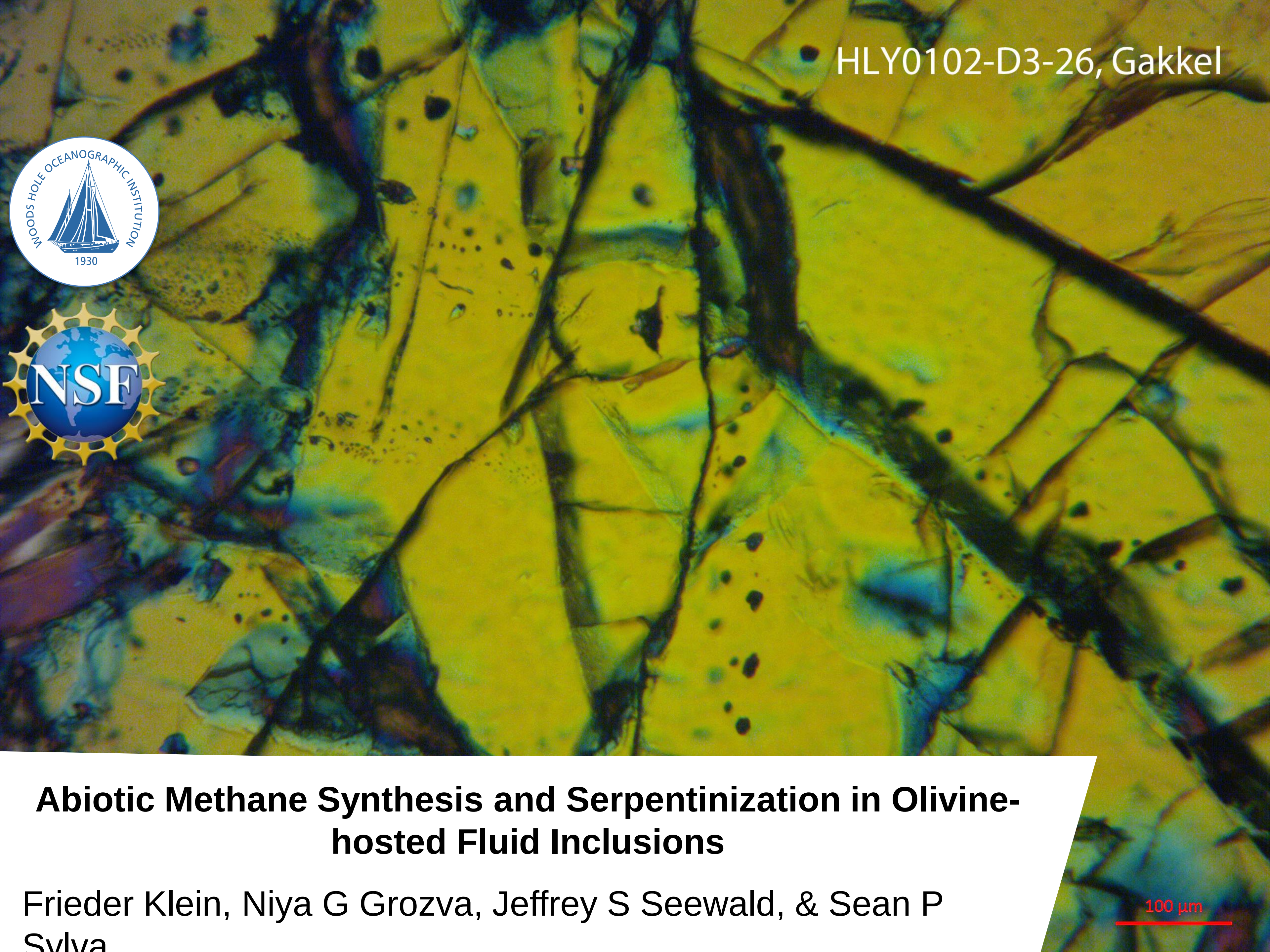
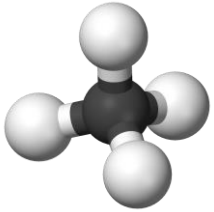


Abiotic Methane Synthesis and Serpentinization in Olivine-hosted Fluid Inclusions

Frieder Klein, Niya G Grozva, Jeffrey S Seewald, & Sean P Sylva



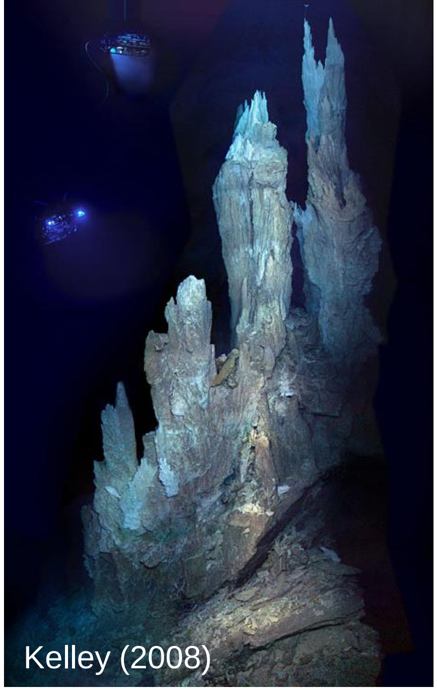
Why Care?

- CH_4 plays key roles in the global C cycle

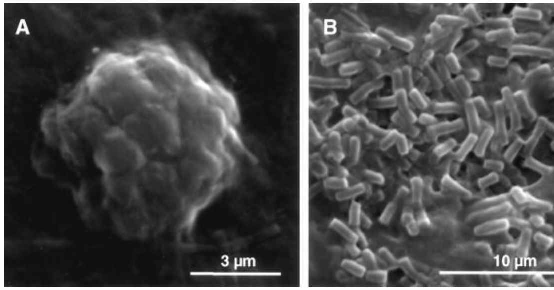
- Oxidation of CH_4 yields catabolic (ATP generating) energy for chemolithoautotrophs

- Abiotic CH_4 on other planetary bodies (Mars, Titan, Enceladus)

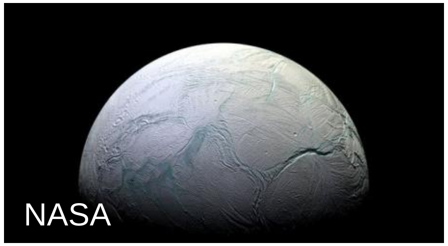
- The source(s) of abiotic CH_4 remain(s) poorly constrained



Kelley (2008)



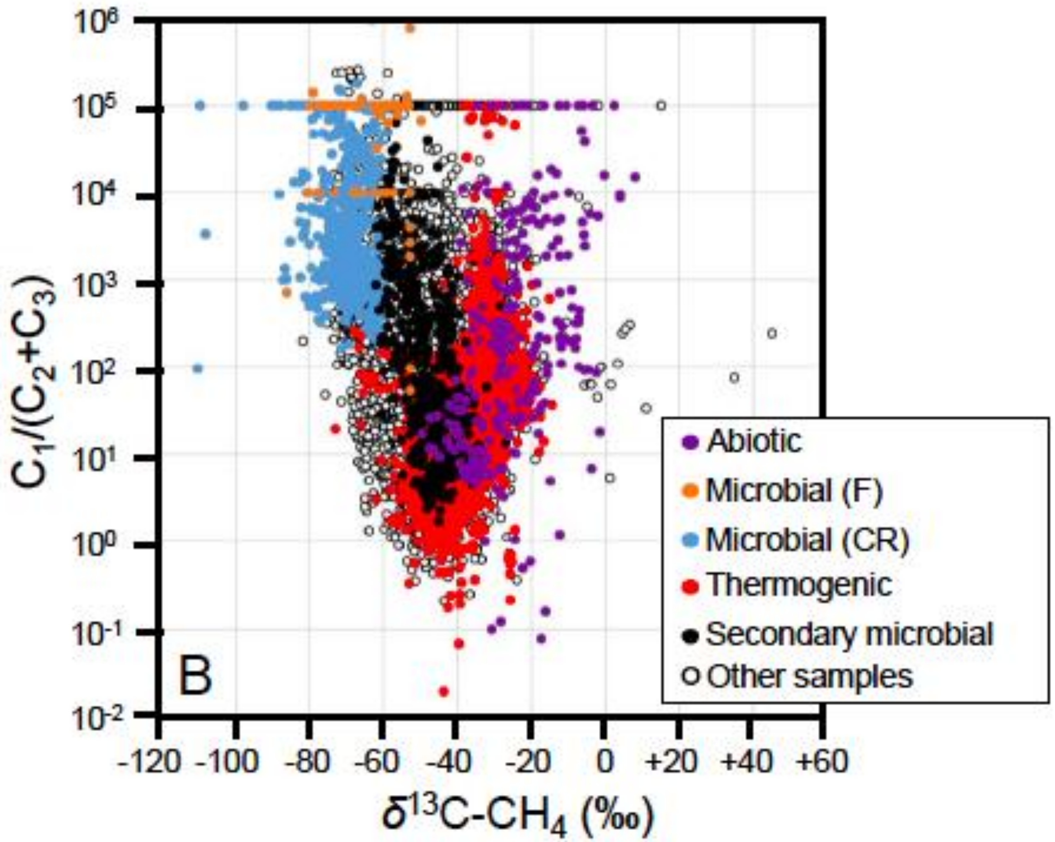
Knittel et al (2005)



NASA

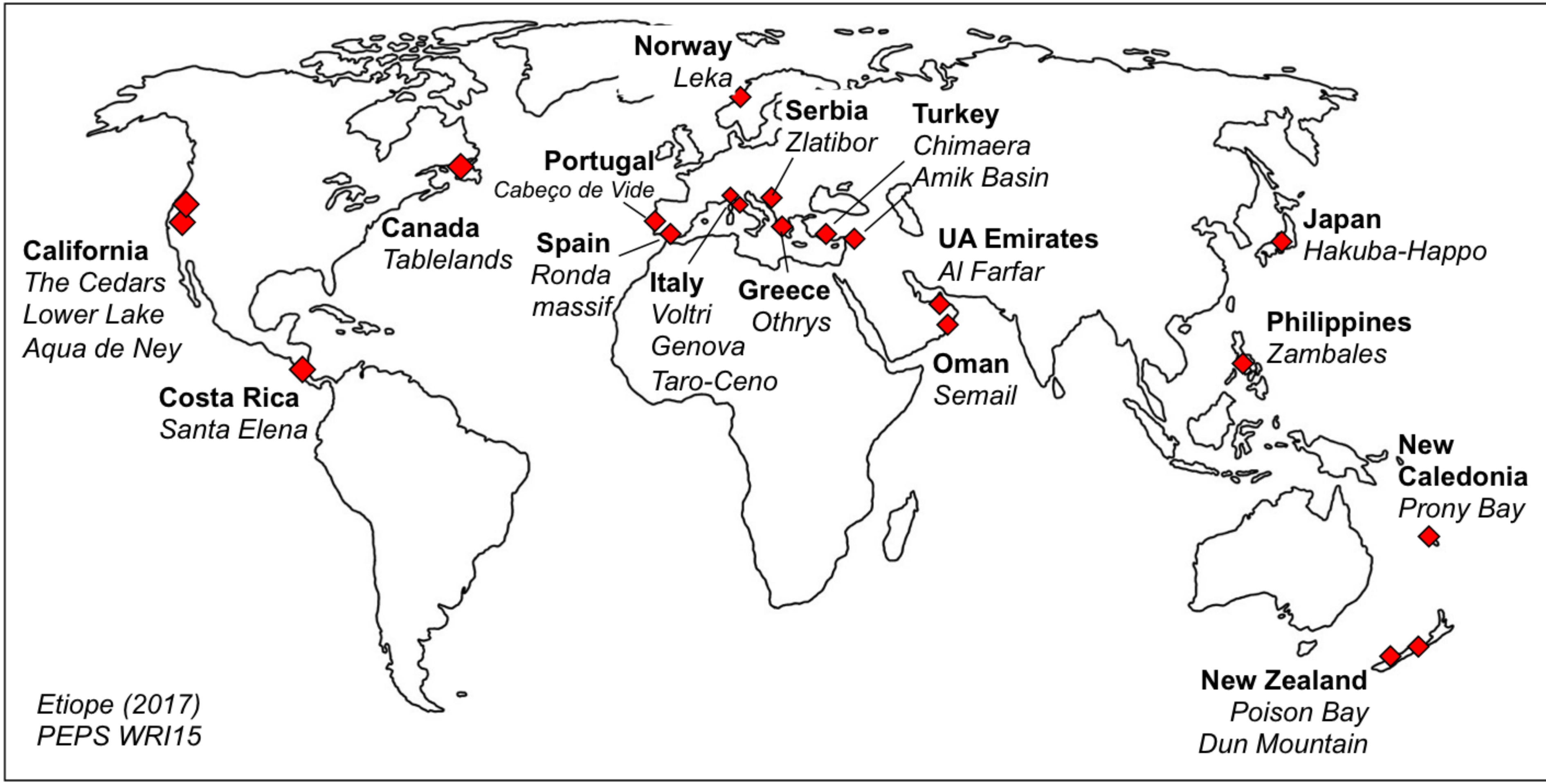
Biogenic, Thermogenic, & Abiotic Methane

- Biogenic: formed by biological organisms
- Thermogenic: formed by thermal decomposition of living organisms or biologically derived compounds
- Abiotic: formed by purely chemical processes with no interference of biological organisms



Milkov & Etiope (2018)

Serpentinite-hosted Methane Seeps



Abiotic CH_4 is leached from basalt or gabbro…!??

Welhan & Craig (1983)

Kelley & Fruh-Green (1999)

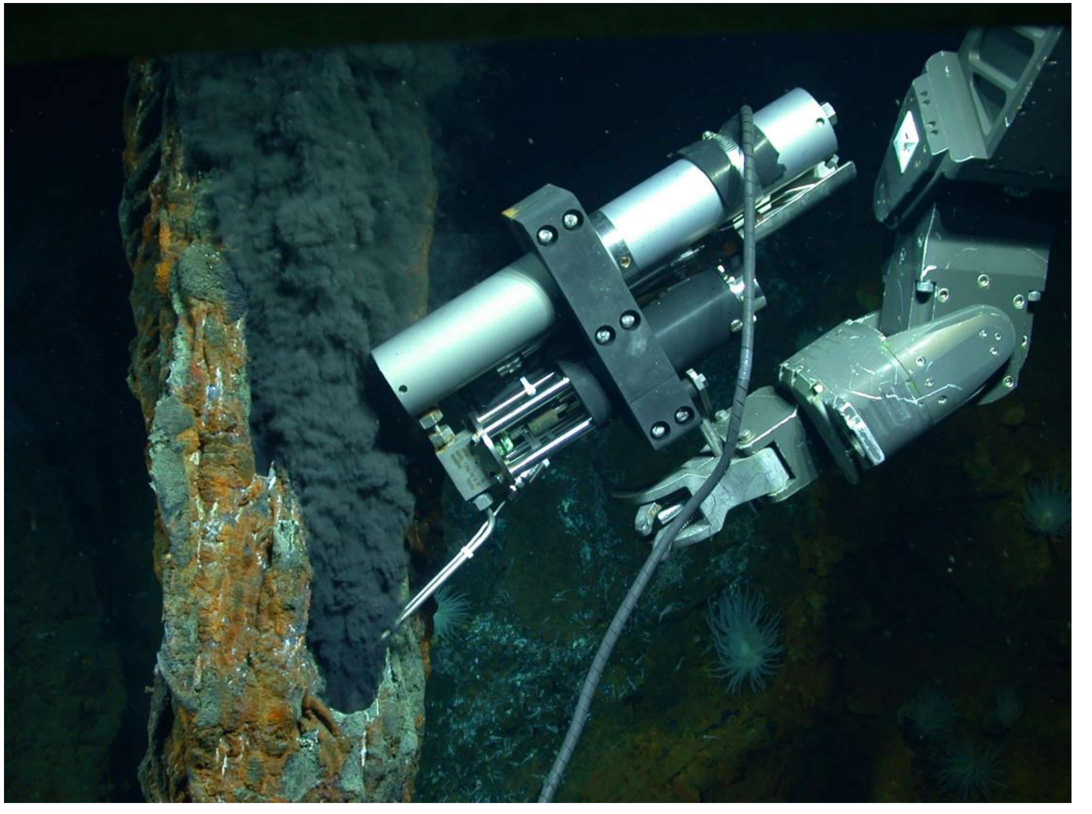
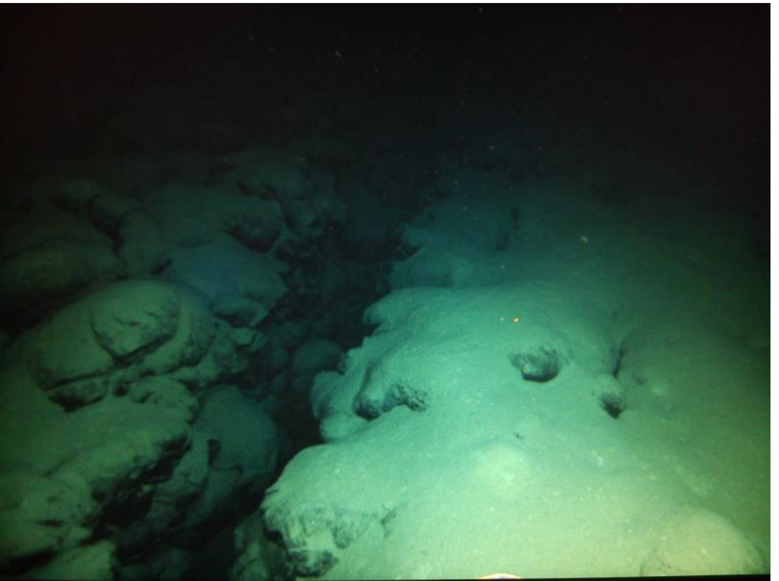
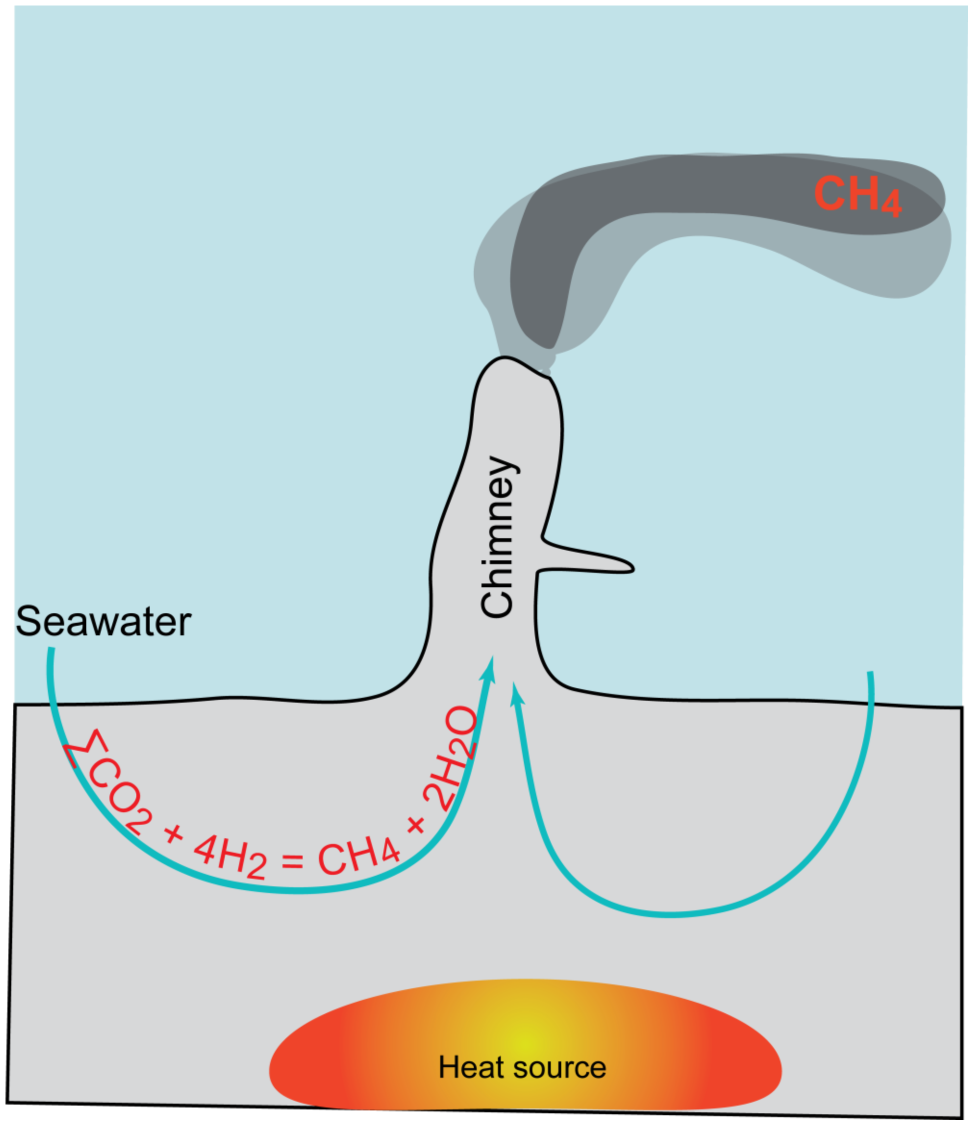
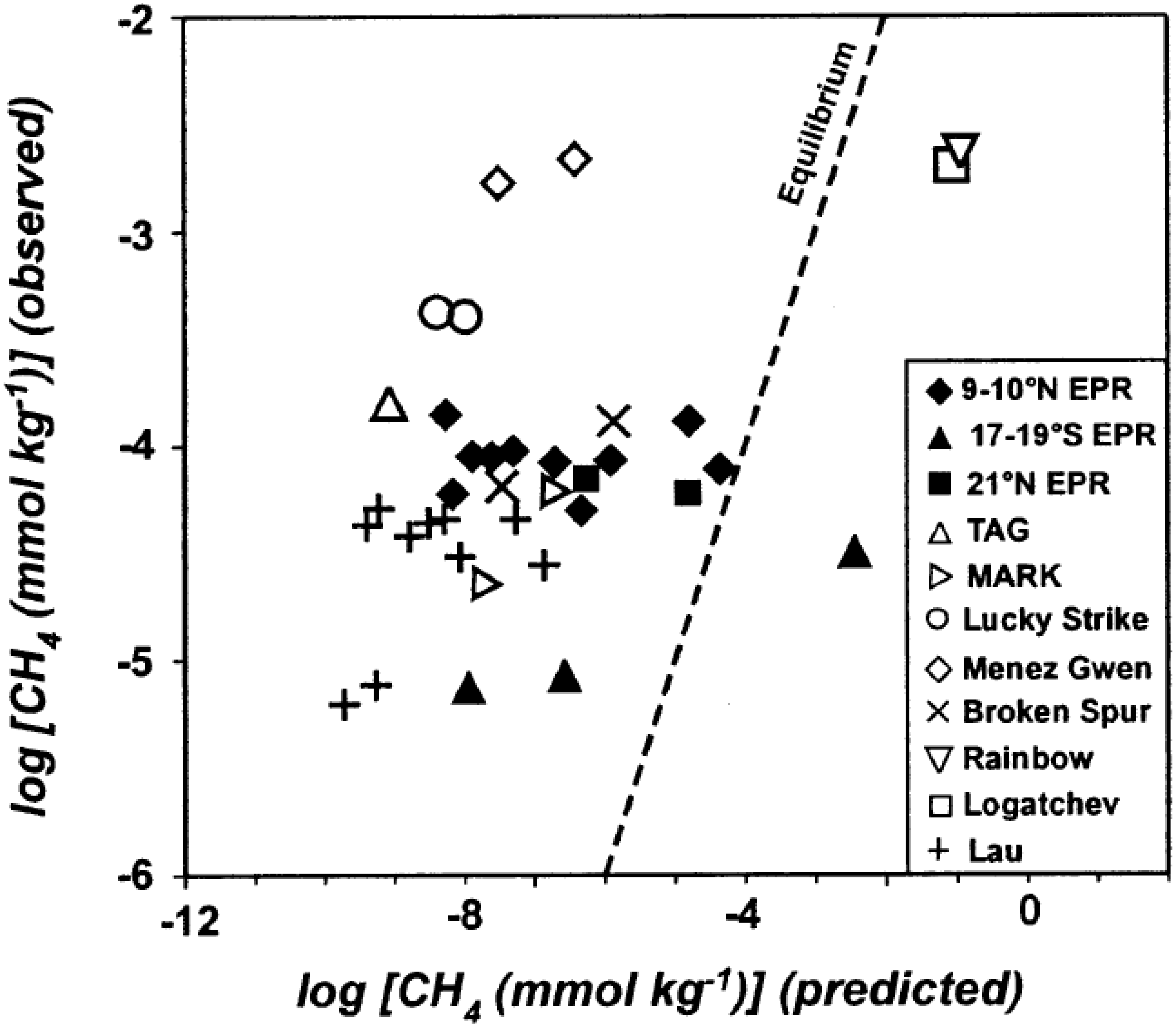


Image courtesy of C. German

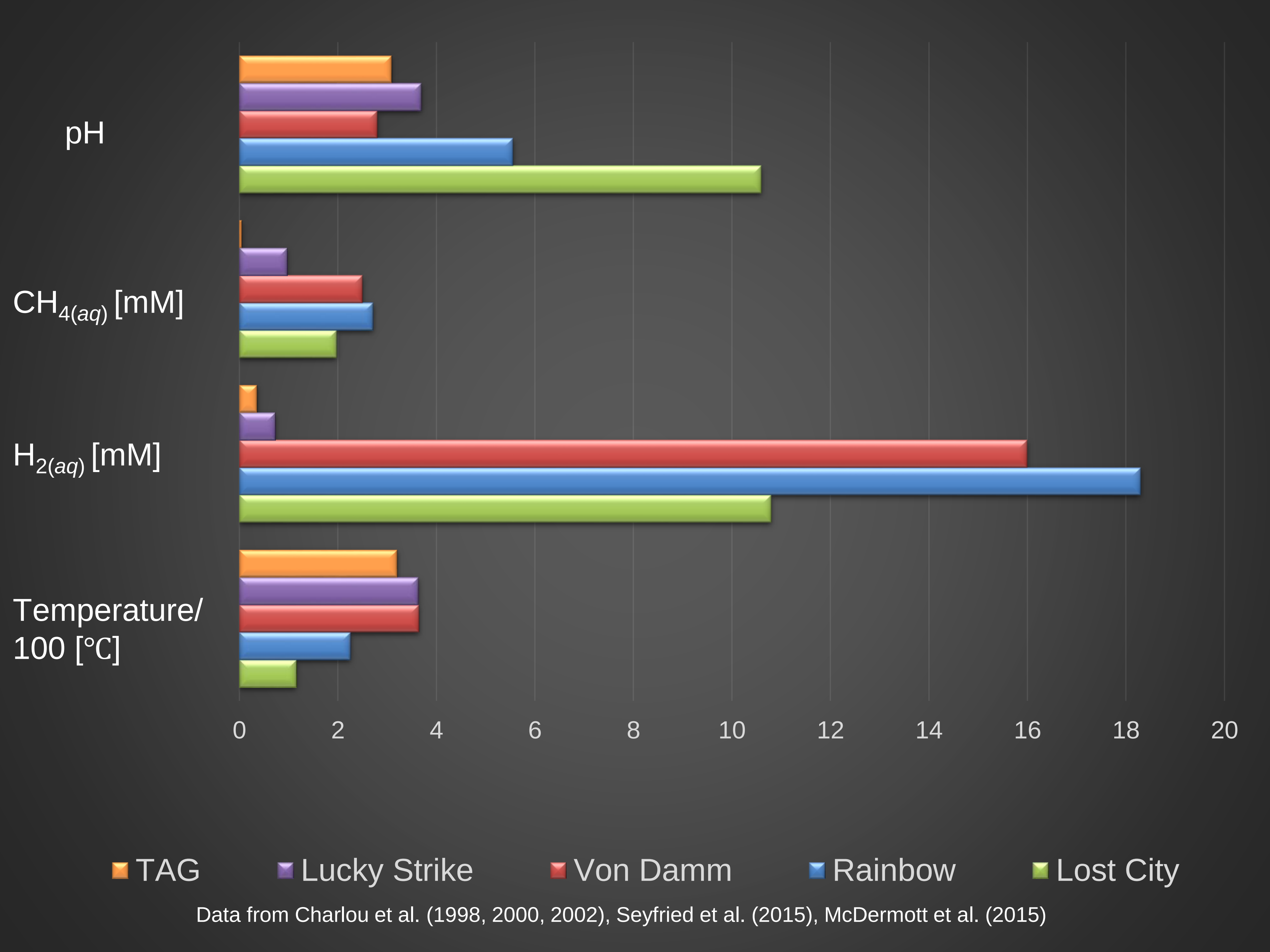


Reduction of dissolved inorganic carbon during hydrothermal circulation!??

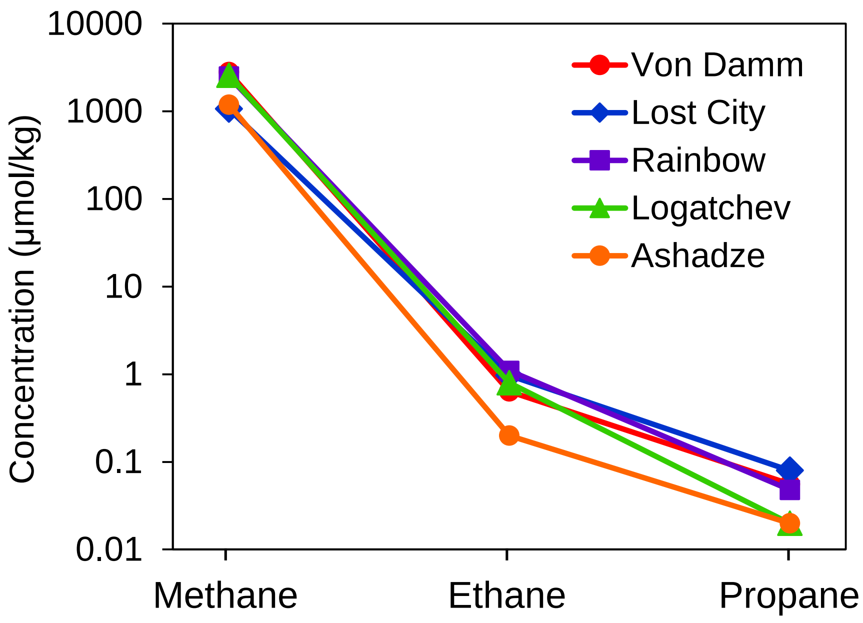


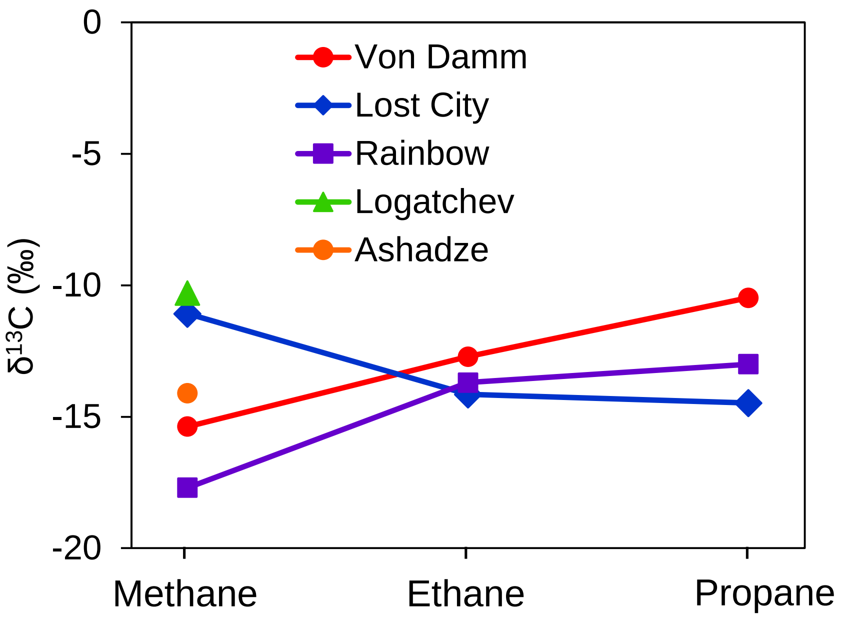


McCollom & Seewald (2007)


pH
CH4(aq) [mM]
H2(aq) [mM]
Temperature/
100 [°C]
0
2
4
6
8
10
12
14
16
18
20
TAG
Lucky Strike
Von Damm
Rainbow
Lost City
Data from Charlou et al. (1998, 2000, 2002), Seyfried et al. (2015), McDermott et al. (2015)

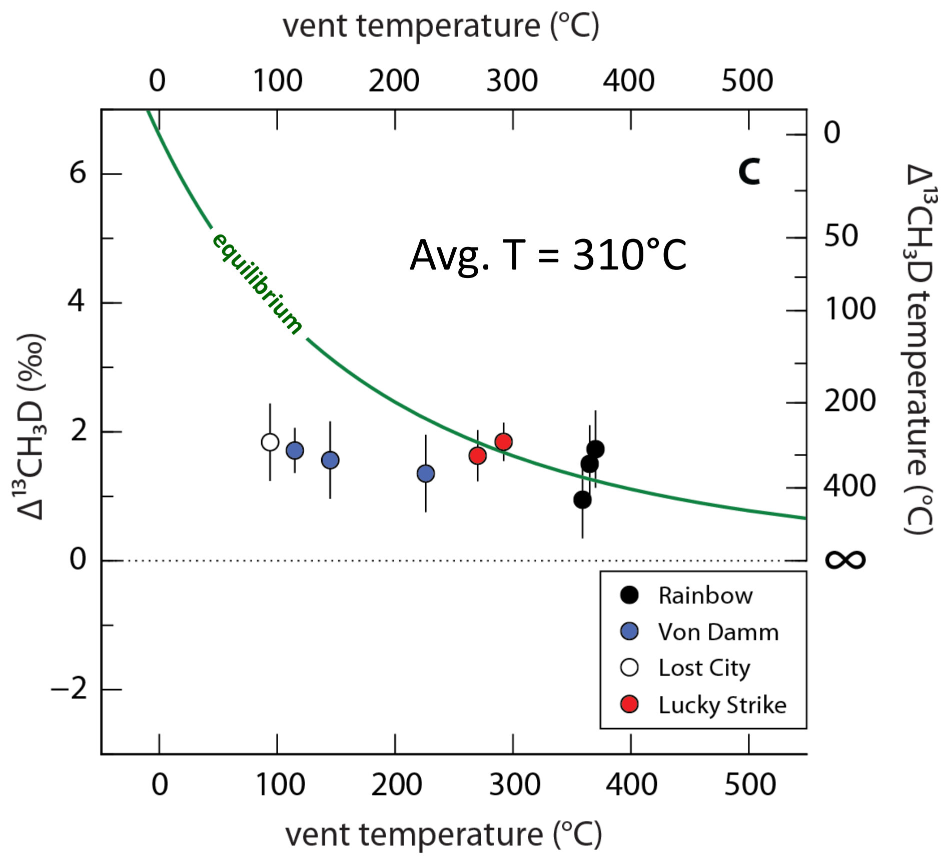
Ultramafic-Influenced Hydrothermal Systems





McDermott et al. (2015)
Proskurowski et al. (2008)
Charlou et al. (2002)

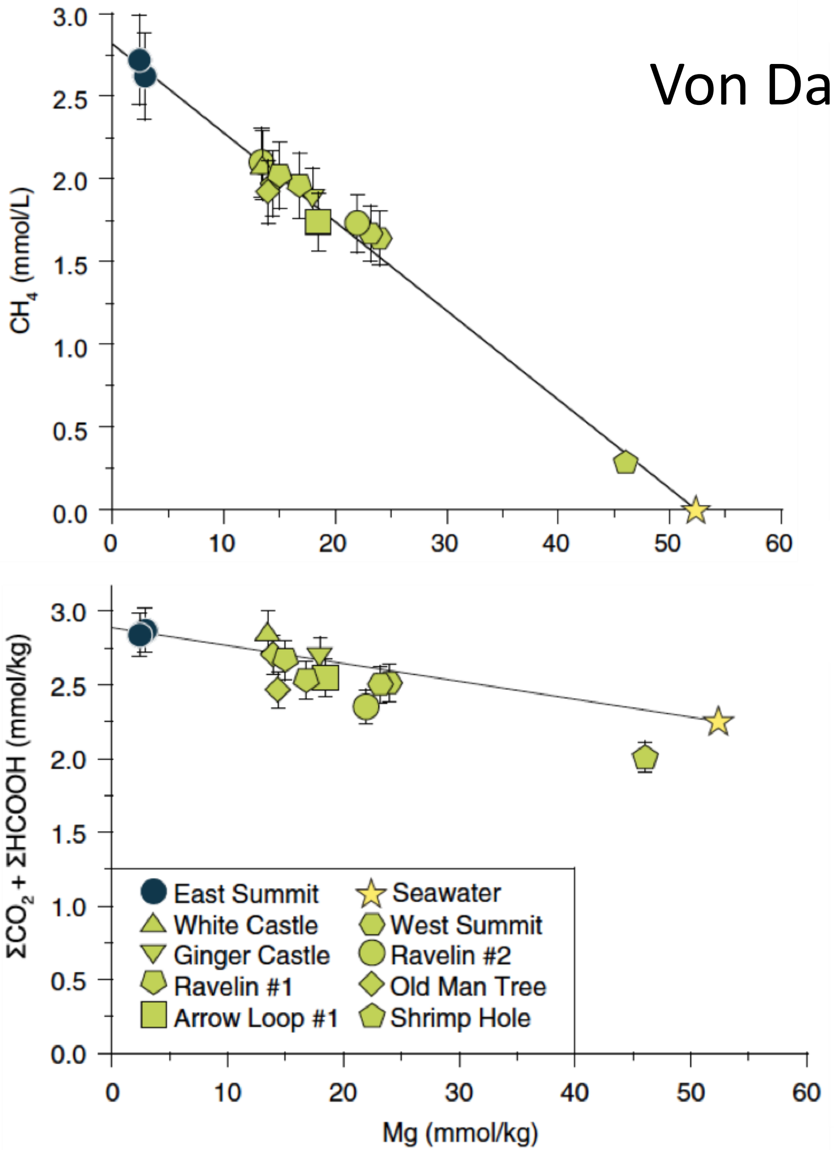
Clumped Isotope Geothermometry



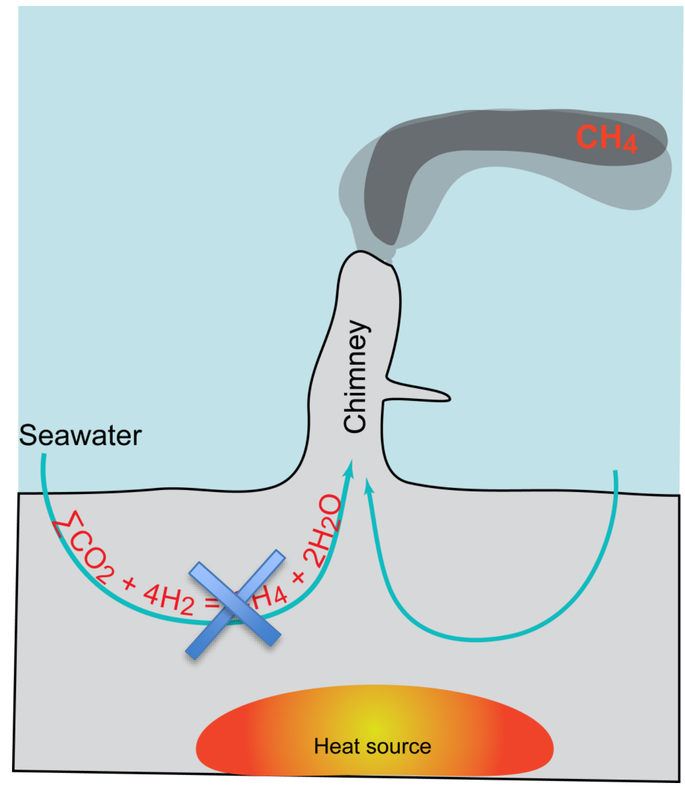
Wang et al. (2018)

$$^{13}CH_4 + {}^{12}CH_3D \rightleftharpoons {}^{13}CH_3D + {}^{12}CH_4$$

Von Damm Vent Field

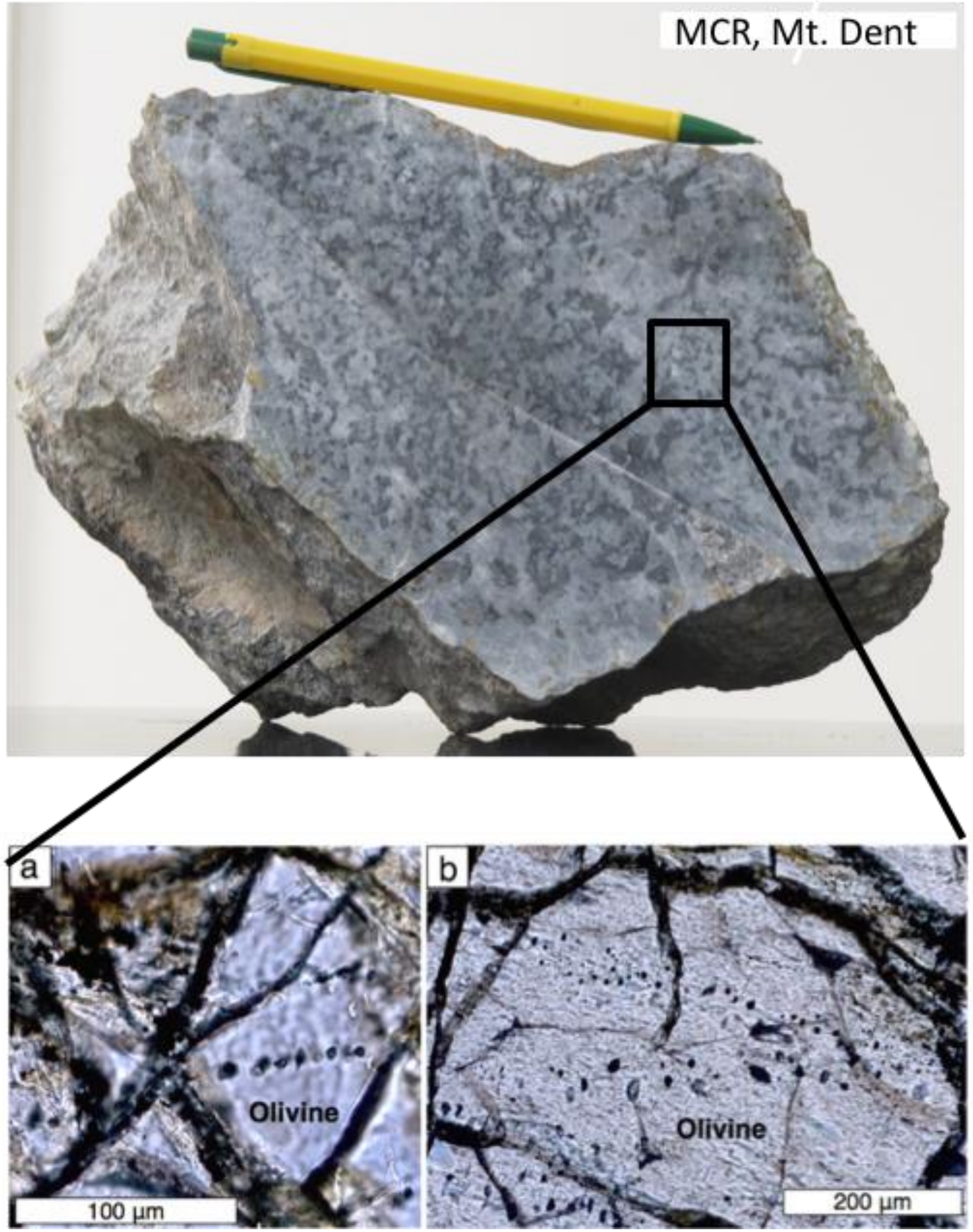


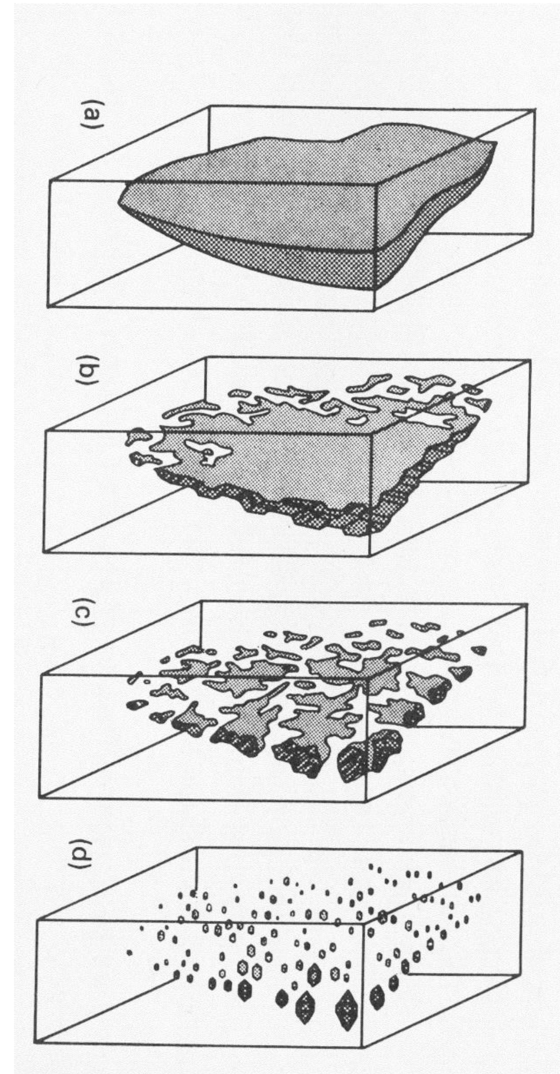
McDermott et al. (2015)



CH_4 is radiocarbon dead

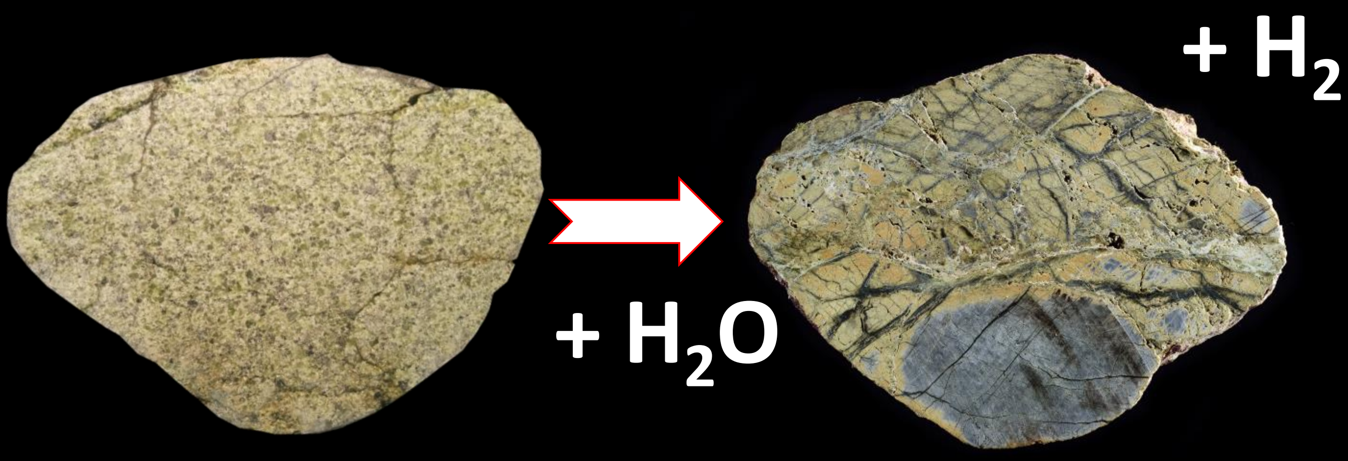
$\delta^{13}C_{CO2}$= +0.9‰ ±0.3
Same as seawater





Roedder (1979)

Serpentinization as a Source of Methane



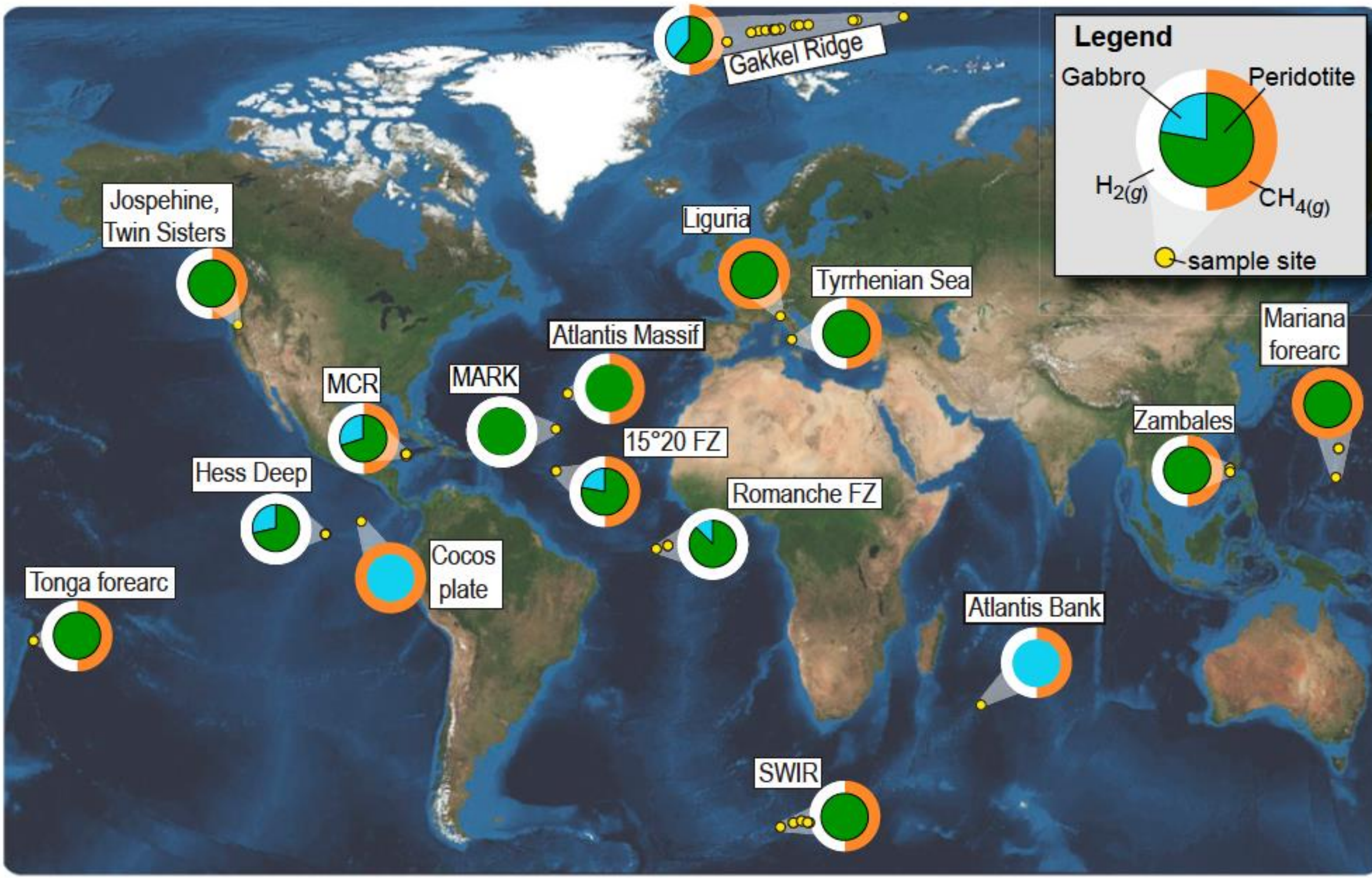
1. $2FeO + H_2O = Fe_2O_3 + H_2$
2. $4H_2 + \Sigma CO_2 = CH_4 + 2H_2O$

Hypotheses

1. Serpentinization within olivine-hosted fluid inclusions creates conditions conducive to abiotic CH_4 formation.
2. Same process takes place in peridotite and gabbroic rocks in distinct geologic settings.
3. CH_4 can be stored over geological timescales and released by dissolution or fracturing of the olivine host.

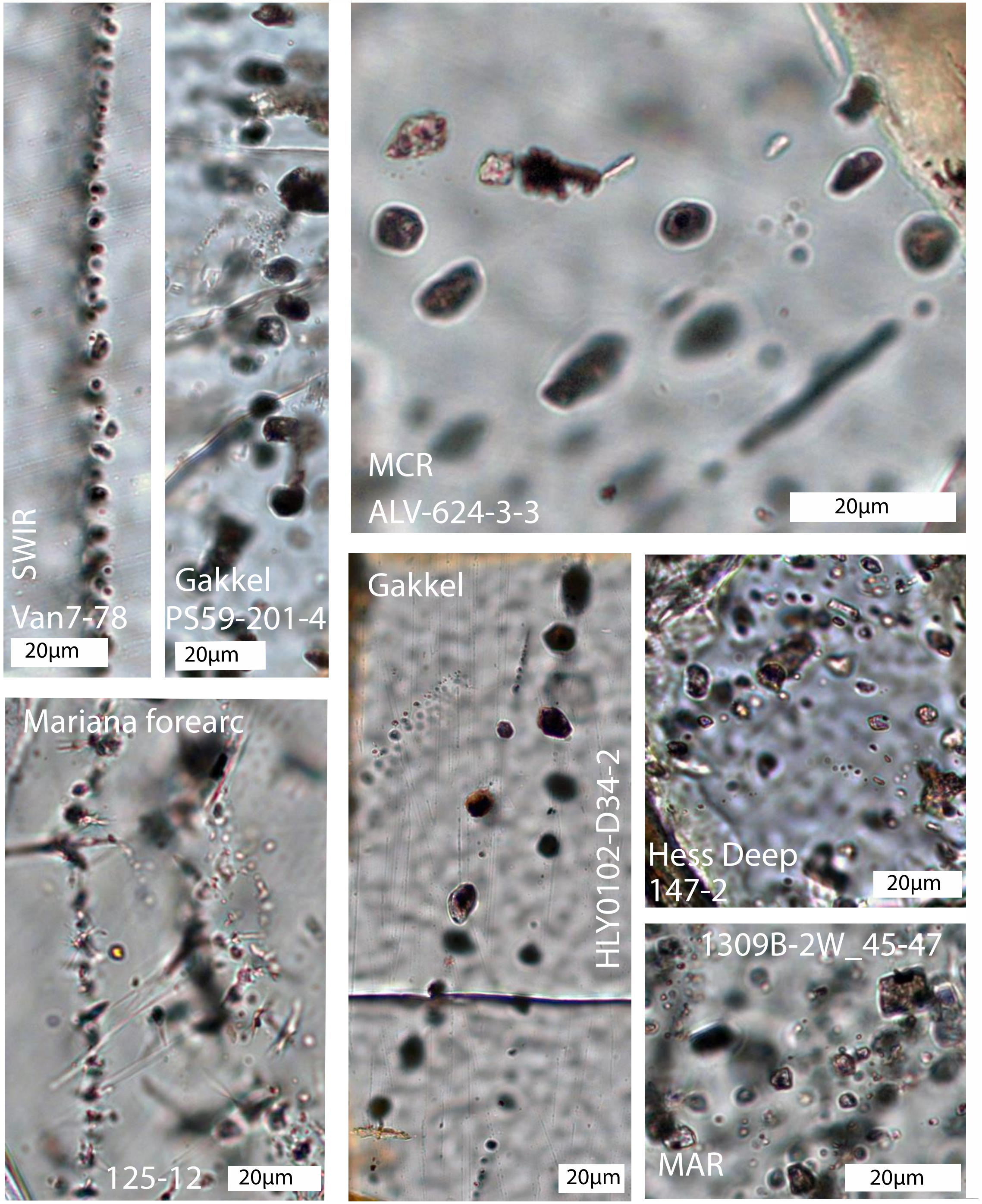
Approach

- survey of fluid inclusions in marine and continental mafic and ultramafic rocks
- examine inclusion contents with SEM, EMPA, and Raman
- analyze volatile contents in crushed rocks with GC-IRMS
- model reaction pathways with EQ3/6



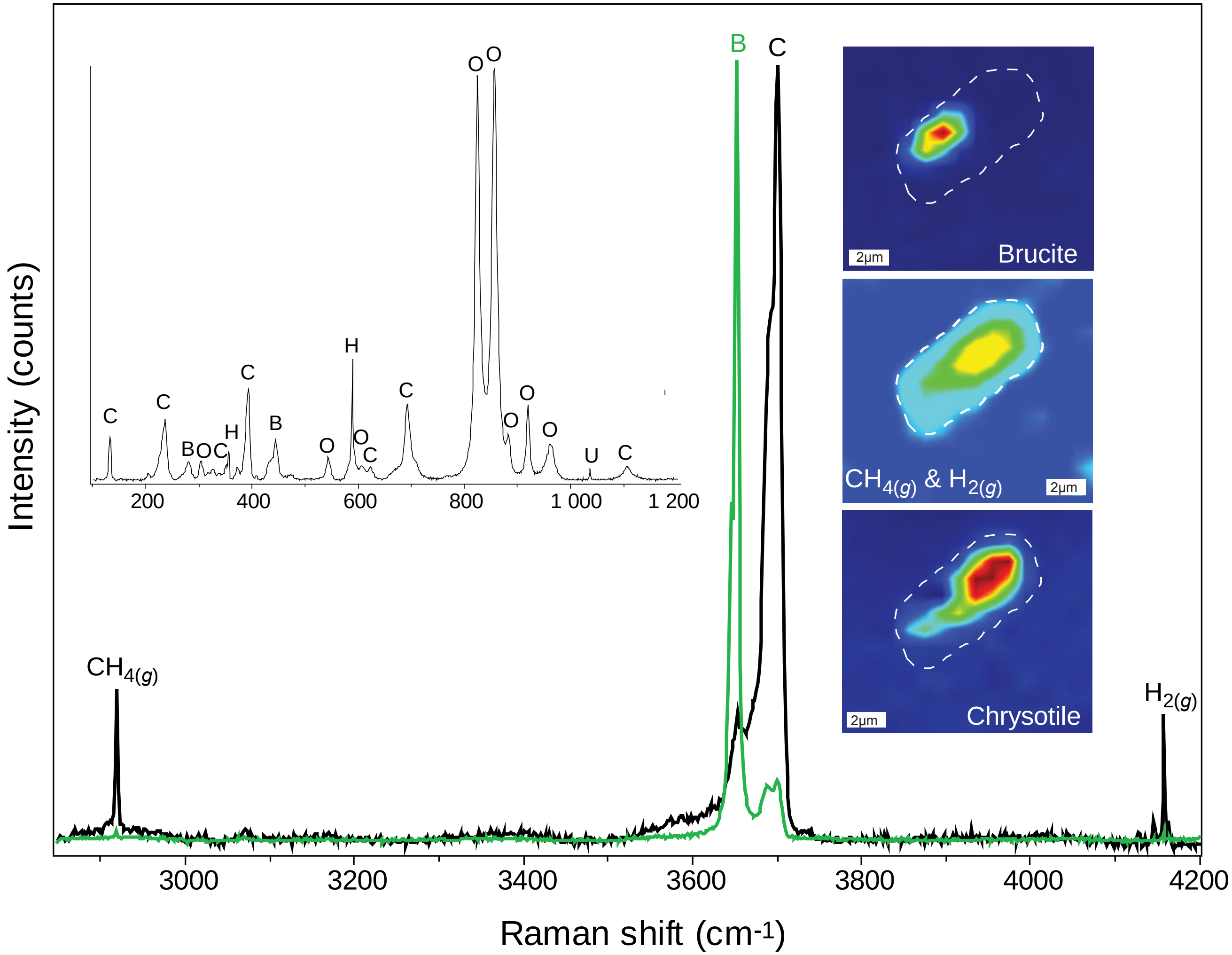
Klein et al. (2019)

- 78% of peridotite and all olivine-bearing gabbros examined contain olivine-hosted inclusions



Klein et al. (2019)

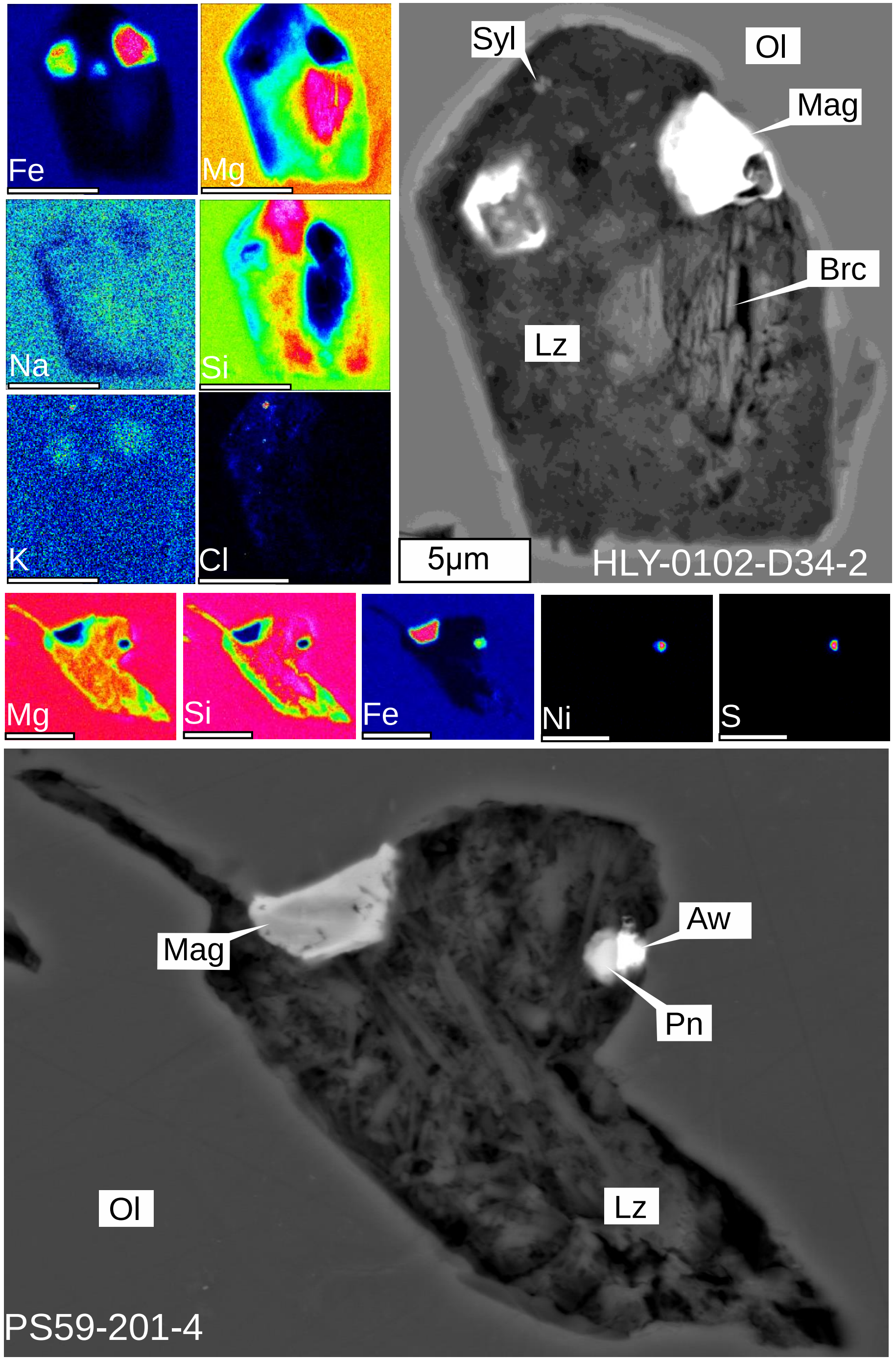
- Volatile contents:
  - $H_{2(g)}$
  - $H_{2(g)}$-$CH_{4(g)}$
  - $CH_{4(g)}$



- $P_{CH4(avg)}$ = 11.5 MPa

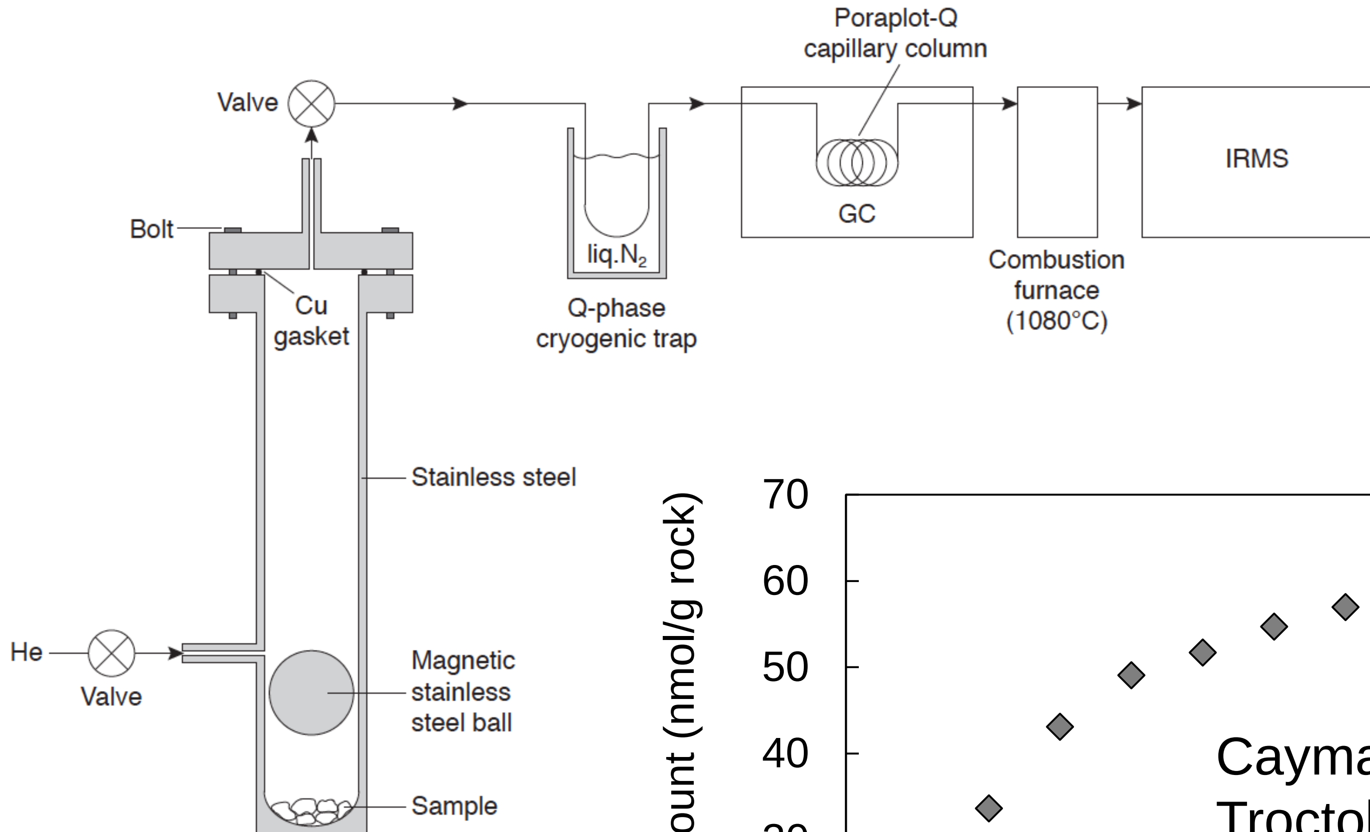
→ 5 Pg CH_4 globally

Klein et al. (2019)

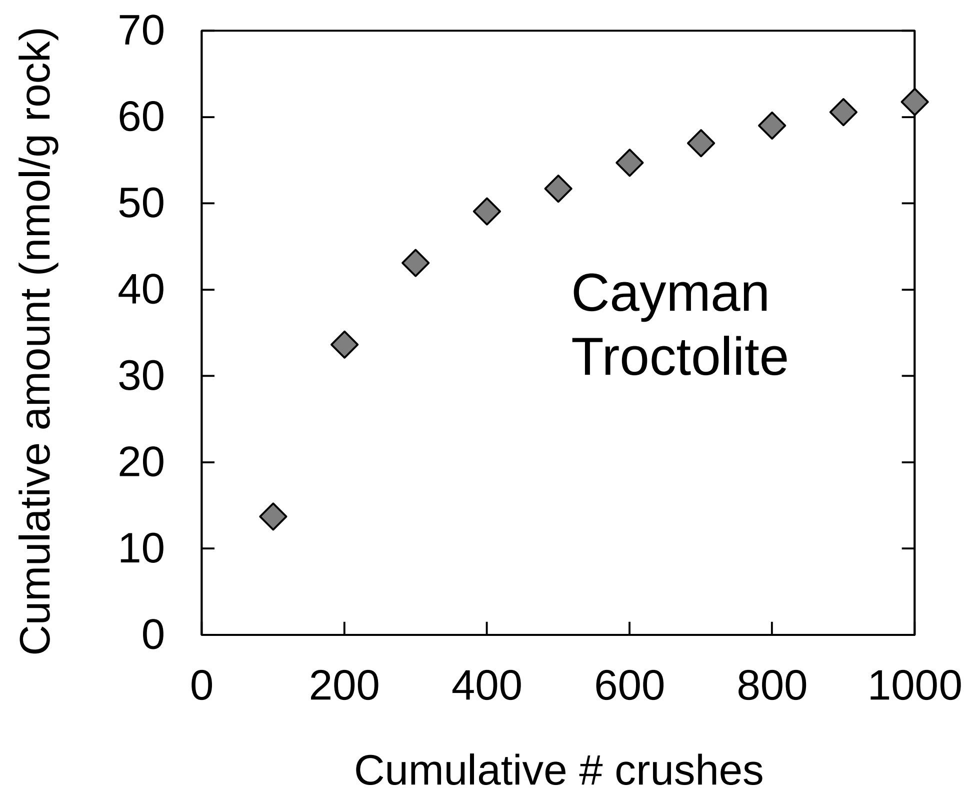


Fe
Mg
Na
Si
K
Cl
Syl
Ol
Mag
Brc
Lz
5μm
HLY-0102-D34-2
Mg
Si
Fe
Ni
S
Mag
Aw
Pn
Ol
Lz
PS59-201-4

Whole-rock CH_4 abundance

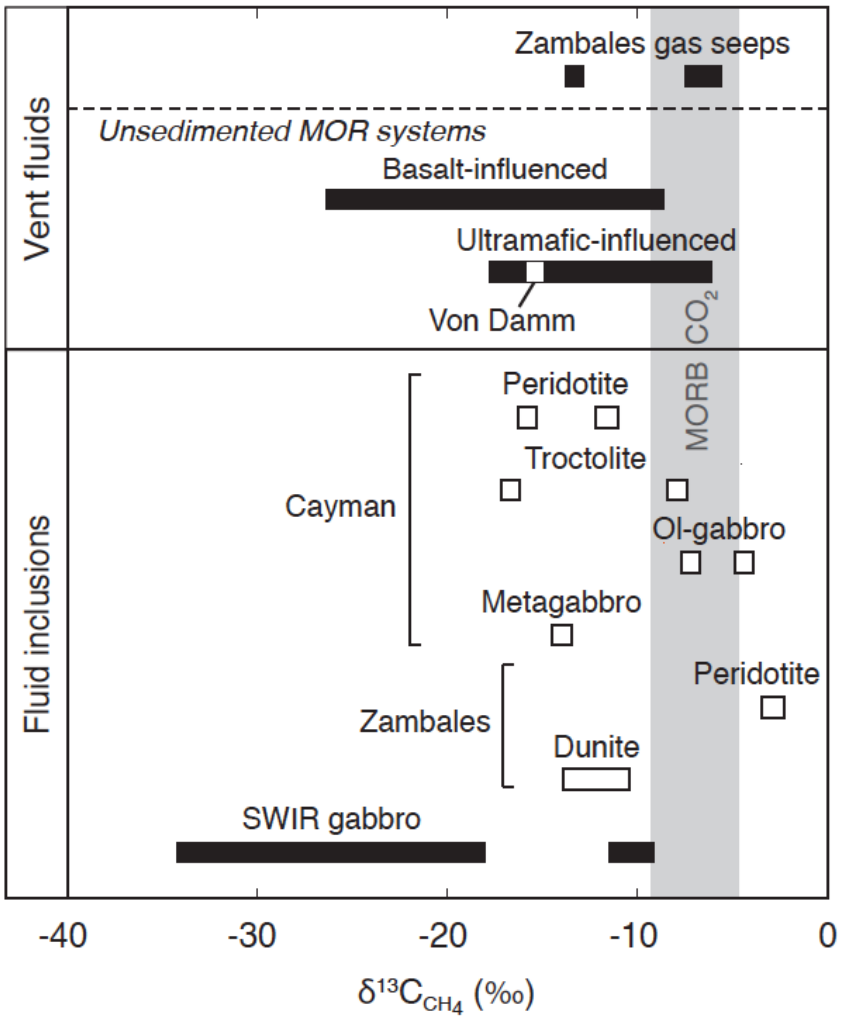


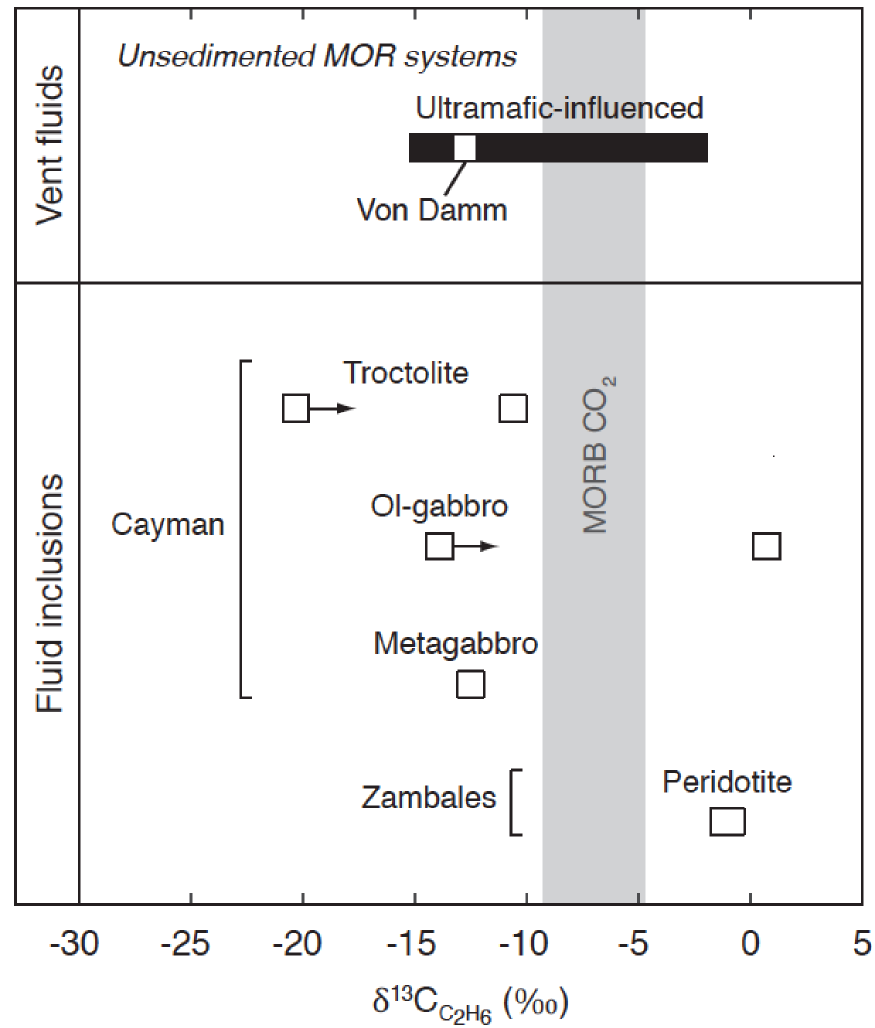
	nmol/g rock
Upper mantle	4-10
Lower crust	60-313



Grozeva et al. (2020)

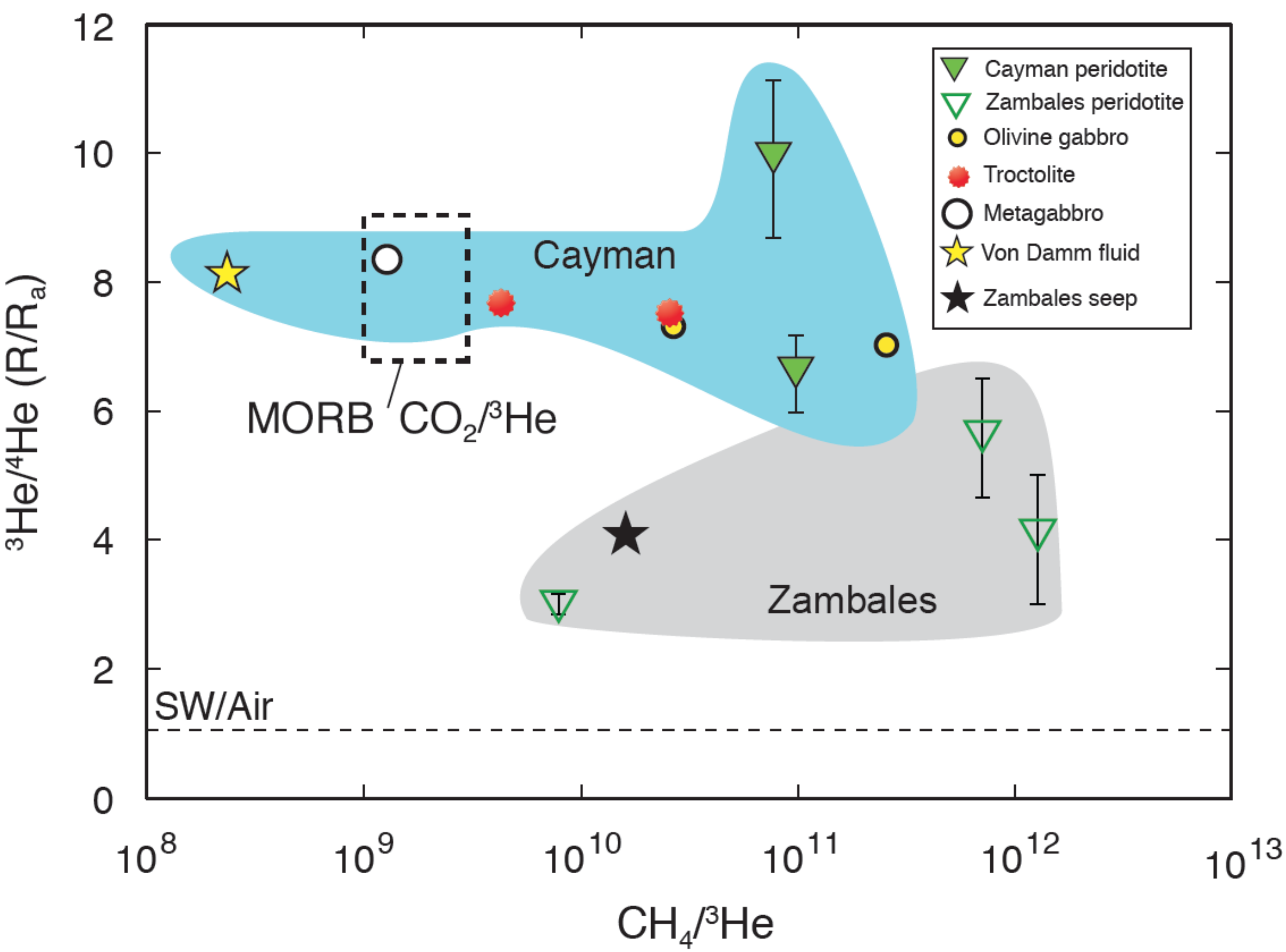
Carbon isotopic compositions





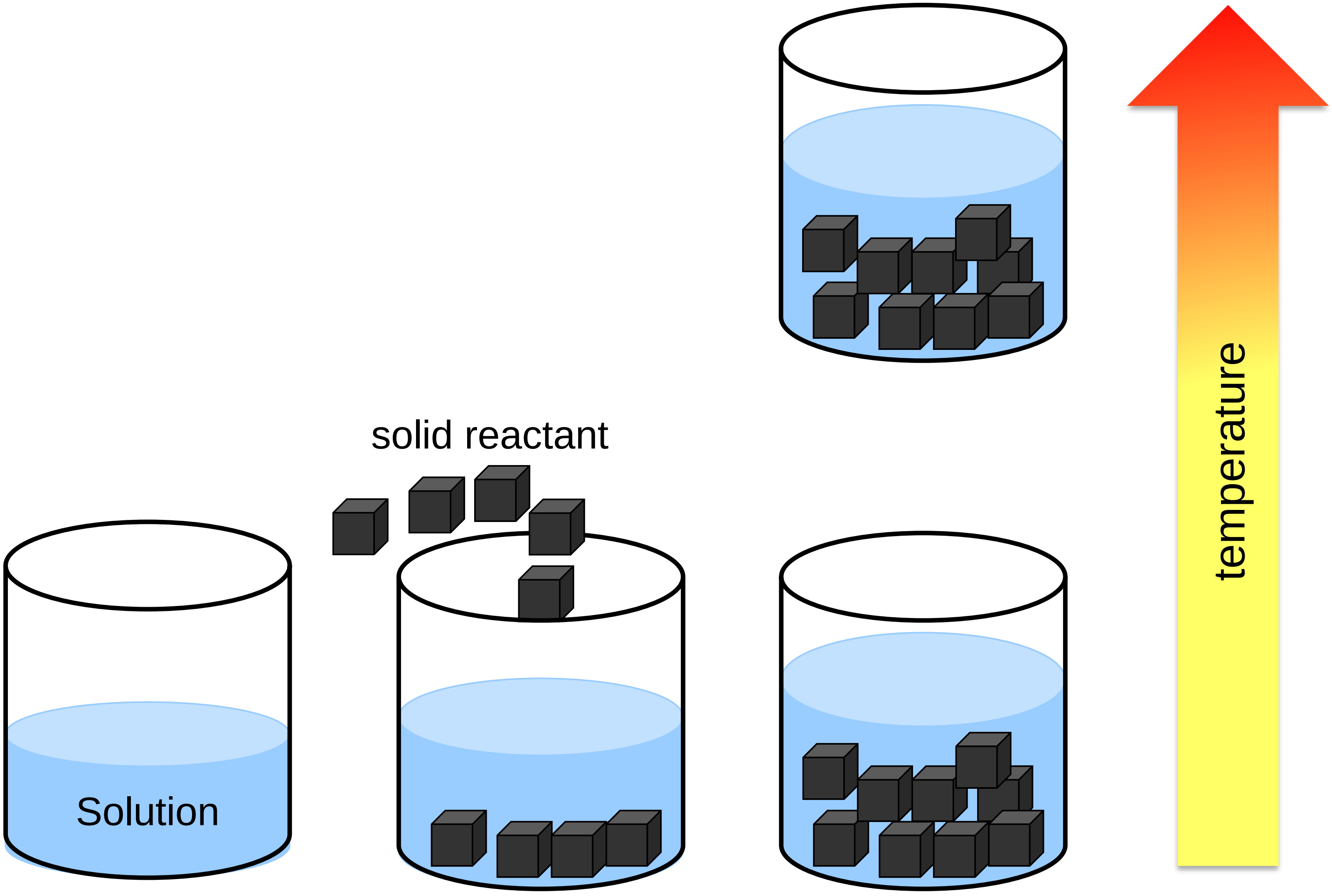
Grozeva et al. (2020)

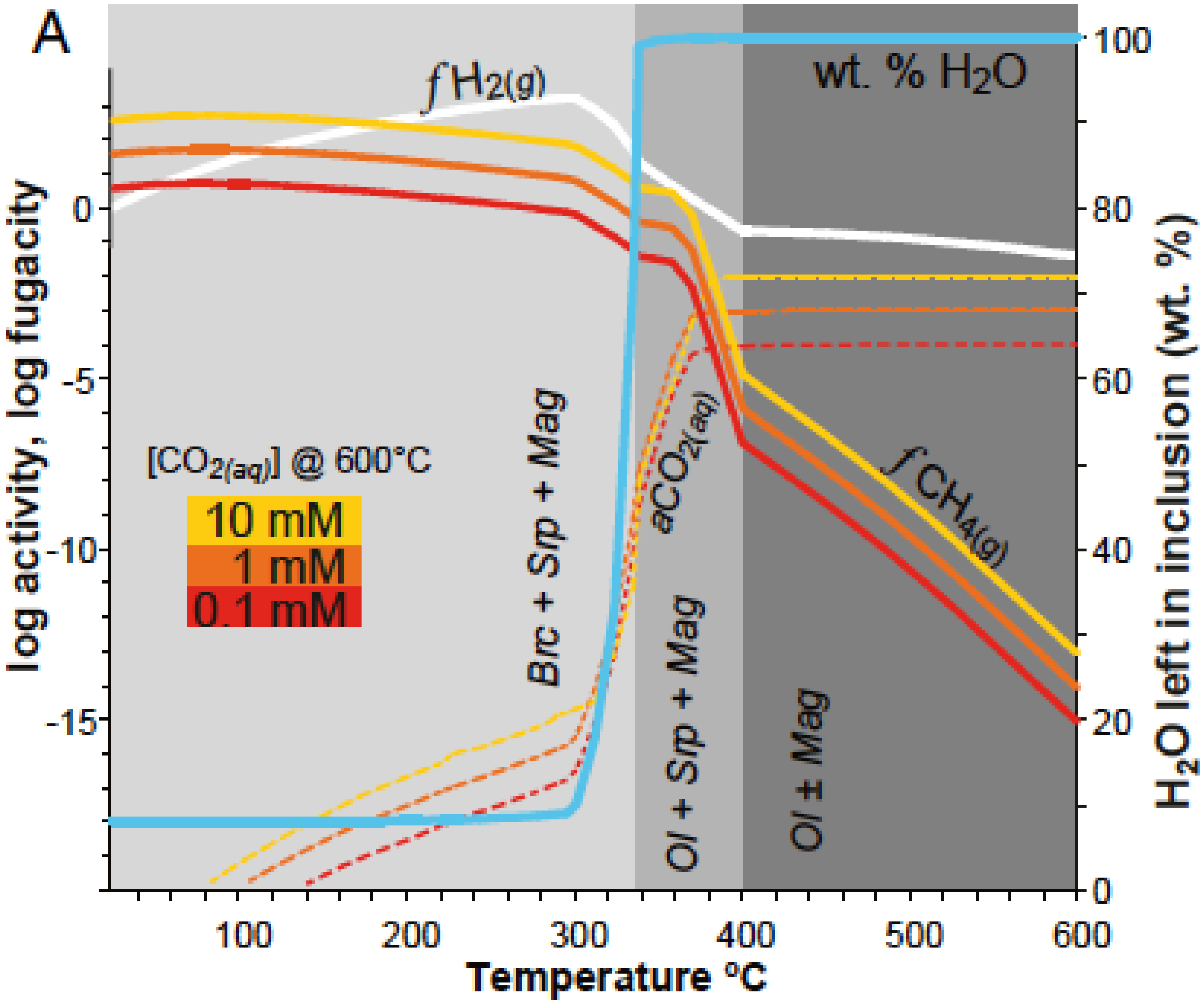
Additional data from Charlou et al. (2010), McDermott et al. (2015), Kelley & Früh-Green (1999, 2001), Vacquand et al. (2018)



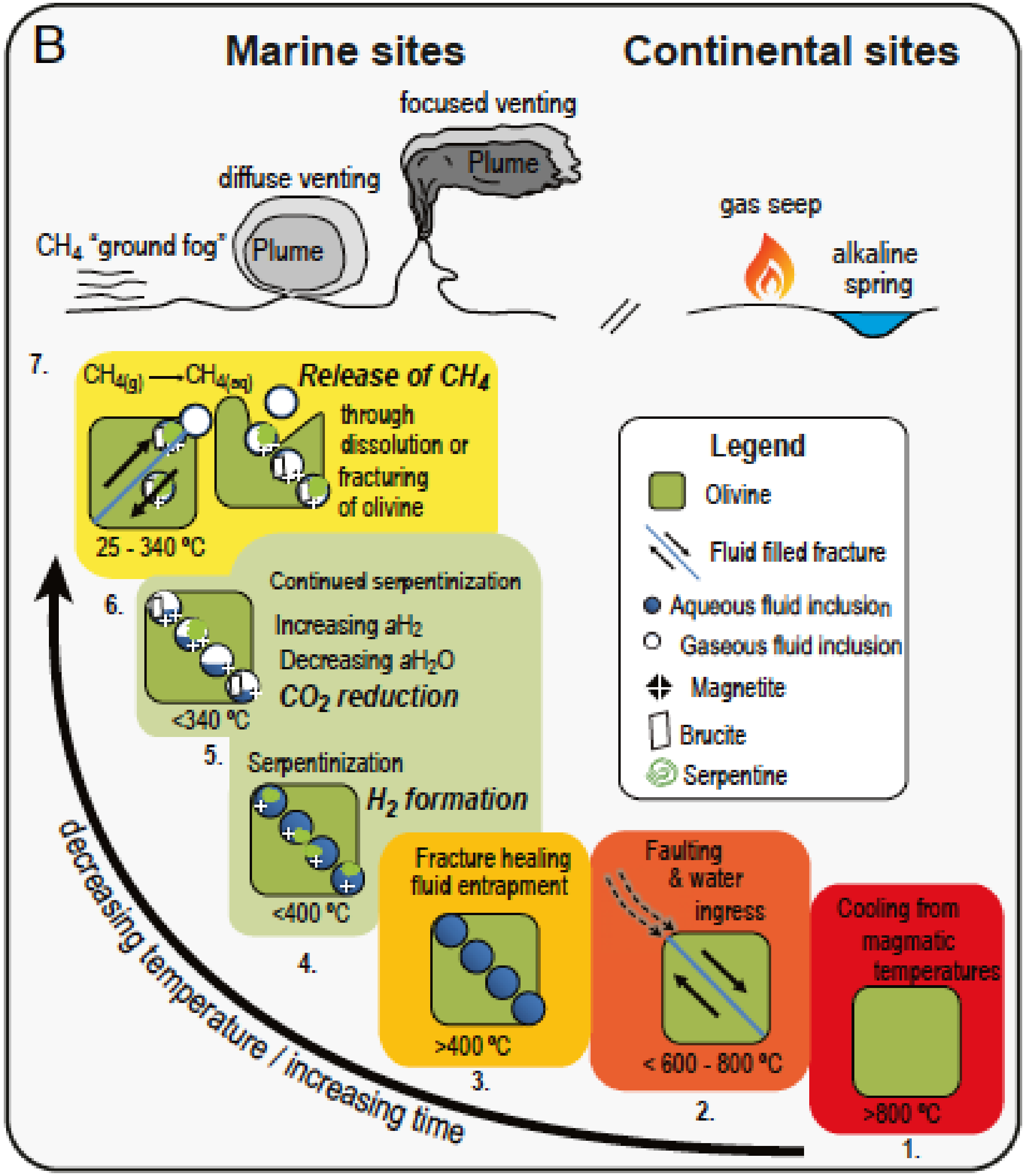
Grozeva et al (2020)

Equilibrium modeling using EQ3/6 (Wolery, 1992)





Klein et al. (2019)



Klein et al. (2019)

Questions

- What is (are) the carbon source(s)?
- What are the clumped isotopologues of CH_4 in olivine-hosted fluid inclusions?
- How much CH_4 is there in olivine-hosted fluid inclusions in intermediate to fast-spreading crust, if any?
- What would happen during subduction of CH_4-bearing fluid inclusions?
- Is there CH_4 in olivine-hosted fluid inclusions on other planetary bodies?

Acknowledgments

- Henry Dick, Karmina Aquinho, Emmanuel Codillo, Mark Kurz
- IODP, captains and crews of JOIDES Resolution, R/V Atlantis, R/V Knorr, R/V Melville, CDC Healy, F/S Polarstern, DSV Alvin
- Curators at the College Station, Bremen, and Kochi core repositories
- NSF