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

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1. **Classification** of geological CH4 emissions

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

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

4. Considerations for unravelling CH4 origin on Mars
1. Classification of geological CH₄ emissions

**HYDROCARBON EARTH’S DEGASSING**

**GEO-CH₄ SOURCES**

**CO₂-rich**

**Submarine seepage**

**CH₄-rich**

**GEOTHERMAL AREAS**

Inorganic/organic methane (high T)

**SEDIMENTARY BASINS**

Microbial and thermogenic gas (low T)

**MANTLE, CRYSTALLINE, METHAMORPHISM**

Inorganic reactions, serpentinization
MACRO-SEEPS MUD VOLCANO

Gas migration along faults

Gas release to the atmosphere

Pressurised gas from hydrocarbon reservoir

Gas

Gas rock

Reservoir

Clay

undercompacted and overpressured sediments

water mud

CH₄

0.1-1000 m
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
FLUX FROM VENTS
(Taiwan)
(macroseepage)
Dahsgil mud volcano (Azerbaijan)

FLUX FROM ERUPTIONS
FLUX FROM ERUPTIONS

Dahsgil mud volcano
(Azerbaijan)
Lokbatan mud volcano (Azerbaijan) October 2001
Lokbatan
(Azerbaijan)
Maggio 2003
GEO-CH$_4$ SOURCES

**GEOTHERMAL AREAS**
- Inorganic/organic methane (high T)

**SEDIMENTARY BASINS**
- Microbial and thermogenic gas (low T)

**MANTLE, CRYSTALLINE, METHAMORPHISM**
- Inorganic reactions, serpentinization

**GEOTCH4 SOURCES**
- Submarine seepage
- Mud volcanoes
- Gas seeps
- Microseepage
- Macro-seeps
MACRO-SEEPS
GAS-SEEPS
Oil-gas seeps, fires, springs

>13000 seeps on the continents
(Clarke abd Cleverly, 1991; Fugro- Robertson database)

Gas release to the atmosphere
Gas migration along faults
Pressurised gas from hydrocarbon reservoir

Reservoir rock
Gas
CH4
water
flames
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
GEO-CH₄ SOURCES

GEOTHERMAL AREAS
Inorganic/organic methane (high T)

SEDIMENTARY BASINS
Microbial and thermogenic gas (low T)

MANTLE, CRYSTALLINE, METHAMORPHISM
Inorganic reactions, serpentinization

Mud volcanoes
Gas seeps
Macro-seeps
Microseepage

Submarine seepage
Reservoir rock
Gas

MICROSEEPAGE

Pressurised gas from hydrocarbon reservoir

Gas migration along faults

Subsoil input
> methanotrophic consumption

Diffuse degassing from soil

CH₄

Reservoir rock

Gas

Dry soil is not always a CH₄ sink!
Microseepage in hydrocarbon basins

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

Closed chamber

\[ f = \frac{\Delta C V}{\Delta t A} \]
Microseepage in hydrocarbon basins

INGV-West Systems prototype (semiconductor sensor)
Microseepage in hydrocarbon basins

Immediate, online measurements of CH4 flux from soil
Microseepage in hydrocarbon basins

Laser sensor
(infrared-absorption spectroscopy)
GEO-CH₄ SOURCES

GEOTHERMAL AREAS
Inorganic/organic methane (high T)

SEDIMENTARY BASINS
Mud volcanoes
Gas seeps
Microseepage

Macro-seeps
Microbial and thermogenic gas (low T)

MANTLE, CRYSTALLINE, METHAMORPHISM
Inorganic reactions, serpentinization

Submarine seepage
Bubble plumes (reaching the atmosphere from seafloor < 200-300 m deep)
GEO-CH$_4$ SOURCES

**GEOTHERMAL AREAS**

- Inorganic/organic methane (high T)

**SEDIMENTARY BASINS**

- Microbial and thermogenic gas (low T)
- Inorganic reactions, serpentinization

**MANTLE, CRYSTALLINE, METHAMORPHISM**

**GEOPHYSICAL FEATURES**

- Mud volcanoes
- Gas seeps
- Microseepage

**Submarine seepage**
VOLCANIC & GEOTHERMAL METHANE

$\text{CO}_2$: 90-99%v
$\text{CH}_4$: 0.01-2%v

$\text{CO}_2 + 4\text{H}_2 = \text{CH}_4 + 2\text{H}_2\text{O}$

+ 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-CH4 emission zones

- Onshore sedimentary seeps
- Marine seeps
- Geothermal-volcanic systems

Gas-oil fields: 112 countries (out of 182)
>900 onshore MV and >13000 oil-gas seeps in > 80 countries
Potential global microseepage area: ~ 4-8 M km²
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) \(10^0 \text{ to } 10^3\) 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
GEOTHERMAL AREAS
Inorganic/organic methane (high T)

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Inorganic/organic methane (high T)

GEOTHERMAL AREAS
Inorganic/organic methane (high T)

TOTAL = 42-64 Mt/y

3-7
Etilope and Klusman (2002)
Lacroix (1993)

19-38
Etilope and Milkov (2004)
Etilope and Klusman (2010)

20
Kvenvolden et al. (2001)
Judd (2004)

Tot abiogenic ~2.3
Serpent. <1
Emmanuel & Ague (2007)

Mud volcanoes
Gas seeps
Microseepage
Macro-seeps

SEDIMENTARY BASINS
Microbial and thermogenic gas (low T)

MANTLE, CRYSTALLINE, METHAMORPHISM
Inorganic reactions, serpentinization

Submarine seeps
No or very low flux,
CH4 oxidised or dissolved

Hydrates

GEO-CH₄ EMISSION ESTIMATES

Kvenvolden et al. (2001)
Judd (2004)

( theoretical estimate )
A revised CH$_4$ source inventory

with Geo-CH$_4$ emission: 42-64 Mt/y

$2^{nd}$ 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

IPCC (2001) – TAR 5-10 Tg y⁻¹ oceanic hydrates and many scientific papers

Fung et al. (1991) Lelieveld et al. (1998) 5-15 permafrost+hydrates+other geologic sources

EPA (1993) only continental hydrates (not oceanic)

IPCC (1992) 5

Kvenvolden (1991) 3-4

Cicerone & Oremland (1988) 5

No experimental data

Hydrates may be important on Mars, but today they are not a source for Earth’s atmosphere

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$_2$H$_6$) and propane (C$_3$H$_8$)

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

ppbv and ppmv levels
Analysis of a robust data set of C₁, C₂, C₃ from 238 sites coupled with published estimates of geo-CH₄ emissions (9 petroleum basins, > 4000 soil-gas samples)
Earth’s degassing accounts for > 17% and 10% of total C2 and C3 emissions
3. Gas origin

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

143 MV from 12 countries

60 seeps from 8 countries

~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)

$\text{PGP} = \text{modification of genetic features}$

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 $\rightarrow$ 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 (Fe$^{3+}$)-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$_2$S concentrations (>1 %) and increased $\delta^{13}C$ values of $C_1$–$C_5$ hydrocarbons.
- not typical of MV systems (low T fluids, H$_2$S 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)

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)

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

- Reduction
- Fermentation
- Oxidation
- Diffusion
- Advection
- Biodegradation

Microbial

Thermogenic

Kerogen type II

Kerogen type III

Bernard plot

$\delta^{13}$C-CH$_4$ per mil (PDB)

$C_1/(C_2+C_3)$
GENETIC ZONATION PLOTS CAN BE MISLEADING WHEN APPLIED TO SEEPS

Schoell plot

Bernard plot

Molecular segregation

Mixing or secondary methanogenesis
And there is an unusual seep in Turkey…..CHIMAERA

CH$_4$: 87% $\delta^{13}$C$_1$ = -8 to -12 ‰
H$_2$: 11%

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. Hosgorman, G. Etope and M. N. Yalçın

CO$_2$ + 4H$_2$ = CH$_4$ + 2H$_2$O

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)


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


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 CH4 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:

\[ \delta^{13}C_1 \text{ and } \delta D_1 \]
\[ \text{C}_2\text{H}_6 \text{ (ethane)}, \quad \text{C}_3\text{H}_8 \text{ (propane)} \text{ concentrations} \]
\[ \text{H}_2 \text{ concentration (indication of serpentinization)} \]

\( \text{Can they be measured by present or future instrumentation?} \)

**BUT, CAUTION!**:

\( \text{C}_1/\text{C}_2 \text{ cannot help to distinguish between biotic and serpentinization gas (similar ratios, and possibility of molecular fractionation)} \)

\[ \delta^{13}C_1 \text{ and } \delta D_1 \text{ may not be decisive: possible occurrence of isotopic fractionations (in subsoil, soil, atmosphere) must be assessed} \]
4. Unravelling CH4 origin on Mars
(GENETIC FEATURES)

Bad news?

Sorry, but it is likely that analysing CH4 isotopes and other trace gas in the atmosphere will not be decisive to understand CH4 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 2002-2007
Romania 2004
Azerbaijan 2004
Greece 2004
Europe 2009

Global emission estimates

Mud volcanoes 2004
Total 2004
Past changes 2008
Microseepage 2009
Fossil-CH4 budget 2008
Ethane-propane emissions 2009

THANKS
CO$_2$ and CH$_4$
geo-sources vs man-made vs natural

CO$_2$

- Atmosphere: 70,000,000 Mt/y
- Geosphere: 26,000 Mt/y

26,000 Mt/y is 43 times the 600 Mt/y from geosphere

CH$_4$

- Atmosphere: 360 Mt/y
- Geosphere: 53 Mt/y

360 Mt/y is 6.8 times the 53 Mt/y from geosphere

180 Mt/y