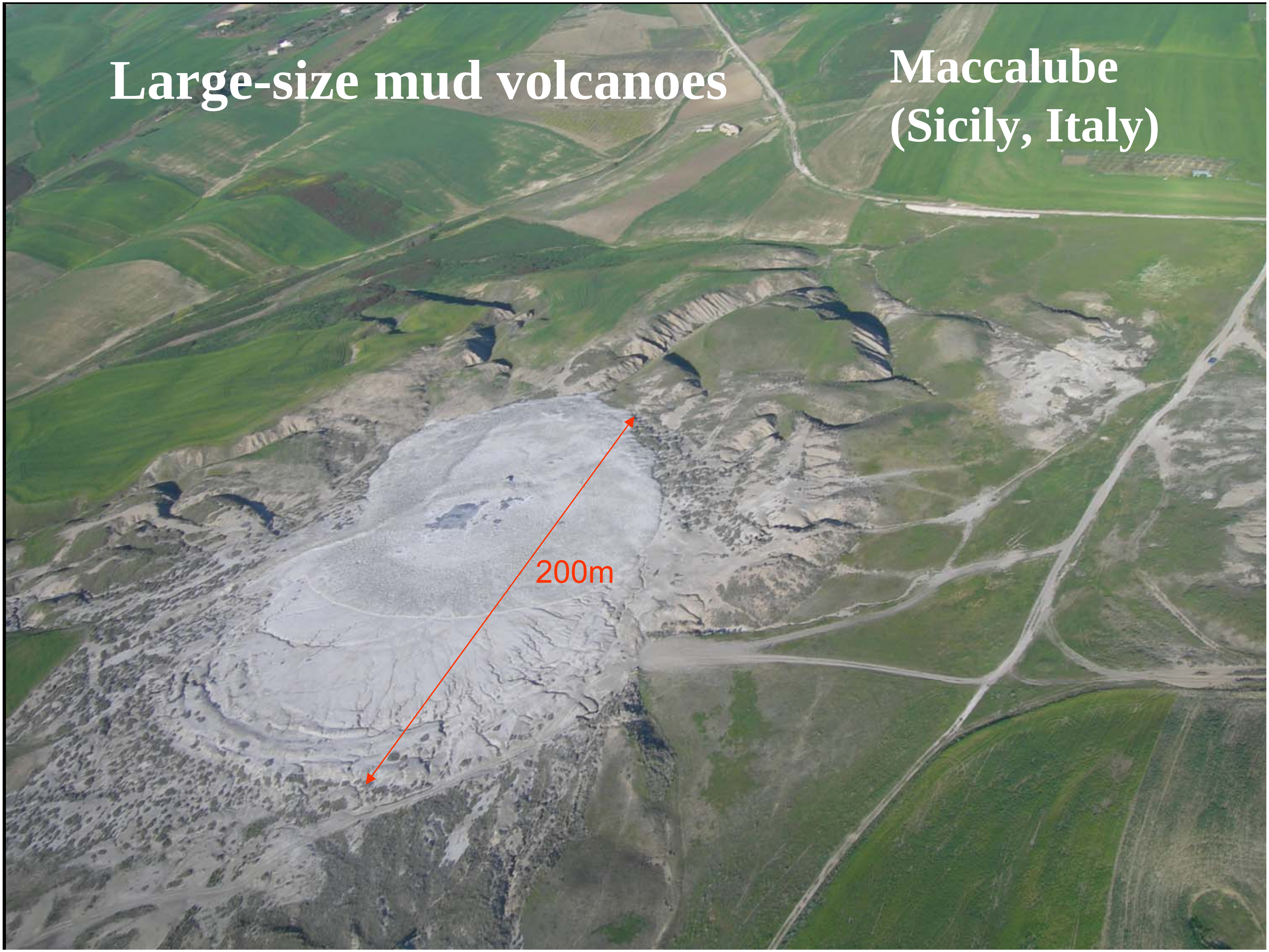
3 types of MV gas emissions

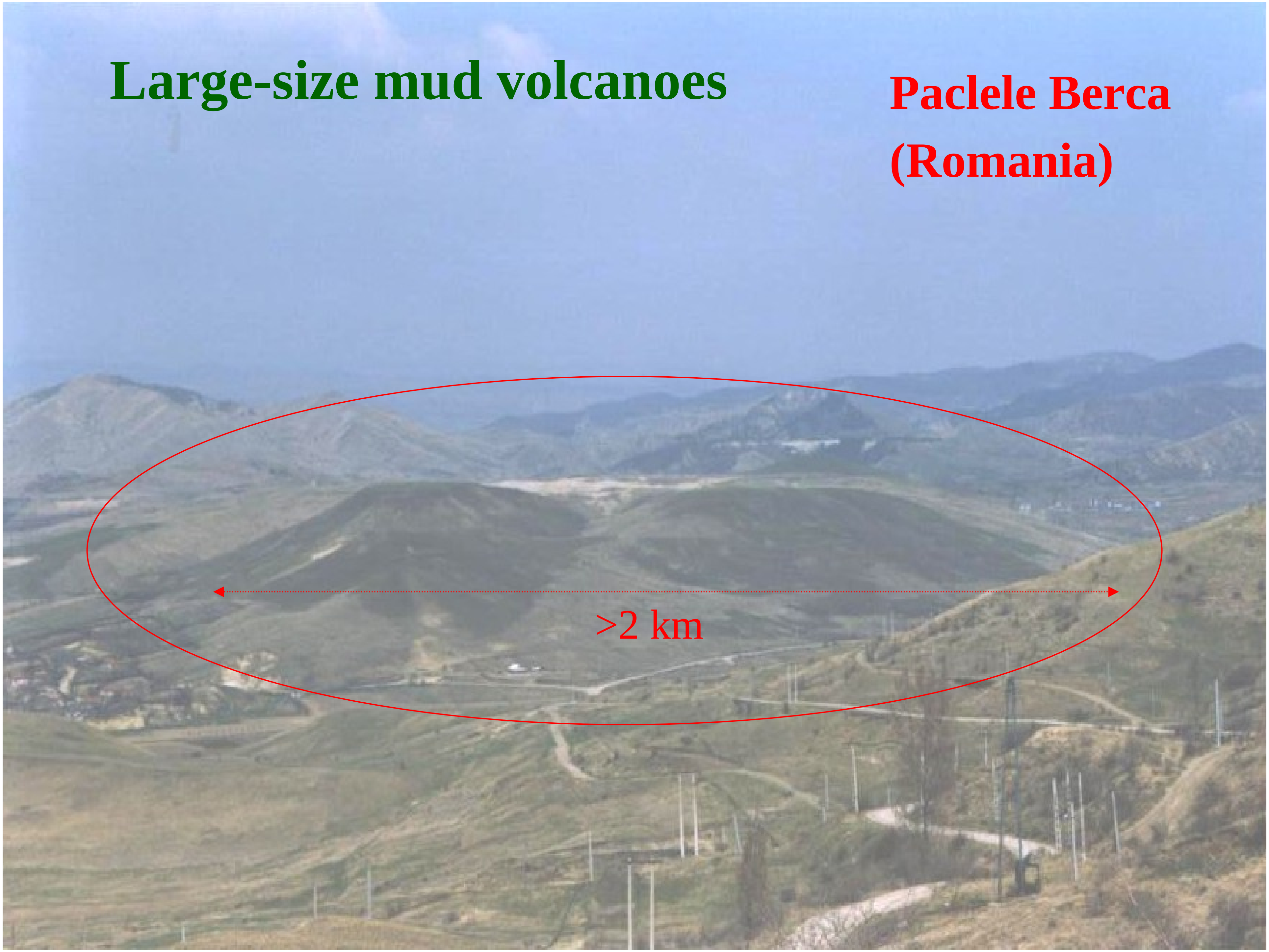
ERUPTIONS

VENTS

MICROSEEPAGE

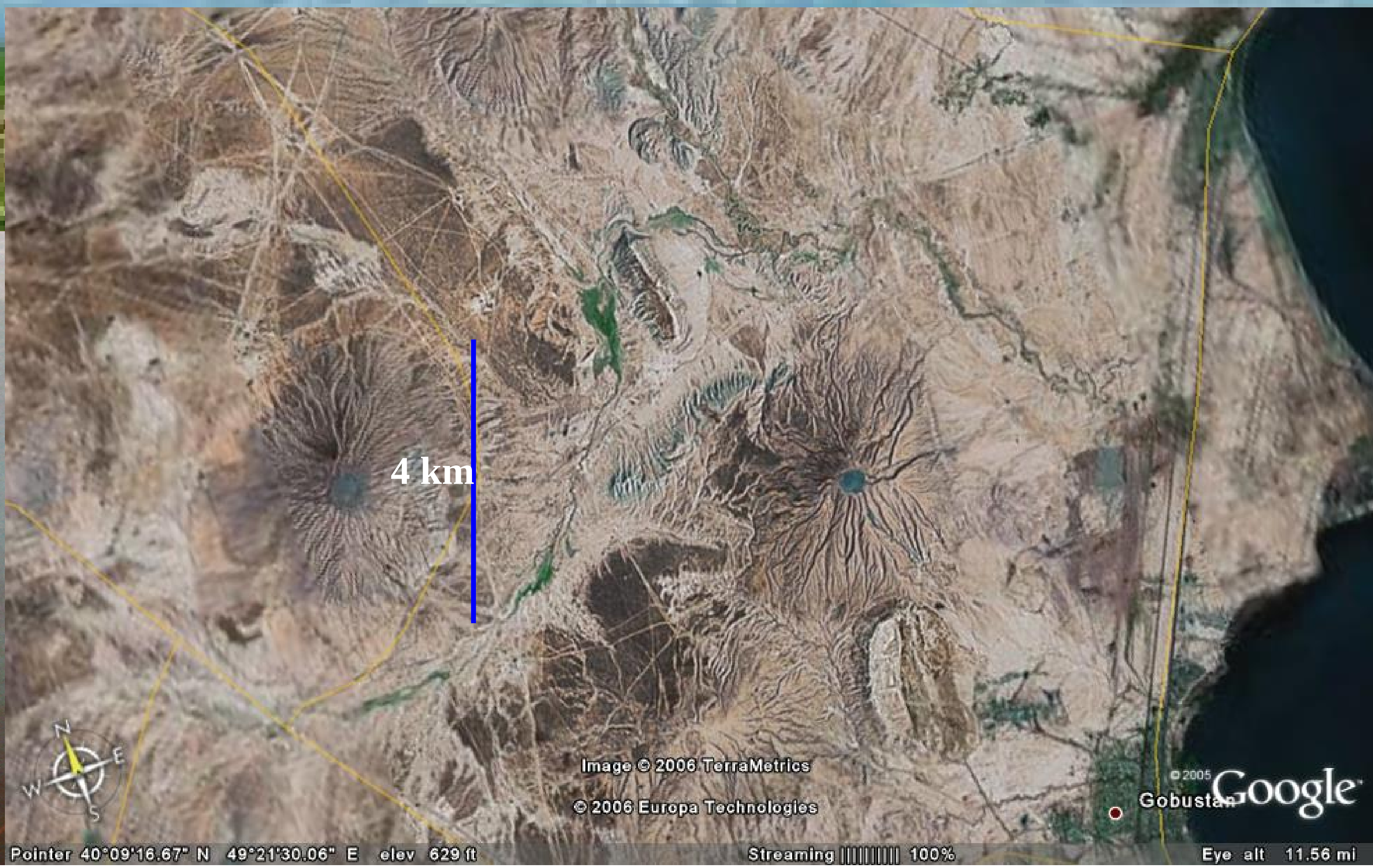



Large-size mud volcanoes
Maccalube
(Sicily, Italy)
200m


Large-size mud volcanoes
Paclele Berca
(Romania)
>2 km

Giant mud volcanoes

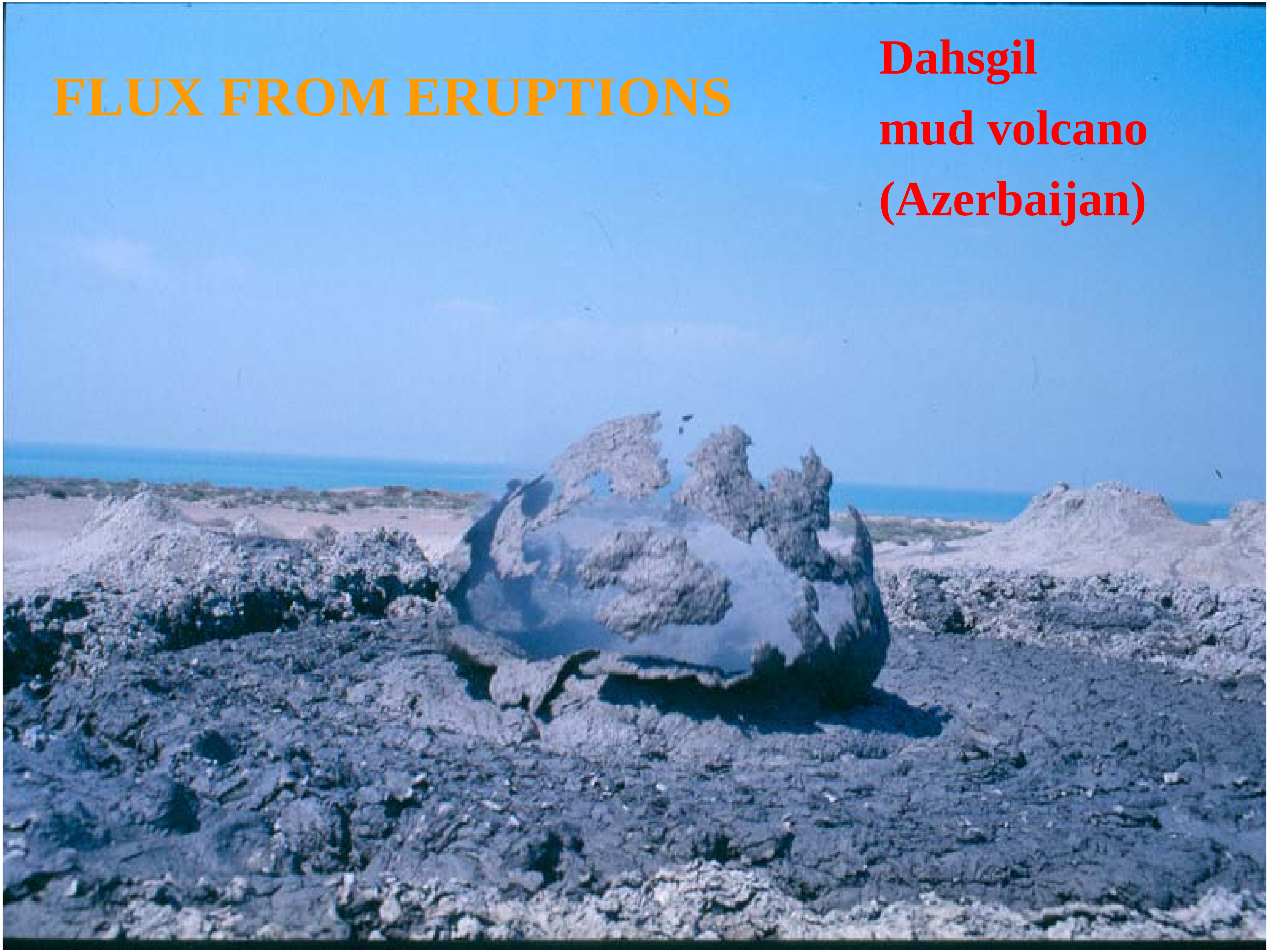
Azerbaijan

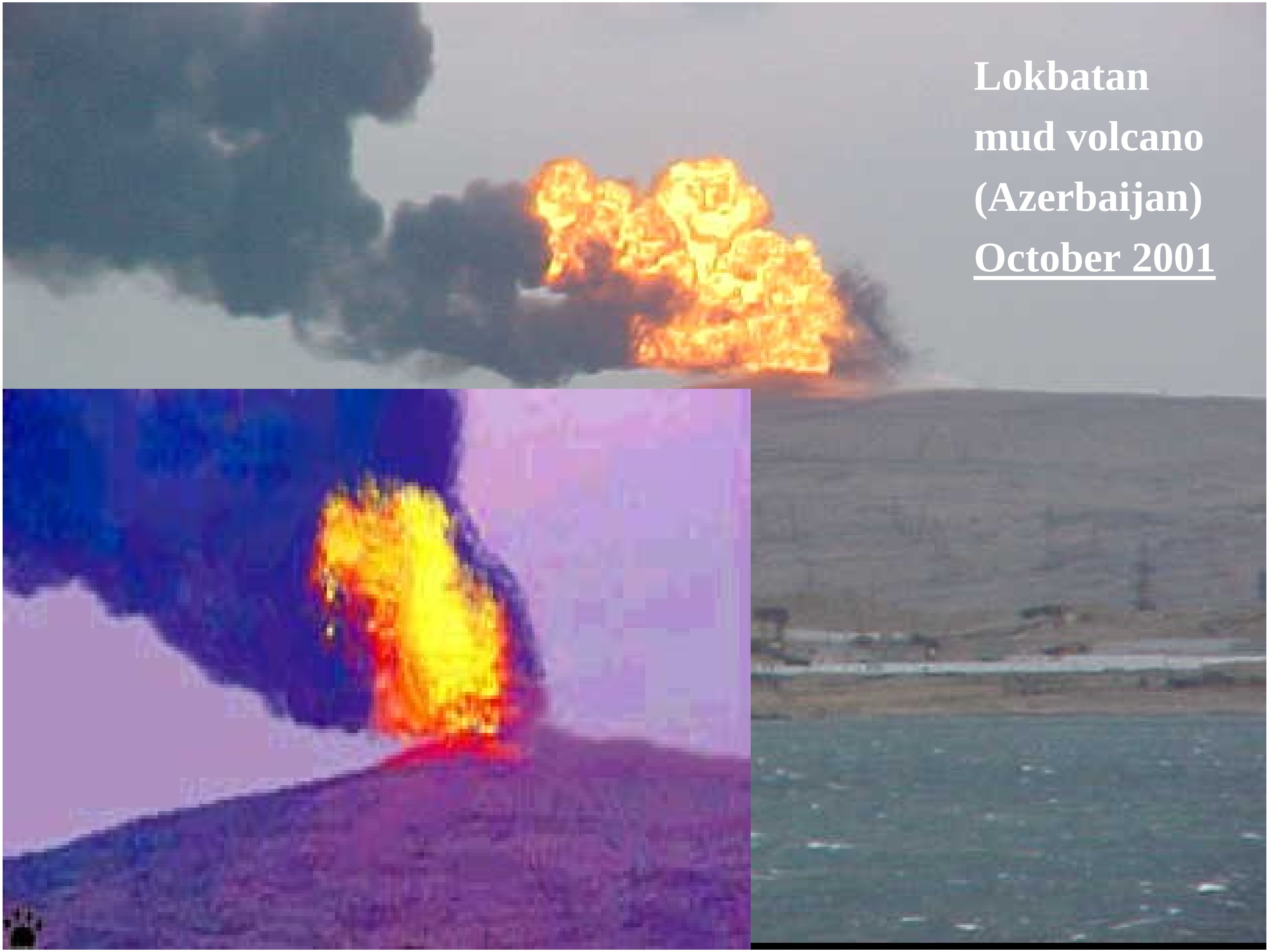


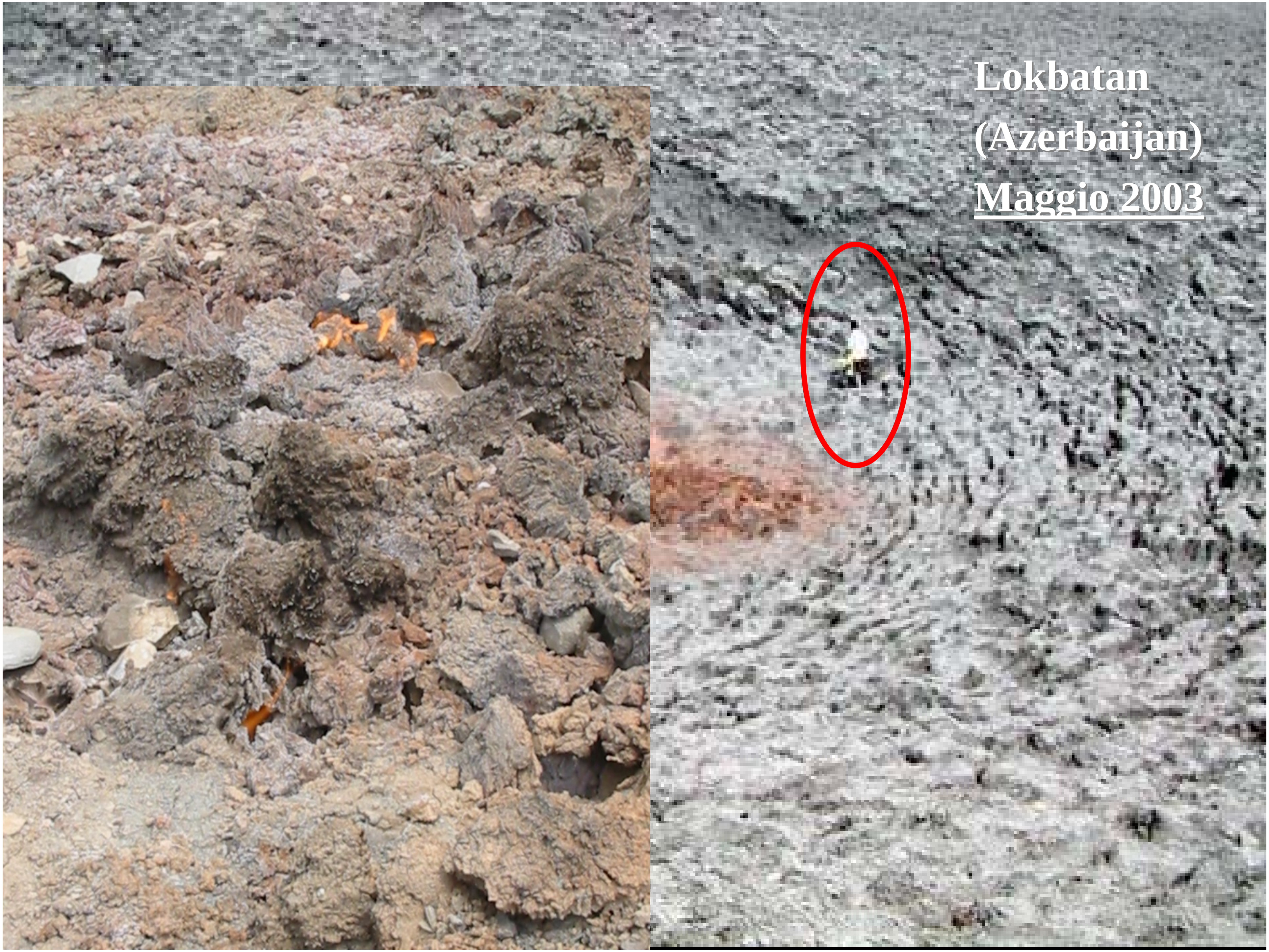
Taiwan

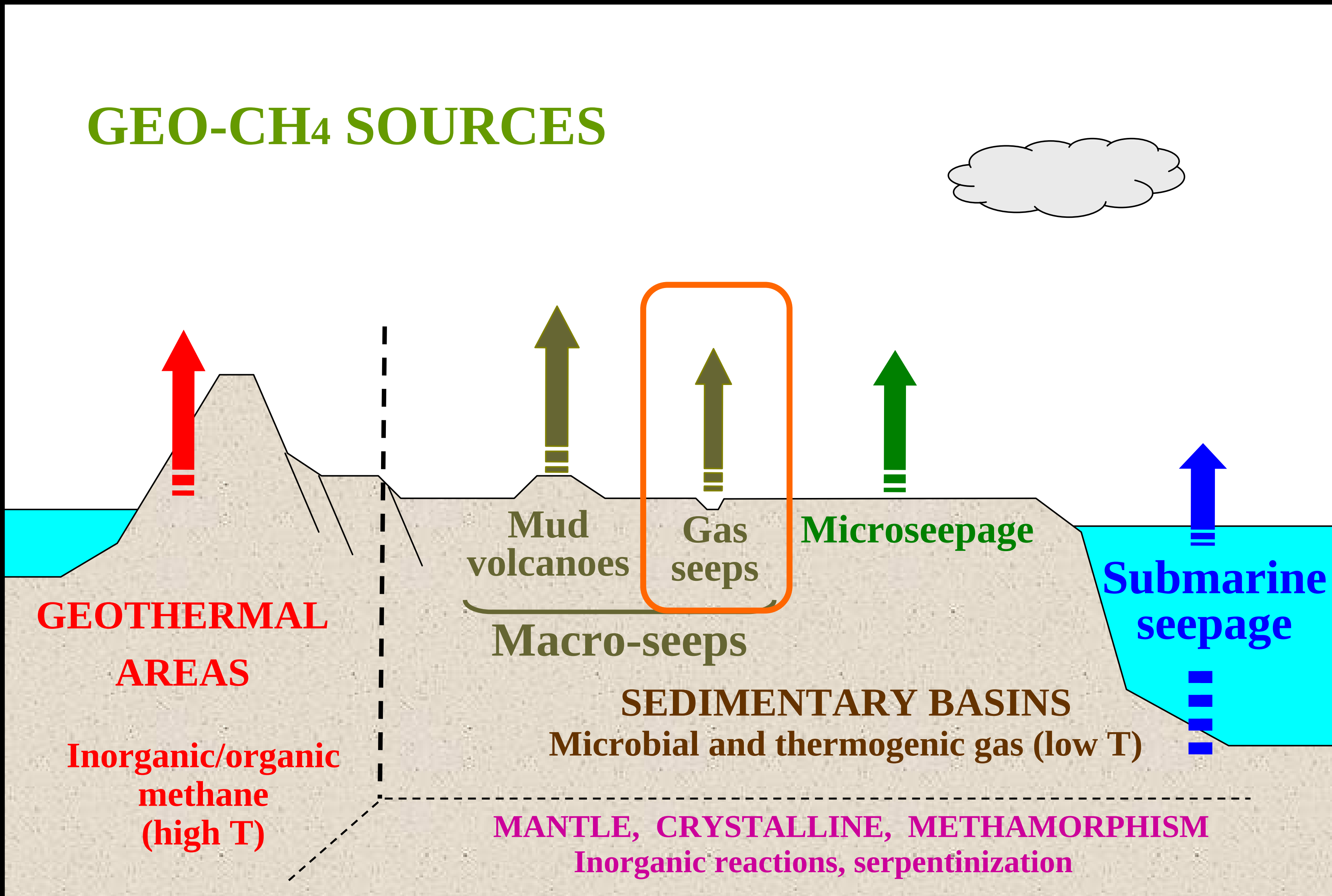
FLUX FROM VENTS
(macroseepage)


FLUX FROM ERUPTIONS
Dahsgil
mud volcano
(Azerbaijan)


FLUX FROM ERUPTIONS
Dahsgil
mud volcano
(Azerbaijan)


Lokbatan
mud volcano
(Azerbaijan)
October 2001

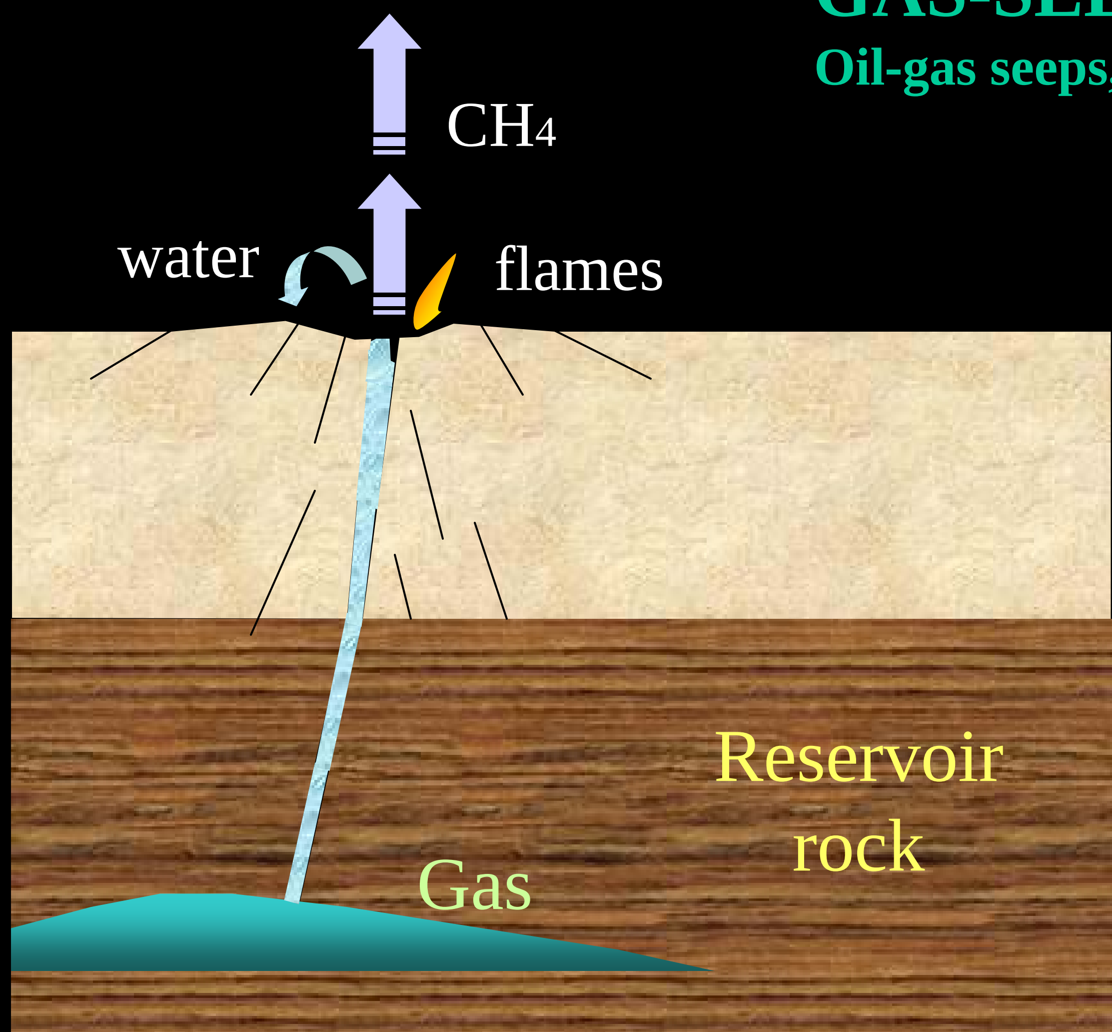

Lokbatan
(Azerbaijan)
Maggio 2003


GEO-CH4 SOURCES
Mud volcanoes
Gas seeps
Microseepage
Submarine seepage
Macro-seeps
GEOTHERMAL AREAS
Inorganic/organic methane (high T)
SEDIMENTARY BASINS
Microbial and thermogenic gas (low T)
MANTLE, CRYSTALLINE, METHAMORPHISM
Inorganic reactions, serpentinization

MACRO-SEEPS

GAS-SEEPS

Oil-gas seeps, fires, springs



Gas release to the atmosphere

Gas migration along faults

Pressurised gas from hydrocarbon reservoir

>13000 seeps on the continents

(Clarke abd Cleverly, 1991; Fugro- Robertson database)

MACRO-SEEPS
GAS-SEEPS
Bubbling water, fires

Italy

MACRO-SEEPS

GAS-SEEPS

Bubbling pools, fires

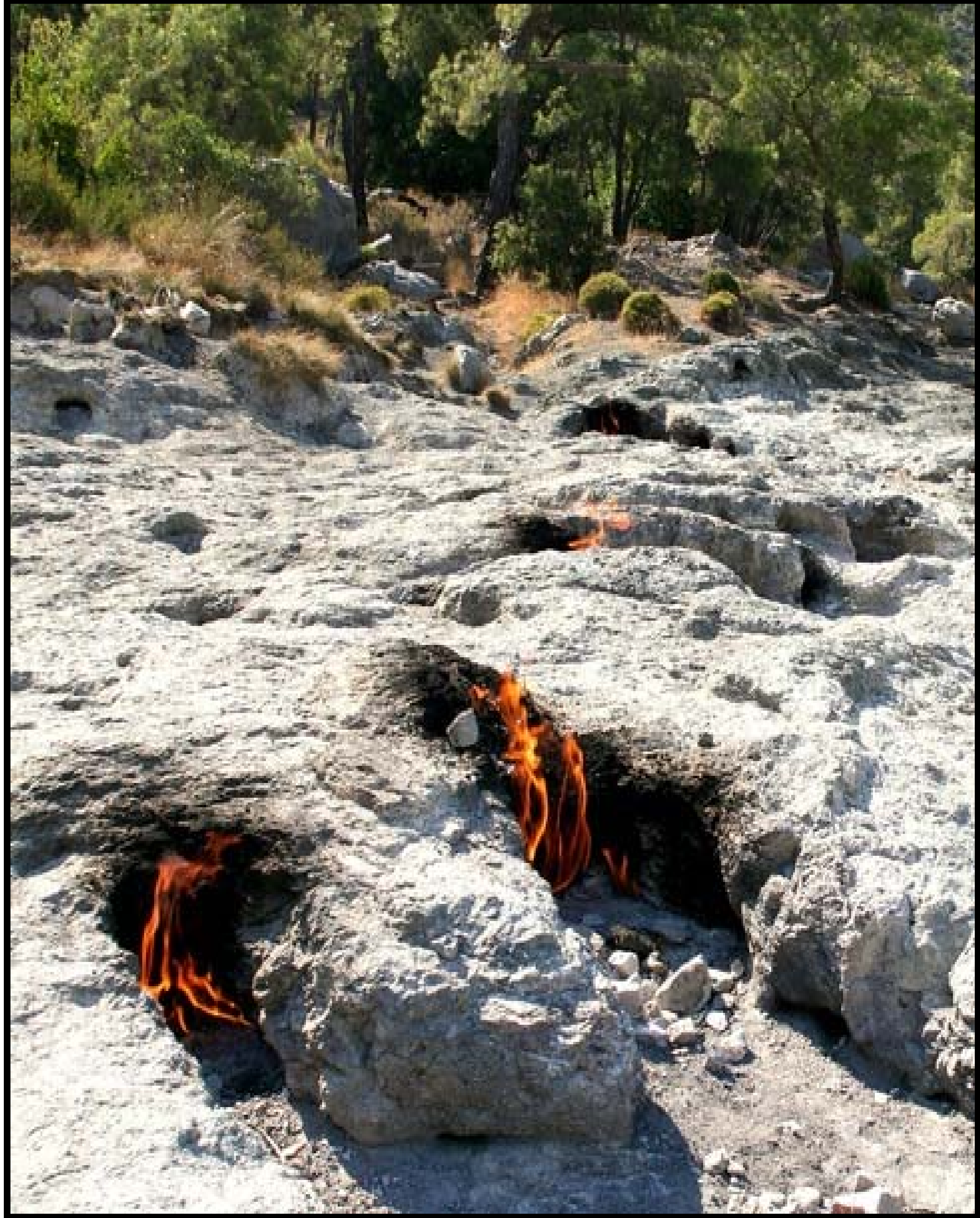
Romania

MACRO-SEEPS

GAS-SEEPS

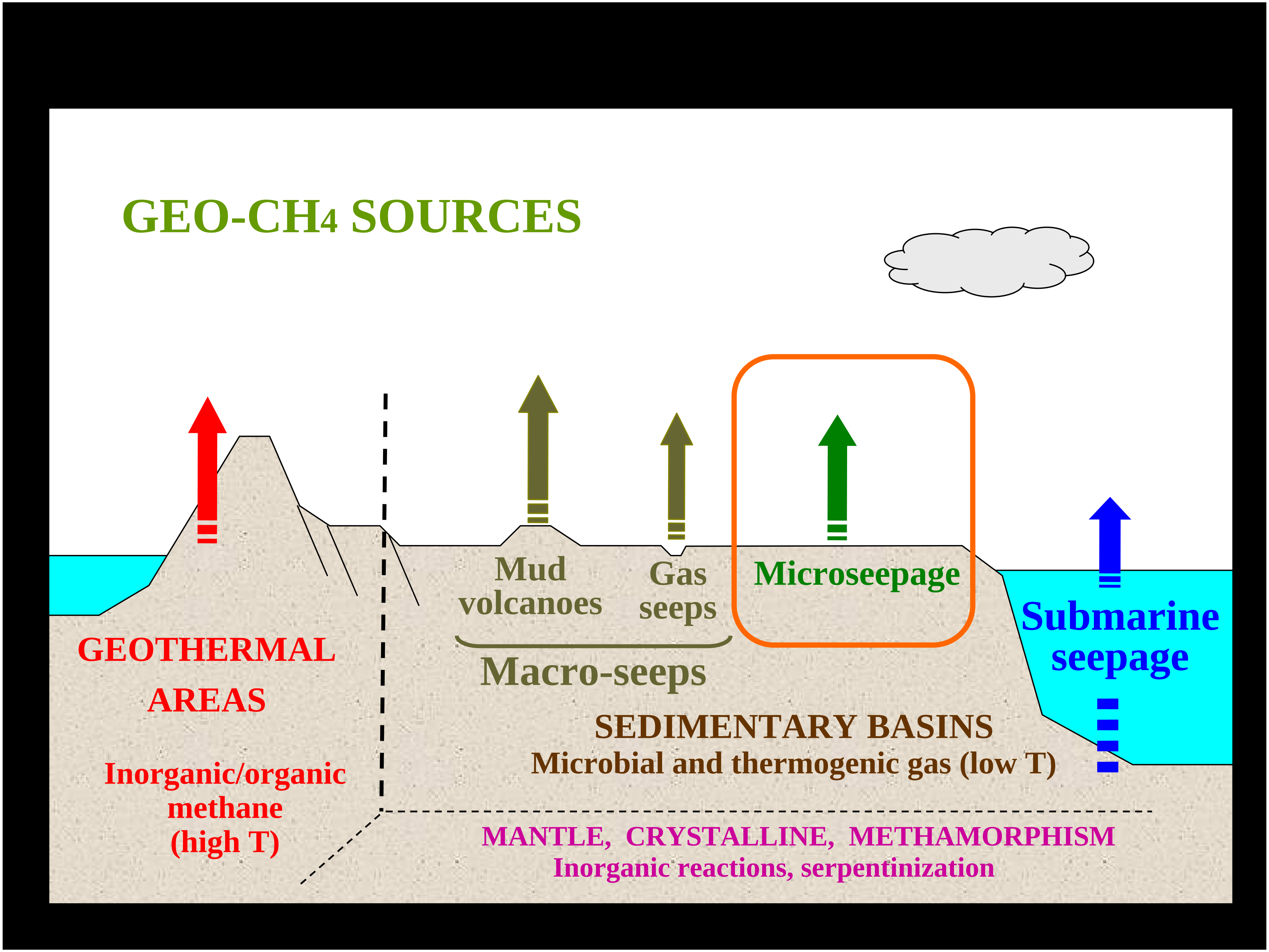
Everlasting fires

Turkey




Iraq
MACRO-SEEPS
GAS-SEEPS
Everlasting fire


MACRO-SEEPS
GAS-SEEPS
Everlasting fires
Azerbaijan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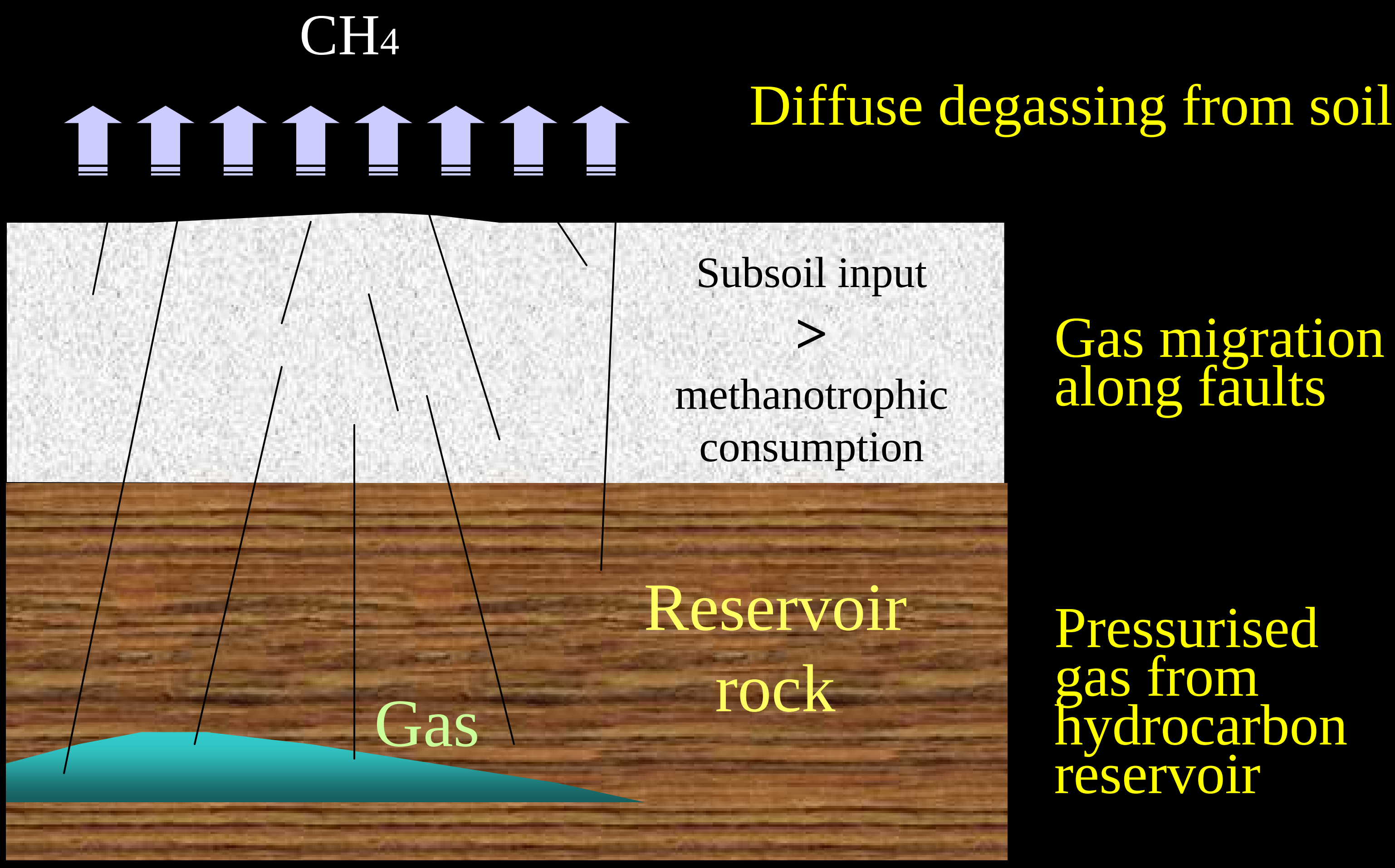
MICROSEEPAGE

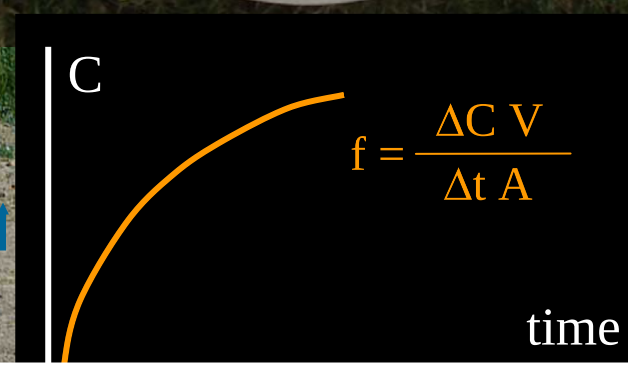


DRY SOIL IS NOT ALWAYS A CH_4 SINK!

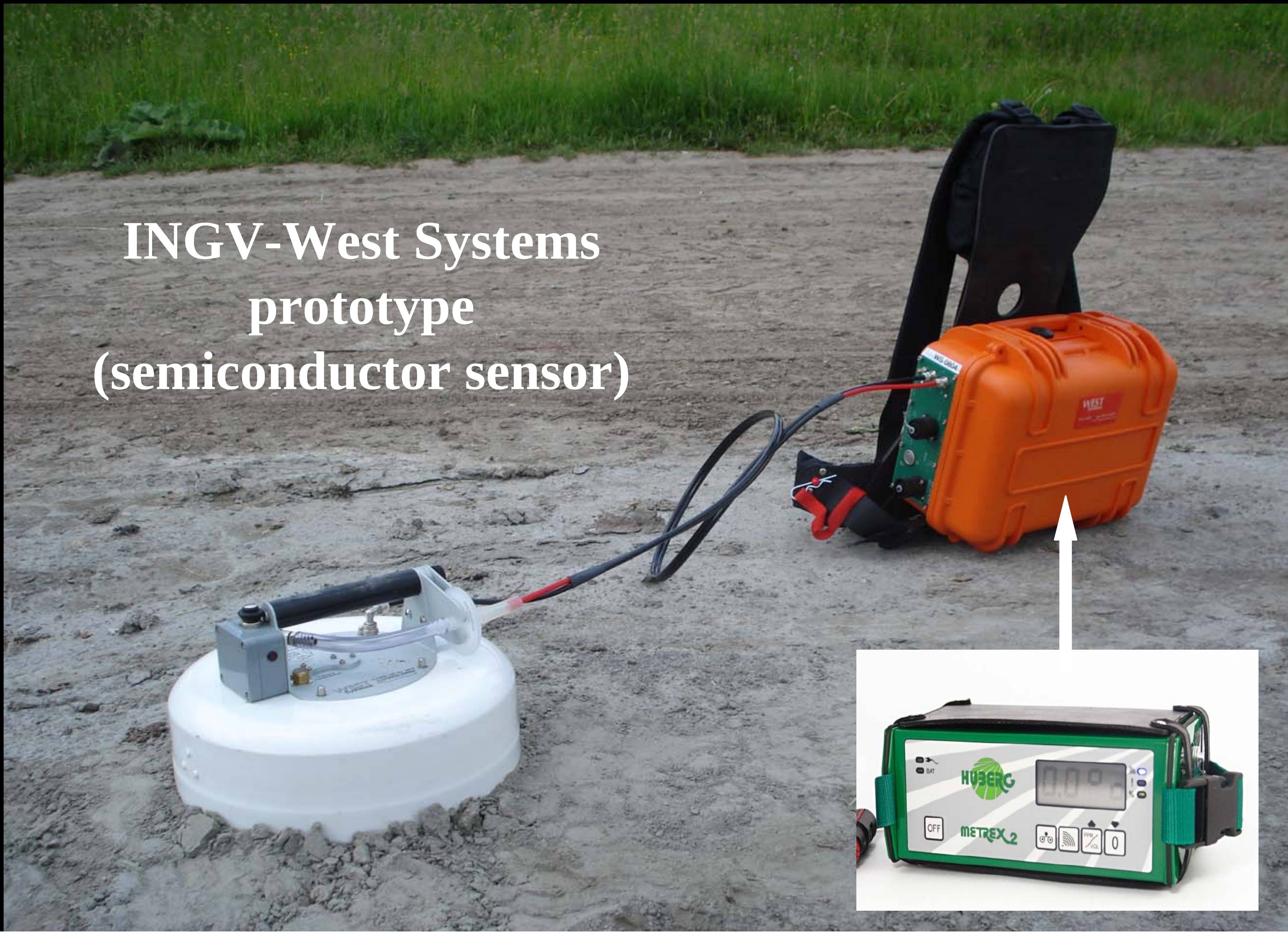
Microseepage in hydrocarbon basins

Positive fluxes of methane
(>1 mg m^{-2} d^{-1})

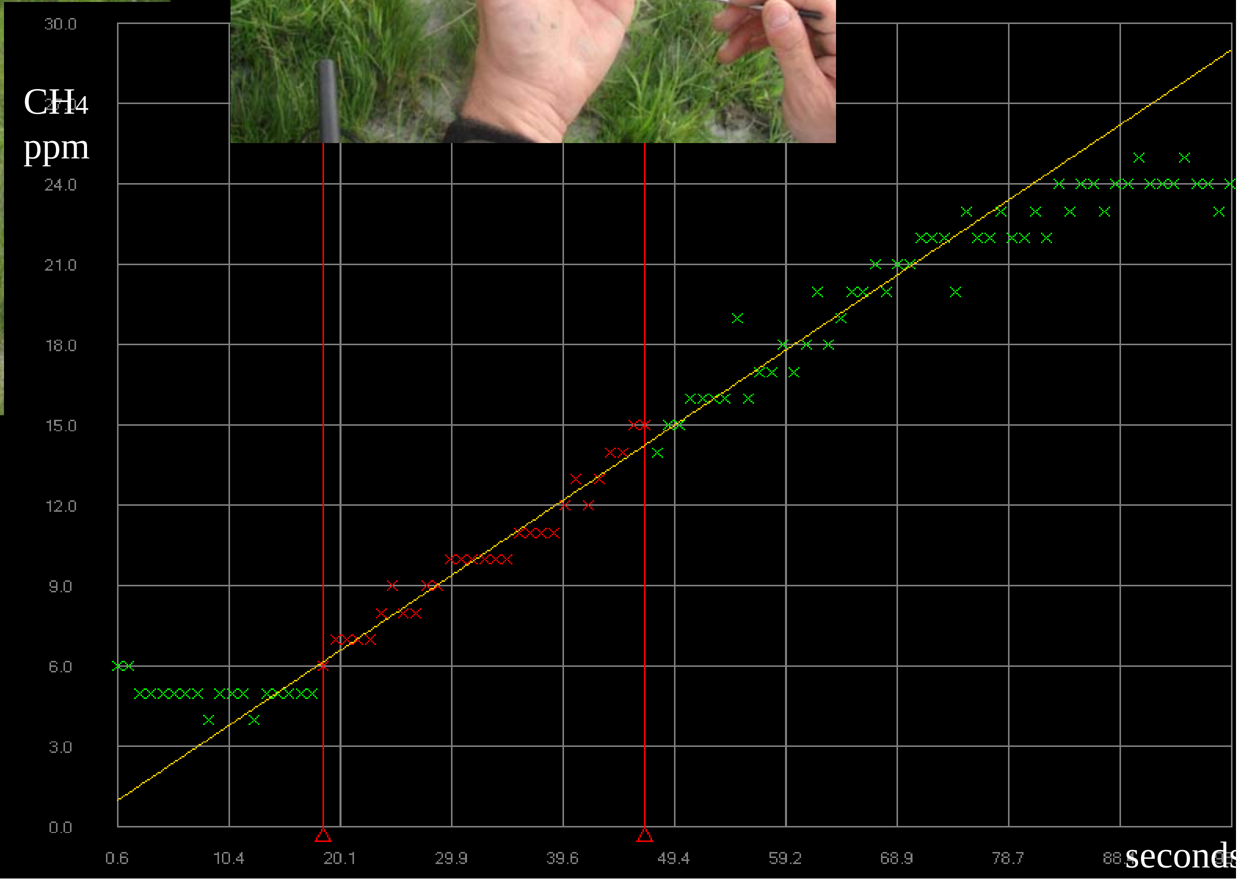
Closed chamber



Microseepage in hydrocarbon basins

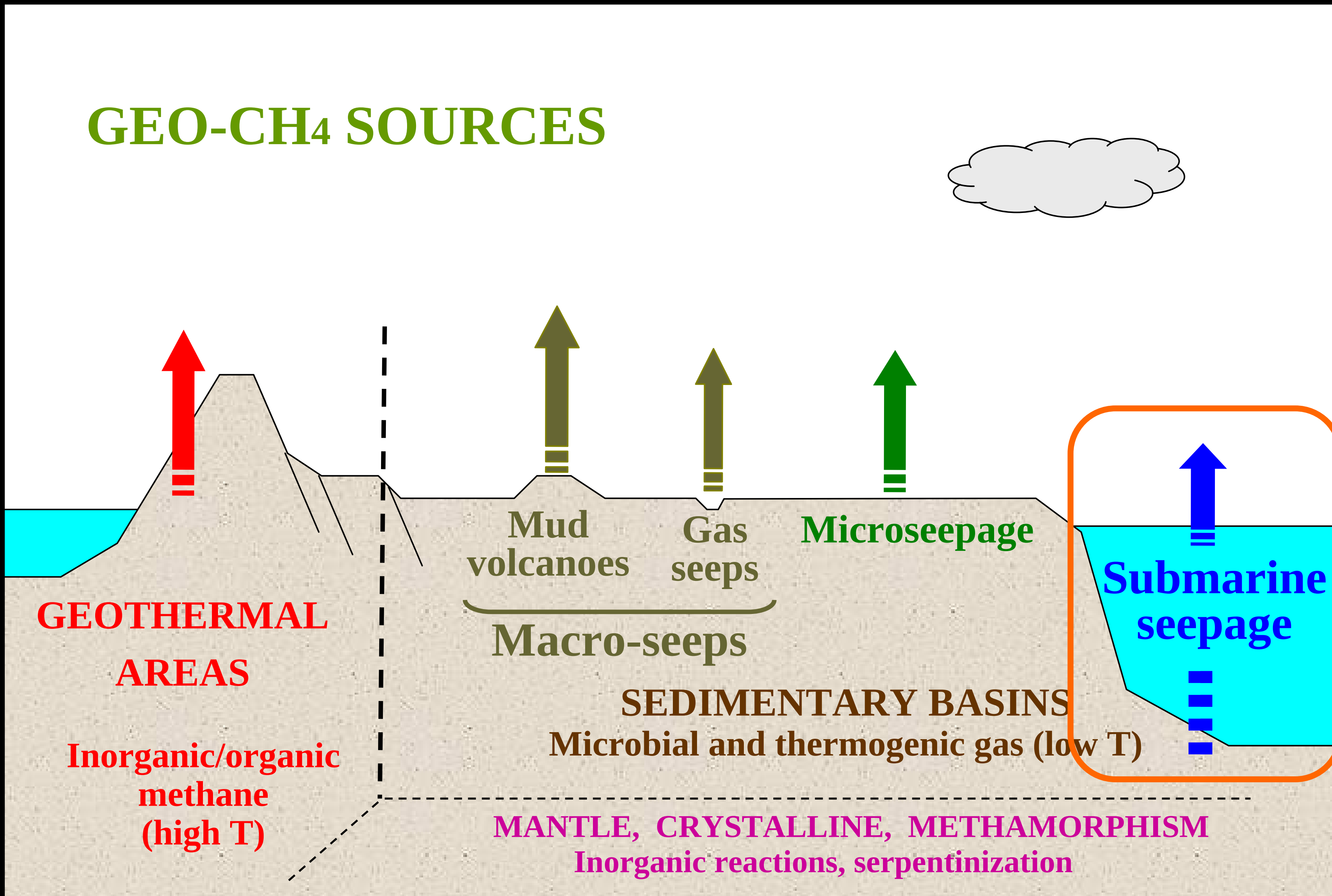


Microseepage in hydrocarbon basins



Immediate, online measurements of CH_4 flux from soil

Microseepage in hydrocarbon basins



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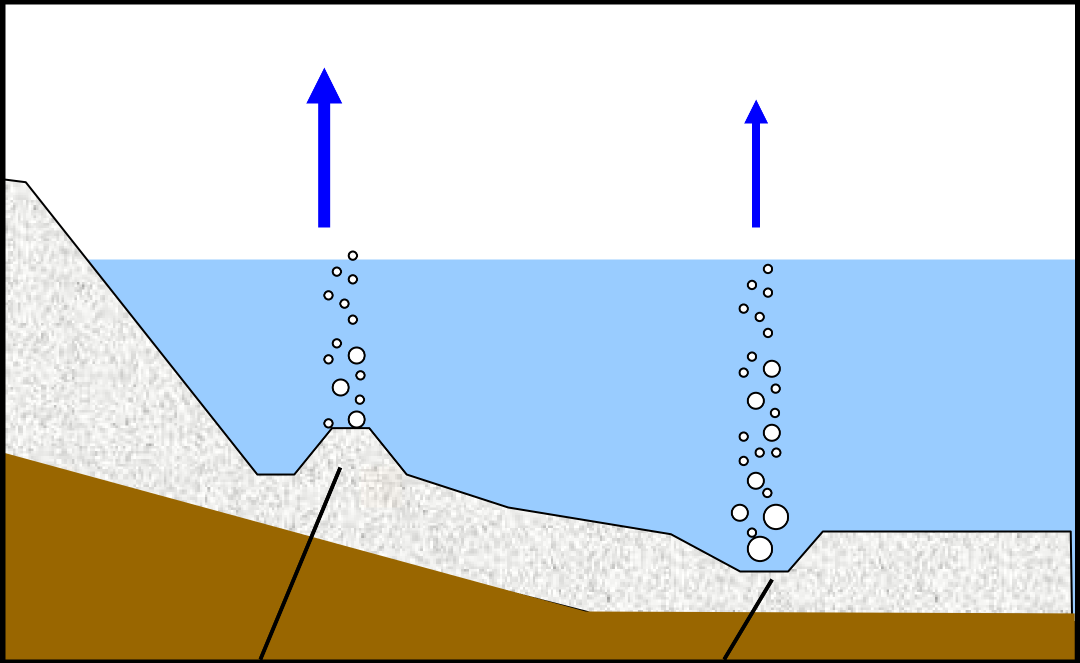
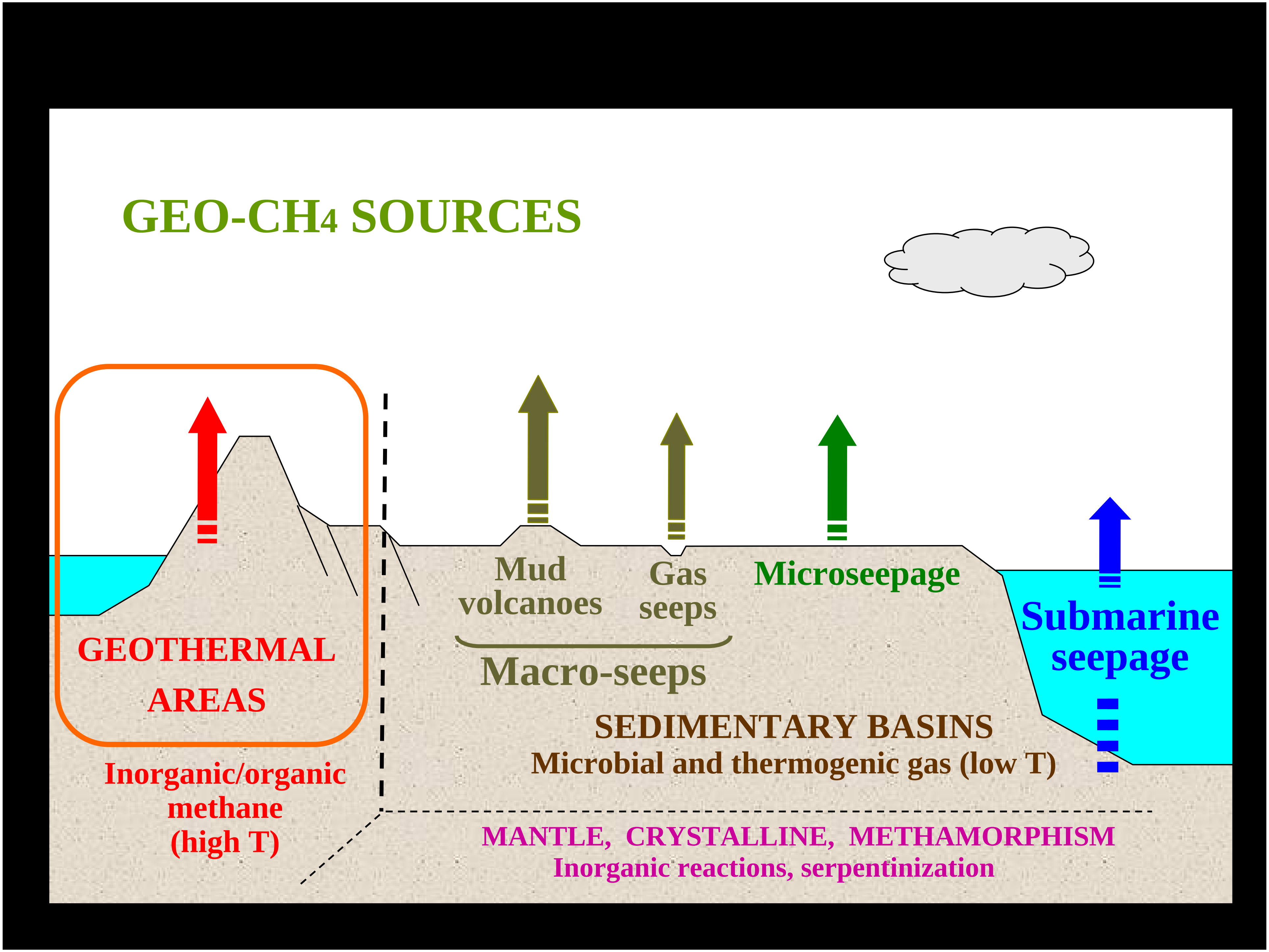
MARINE SEEPS

Bubble plumes
(reaching the atmosphere from seafloor < 200-300 m deep)

Cold seeps, mounds, pockmarks…

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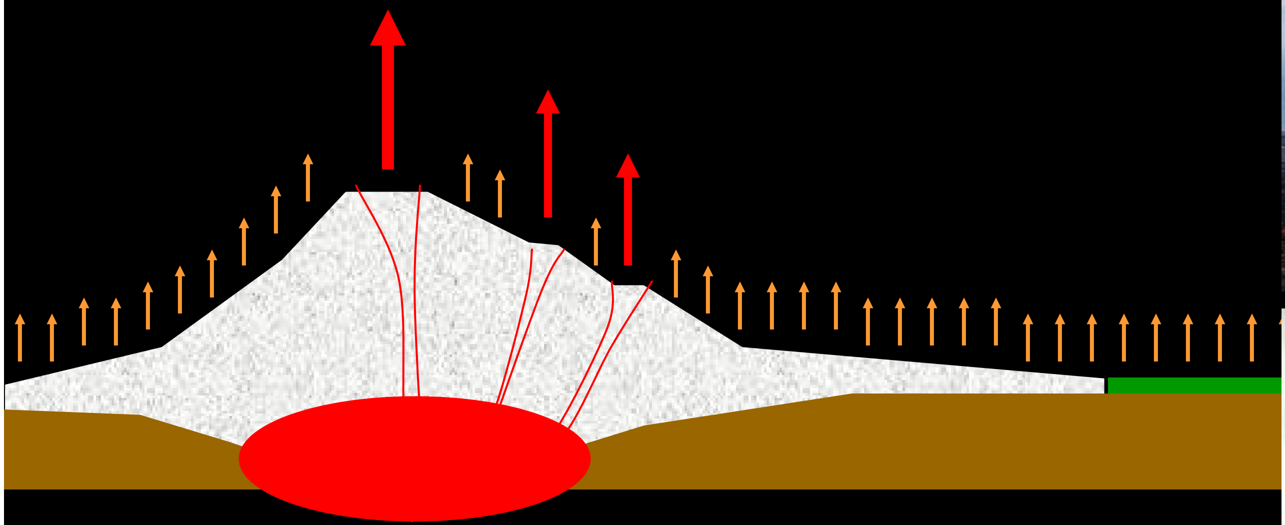
VOLCANIC & GEOTHERMAL METHANE

CO_2: 90-99%v
CH_4: 0.01-2%v

$CO_2 + 4H_2 = CH_4 + 2H_2O$

+ thermogenic (organic matter breakdown)

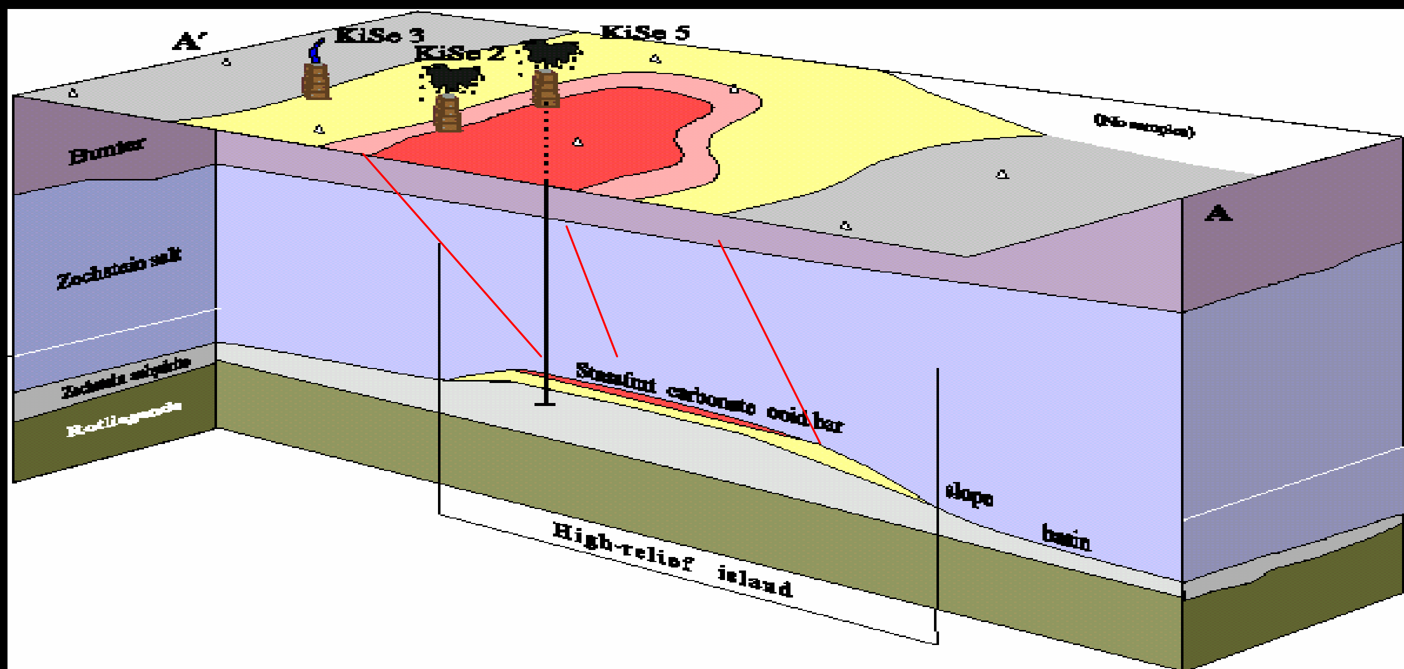
Magmatic, hydrothermal CO_2-rich vents (fumaroles, mofettes) and soil degassing



SEEPAGE AND MICROSEEPAGE

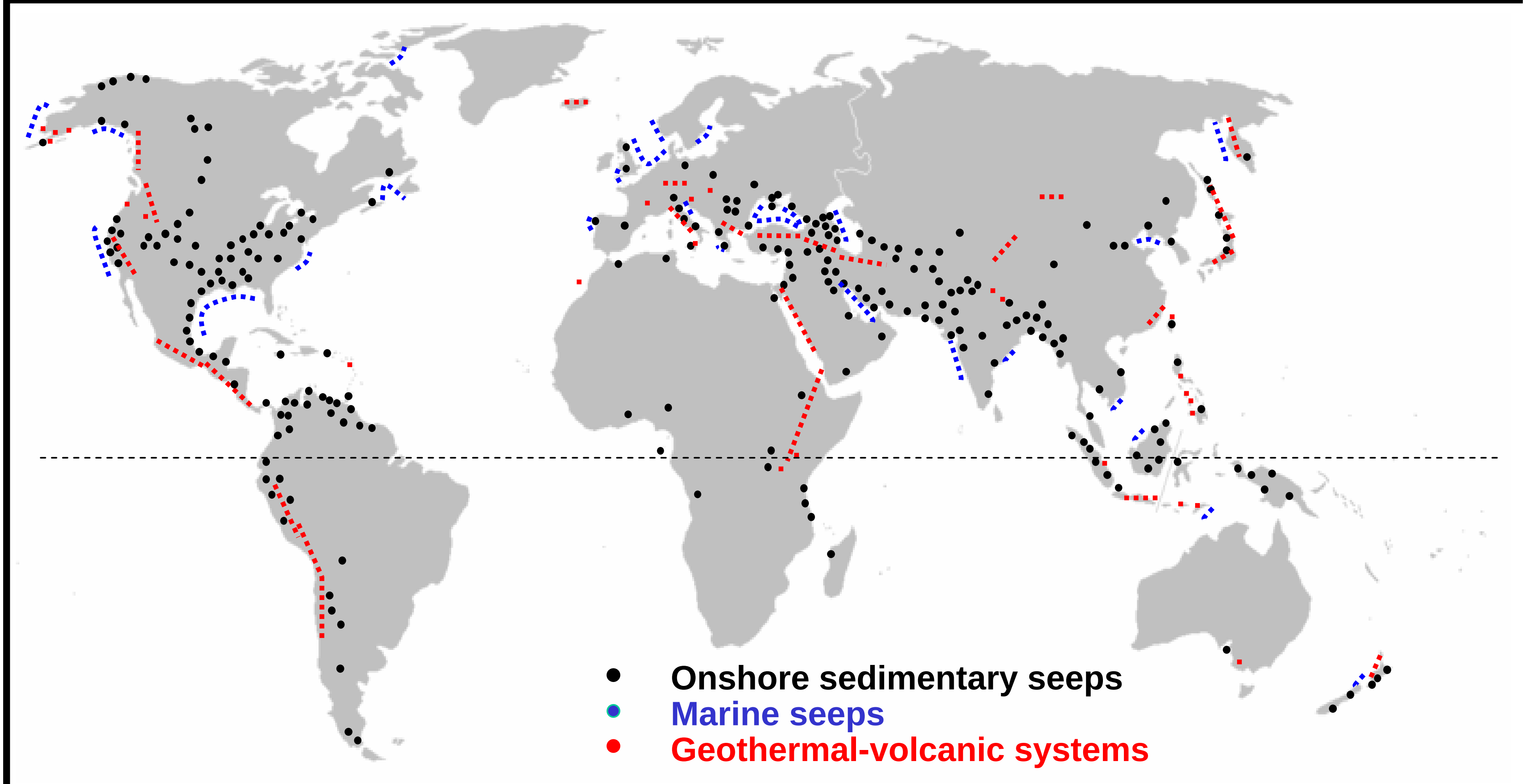
widespread and detectable in correspondence with any gas-oil field

(or Total Petroleum System)



Many petroleum fields discovered thanks to HC seepage

Global distribution of all geo-CH_4 emission zones



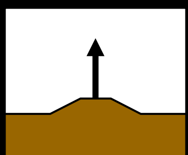
Gas-oil fields: 112 countries (out of 182)

>900 onshore MV and >13000 oil-gas seeps in > 80 countries

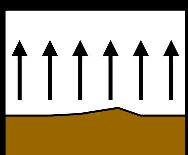
Potentail global microseepage area: ~ 4-8 M km^2

2. Gas fluxes: emission factors and global emission

Emission factor = specific flux



Point sources (vents): **ton/year**

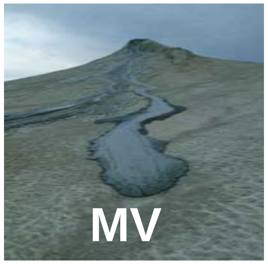


Area sources (with microseepage): **$t\ km^{-2}\ y^{-1}$**

$mg\ m^{-2}\ d^{-1}$

A LARGE FLUX DATABASE – Emission factors are today well known

Hundreds of flux data from USA, EUROPE, AZERBAIJAN, CHINA, TAIWAN



Gas flux from vents & ground is similar in all MV surveyed

Typical EF (including microseepage around vents): **10^2 - 10^3** t km^{-2} y^{-1}

Single vents or craters of small MV (1-5 m high) **10^0-10^1** t/y

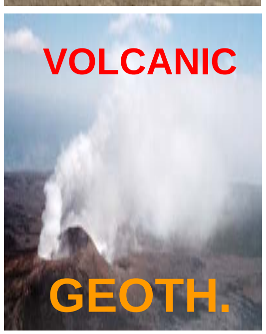
A whole MV (with tens or hundreds of vents) **10^2** t/y

Eruptions of big MV **10^3** t in a few hours

Individual gas seeps (natural fires, bubbling pools) **10^0 to 10^3** t/y.

Typically **10^1-10^2** mg m^{-2} d^{-1} (similar to wetlands),

Around macro-seeps **10^3–10^5** mg $m^{-2}d^{-1}$,



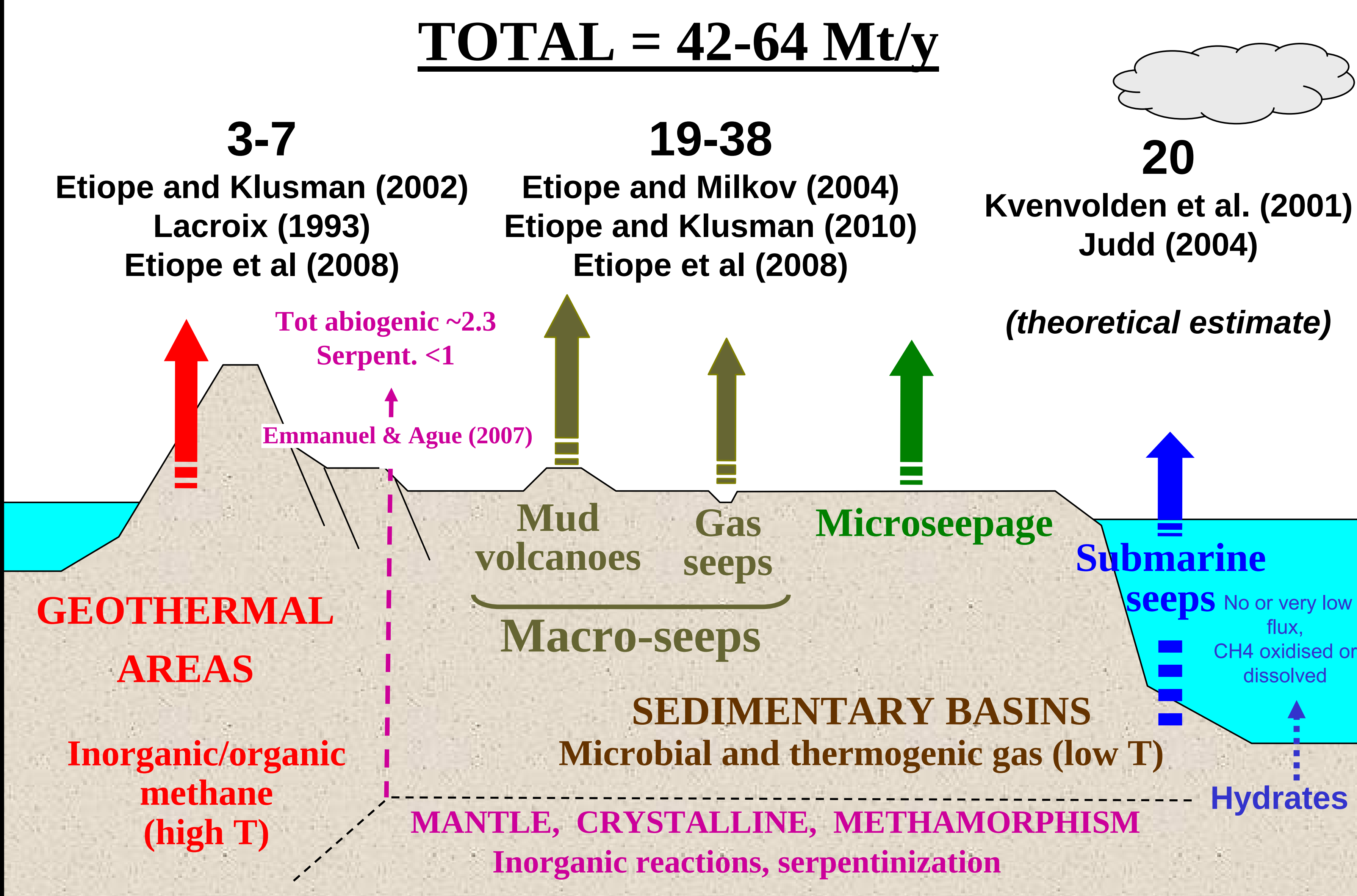
Volcanoes are not important CH_4 contributors

(CH_4 concentration 0.0001 - 0.1%) **<10^0-10^1** t/y by volcano

Geothermal manifestations are more important,

up to **10^2** t/y for individual vents

GEO-CH4 EMISSION ESTIMATES

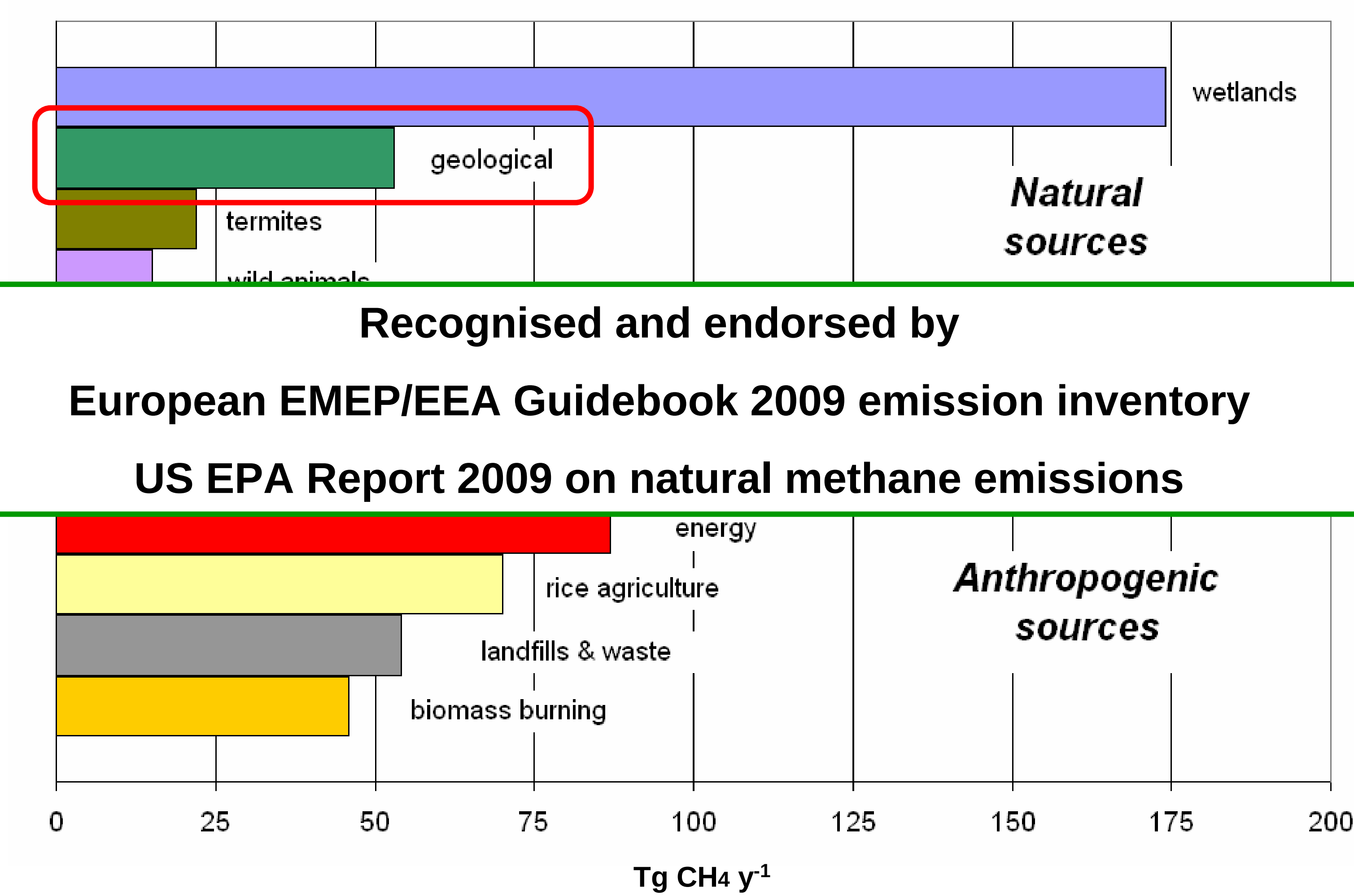


A revised CH_4 source inventory

with Geo-CH_4 emission: 42-64 Mt/y

2nd natural CH_4 source

9% of total CH_4 source

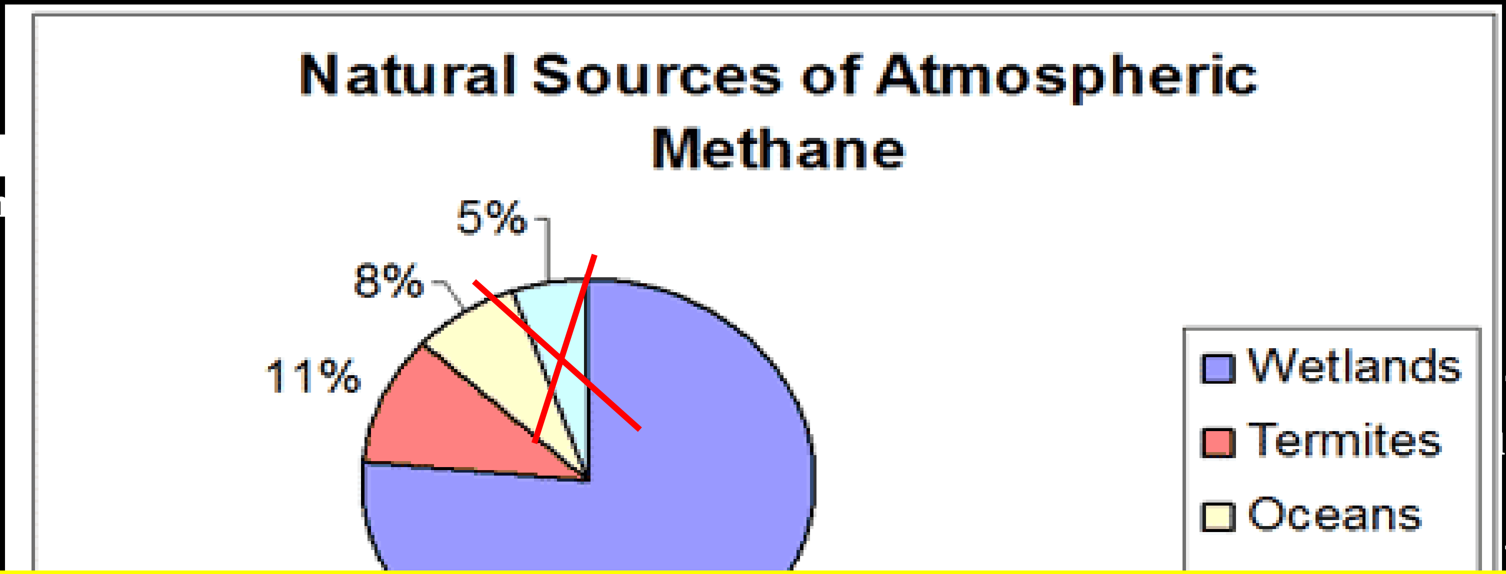


Recognised and endorsed by

European EMEP/EEA Guidebook 2009 emission inventory

US EPA Report 2009 on natural methane emissions

GAS-HYDRATES MISQUOTATION and SPECULATION



Hydrates may be important on Mars,

but today they are not a source for Earth's atmosphere

5

Kvenvolden (1991) 3-4

No experimental data

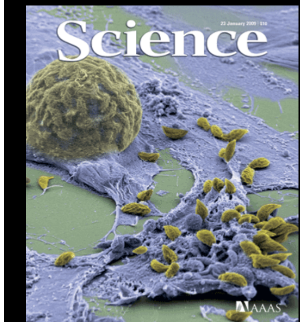
Sedimentary gas seepage
CH_4 rich (>80 %)

volcanic-geothermal exhalations
CO_2 dominant (>90 %)

both have ethane (C_2H_6) and propane (C_3H_8)

10^2 -10^3 ppmv in petroleum gas
(often > 1% in deep gas and oil seeps)

ppbv and ppmv levels



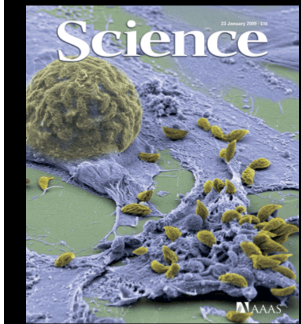
23 JANUARY 2009 VOL 323 SCIENCE www.sciencemag.org

Earth's Degassing: A Missing Ethane and Propane Source

Giuseppe Etiope[1]* and Paolo Ciccioli[2]

Analysis of a robust data set of C_1, C_2, C_3 from 238 sites coupled with published estimates of geo-CH_4 emissions
(9 petroleum basins, > 4000 soil-gas samples)

	Global CH_4 emission	Median C_2/C_1	Ethane emission	Median C_3/C_1	Propane emission
Mud volcanoes	6-9	0.0007	0.008-0.012	0.00008	0.001-0.002
Onshore seeps	3-4	0.018	0.10-0.14	0.009	0.074-0.1
Microseepage	10-25	0.068	1.28-3.21	0.031	0.85-2.13
Marine seeps	20	0.012	0.45	0.0017	0.09
Geothermal	2.5-6.3	0.013	0.06-0.15	0.0013	0.009-0.022
Volcanic	<1	0.022	<0.041	0.010	<0.027
Total geologic	**42 – 64**		**~ 2 – 4**		**1 - 2.4**
Biogenic			0.80		1.63
Oceans			0.78		1.06
Anthropogenic			5.70		6.51
Forest-savanna burning			2.29		0.41
Total POET			**9.57**		**9.61**



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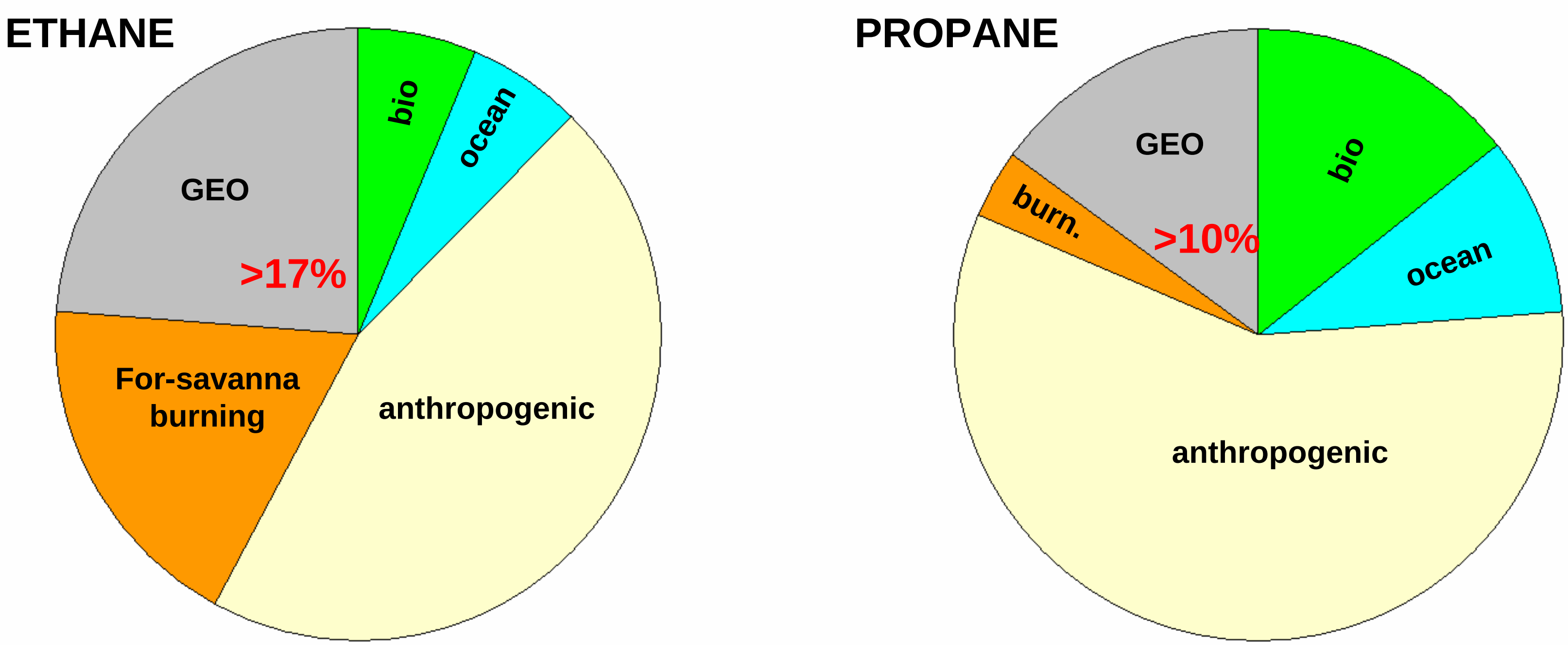
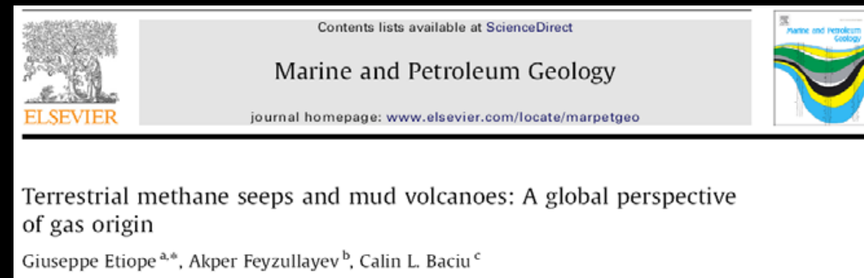


Earth's degassing accounts for > 17% and 10% of total C_2 and C_3 emissions

3. Gas origin

Global analysis of onshore seeping $\delta^{13}C_1$, δD, C_1/C_2+C_3


Contents lists available at ScienceDirect

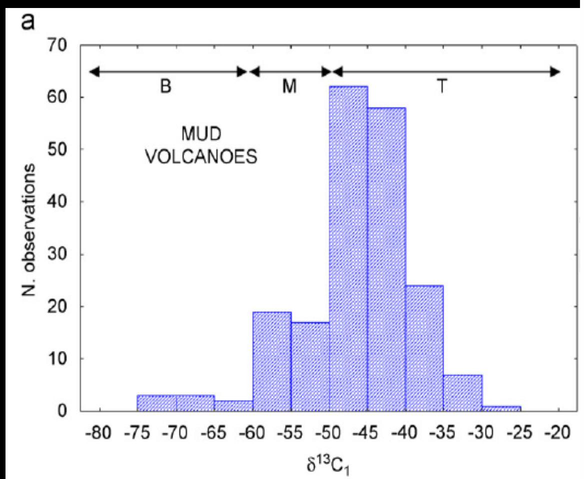
Marine and Petroleum Geology

journal homepage: www.elsevier.com/locate/marpetgeo

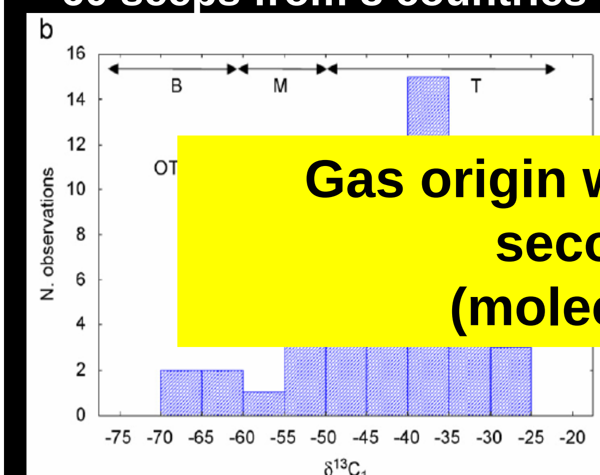
Terrestrial methane seeps and mud volcanoes: A global perspective of gas origin

Giuseppe Etiope [a,*], Akper Feyzullayev [b], Calin L. Baciu [c]

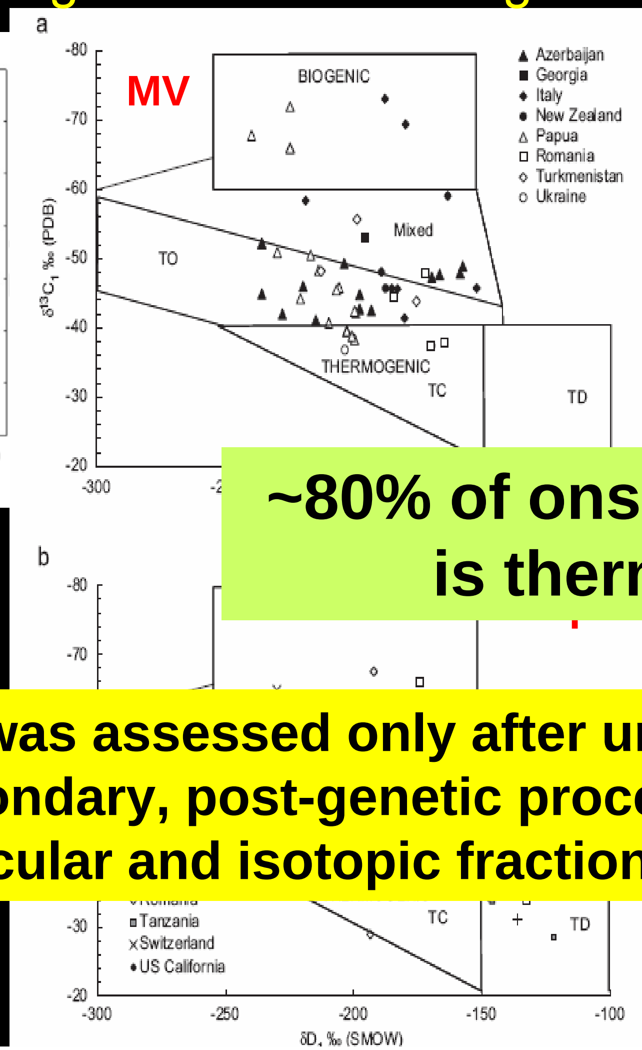
143 MV from 12 countries



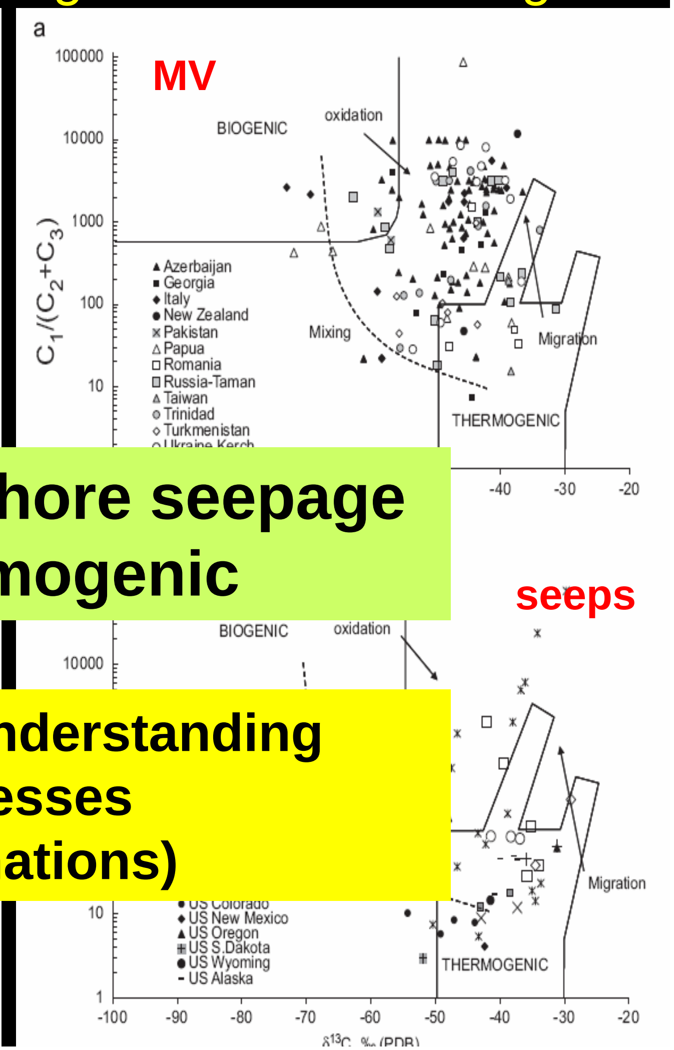
60 seeps from 8 countries



global "Schoell" diagram



global "Bernard" diagram



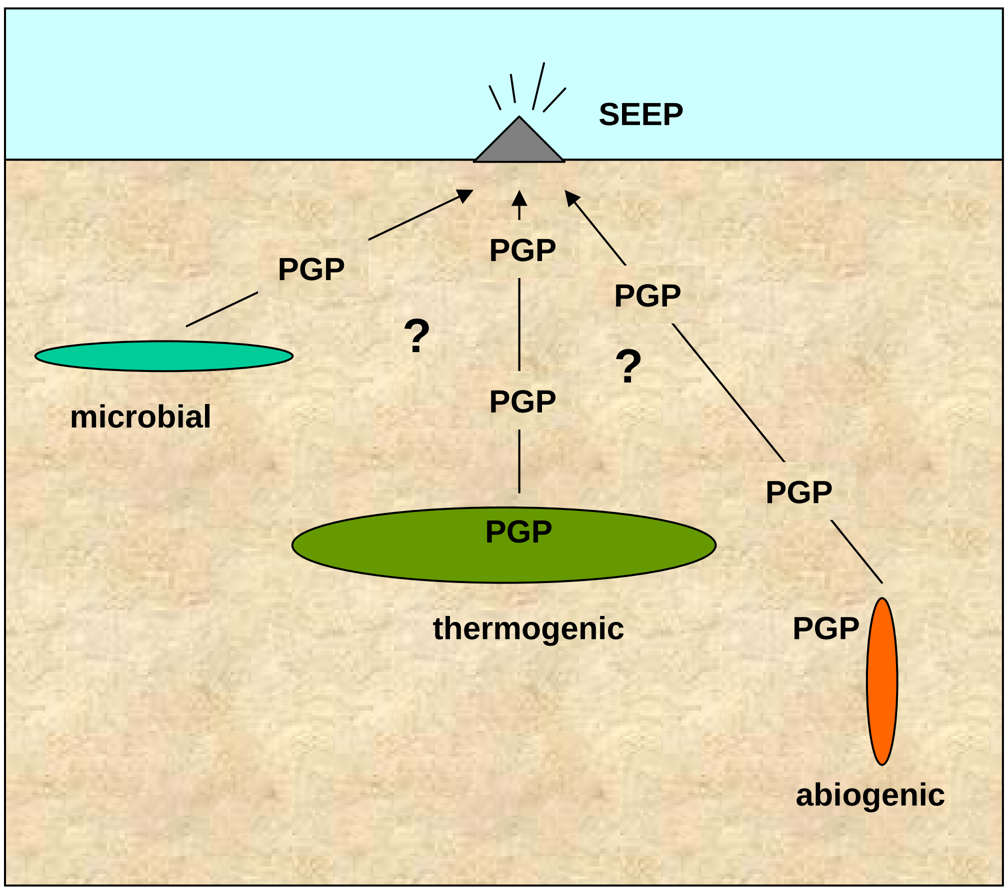
~80% of onshore seepage is thermogenic

Gas origin was assessed only after understanding secondary, post-genetic processes (molecular and isotopic fractionations)

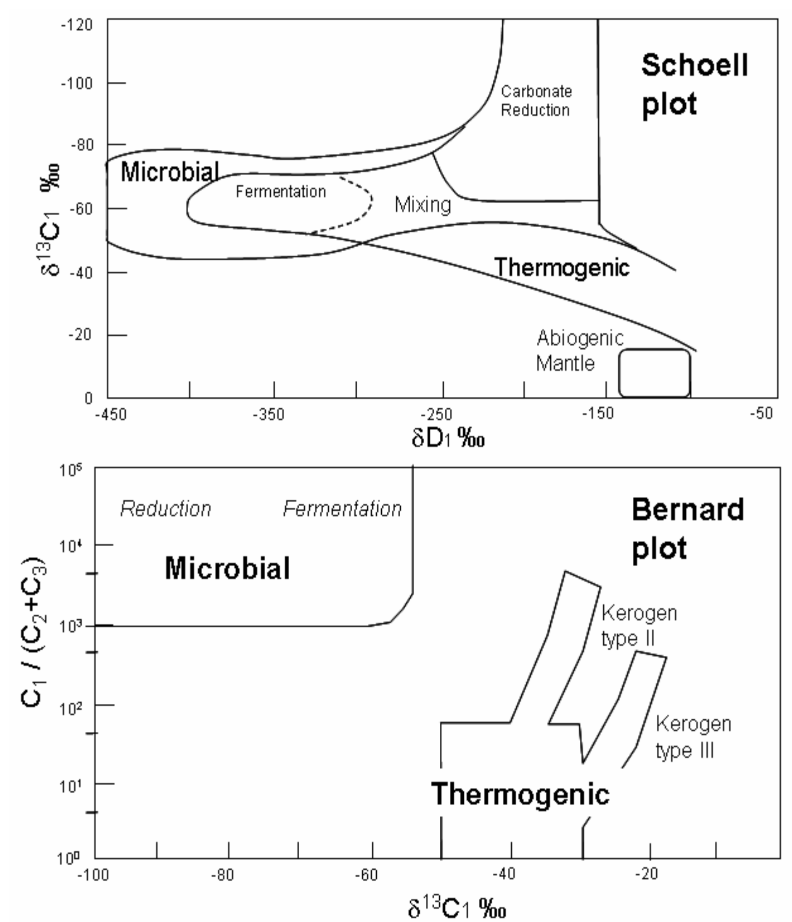
ASSESSING GAS ORIGIN

Schoell and Bernard plots (genetic zonation)

Recognition of Post-Genetic Processes (PGP)
PGP = *modification of genetic features*



GENETIC ZONATION PLOTS



SEVEN PGP AFFECTING GAS HC

1) aerobic microbial oxidation of methane

2) anaerobic microbial oxidation of methane

3) abiogenic oxidation

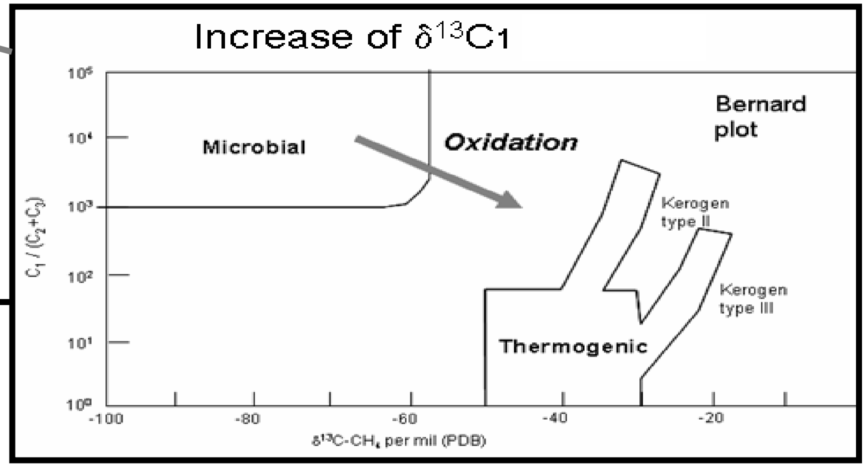
4) isotopic fractionation by diffusion

5) molecular fractionation by advection

6) gas mixing

7) anaerobic biodegradation of petroleum and secondary methanogenesis

1. Aerobic microbial oxidation (*Coleman et al. 1981; Schoell 1983; Whiticar, 1999*).



Recognizable by comparing MV vs reservoir gas
may occur in some MV but it is not significant,
generally leading to slight increases of $\delta^{13}C_1$ < 5 ‰.

2. Anaerobic microbial oxidation

Widely documented in submarine MV → methane consumption at seafloor (e.g. *Niemann et al., 2006*)
Poorly documented In terrestrial MV (with different results:
yes in Romania MV (*Alain et al., 2006*)
no in Taiwan MV (*Chu et al., 2007*).
Diffuse microseepage throughout the muddy cover (*Etiope et al., 2004; Hong and Yang, 2007*) suggests that C_1 consumption, if any, is not pervasive but local

3. Abiogenic oxidation

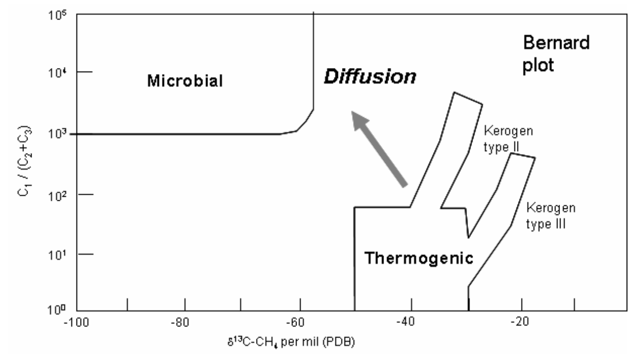
- thermochemical sulphate reduction (TSR)
- oxidation by ferric (Fe3+)-bearing minerals (hematite, magnetite; *Pan et al., 2006; Seewald, 2003*).
at relatively high temperatures (80°C - 400°C);

- in very deep reservoirs (and in high heat flow regions)
- TSR produces high H_2S concentrations (>1 %) and increased $\delta^{13}C$ values of C_1–C_5 hydrocarbons.
- not typical of MV systems (low T fluids, H_2S generally absent)

4. Isotopic fractionation by diffusion (Fick's law gas motion)

well known during primary migration (from source rock to res.) and secondary migration (between reservoirs).
- depletion of ^{13}C in diffusing CH_4
- ^{13}C enrichment in residual CH_4

not important in seeps (advection is dominant)
(*Deville et al., 2003; Etiope et al., 2007; Etiope et al., 2009*)



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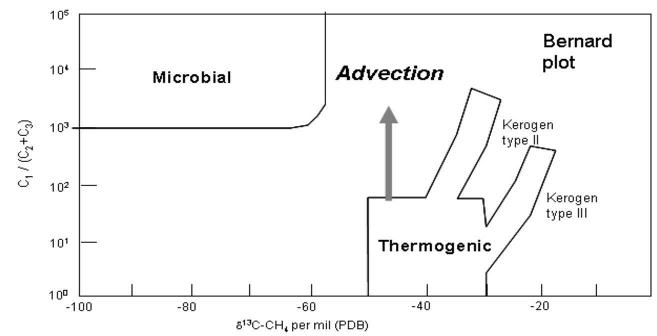
5. Molecular fractionation by advection (Darcy's law gas motion)

Distillation of light HC by adsorption and solubility properties

characteristic of many MV systems
not observed in high flow "dry" seeps
sometimes observed in low flow seeps (*Etiope et al., 2009*)



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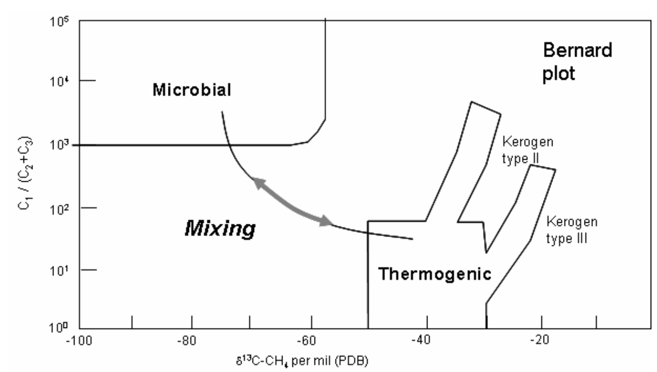
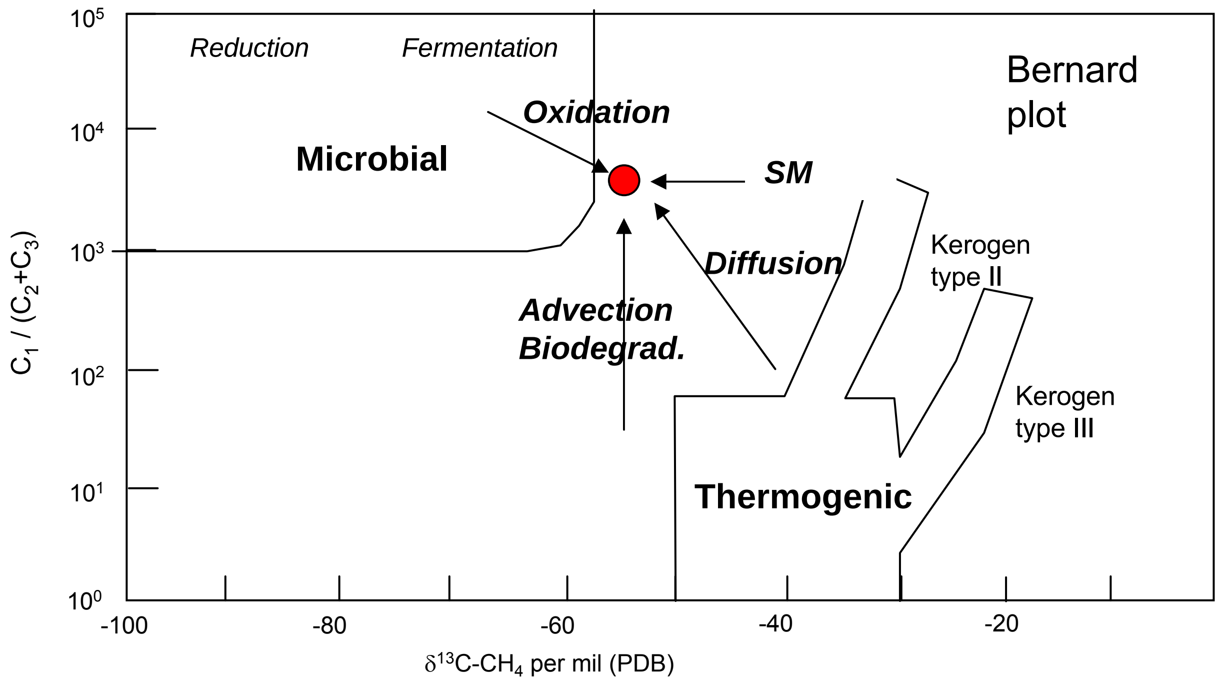
6. Gas mixing (thermogenic + microbial)

Observed in 20% of onshore MV (*Etiope et al., 2009*).
in reservoir or during the ascent of gas
Its recognition is not immediate: $\delta^{13}C_1$ alone can be misleading

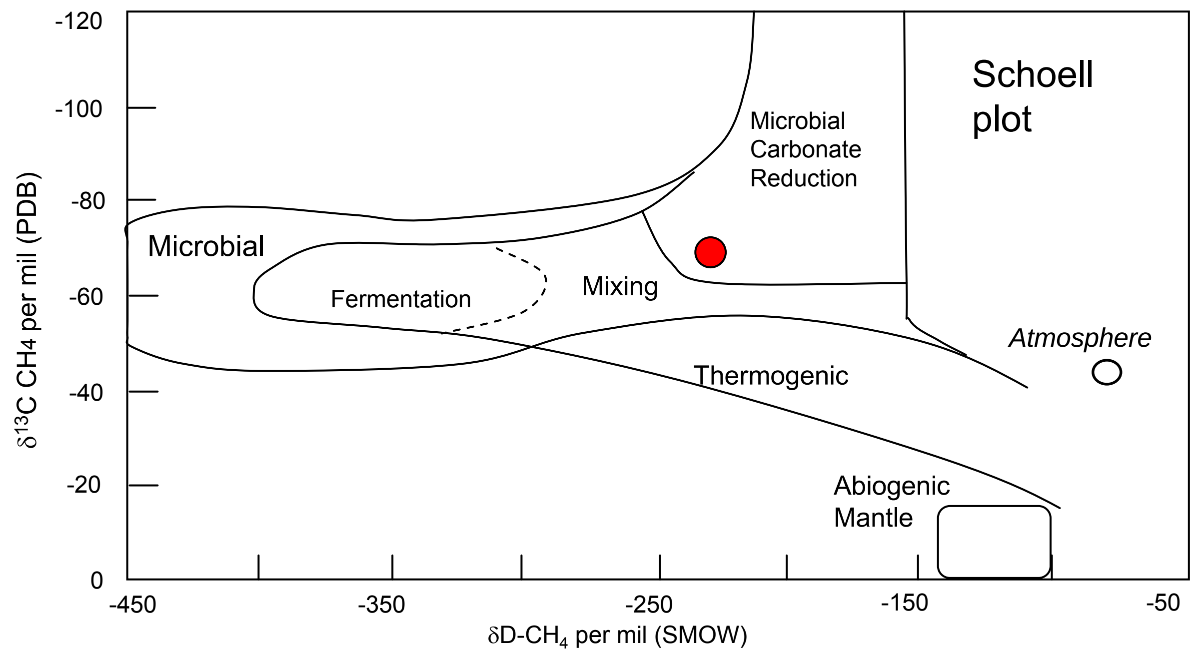


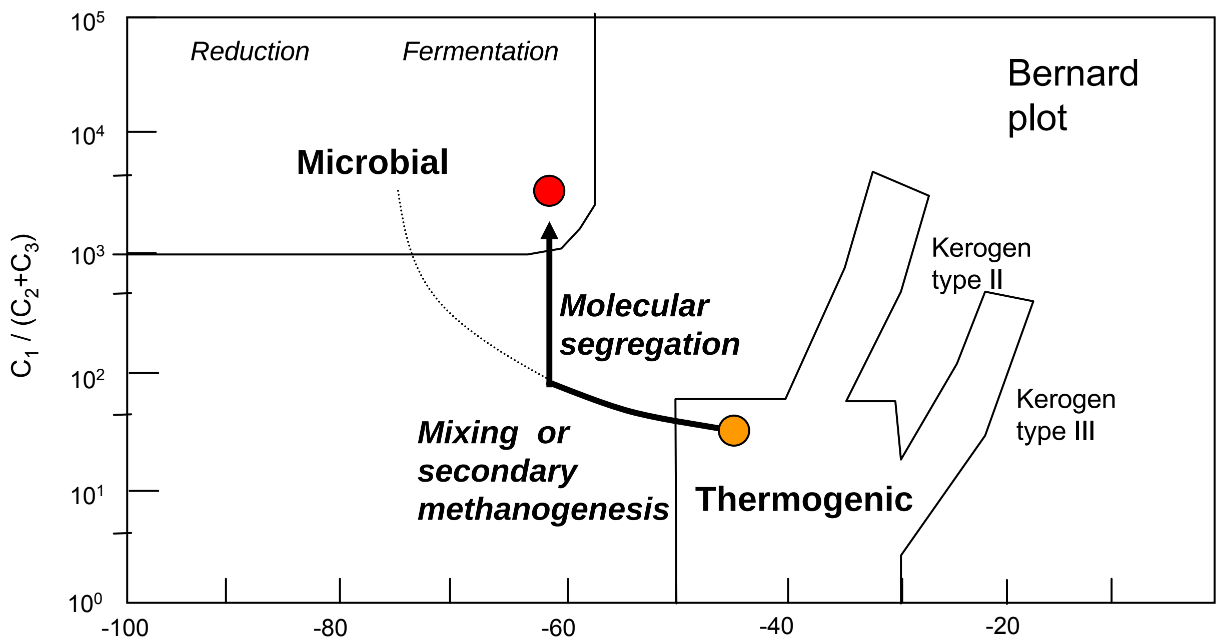
GENETIC ZONATION PLOTS

Effects of post-genetic processes

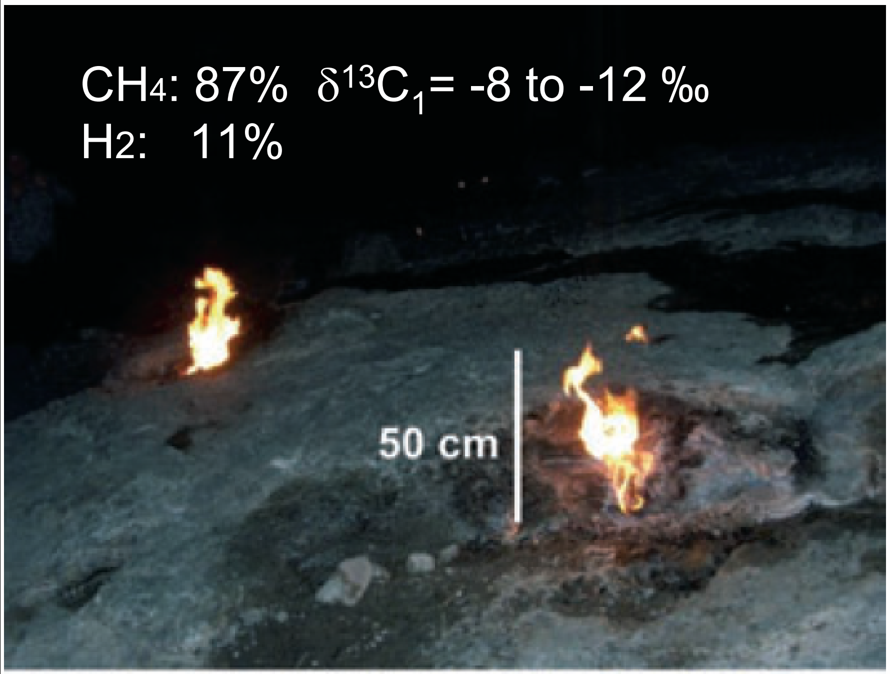


GENETIC ZONATION PLOTS CAN BE MISLEADING WHEN APPLIED TO SEEPS





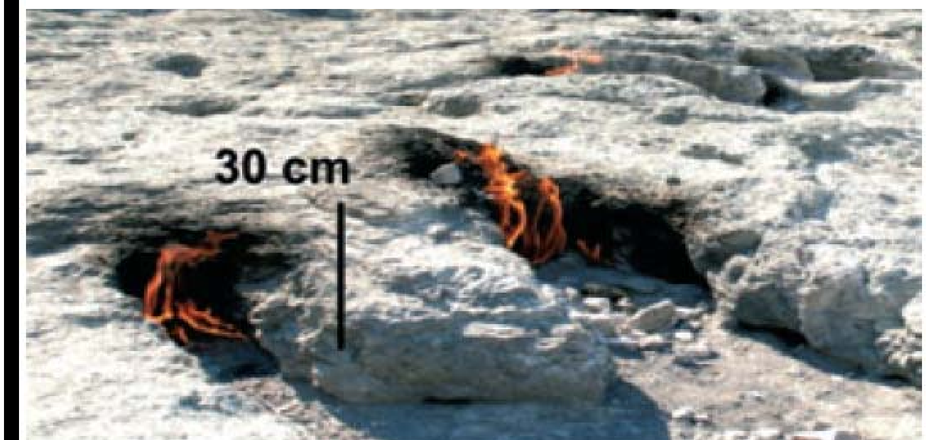
And there is an unusual seep in Turkey…..CHIMAERA

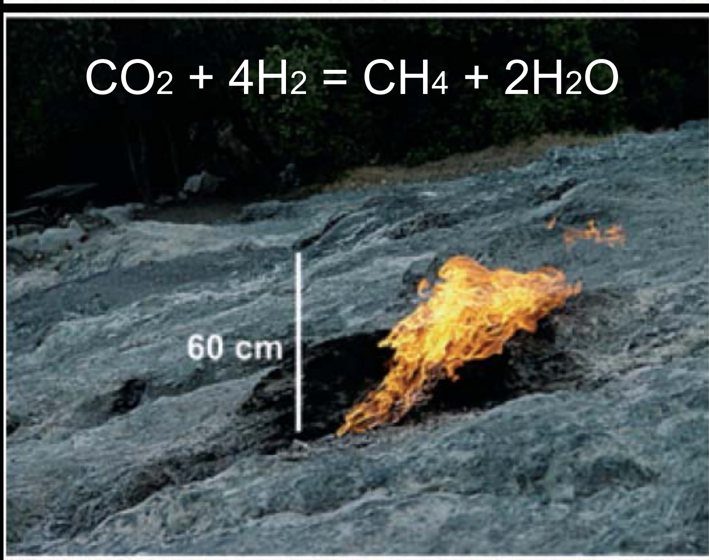


New evidence for a mixed inorganic and organic origin of the Olympic Chimaera fire (Turkey): a large onshore seepage of abiogenic gas

Geofluids (2008) 8, 263–273

H. HOSGORMEZ[1], G. ETIOPE[2] AND M. N. YALÇIN[1]





Total CH_4 flux >>50 ton/year

~ 50% of gas is ABIOGENIC
(low T serpentinization)

Abiogenic CH_4 flux >>25 ton/year

THE BIGGEST TERRESTRIAL (onshore) ABIOGENIC GAS SEEP IN THE WORLD!

Other abiogenic (serpentinization) gas seeps

Mid-Ocean Ridges: but they are high T serpentinization (hydrothermal)

Charlou et al (2002) *Geochemistry of high H2 and CH4 vent fluids issuing from ultramafic rocks at the Rainbow hydrothermal field.* Chem. Geol., 191, 345.

Proskurowski et al (2008) *Abiogenic hydrocarbon production at Lost City Hydrothermal Field*. Science, 319

Onshore, low T serpentinization seeps are only in the Philippines and Oman, but they are quite weak (no flux data)

Abrajano et al (1988) *Methane-hydrogen gas seeps, Zambales Ophiolite, Philippines: deep or shallow origin?* Chem. Geol., 71, 211.

Sano et al (1993) *Origin of hydrogen-nitrogen gas seeps, Oman*. Appl.Geoch., 8, 1.

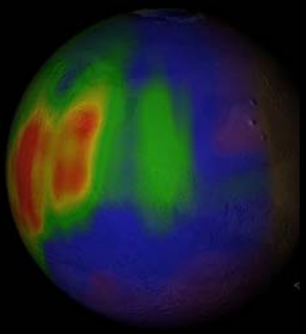
And low T serpentinization occurs in New Caledonia and Bosnia (Barnes et al., 1978) – no news about seeps

4. Unravelling CH_4 origin on Mars
(FLUXES)

1. CH_4 from seeps (point sources): 10^0 to 10^3 t/y
   Fluxes of terrestrial seeps are a reference for eventual Mars analogues.

   Potential (not actual) amount of gas (orders of magnitude) from Martian seeps can be inferred by their size (area), applying terrestrial emission factors.

2. CH_4 can also be released by diffuse exhalation (microseepage) from Martian soil (area source), even if macro-seeps are lacking; typical fluxes from soil in petroleum basins: 1-100 mg $m^{-2}d^{-1}$

3. 

   N.Summer 2003 CH_4 plume can be produced by ≥52 t/day (*Mumma et al 2009*). On the Earth, ≥52 t/day are provided by gas seepage zones of the order of 10^1-10^3 km^2 (or microseepage area 500 to 5000 km^2 wide).

   If a global Martian CH_4 source of ~100-300 t/y is required to maintain 10 ppb in the atmosphere, then only a few (or just one) terrestrial-type seeps may be requested.

4. Unravelling CH_4 origin on Mars
(GENETIC FEATURES)

- Most of gas seeping on the Earth's surface (thousands of seeps) is thermogenic (80%). Microbial only 4%

- Only a few seeps are abiogenic (low T serpentiniz.): but a large abiotic gas emission (>25 t/y) has been discovered in Turkey

Useful parameters:

$\delta^{13}C_1$ and δD_1

may help

C_2H_6 (ethane), **C_3H_8 (propane)** concentrations

H_2 concentration (indication of serpentinization)

Can they be measured by present or future instrumentation?

BUT, **CAUTION!**:

C1/C2 cannot help to distinguish between biotic and serpentinization gas (similar ratios, and possibility of molecular fractionation)

$\delta^{13}C_1$ and δD_1 may not be decisive: possible occurrence of isotopic fractionations (in subsoil, soil, atmosphere) must be assessed

4. Unravelling CH_4 origin on Mars
(GENETIC FEATURES)

Bad news?

Sorry, but it is likely that analysing CH_4 isotopes and other trace gas in the atmosphere will not be decisive to understand CH_4 origin (probably you'll get more questions than answers)

Gas should be analysed in the Martian soil or (better) subsoil, (before eventual migration- or atmospheric-induced fractionations)

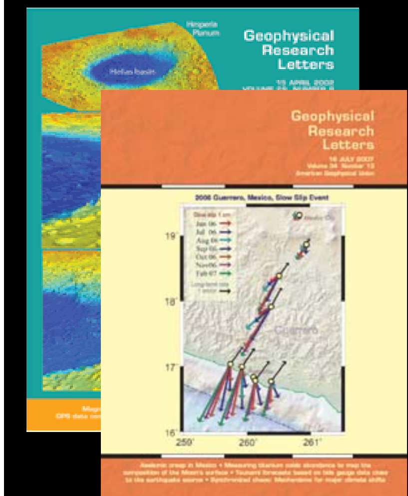
The best:

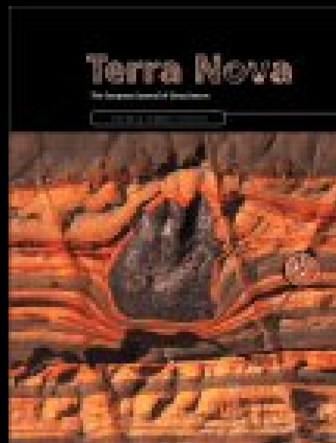
- **fluid sampling/analysis directly in a mud volcano (if fluids exist there)**
- **drilling in the Martian subsoil.**

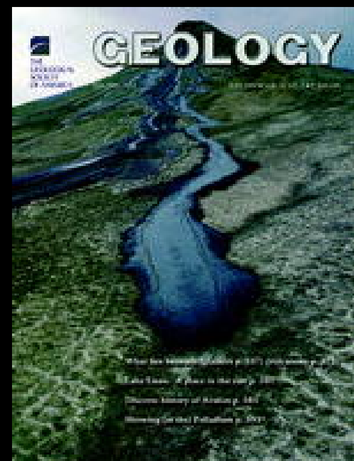
Possible in future missions?

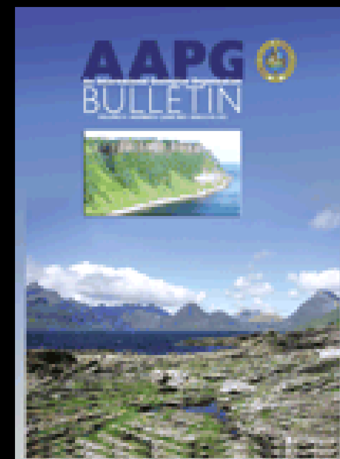
MAIN PAPERS PUBLISHED

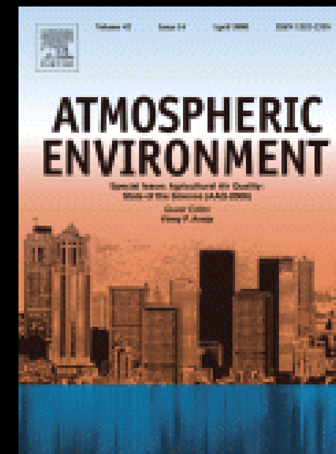
Italy	Romania	Azerbaijan	Greece	Europe
2002-2007	2004	2004	2004	2009





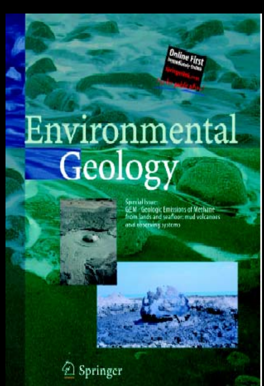


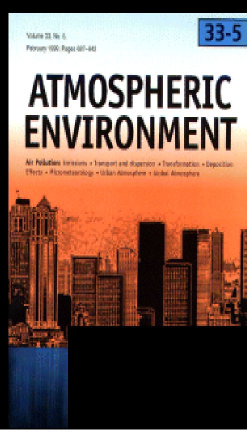


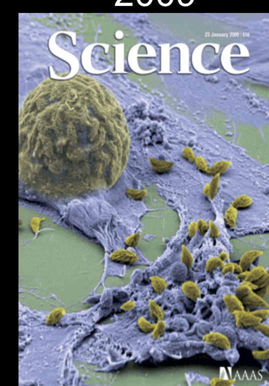


Global emission estimates

Mud volcanoes	Total	Past changes	Microseepage	Fossil-CH_4 budget	Ethane-propane emissions
2004	2004	2008	2009	2008	2009







T H A N K S

CO_2 and CH_4
geo-sources vs man-made vs natural