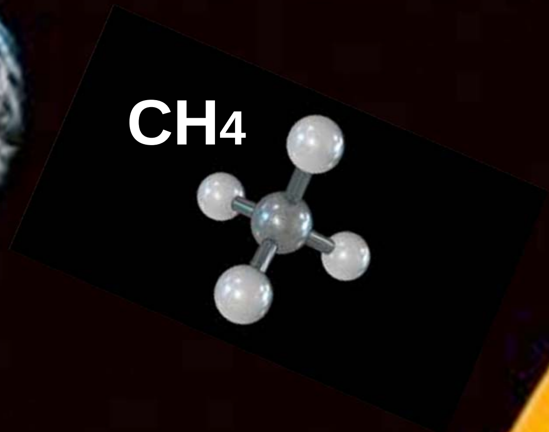

UNDERSTANDING THE ORIGIN OF METHANE ON MARS THROUGH ISOTOPIC AND MOLECULAR DATA FROM NOMAD (EXOMARS):

WILL THERE BE MORE ANSWERS OR QUESTIONS?

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Knowing geologic methane release on Earth is a necessary step towards understanding why and where methane can be on Mars

Geologic and geochemical concepts of methane seepage on Earth….

….are used to recognize potential methane release and origin on Mars

NOMAD can

- detect CH_4
- measure its stable C isotope ratio ($^{13}C/^{12}C$)
- measure the isotopologue $^{13}CH_3D$
- detect ethane (C_2H_6)

ACS can also detect CH_4

Useful parameters to identify the methane origin, which may be biotic or abiotic

ExoMars programme's scientific objectives
n.3 - martian atmospheric trace gases and their sources
n.4 - characterisation of the surface environment

Are these parameters sufficient? And how can / should we interpret the values?

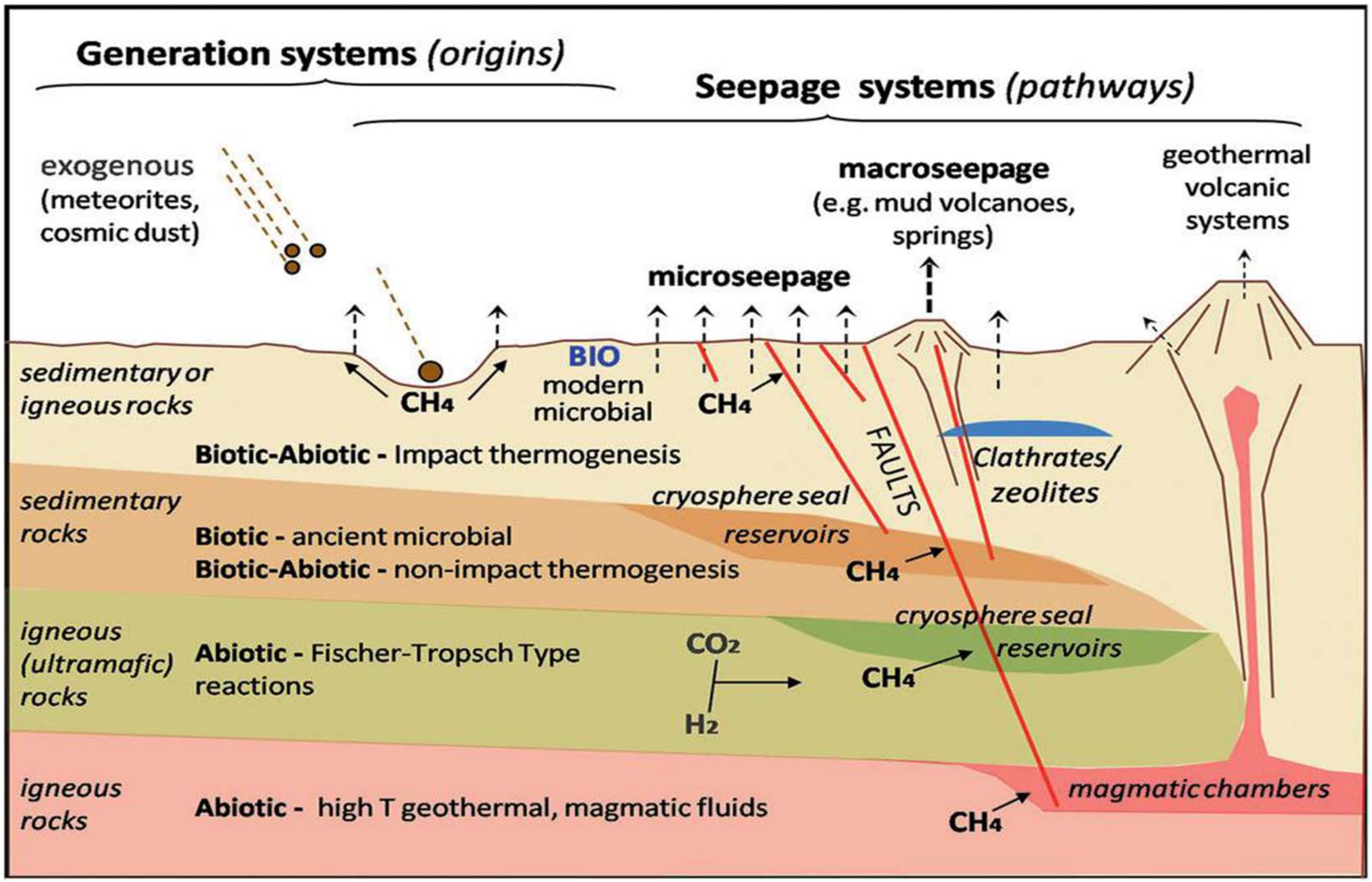
Updated scheme of geologic CH_4 sources on Mars
(and some definitions)

BIOTIC
- biogenic or microbial
  - living microbial
  - fossil microbial
- thermogenic (organic matter)

← **LIFE** ←

ABIOTIC (magmatic, FTT reactions)

CH_4 energy source for prebiotic chemistry

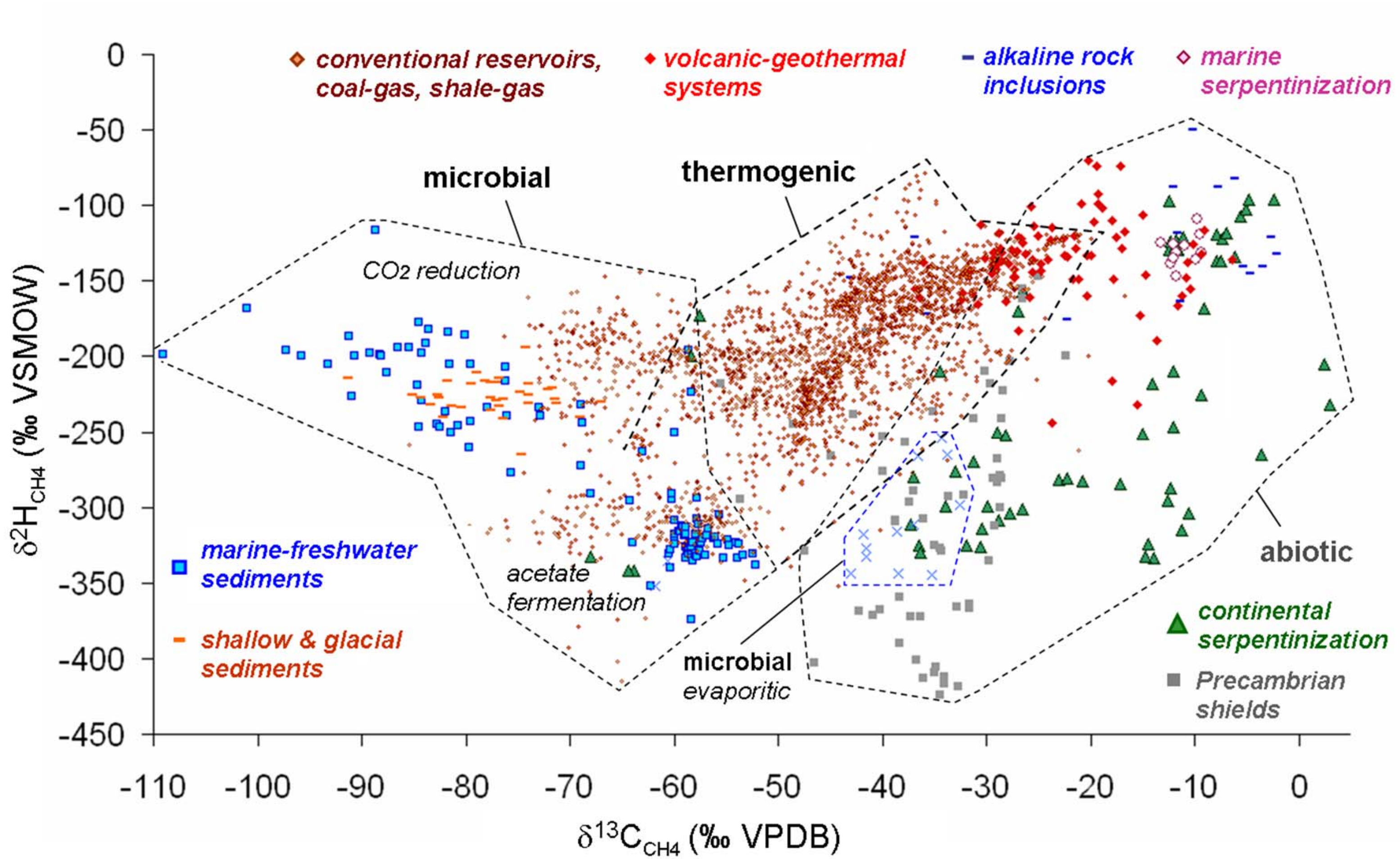


Oehler and Etiope, 2017

Stable C isotope ratio $^{13}C/^{12}C$

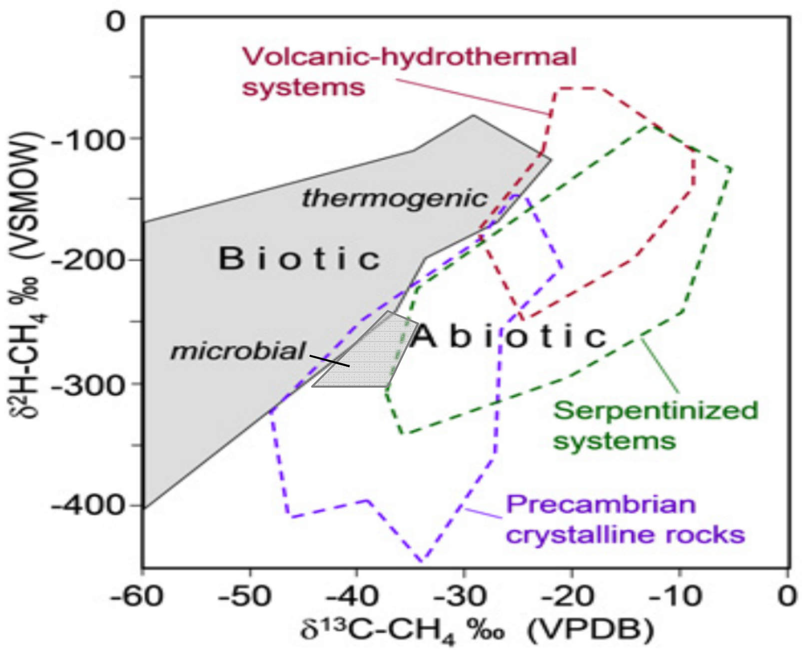
$$\delta^{13}C = \left(\frac{\left(\frac{^{13}C}{^{12}C}\right)_{sample}}{\left(\frac{^{13}C}{^{12}C}\right)_{standard}} - 1 \right) * 1000\ ‰$$

CH_4 on Earth



Etiope (2017) Encyclopedia of Geochemistry

Abiotic CH_4 isotopic composition, quite different from biotic gas, but resolved only knowing stable H isotope ratio



Etiope and Schoell (2014)

$^{13}C/^{12}C$ similar values for different origins

- **abiotic CH_4** is not always ^{13}C-enriched, resembling microbial gas

(abiotic gas with $\delta^{13}C_{CH4}$ as low as -140‰ obtained in laboratory)

- **microbes** can produce ^{12}C-depleted CH_4, resembling abiotic gas

$^{13}C/^{12}C$ of CH_4 depends on $^{13}C/^{12}C$ of its precursor (carbonate, CO_2), quite variable on Mars

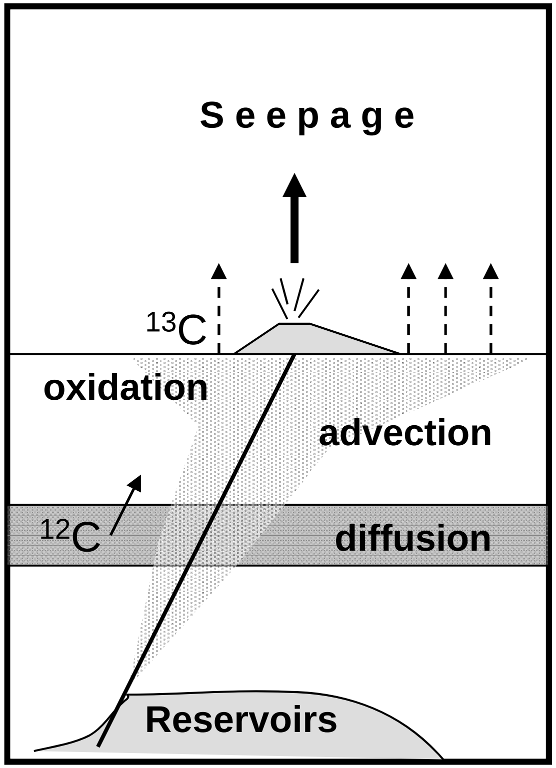
- atmospheric fractionated CO2 ($\delta^{13}C$~+46‰) ⇨ very ^{13}C-enriched CH4 (regardless the genetic mechanism)
- atm. unfraction. or magmatic CO2 (e.g. Zagami meteor.; $\delta^{13}C$ -20 to 0‰) ⇨ $\delta^{13}C_{CH4}$ like on Earth

Post-genetic alterations complicate the story

- oxidation (e.g., by hydrogen peroxide in the regolith) can increase $\delta^{13}C$ value, transforming an apparent “microbial” signature into an “abiotic” one

- isotopic fractionation during diffusion in low permeability rocks can lead to ^{12}C-enrichment in the released gas

Advection is the dominant mechanism of gas migration to the surface (seepage), but diffusion steps may take place through less permeable, sealing rocks.

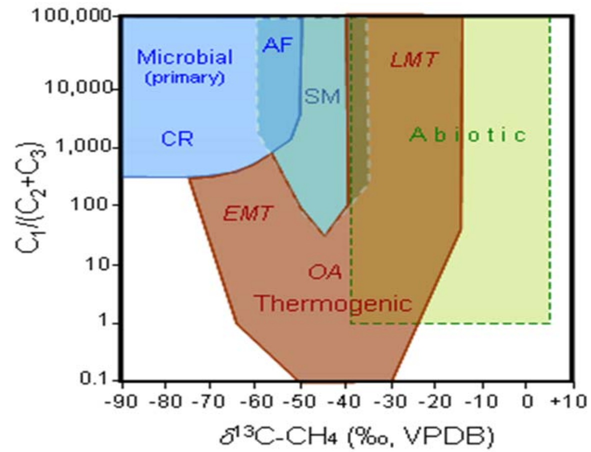


Methane/ethane (C_1/C_2) ratio

ethane (C_2H_6) is also important, although not decisive, for determining gas origin; often considered that high C_1/C_2 ratios indicate microbial CH_4 Wrong!

- dry thermogenic gas, in overmature source rocks, may have high C_1/C_2 ratios, similar to microbial gas

- abiotic gas has a wide range of C_1/C_2 ratios, overlapping microbial ranges



CR: CO_2 reduction

AF: acetate (CH_3COO) fermentation

SM: Secondary Microbial

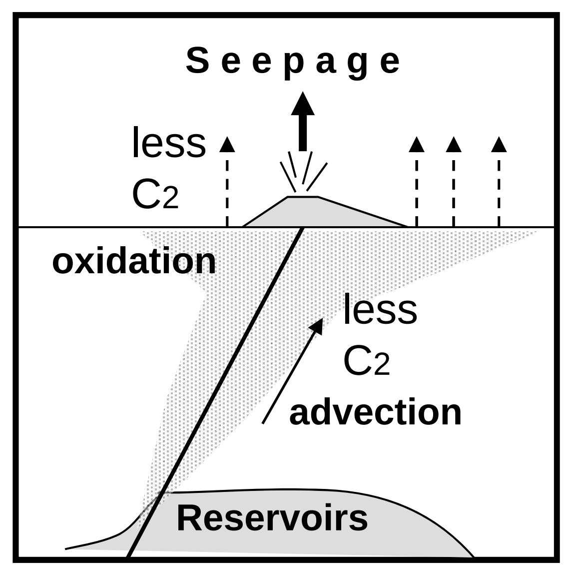
EMT: early mature thermogenic

OA: oil-associated thermogenic

LMT: late mature thermogenic

- molecular fractionation (lost of C2+) during advection *(C_1/C_2 at the surface > original ratio at the source rock)*

- once in the atmosphere, C_2 is more rapidly oxidised than C_1, resulting in a further increase of the C_1/C_2 ratio



Ethane shall be examined together with other geochemical data, taking into account the geological context

CH_4 isotopologue $^{13}CH_3D$

doubly substituted isotopologue of methane

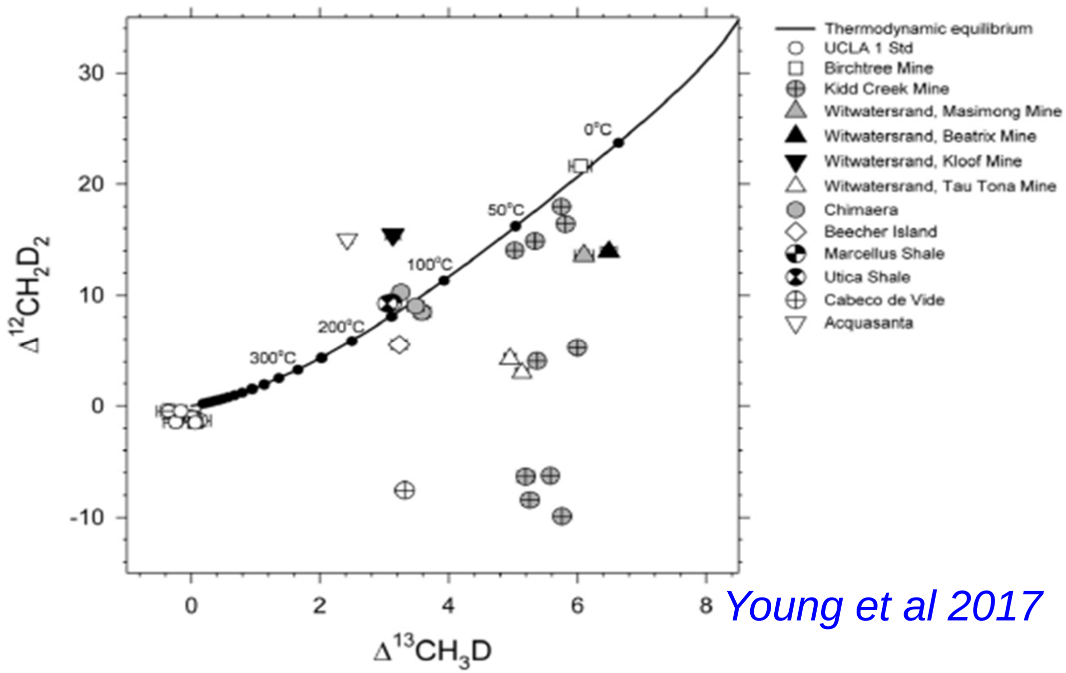
Several papers claim that isotopologues can identify the origin of methane – not true!

Clumped isotopes can only determine the **temperature** of CH_4 formation and only if they are in thermodynamic equilibrium (which happens only at high temperatures)

abiotic and microbial gas can be formed at the same T!

They could reveal biological re-processing….but with many assumptions and uncertainties

And the other isotopologue $^{12}CH_2D_2$ is necessary to understand if there is equilibrium



Young et al 2017

So, considerable uncertainties in the interpretation of methane origin

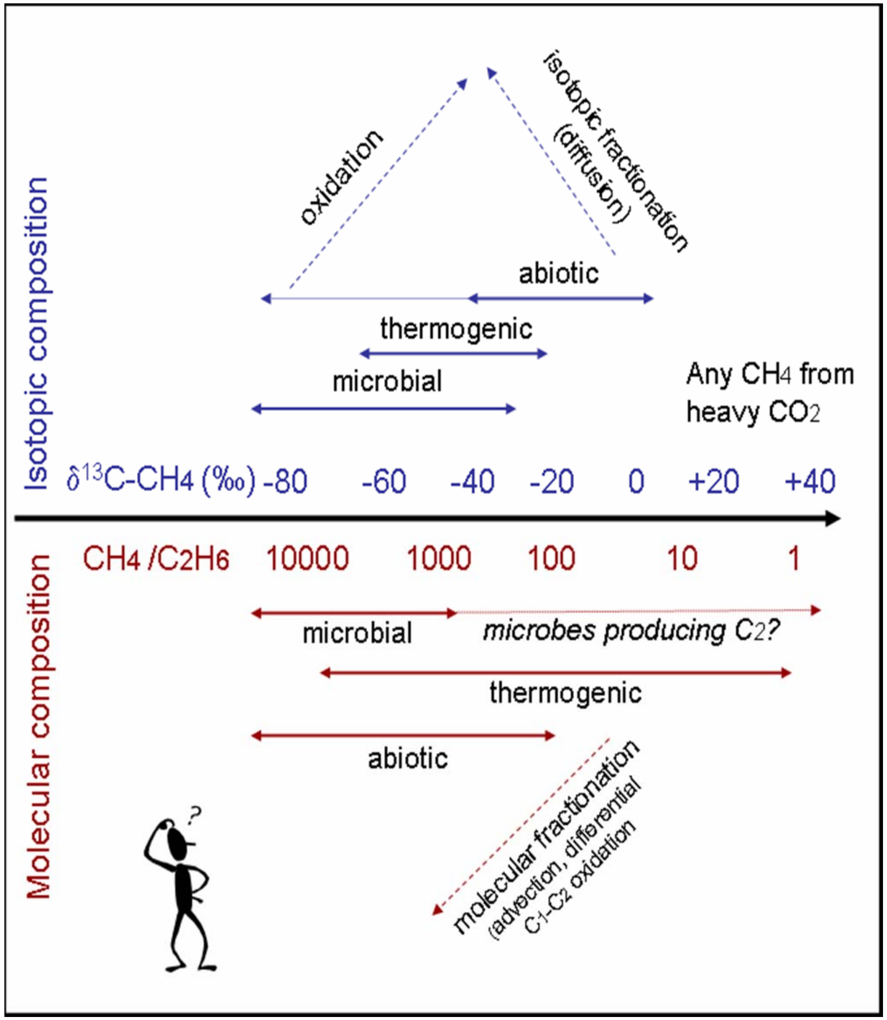
$^{13}C/^{12}C$ of CH_4 could be similar to that on Earth only if it is from unfractionated or magmatic CO_2, or a C precursor with negative $\delta^{13}C$ values

If both C_1 and C_2 are detected, gas could be abiotic, assuming that

- there are no ethane-producing microbes on Mars
- there is no ancient organic matter in rocks

If ethane is not detected, gas could be:

(a) microbial
(b) abiotic or thermogenic, molecularly fractionated
(c) dry thermogenic (overmature)
(d) abiotic generated at very low T



Conclusions

CH_4 isotopic ratio and C_1/C_2 ratio observable by NOMAD

(a) may have a wide range of values; each value could reflect a number of possible genetic mechanisms (microbial, thermogenic and abiotic).

(b) can be totally different from those of the original gas produced in the subsurface because of post-genetic alterations

(the atmosphere is not the best place to study the origin of methane)

Probably we'll get more questions than answers

Only preliminary interpretations can be provided

Hydrogen data from FREND neutron detector can also be of support

possible associations with hydrated olivine-rich rocks, which may suggest abiotic methane

….but we'll do our best integrating TGO data with geological evaluations