Methanogenic Microbial Degradation of Organic Matter in Indiana Coal Beds

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Abstract

We investigated the phylogenic and geochemical characteristics of biogenic coalbed methane (CBM) in the Indiana part of the Illinois Basin to identify the organisms responsible for methane generation and to determine the biogeochemical constraints on production of methanogenic substrates, such as H_2 and CO_2. 16S rRNA analysis of in-situ microbial community and methanogen enrichments indicate that *Methanocorpusculum* is the dominant methanogenic genus. This microorganism was characterized by its distribution of intact polar cell membrane lipids (IPLs) and by scanning electron microscopy. Typical characteristics of *Methanocorpusculum* were rapid growth in the H_2 and CO_2 environment, small 0.4 μm spherical cells, and a 2:1 ratio of diethers to tetraethers in the cell membrane. Within the clone library of water co-produced from a CBM well, we also found species capable of anaerobic degradation of a variety of molecules, including polyaromatic, aromatic, and aliphatic hydrocarbons. Oil extracted from co-produced coalbed water shows a high level of biodegradation. We calculated free energies available for in-situ subsurface conditions for CO_2-reduction and acetoclastic methanogenesis, homoacetogenesis, and syntrophic acetate oxidation that represent terminal microbial biodegradation reactions. Methanogenesis via CO_2-reduction appears to be the dominant terminal biodegradation process affecting coal organic matter. We suggest that post-uplift influx of fresh water, most likely during inter- and post-glacial periods, decreased the salinity of the original basinal brine and allowed inoculation of previously sterile Indiana coals with a diverse biodegrading microbial community. Further integrated biogeochemical analysis will more precisely define the role of the microbial community on the rate-limiting steps of biogenic methane formation.

Methanogenic microbial degradation of organic matter in Indiana coal beds

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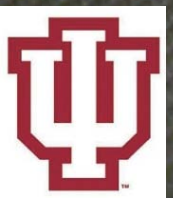
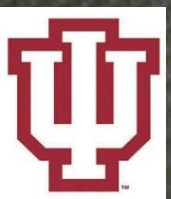
Chris Reddy, Robert Nelson – *Woods Hole Oceanographic Institution*
Albert Holba – *ConocoPhillips*
Tom Hite and Indiana coal companies



- Introduction and study area – eastern Illinois Basin (Indiana)
- Microbial origin of CBM and its distribution
- Ongoing microbial methanogenesis in Indiana coals
- Biodegradation of organic matter in coal (gases, oil, and the coal itself)



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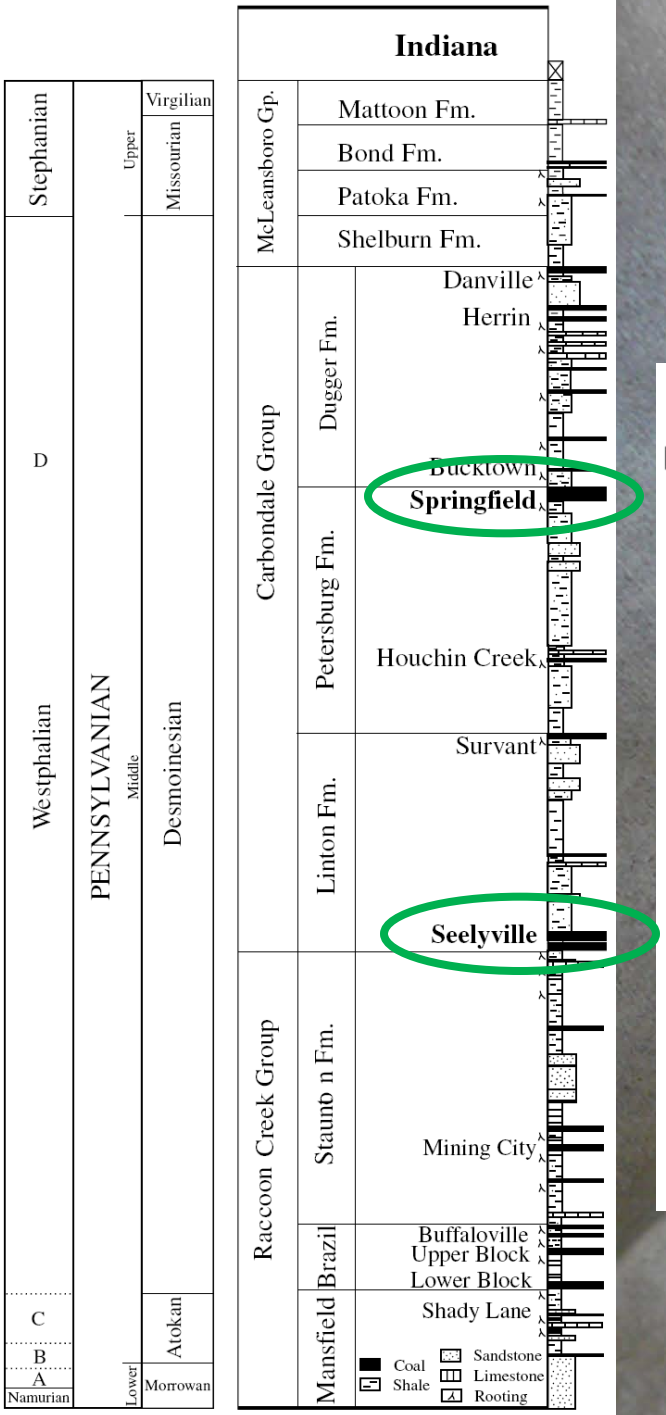
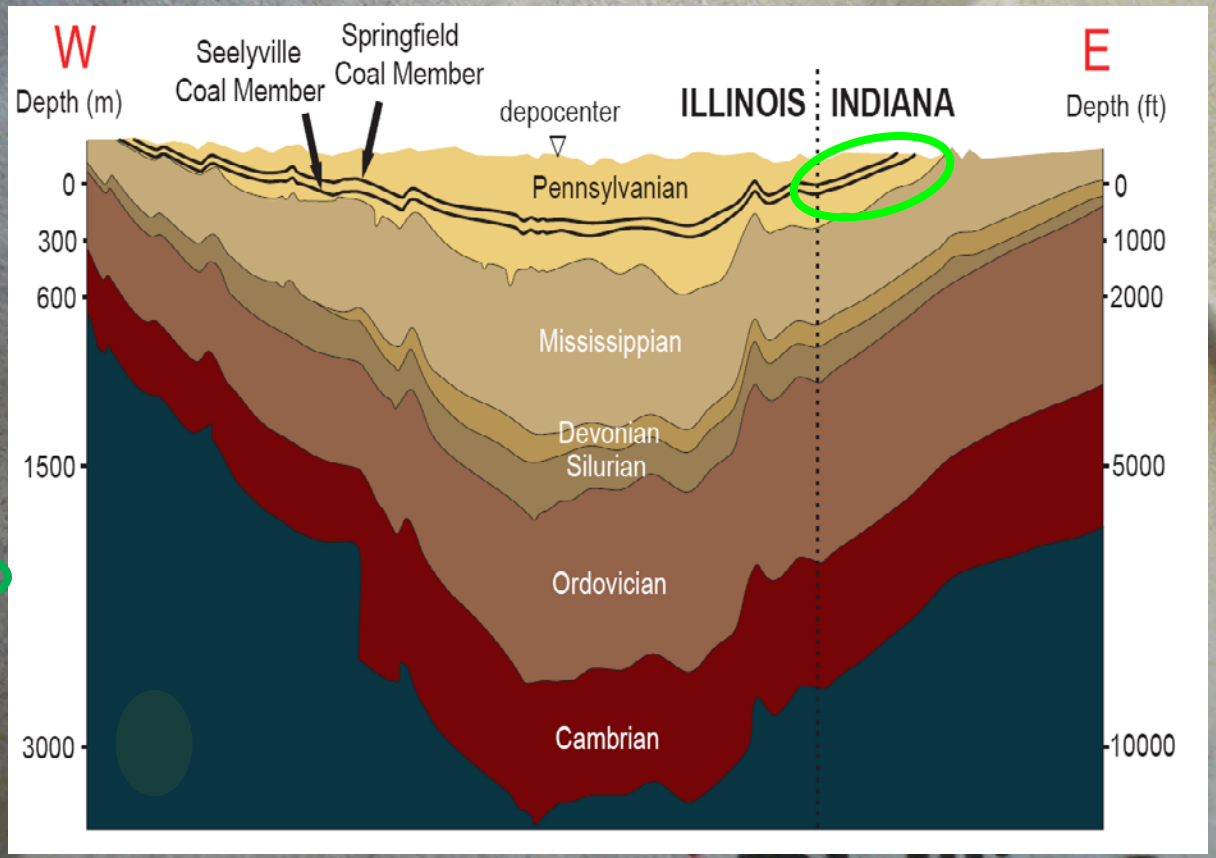
Illinois Basin coals
Springfield and Seelyville





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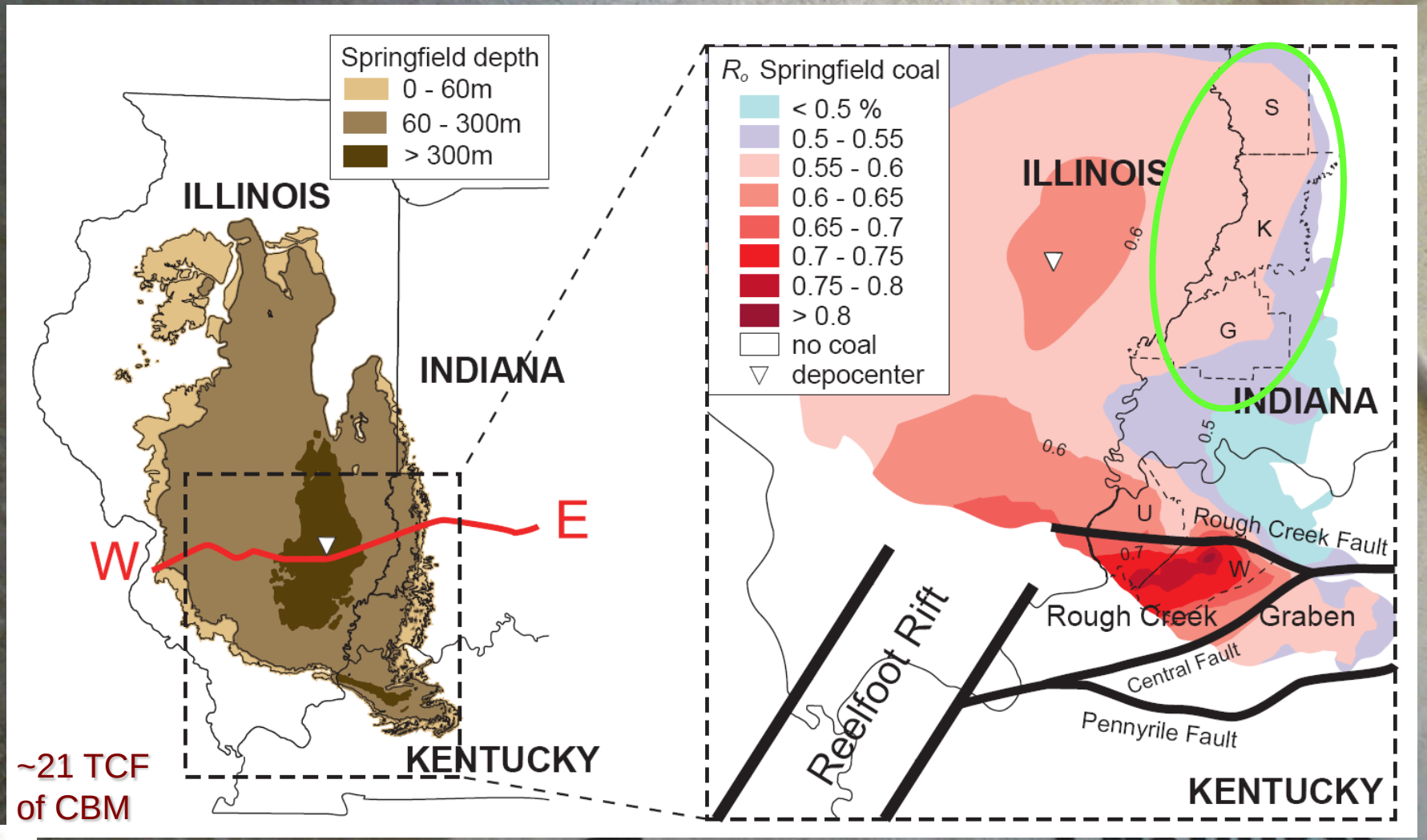
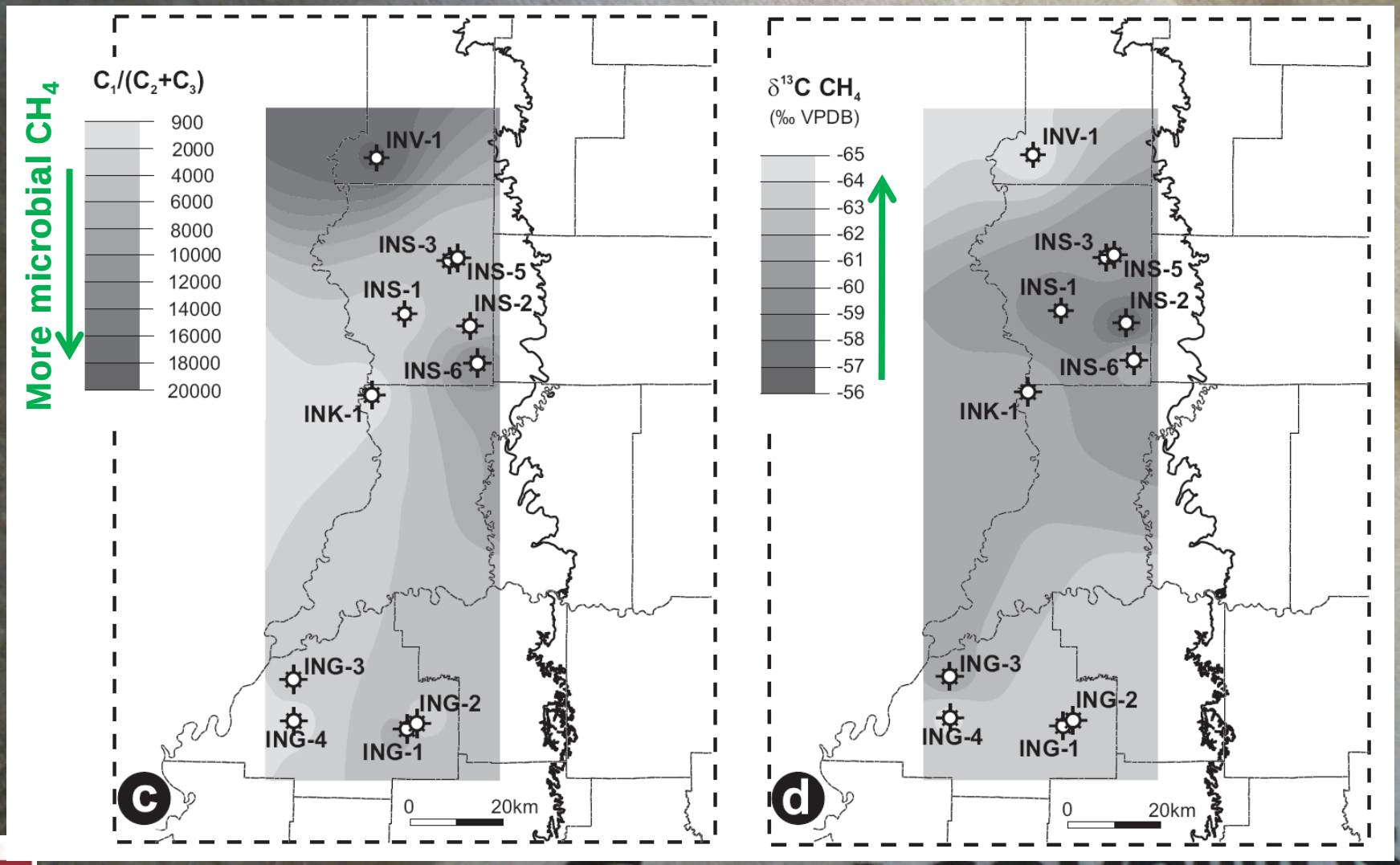
Eastern Illinois Basin – shallow low maturity coals in Indiana



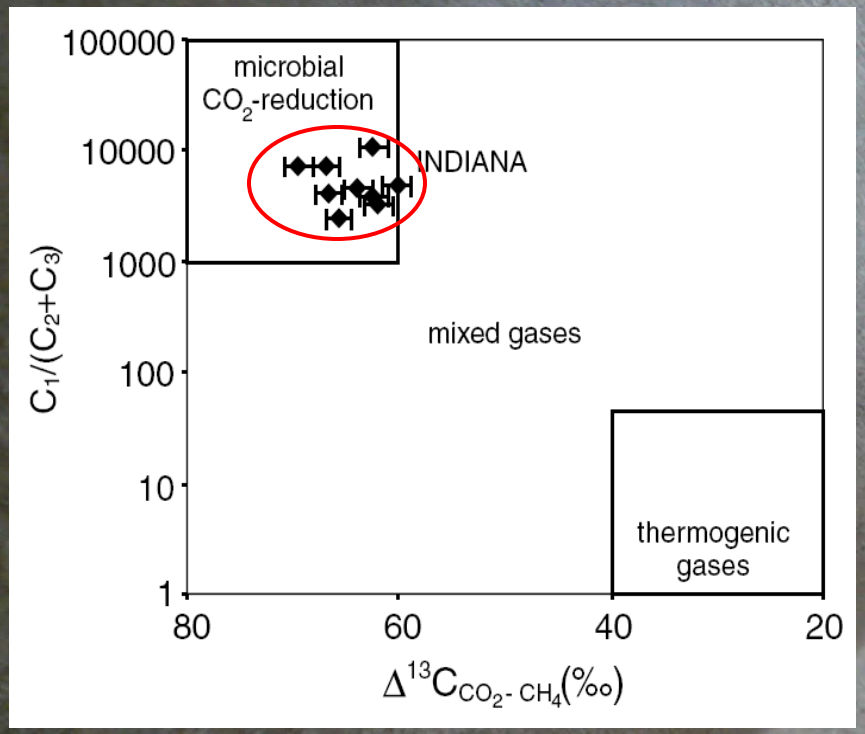
Distribution of coal gas compositional and isotopic fingerprints – predominantly microbial CH_4

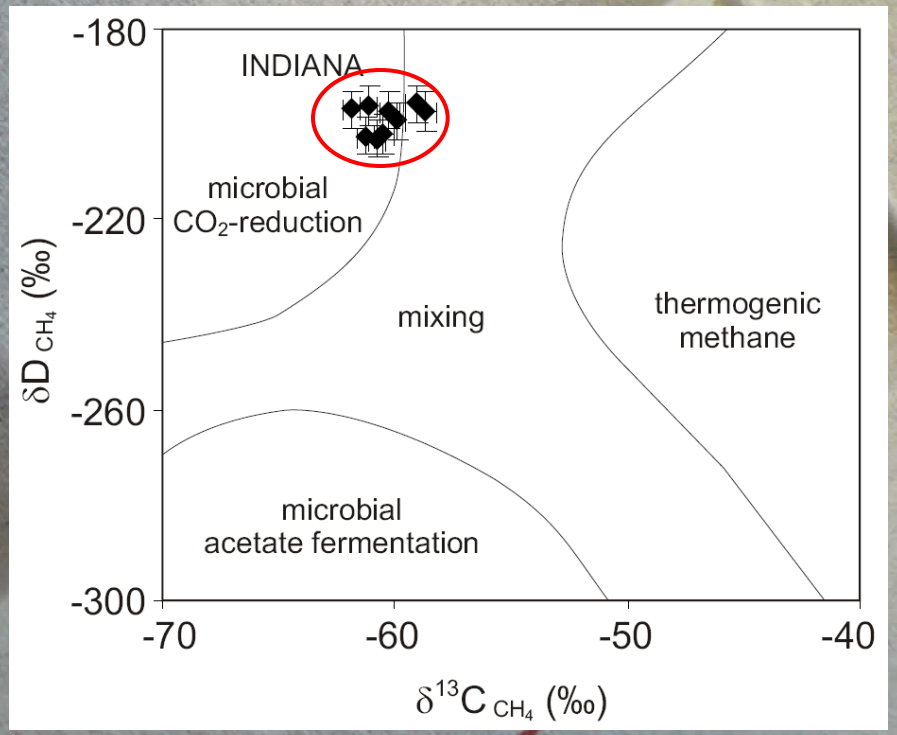


~ 3 cm^3/g (100 scf/ton), ~ 99% of microbial origin

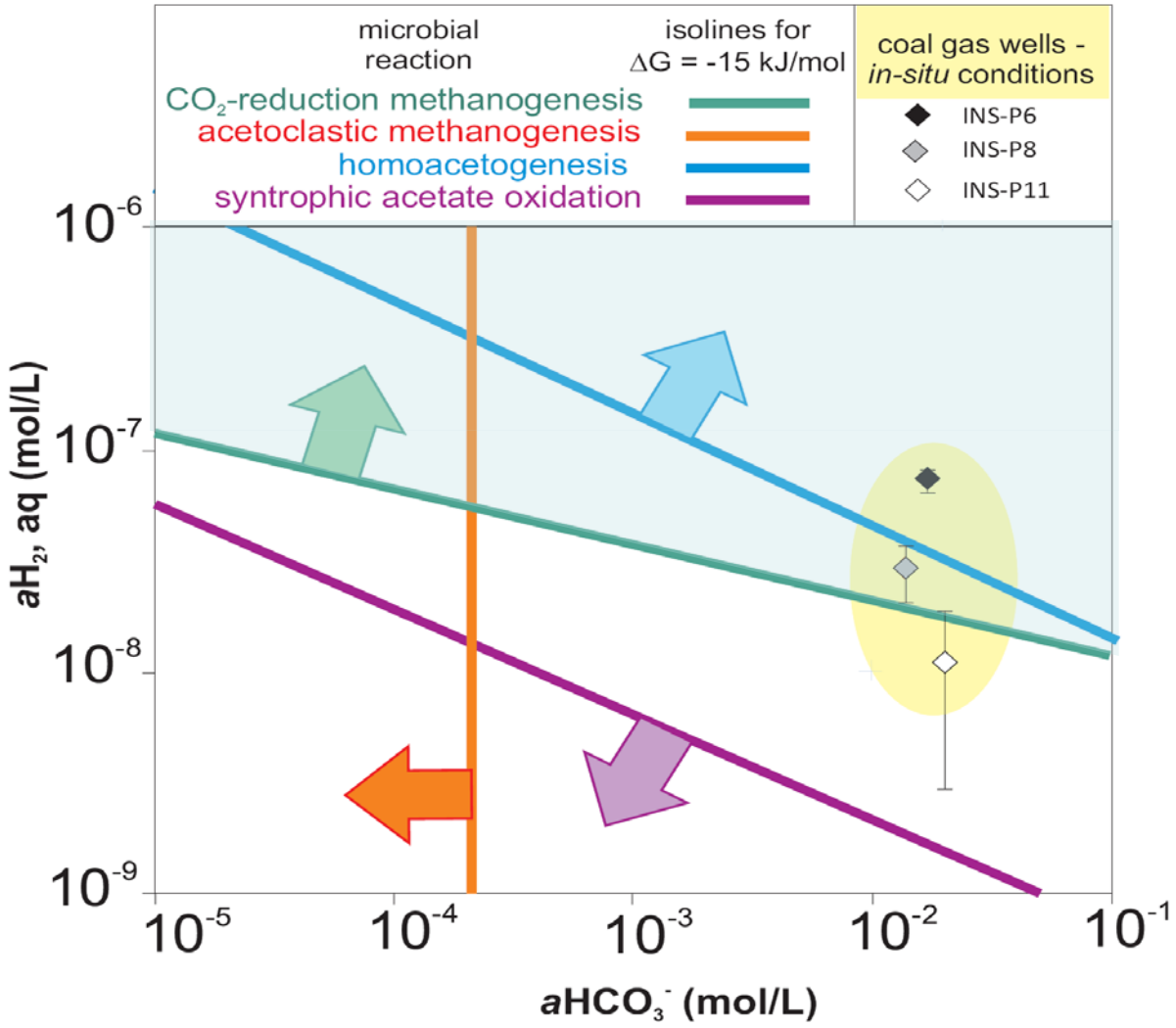
Strąpoć et al., 2008, IJCL

Geochemical and isotopic signatures of coal gas: CH_4 generated microbially via CO_2-reduction





Strąpoć et al., 2007, OG

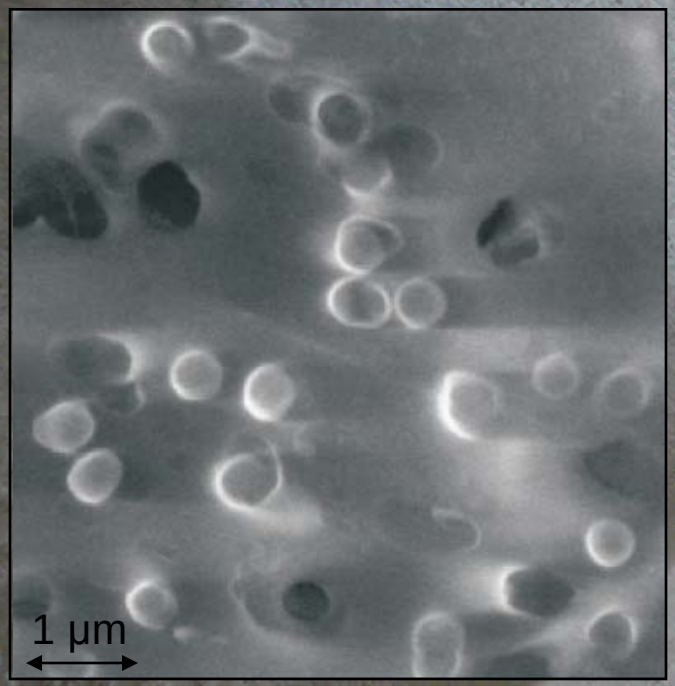


Free energy available for terminal biodegradation reactions: H_2/CO_2-utilizing methanogenesis wins over homoacetogenesis and acetoclastic methanogenesis

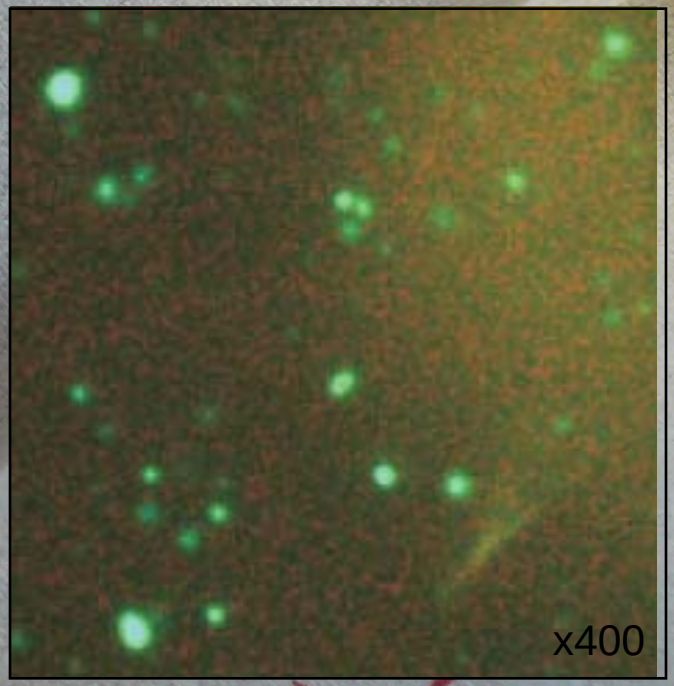
			$\Delta G^\circ_{P,T}$ (kJ) 10.5 atm, 17°C	ΔG (kJ) *in situ*[&]
1	CO_2-reduction methanogenesis	$HCO_3^- + 4H_{2,aq} + H^+ \rightarrow CH_4 + 3H_2O$	-230.2	-19.8
2	Acetoclastic methanogenesis	$CH_3COO^- + H_2O \rightarrow CH_{4,aq} + HCO_3^-$	-14.7	-4.8
3	Homoacetogenesis	$2HCO_3^- + 4H_{2,aq} + H^+ \rightarrow CH_3COO^- + 4H_2O$	-215.6	-15.1
4	Syntrophic acetate oxidation	$CH_3COO^- + 4H_2O \rightarrow 2HCO_3^- + 4H_{2,aq} + H^+$	+215.6	+15.1

Microscopic features of methanogenic enrichments of the CBM co-produced water suggest presence of methanogenic Archaea

Very small cell size typical of Archaea



Epifluorescence of F420 coenzyme



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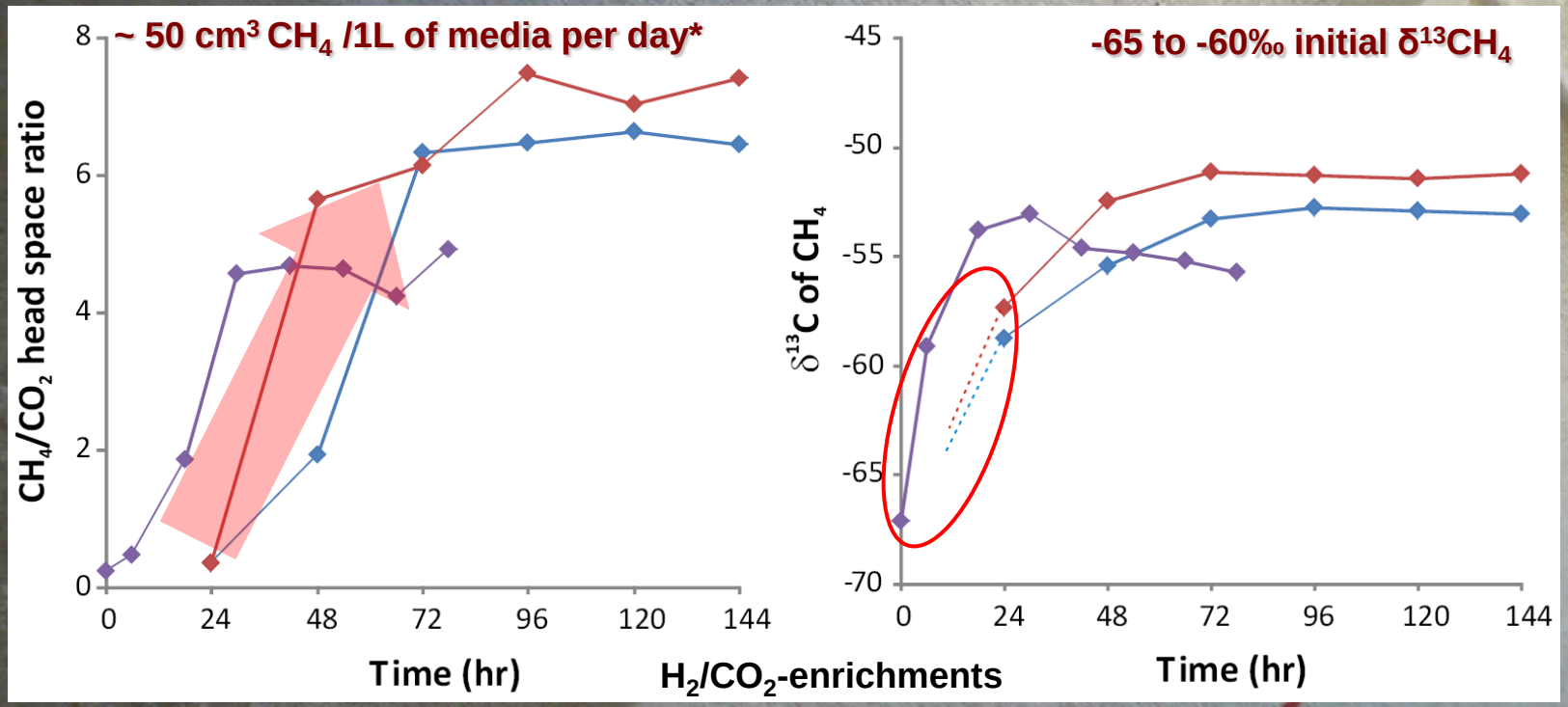
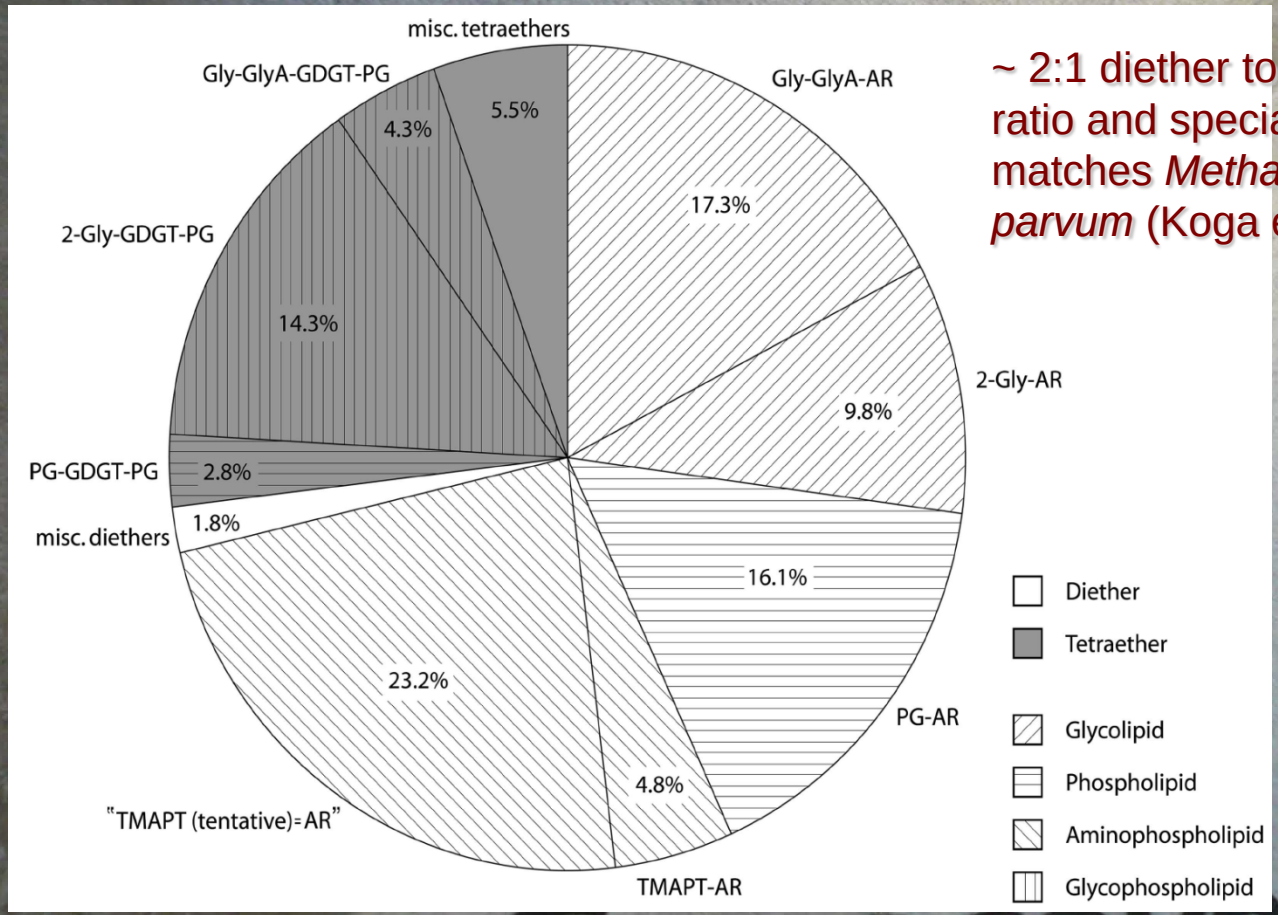
Microbiological enrichments of the CBM co-produced water confirm CH_4 production via CO_2-reduction



* estimated *in-situ* (mostly post-Pleistocene) CH_4 generation was ~ 1 scf/ton per 100 years (Strąpoć et al., 2007)

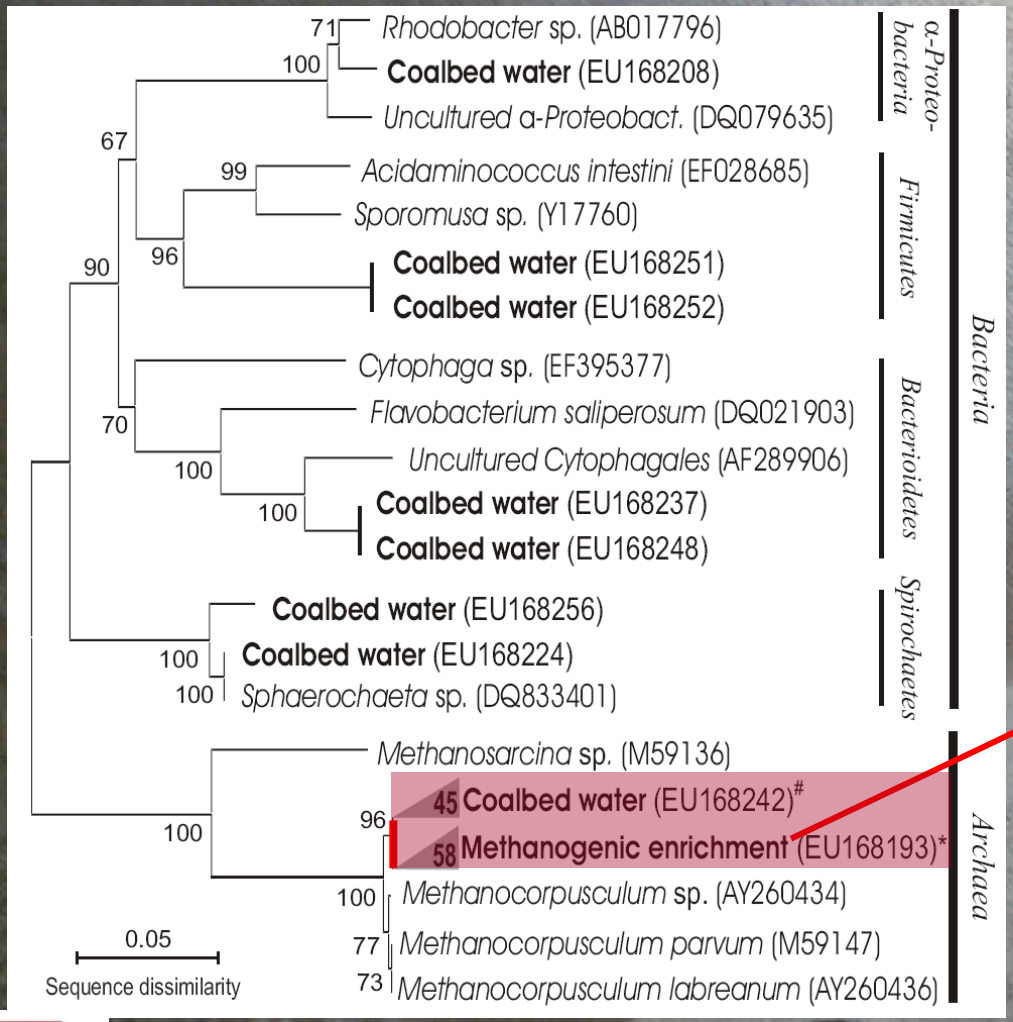
Cell membrane intact polar lipids (IPLs) of the methanogenic enrichment point to *Methanocorpusculum*, H_2/CO_2 utilizing methanogen

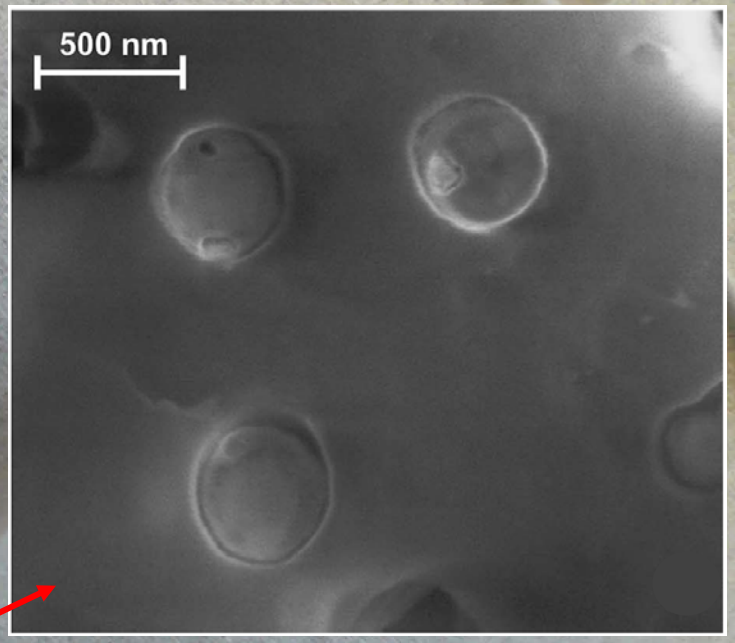


~ 2:1 diether to tetraether ratio and speciation of both matches *Methanocorpusculum parvum* (Koga et al., 1998)

Strąpoć et al., 2008, AEM

16S rRNA study of coal water and methanogenic enrichment: dominant methanogen - CO_2/H_2 utilizing *Methanocorpusculum*





SEM image of the CO_2-reduction methanogenic enrichment *(Methanocorpusculum)*

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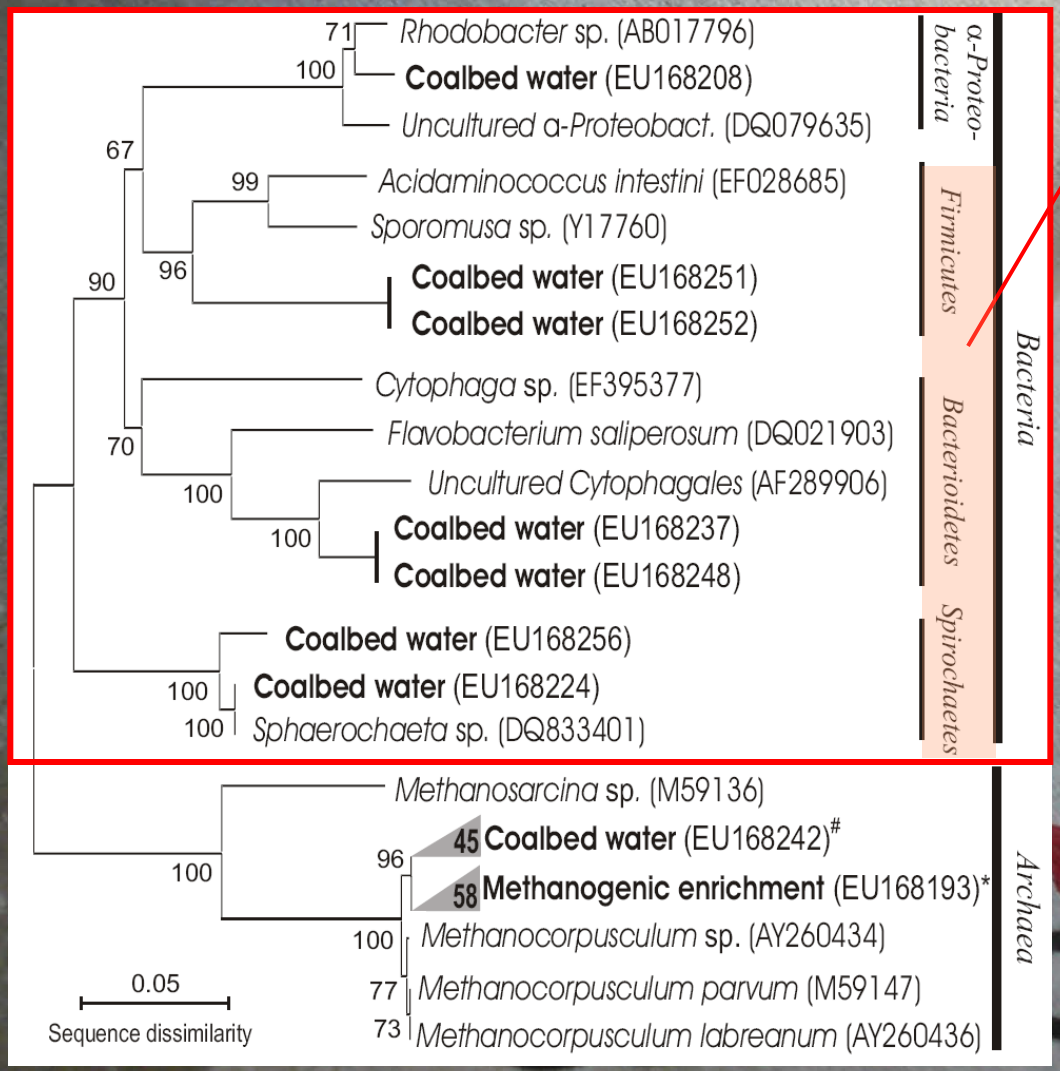
Strąpoć et al., 2008, AEM

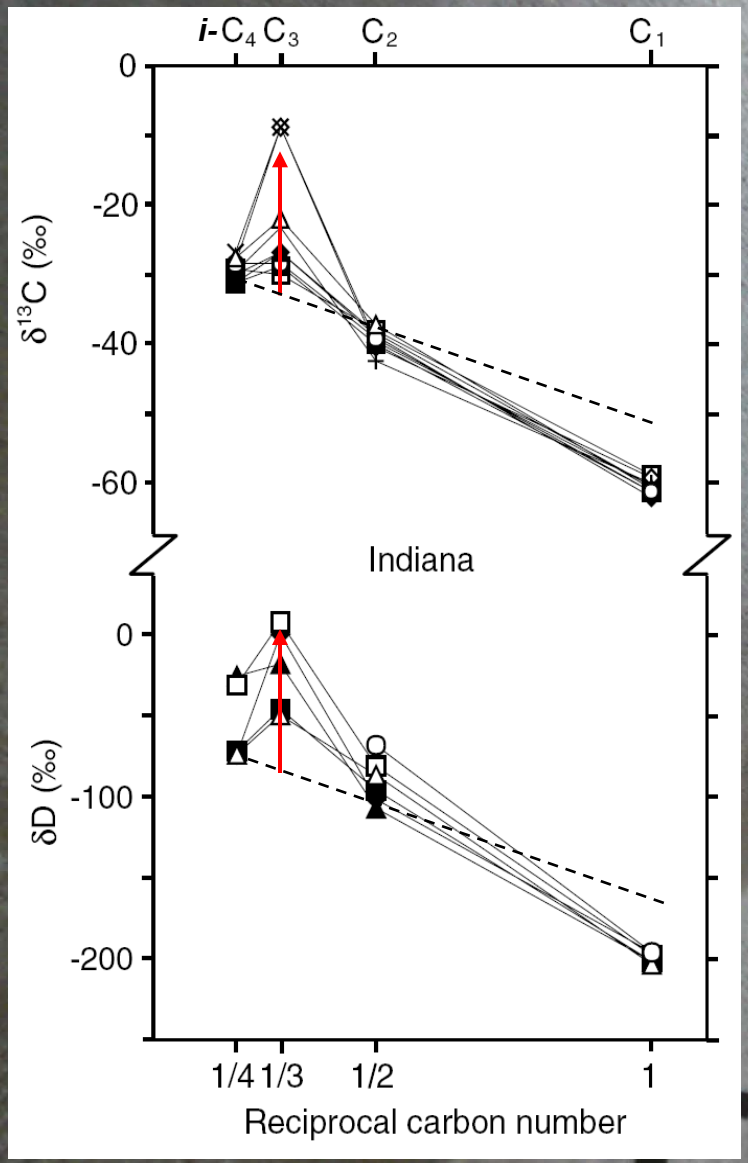
Variety of bacteria in Indiana coals can provide simple substrates (CO_2, H_2, acetate) for methanogens

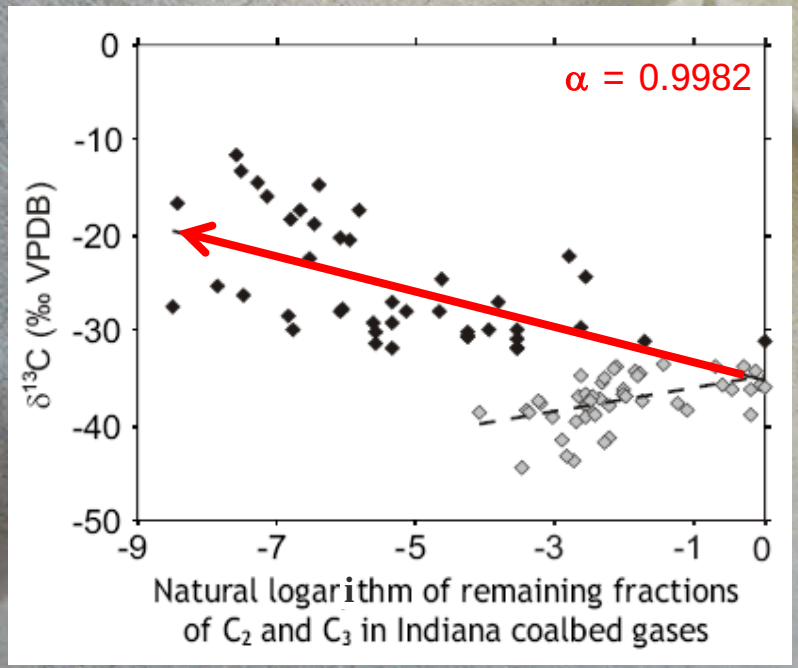


These bacteria can participate in enzymatic defragmentation of coal geomacromolecules followed by fermentation of smaller compounds; **fermentation** delivers **H_2, CO_2, and acetate** – methanogenic substrates

Biodegradation of gaseous hydrocarbons:

* Propane heavily altered
* n-Butane gone

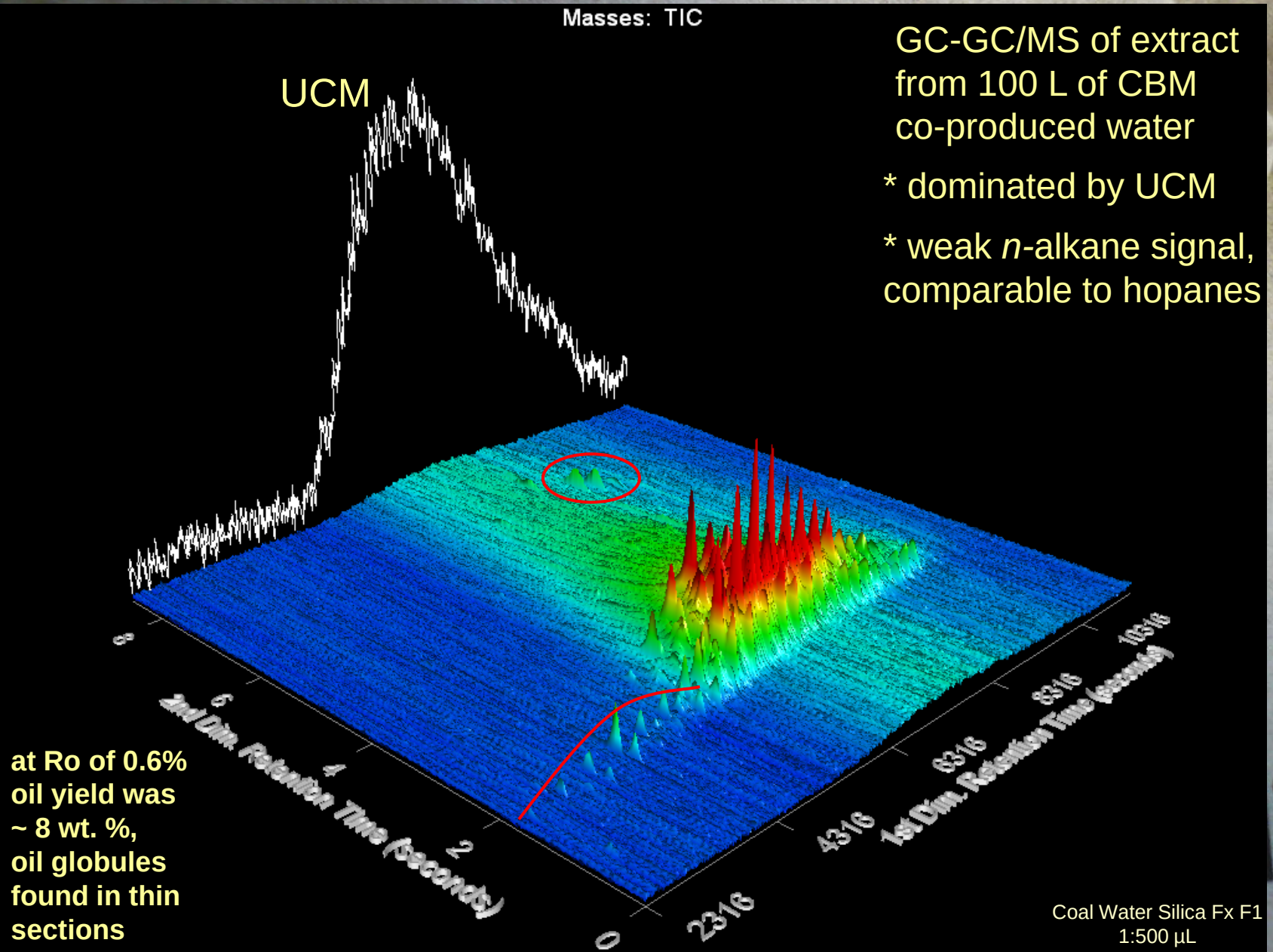




C diagram after Chung et al., 1988

Strąpoć et al., 2007, OG

Biodegradation of liquid hydrocarbons present in coal



GC-GC/MS of extract from 100 L of CBM co-produced water

* dominated by UCM

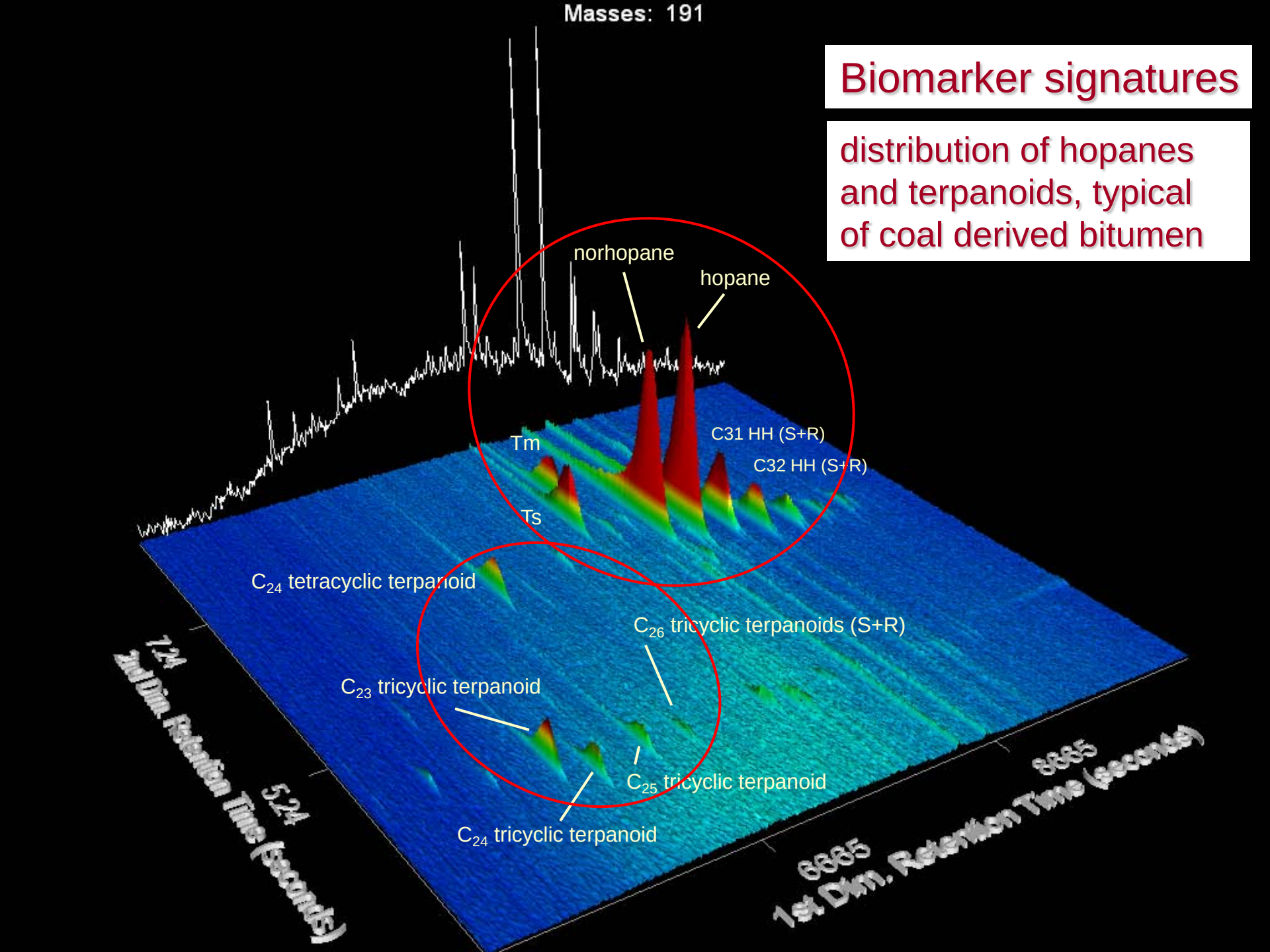
* weak *n*-alkane signal, comparable to hopanes

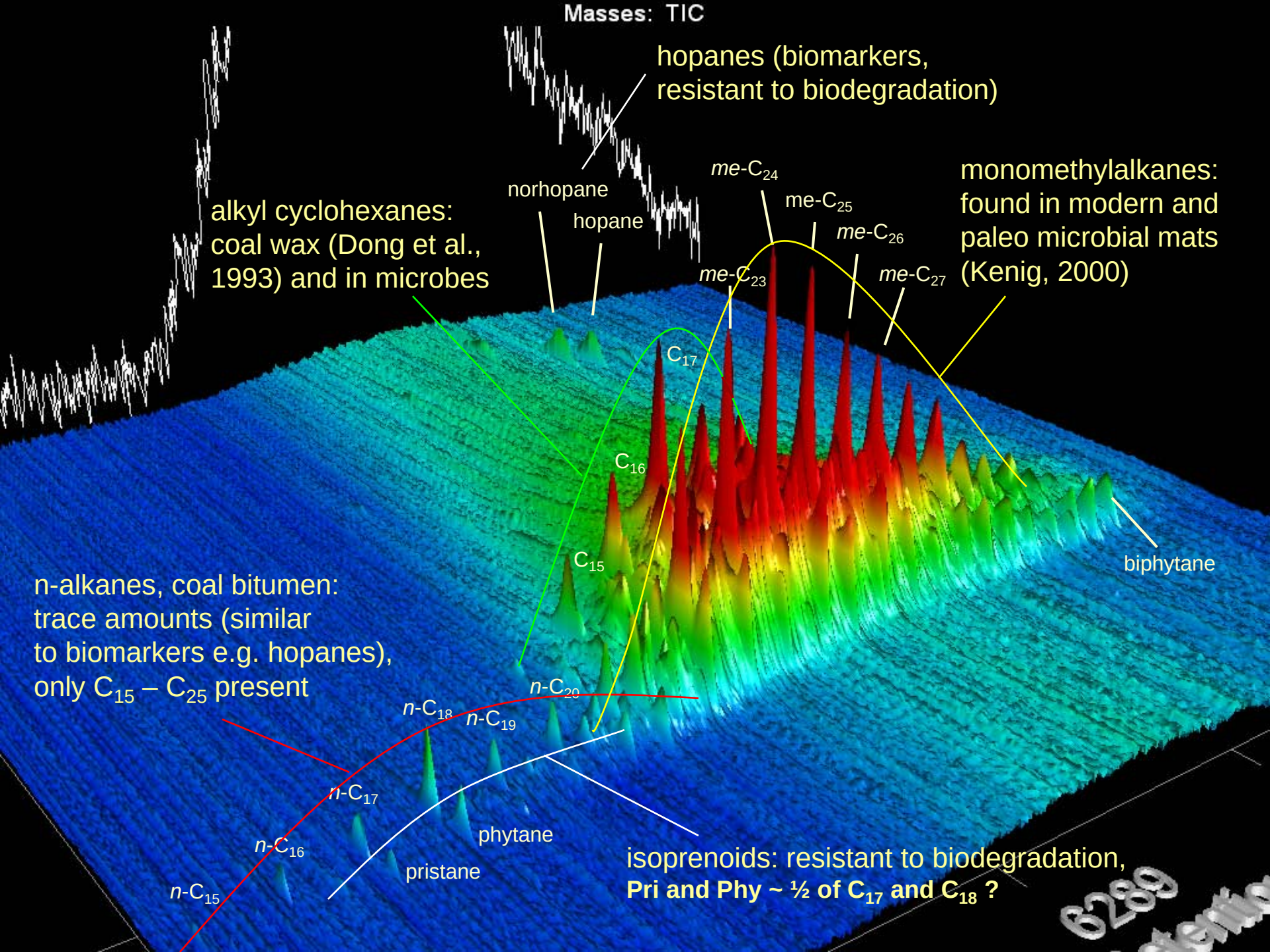
at Ro of 0.6% oil yield was ~ 8 wt. %, oil globules found in thin sections

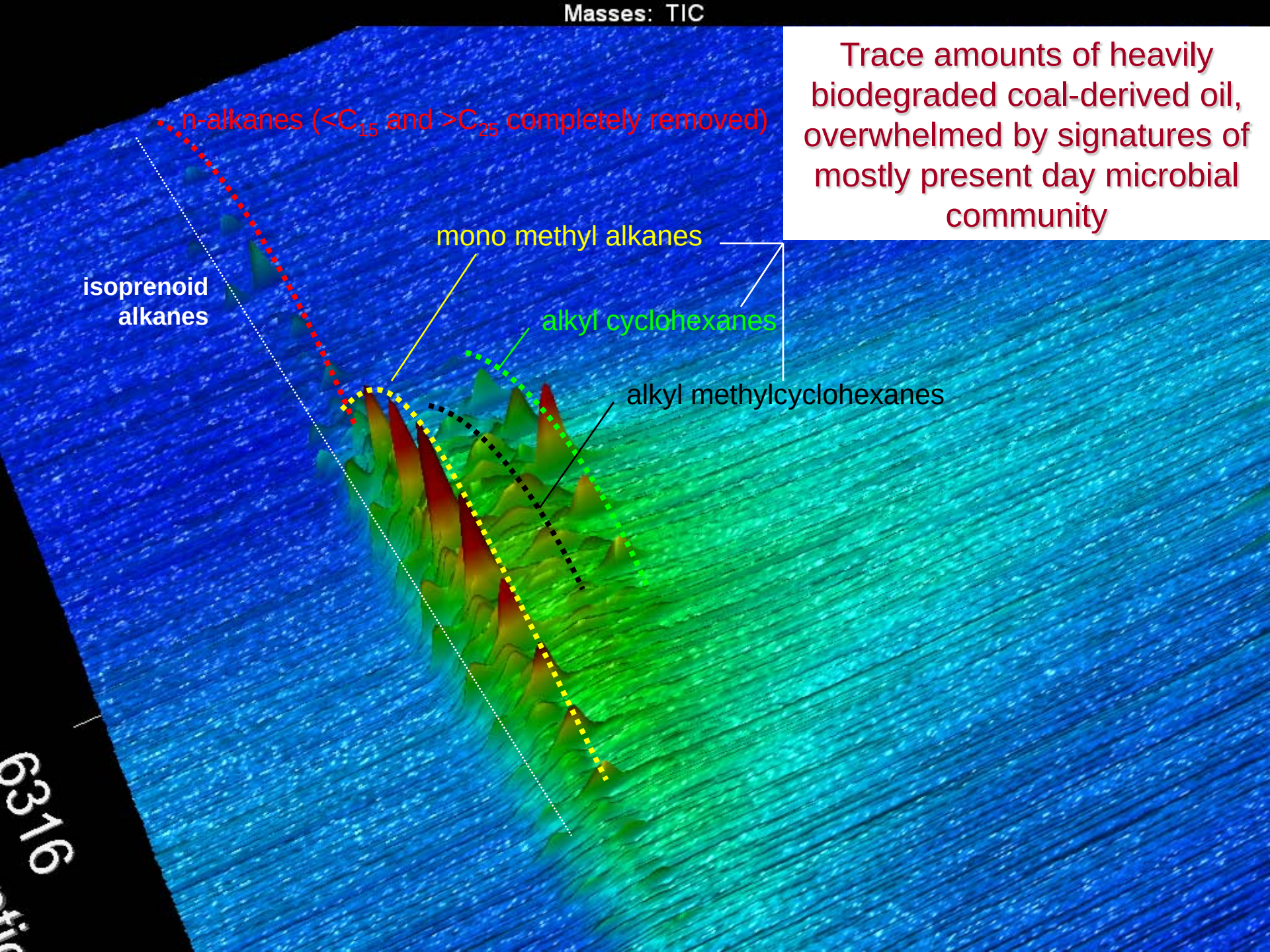
Coal Water Silica Fx F1
1:500 µL

Biomarker signatures

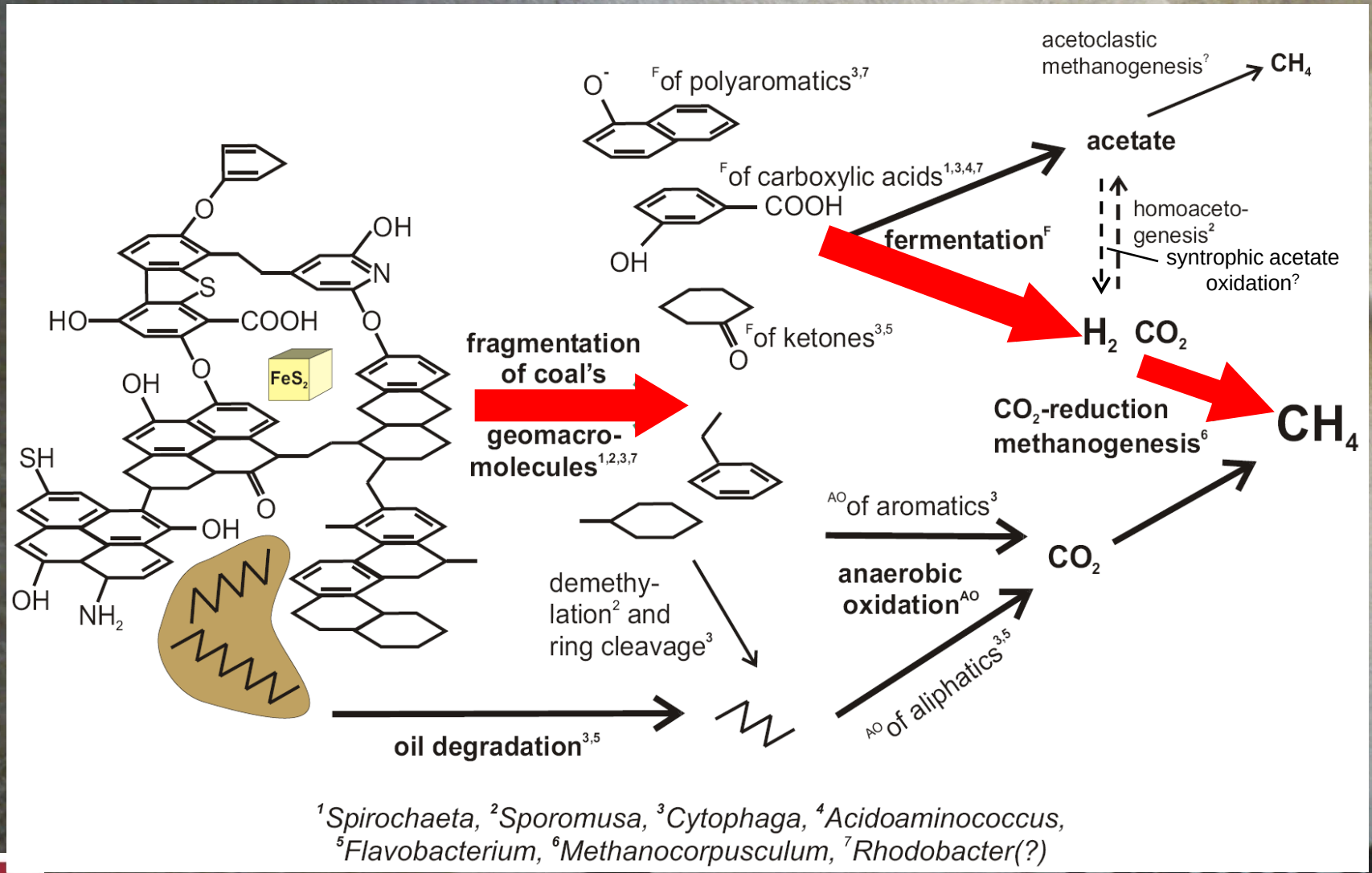
distribution of hopanes and terpanoids, typical of coal derived bitumen




Masses: TIC
hopanes (biomarkers, resistant to biodegradation)
norhopane
hopane
alkyl cyclohexanes: coal wax (Dong et al., 1993) and in microbes
me-C24
me-C25
me-C26
me-C27
me-C23
monomethylalkanes: found in modern and paleo microbial mats (Kenig, 2000)
C17
C16
C15
biphytane
n-alkanes, coal bitumen: trace amounts (similar to biomarkers e.g. hopanes), only C15 – C25 present
n-C20
n-C18
n-C19
n-C17
n-C16
n-C15
phytane
pristane
isoprenoids: resistant to biodegradation,
Pri and Phy ~ ½ of C17 and C18 ?

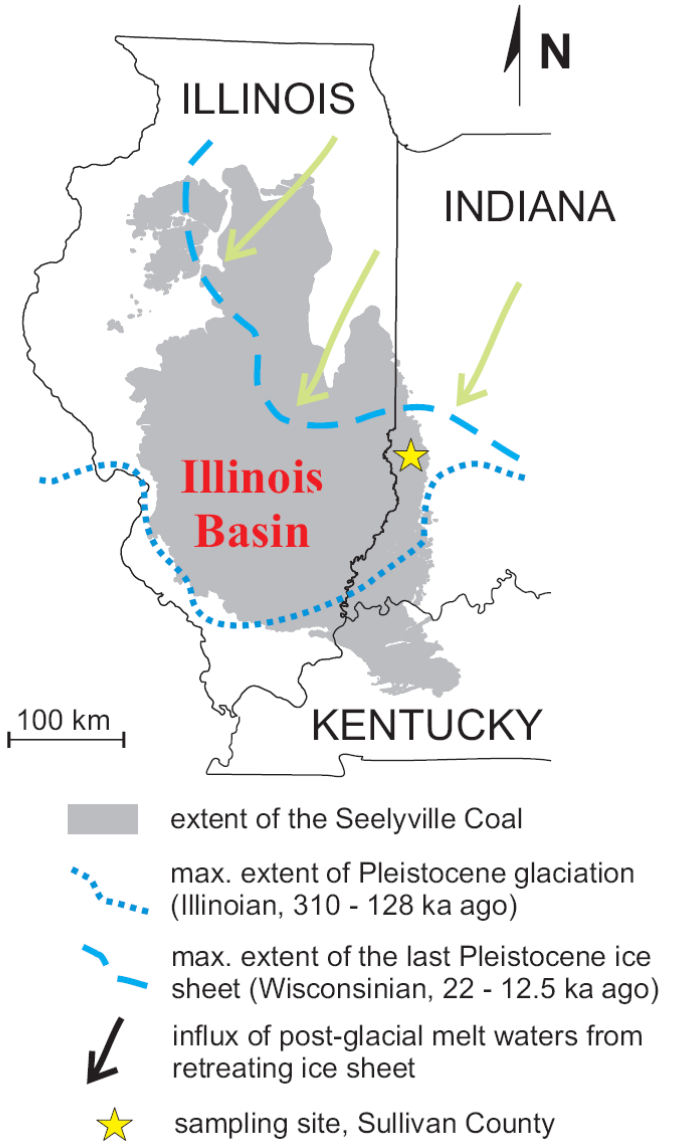

Masses: TIC
n-alkanes (<C15 and >C25 completely removed)
mono methyl alkanes
isoprenoid alkanes
alkyl cyclohexanes
alkyl methylcyclohexanes
Trace amounts of heavily biodegraded coal-derived oil, overwhelmed by signatures of mostly present day microbial community
6316

Biodegradation of solid organic matter of coal by complex microbial community – a model



[1]*Spirochaeta*, [2]*Sporomusa*, [3]*Cytophaga*, [4]*Acidoaminococcus*, [5]*Flavobacterium*, [6]*Methanocorpusculum*, [7]*Rhodobacter(?)*

Concept of the microbial colonization and onset of methanogenesis



- Inter- and post-glacial colonization and onset of CH_4-generation in the Illinois Basin (similarly to the New Albany Shale and Antrim Shale in Michigan Basin (McIntosh, 2003)
- Initiated by brine dilution with ice sheet melt waters
- Similar activation of methanogenesis in coal beds observed in other basins: Black Warrior, San Juan, Alberta

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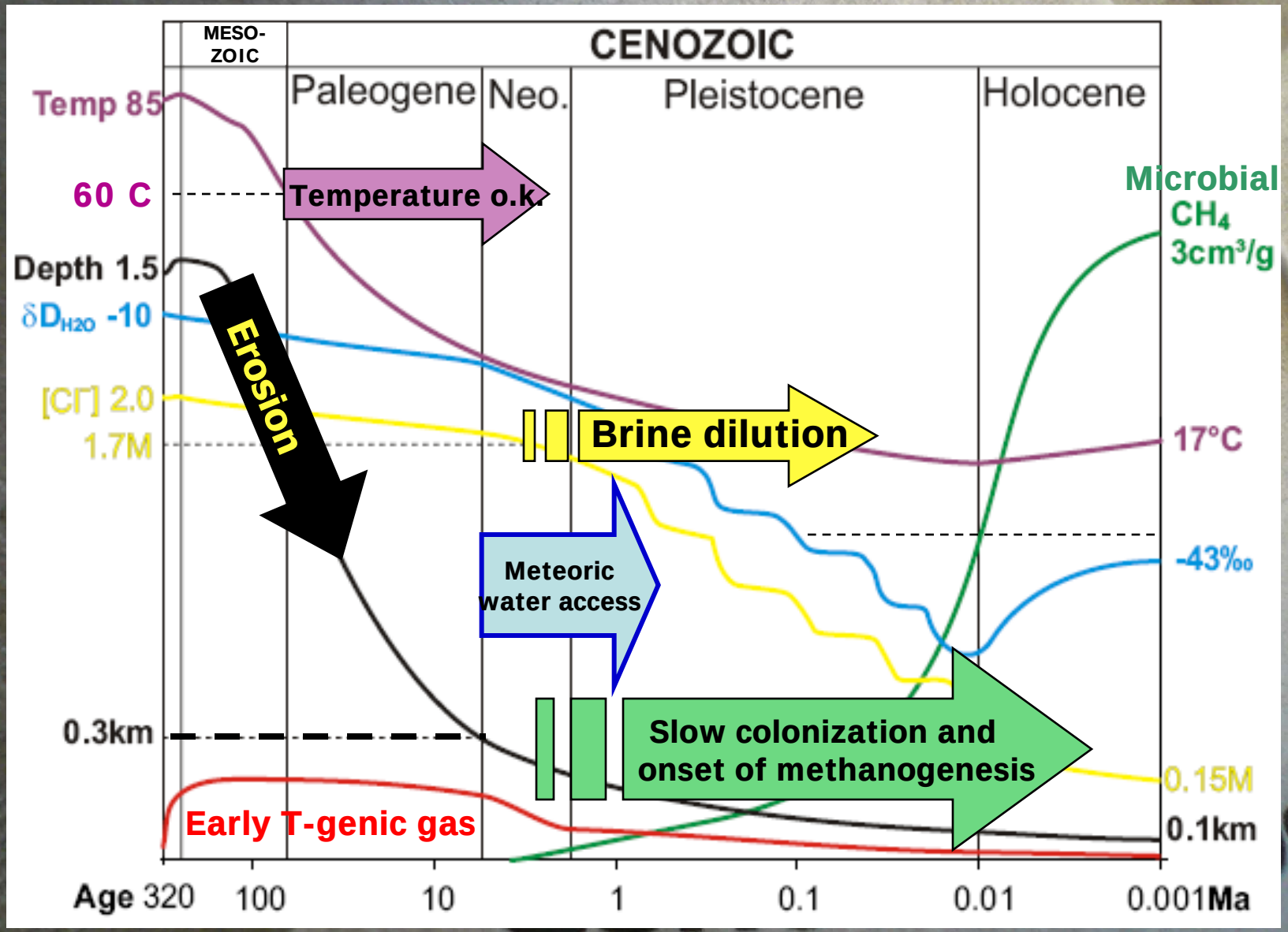
Basin history and multi-parameter model for microbial methanogenesis



SUMMARY

- CBM reserves in the eastern margin of the Illinois Basin are predominantly of microbial and likely recent origin.

- Ongoing methanogenesis is dominated by CO_2-reduction pathway utilized by *Methanocorpusculum* genus, supported by geochemistry, isotopes, enrichments,16S rRNA, IPLs, and free energy calculations.

- Complex microbial community degrades gaseous (C_3 and *n*-C_4) and liquid hydrocarbons (coal derived oil), and potentially solid organic compounds present in coal.

- Microbes play a key role in anaerobic biodegradation of subsurface OM. Microbes (Firmicutes, Bacterioidetes, Spirochetes) defragment and ferment larger organic moieties, and provide substrates (especially H_2) for the terminal step – METHANOGENESIS.

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Thank YOU

questions?