Differentiation of Biotic and Abiotic CH_4: Lessons from terrestrial analogs

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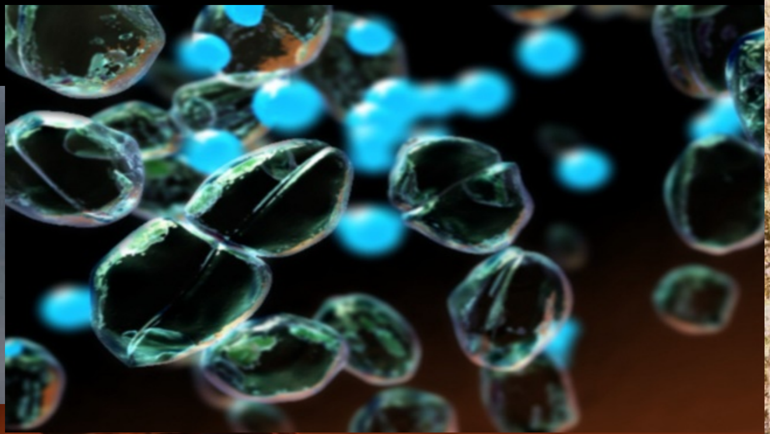
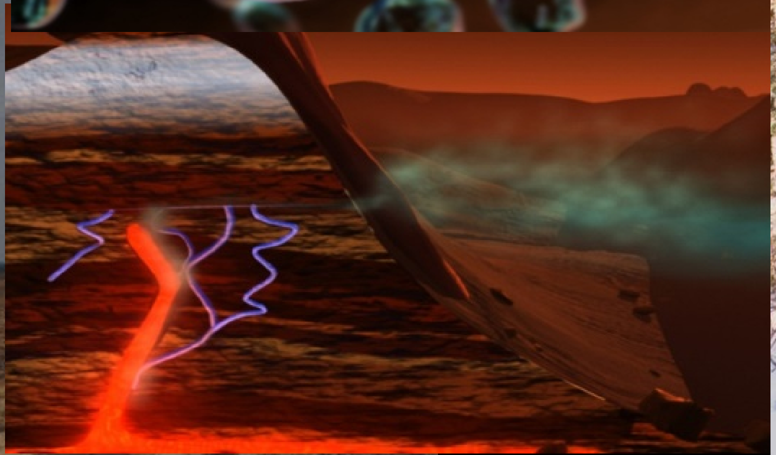


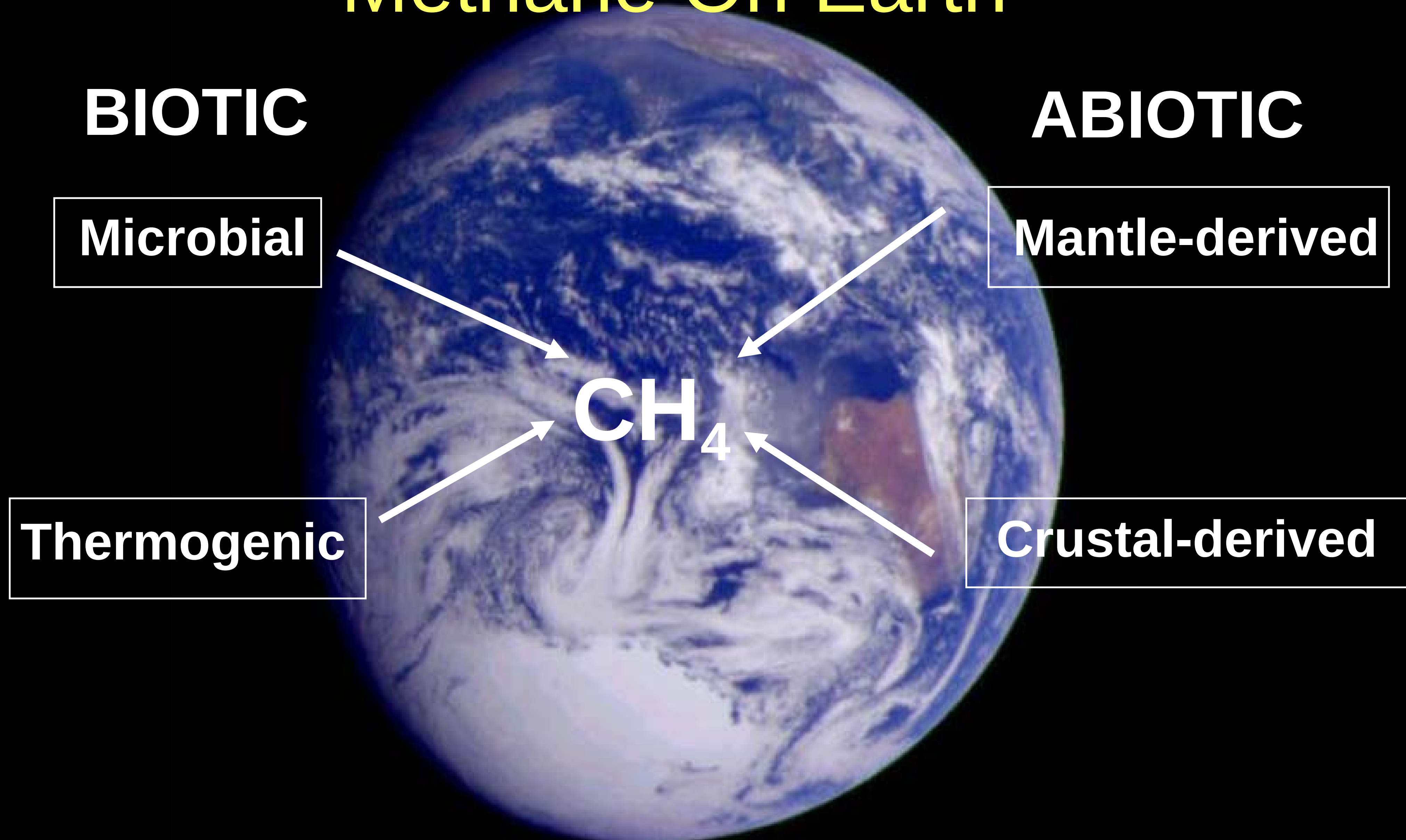


What can we learn from Earth analogs about differentiation?

Outline

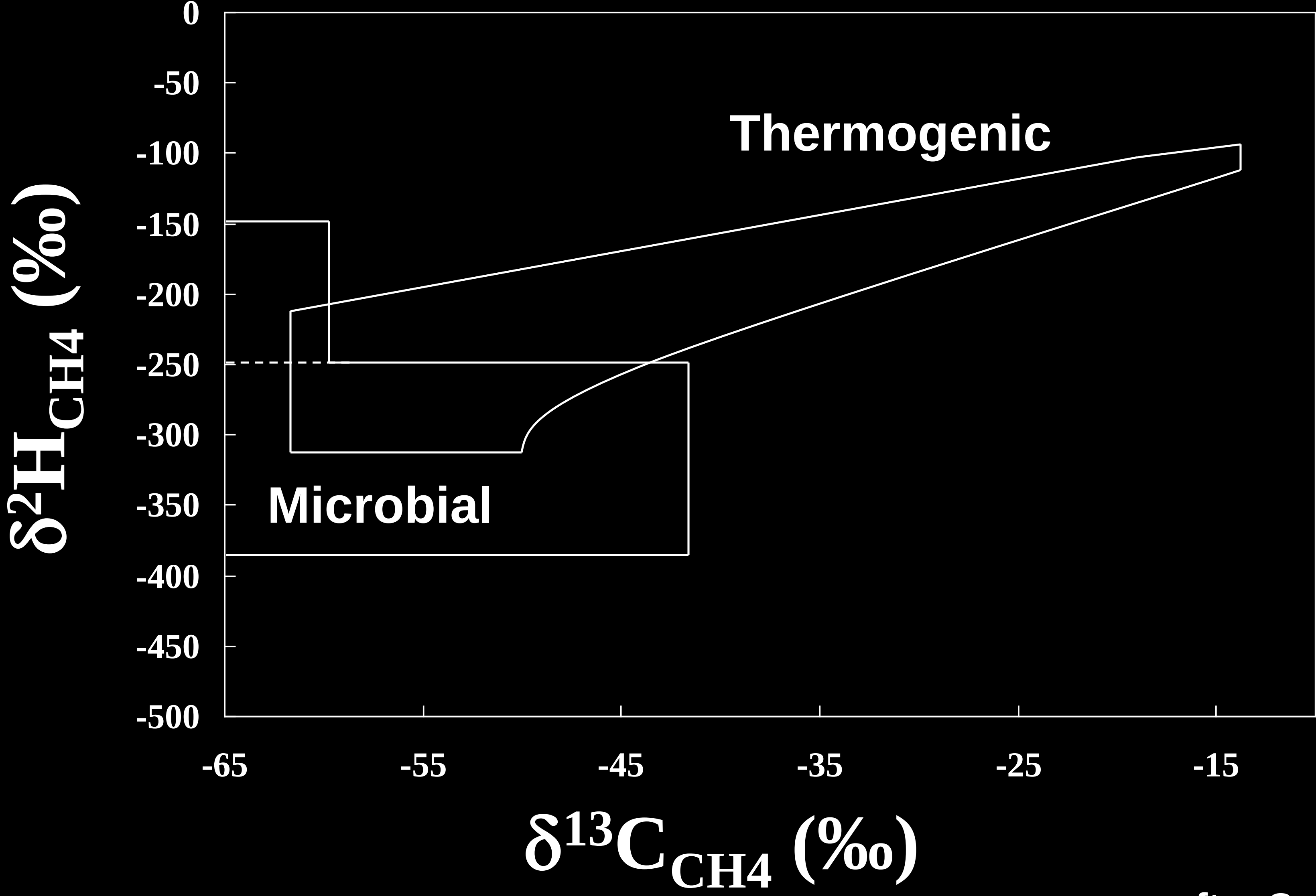
- Overlapping Definitions and Signatures
- Success requires multiple lines of evidence, and contextual evidence
- New technologies (e.g. clumped isotopologues, PSIA) enabling a renaissance in the field
- For Mars - helps to consider the Parsimonious approach
- Test case from Earth analogs for differentiating biotic and abiotic CH_4
- Conclusions

Methane On Earth



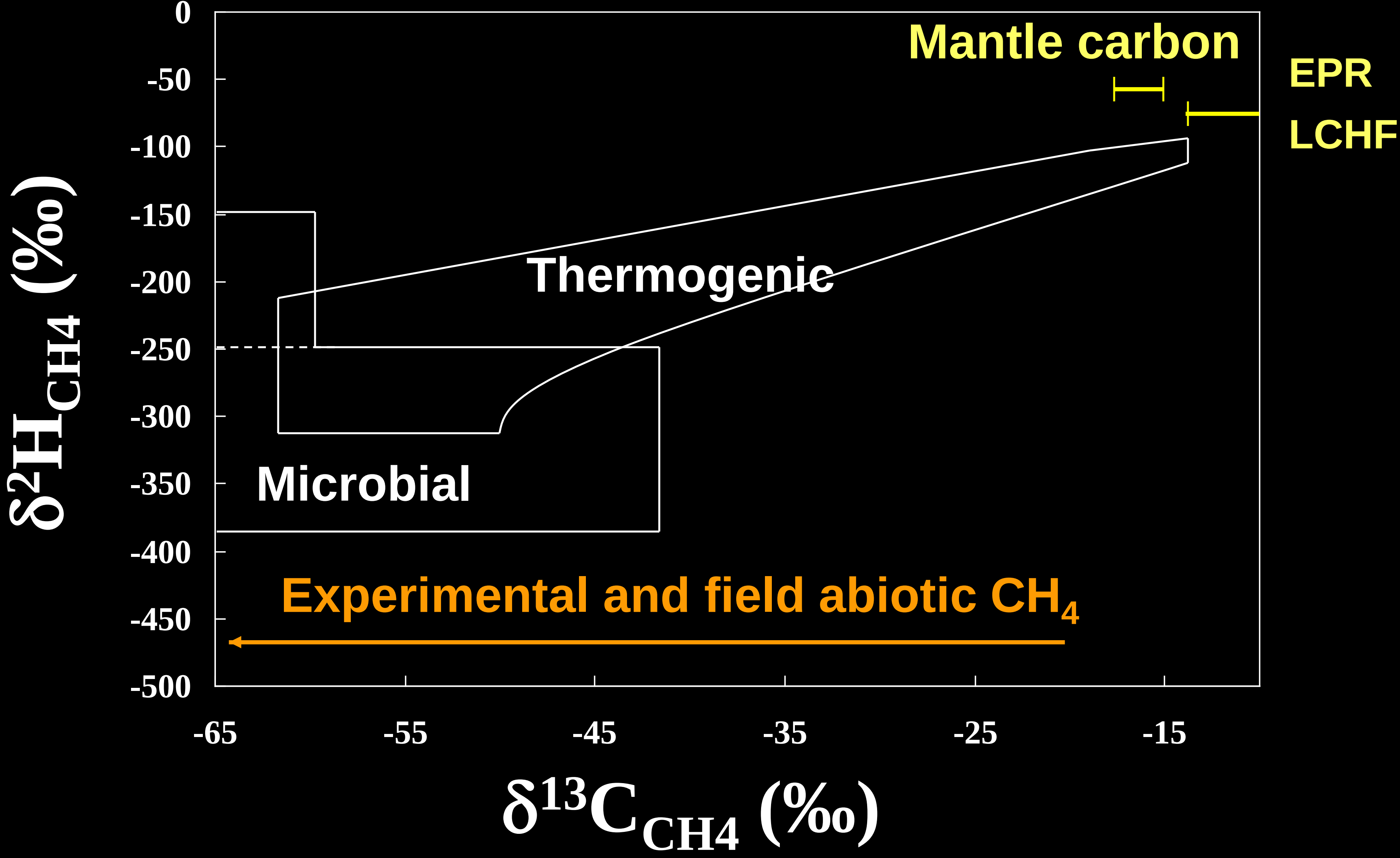
Many overlapping definitions

Overlapping $\delta^{13}C$ Signatures - *Biotic*



after Schoell (1988)

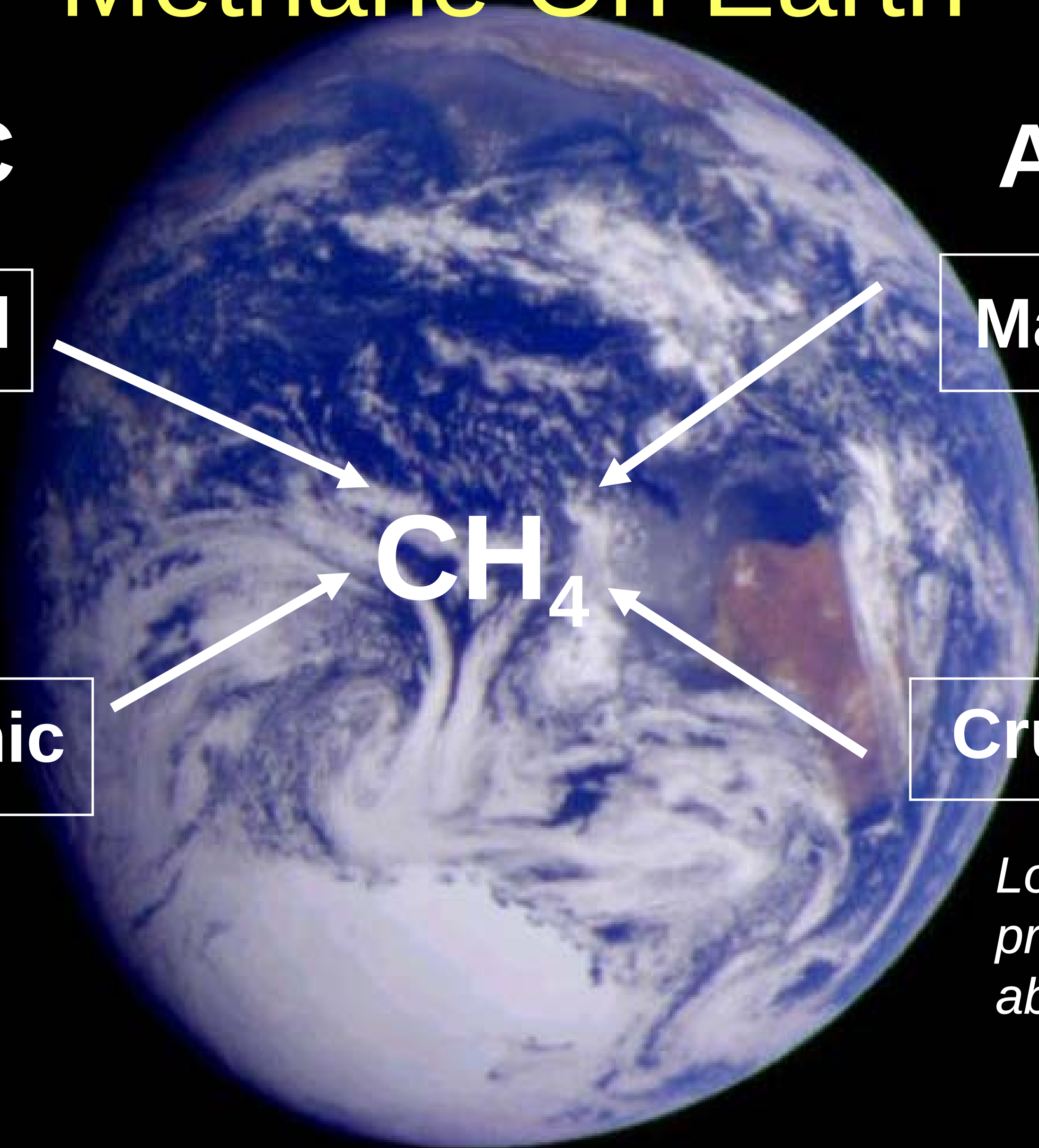
Overlapping $\delta^{13}C$ Signatures - *Abiotic*



Biotic vs Abiotic CH_4

- $\delta^{13}C$ (or $\delta^{2}H$) value alone not diagnostic
- Abiotic CH_4 will have a $\delta^{13}C$ value that reflects the local carbon source
- Enriched – if mantle-derived
- Wide possible range of $\delta^{13}C$ values in crustal environments
- Mantle-derived = abiotic
- Abiotic is not necessarily mantle-derived

Methane On Earth



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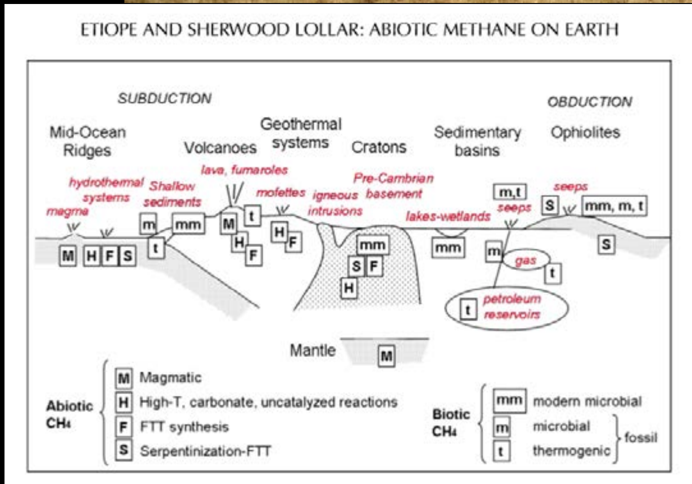
Multiple Lines of Evidence

- 1. Isotopic signatures: including C & H source signatures and reaction products
- 2. Associated species (DIC, H_2O, H_2, higher hydrocarbons, N- or S- compounds)
- 3. Conservative tracers (e.g. noble gases)
- 3. Geologic and hydrogeologic context
- 4. Evaluate end-members and mixing
- 5. Post-genetic alteration and sinks
- 6. New breakthrough technologies (e.g. clumped isotopologues)

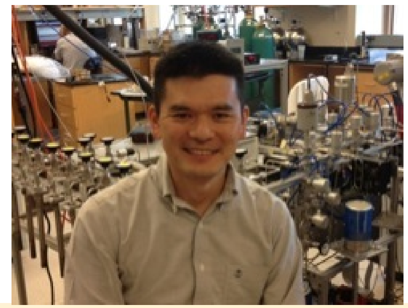


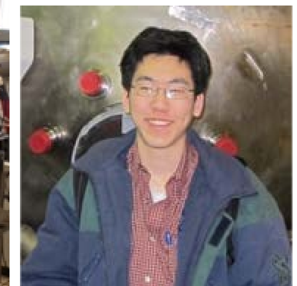
Ed Young in his lab.

SOURCE CODE: The Methane Race

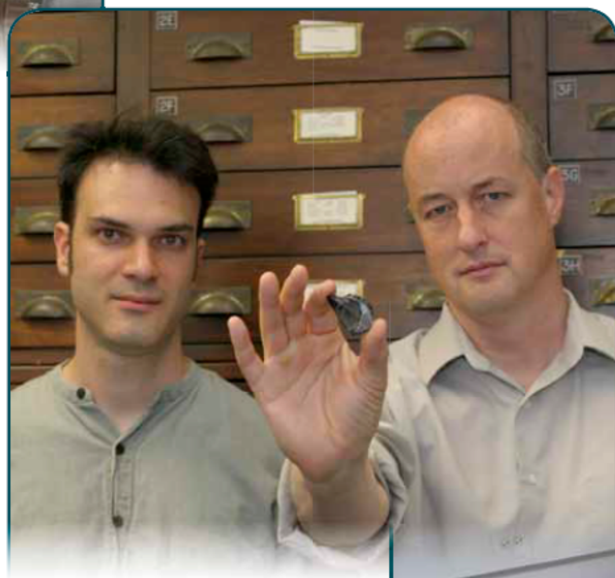
Researchers are developing instruments to determine where molecules come from — revealing everything from the origins of natural gas on Earth to whether there is life on Mars.

Shuhei Ono & D.T. Wang - MIT

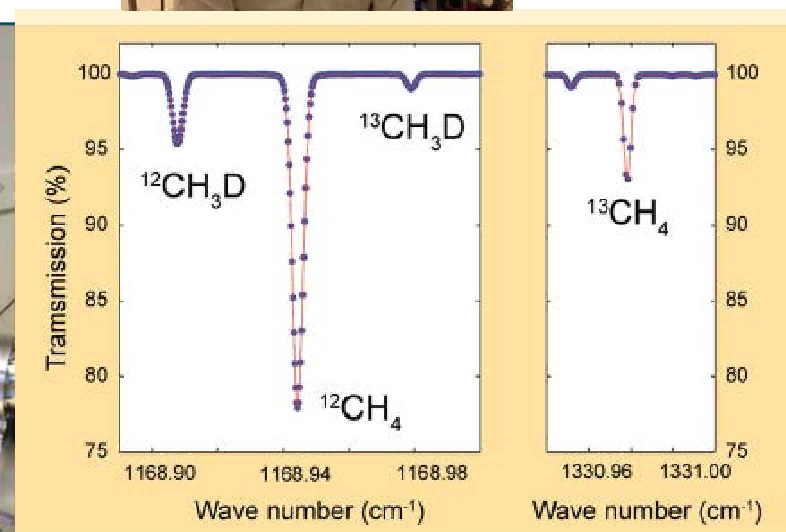




Caltech geochemists Rob Eagle (left) and John Eiler used carbon dioxide isotopologues from dinosaur teeth to determine the body temperature of sauropods.



Doug Rumble stands behind a Nu Instruments' mass spectrometer. Rumble and Ed Young have asked Nu to build a new instrument, similar to the device shown here but with a magnet that is twice as big as usual.



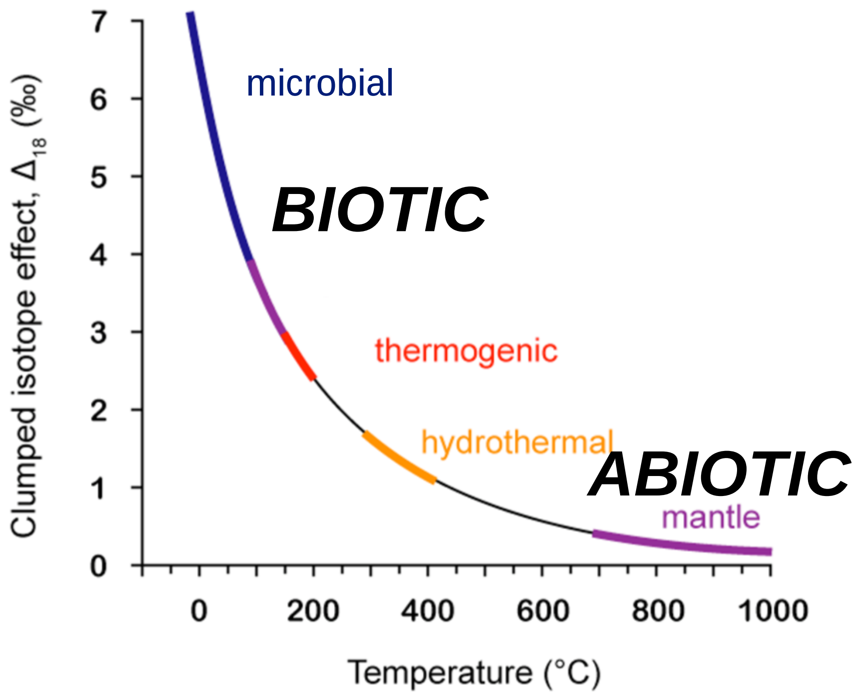
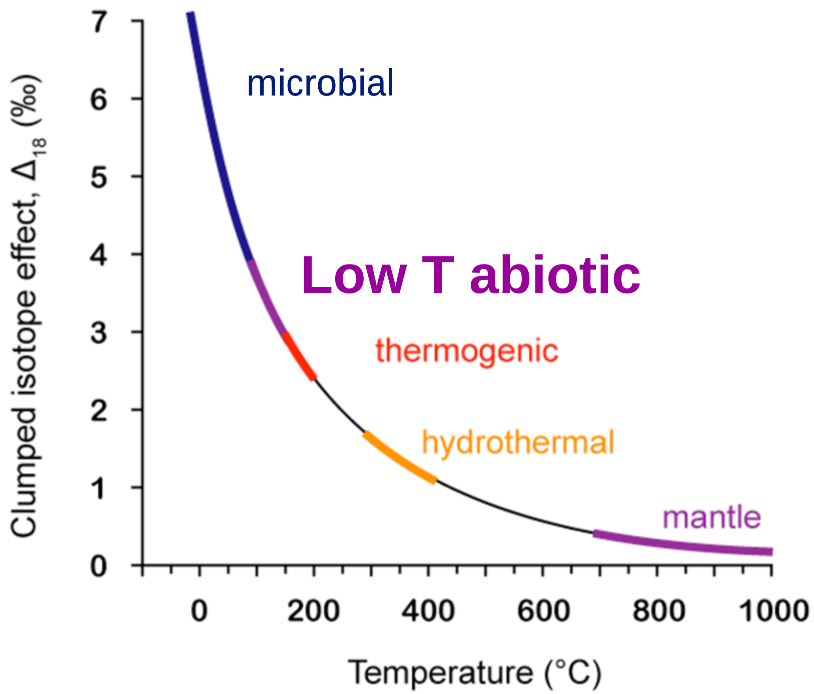


Figure 2: Methane clumped isotope thermometry scale.

The Δ_{18} value measures the deviation of the ratio $^{13}CH_3D/^{12}CH_4$ from that expected for a statistical (i.e., high temperature) distribution. For methane clumped isotope system, Δ_{18} equal to $(K\text{-}1)\times1{,}000$, where K is the equilibrium constant for isotope exchange reaction (R2). Also shown in the figure are T-Δ_{18} relationships expected for various methane sources based on “typical” ranges of formation temperatures.

A new geothermometer for methanogenesis based on $^{13}CH_3D$:



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A new geothermometer for methanogenesis:

- Deeper levels of information available

3 complications and/or opportunities

- Low to moderate T Abiotic organic synthesis from water-rock reaction
- Mixing (e.g. $^{12}CH_2D_2$)
- Kinetic effects of microbial methanogenesis vs. equilibrium geothermometry (*e.g. Wang et al., 2015*)

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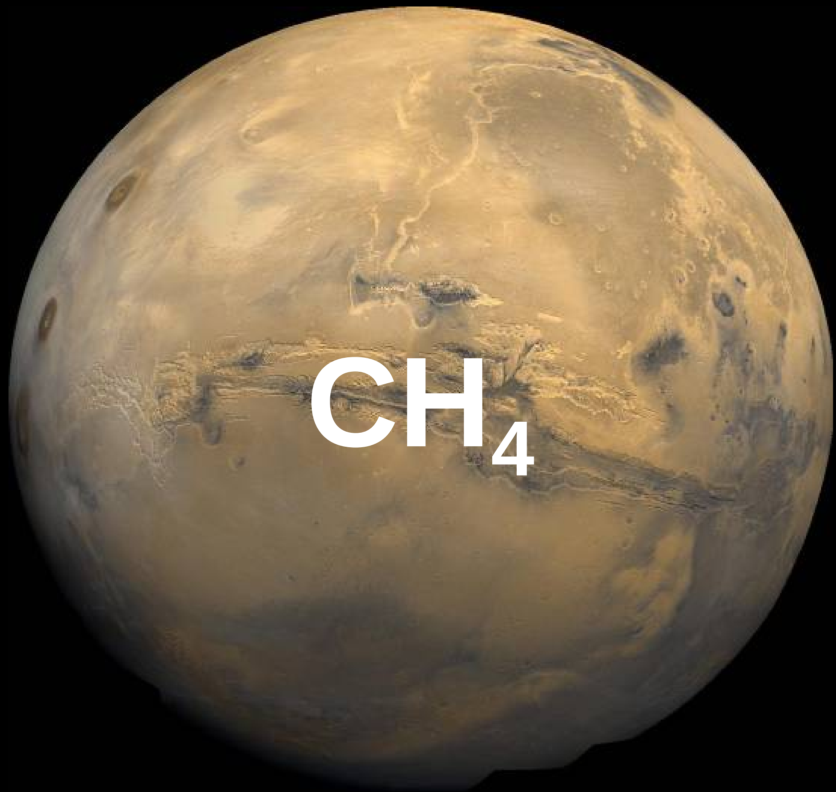
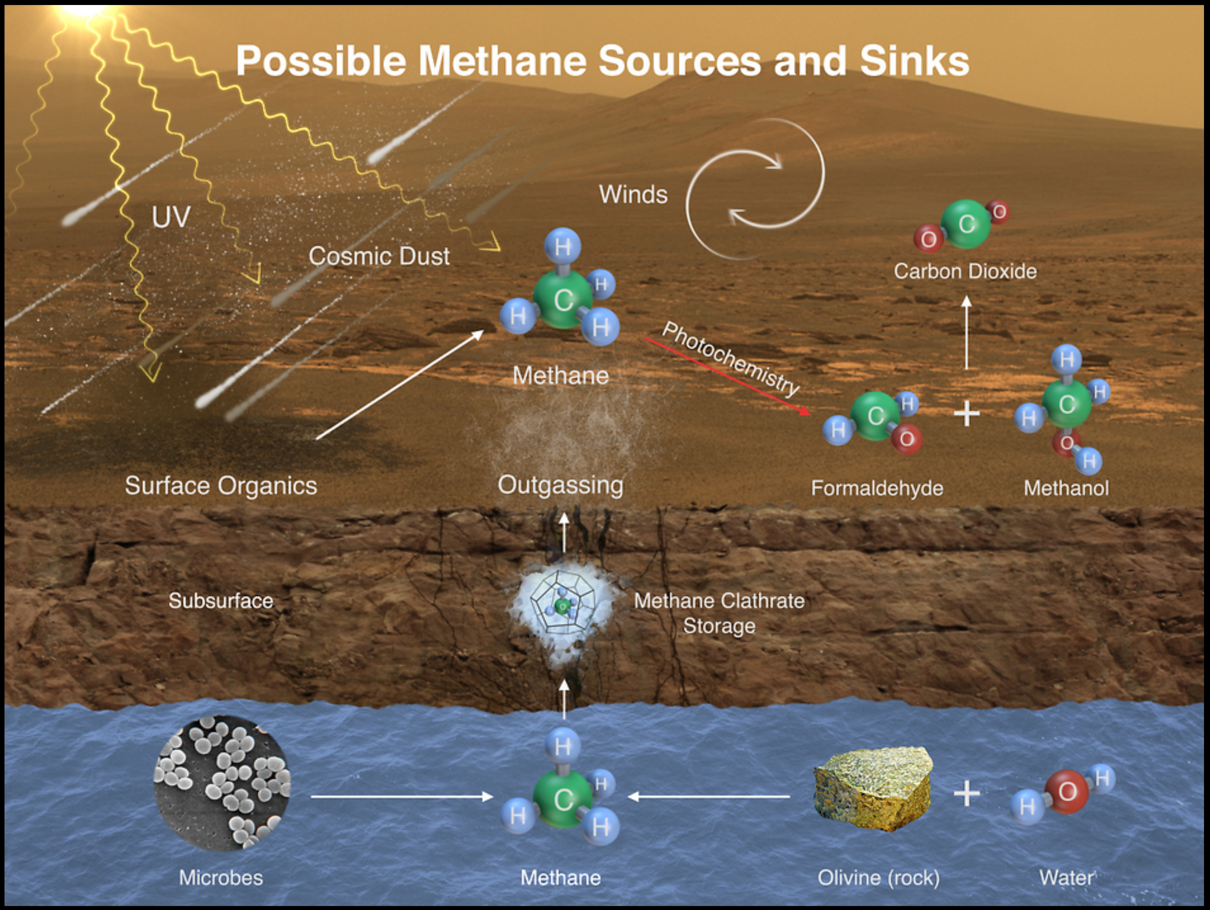
Origin of Methane On Mars?

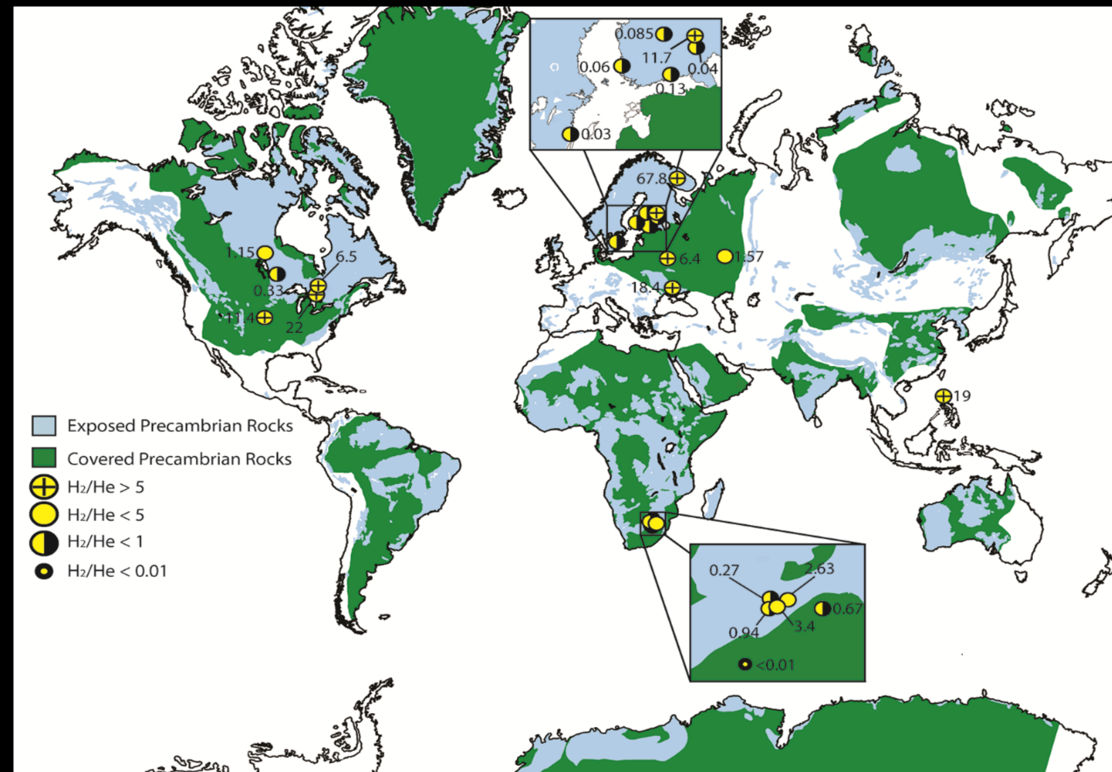




Parsimonious approach – what measurement(s)?

Parsimonious approach

- Associated Gases
- 1. H_2 levels
- 2. Ethane (C_2H_6) levels
- 3. CH_4/H_2 and CH_4/C_2H_6 (CH_4/C_2^+) ratios
- Conservative noble gases
  - constrain origin & sinks
  - constrain production rates & flux for reactive reduced gases (e.g. H_2/He)



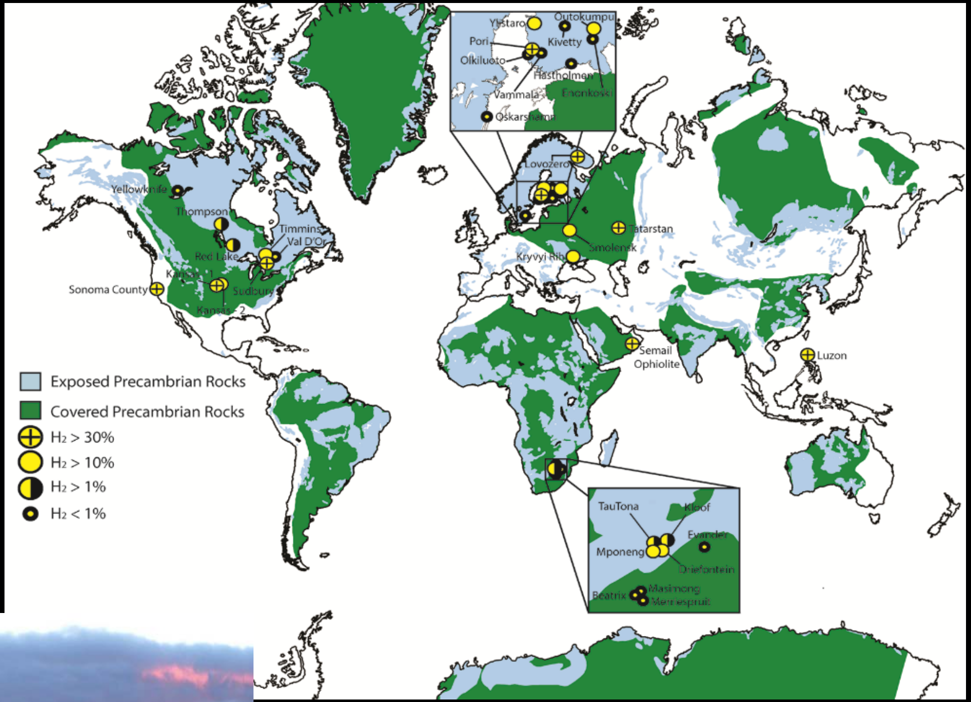
Sherwood Lollar et al., 2014 Nature

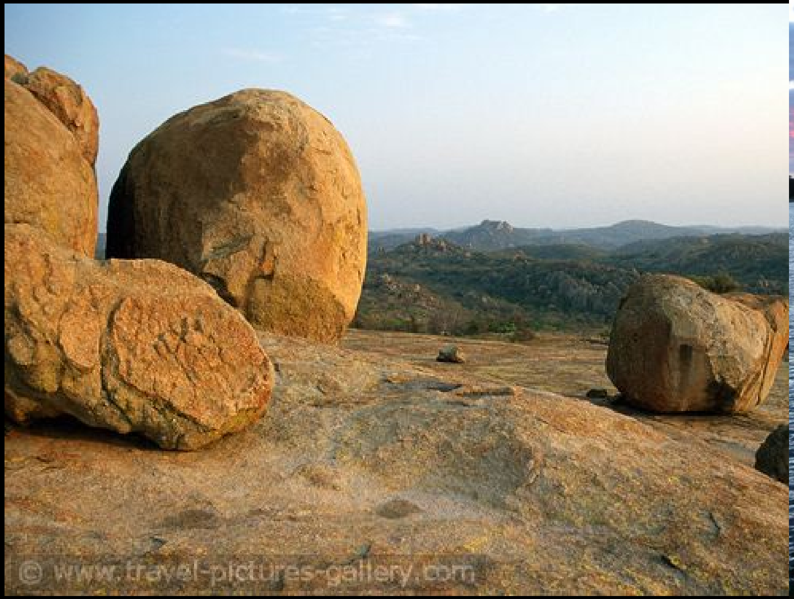
Associated Gases (gas ratios)

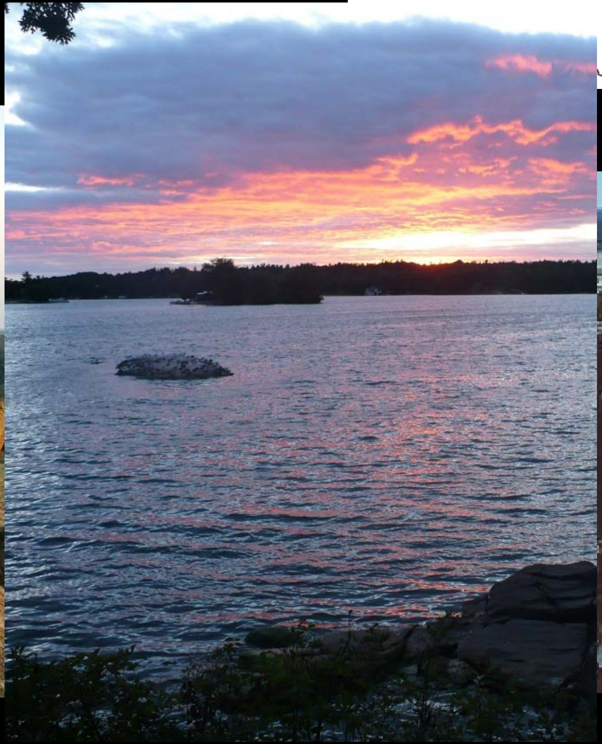
- 1. Abiotic end-members from low T water-rock reaction (e.g. serpentinization) are characteristically H_2-rich
- 2. Microbial metabolisms (sulfate-reducers, methanogens) drive down H_2 concentrations
- 3. Abiotic end-members from low T water-rock reaction (e.g. serpentinization) are often rich in ethane in addition to CH_4 – resulting in low CH_4/C_2^+ ratios (< 100)
- 4. Microbial methanogens produce little ethane and hence high CH_4/C_2^+ ratios (>>1000)

Test case from an appropriate Earth analog?

Test Case: *Ongoing reduced Gas production from billion(s) year old rock with (some) relevant minerology – the Precambrian Shields*

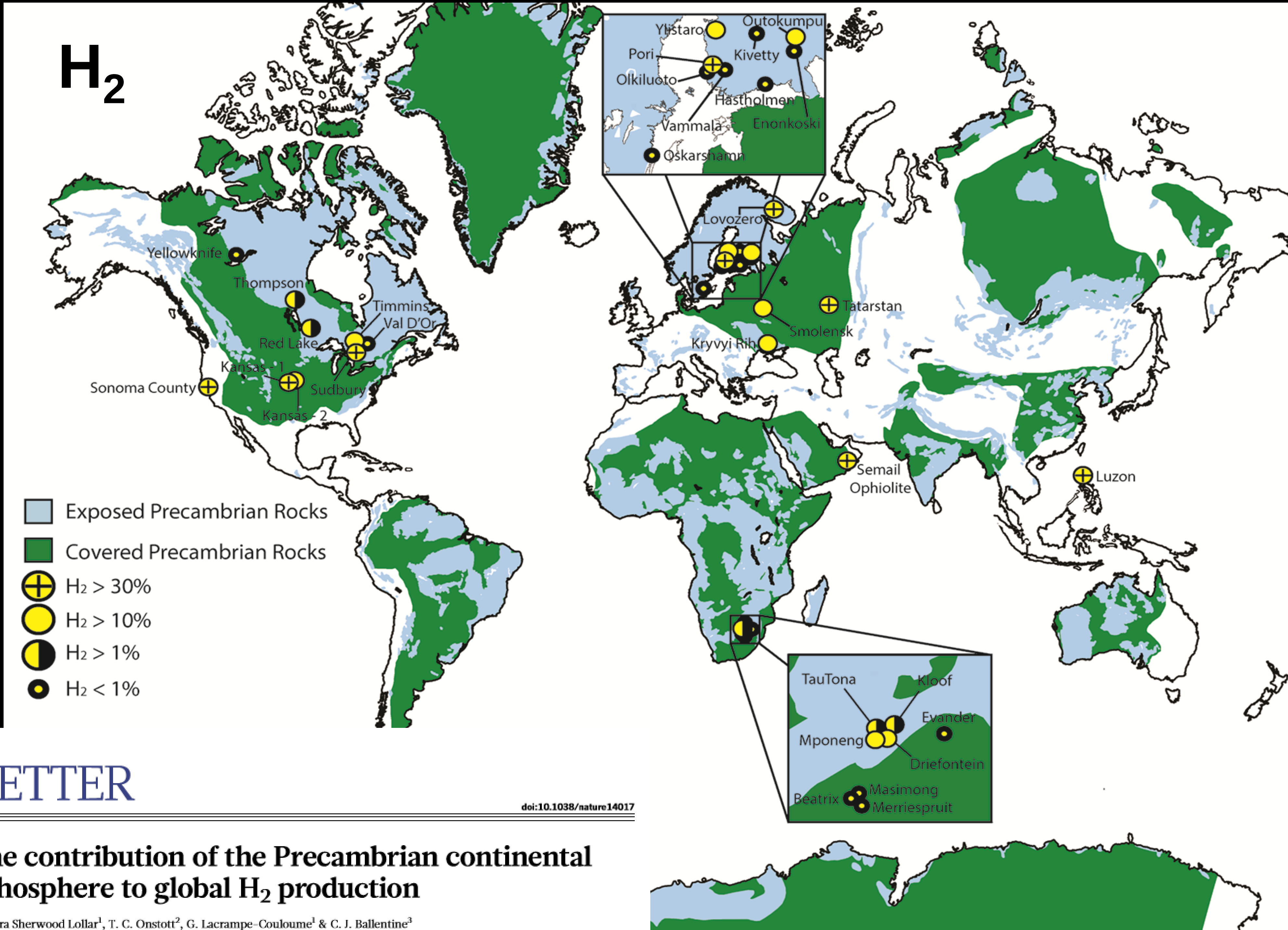






Precambrian > 72% of surface area of Earth's continental crust

Data from Goodwin (1996); Condie (1993); Rudnick and Fountain (1995)



LETTER

doi:10.1038/nature14017

The contribution of the Precambrian continental lithosphere to global H_2 production

Barbara Sherwood Lollar[1], T. C. Onstott[2], G. Lacrampe-Couloume[1] & C. J. Ballentine[3]

Analogs of ongoing processes of water-rock reaction relevant to Mars

- Water-rock reactions such as radiolysis (*Lin et al., 2005*) and serpentinization (*Sherwood Lollar et al, 2006*) producing H_2
- Drives the Deep Carbon cycle *e.g.* methanogenesis

Abiotic Organic Synthesis

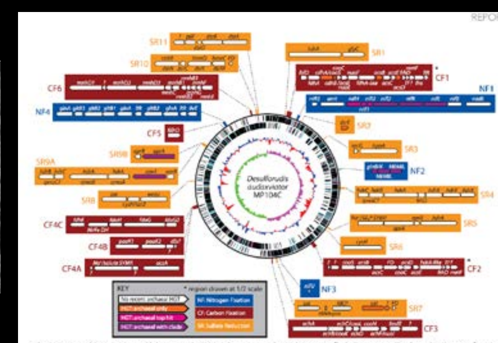
$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$$

Surface catalyzed Fischer Tropsch–Type (Sabatier) Reactions

Microbial Methanogenesis

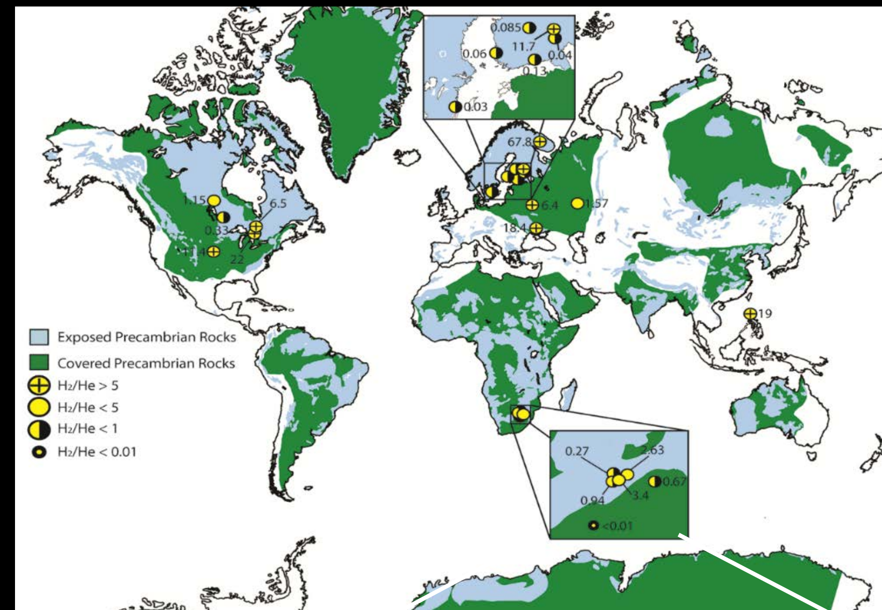
$$CO_2 + H_2 \rightarrow CH_4 + H_2O$$

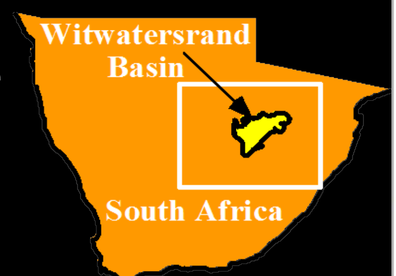
CO_2 reduction

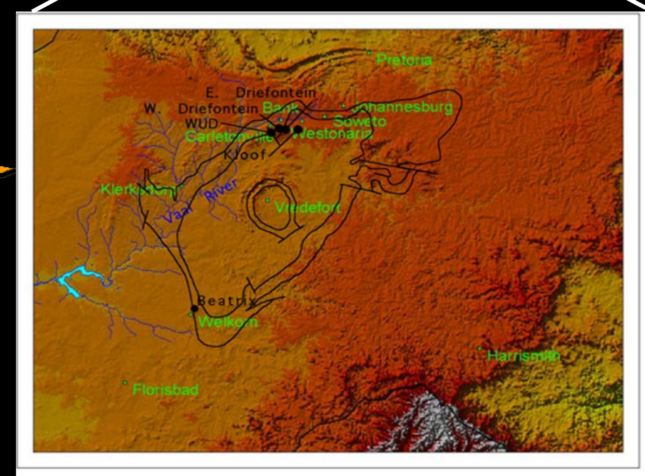


Test Case: Associated Gases

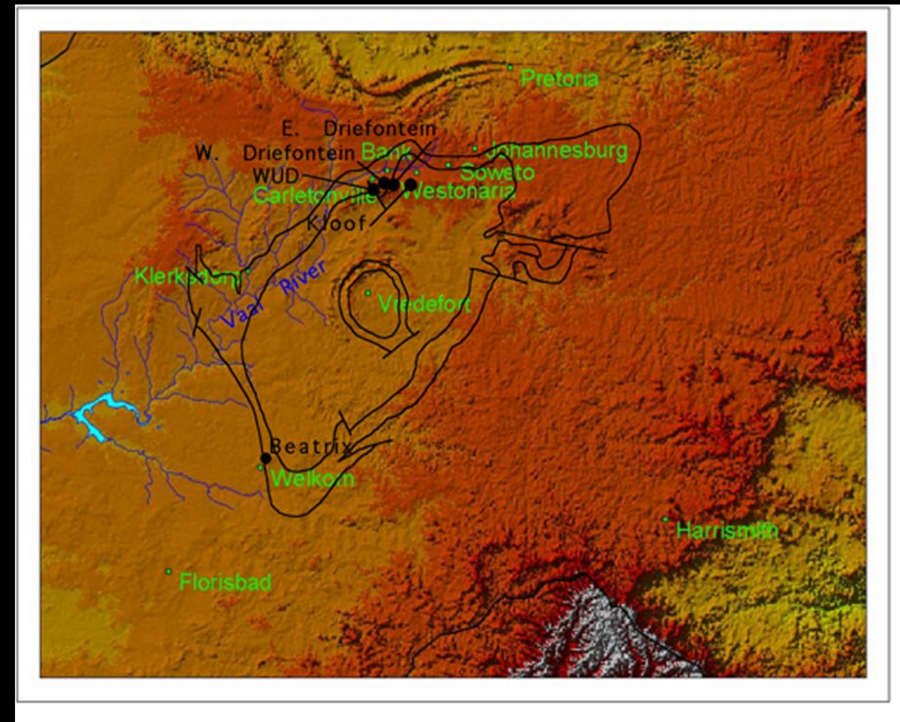
- Carry out this test for biotic vs. abiotic CH_4 on this global database
- 1. H_2 levels
- 2. Ethane (C_2H_6) levels
- 3. CH_4/H_2 and CH_4/C_2H_6 (CH_4/C_2^+) ratios
- 4. Focus: South Africa where greatest contextual evidence gathered over past 20 years







Test Case: Wits Basin



Associated gases (H_2, C_2H_6) successfully identify sites with microbial CH_4

Consistent with sites where multiple lines of evidence (including culture and genomic data) support dominance of microbial methanogenesis

Multiple Lines of Evidence

- 1. Isotopic signatures: including carbon source and reaction products
- 2. Associated species (DIC, H_2O, H_2, higher hydrocarbons, N- or S- compounds)
- 3. Conservative tracers (e.g. noble gases)
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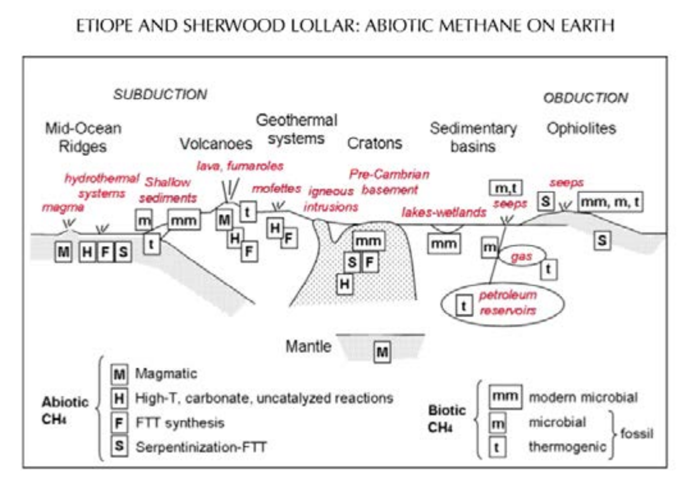
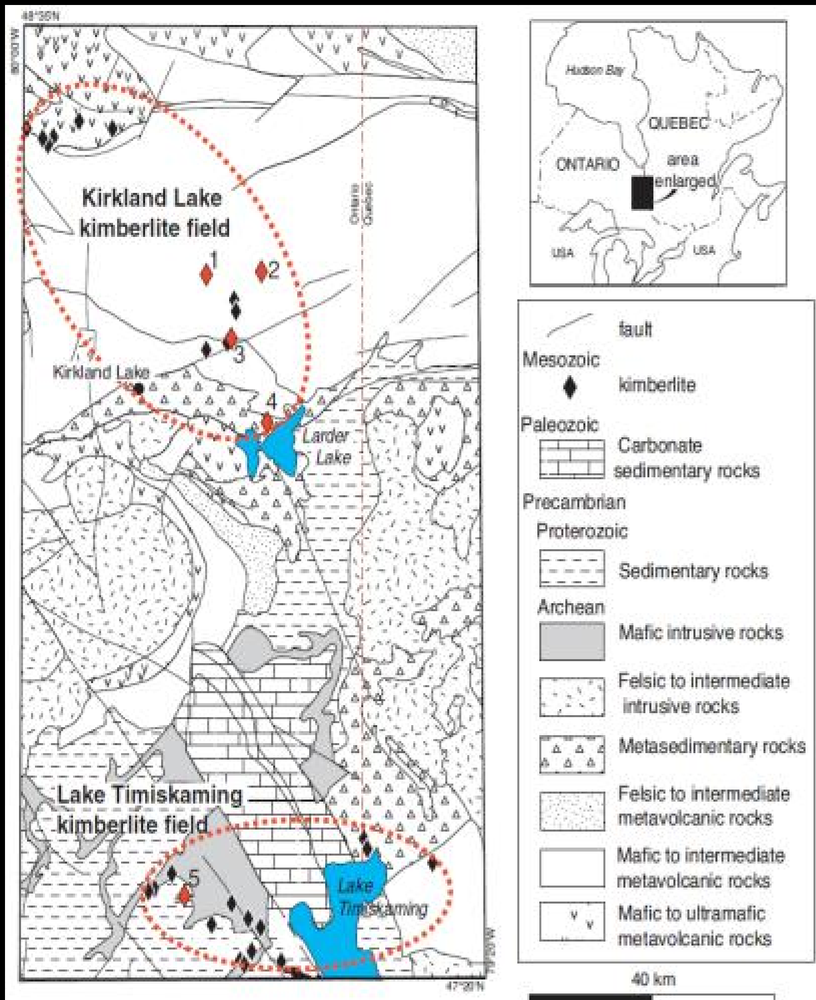


Conduits to Surface

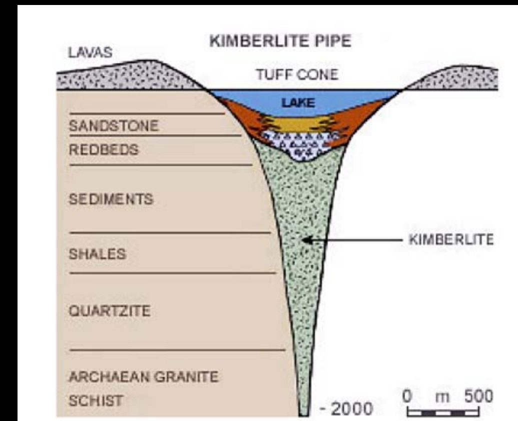
Diffuse gas seeps over cratons

CH_4 gas from perennial springs in high Arctic permafrost

Conduits to Surface



Modified from Sader et al 2007



Reduced gases (H_2 and CH_4) exsolving from groundwaters above kimberlite pipes

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