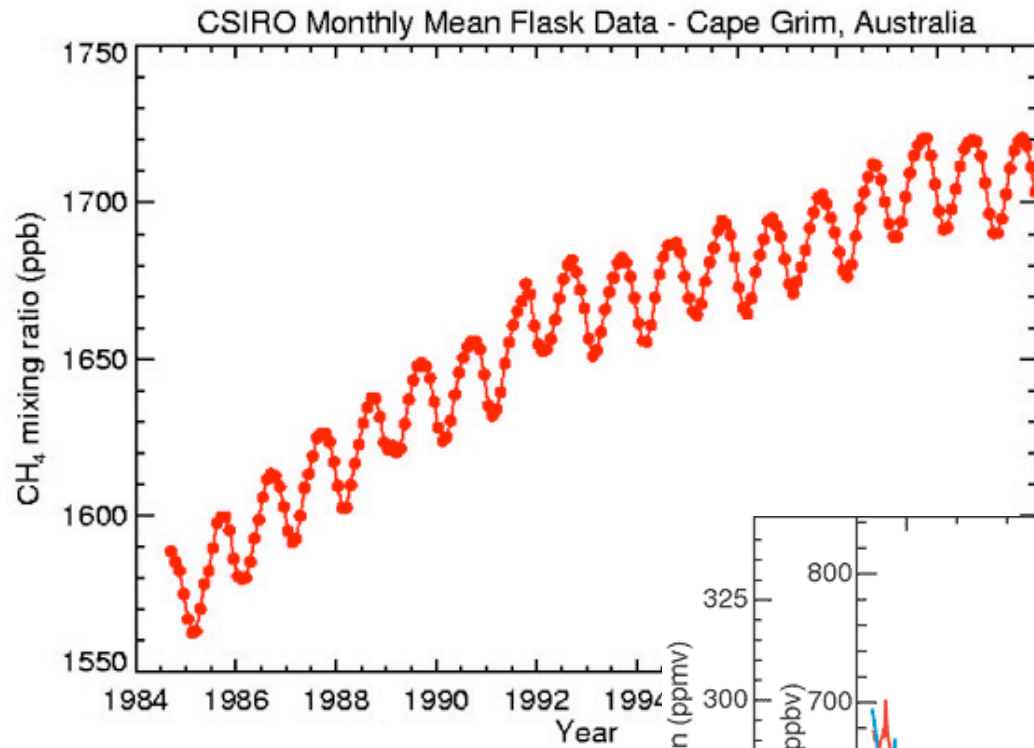
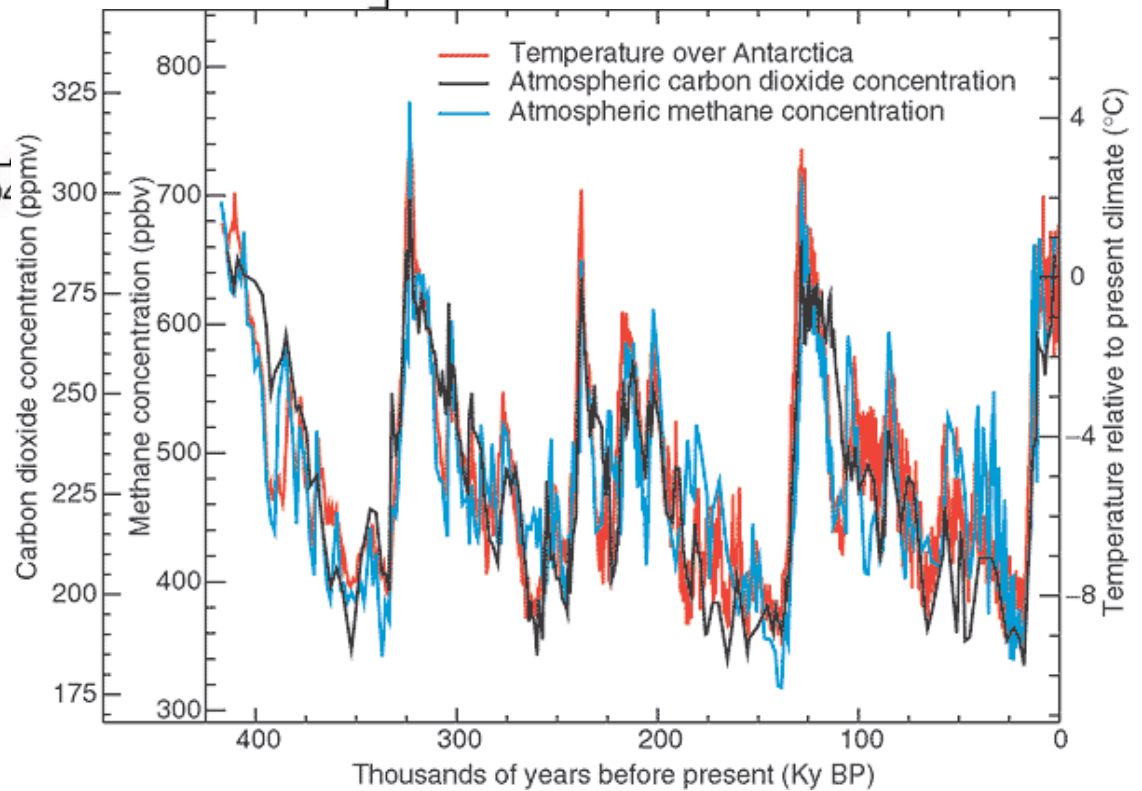


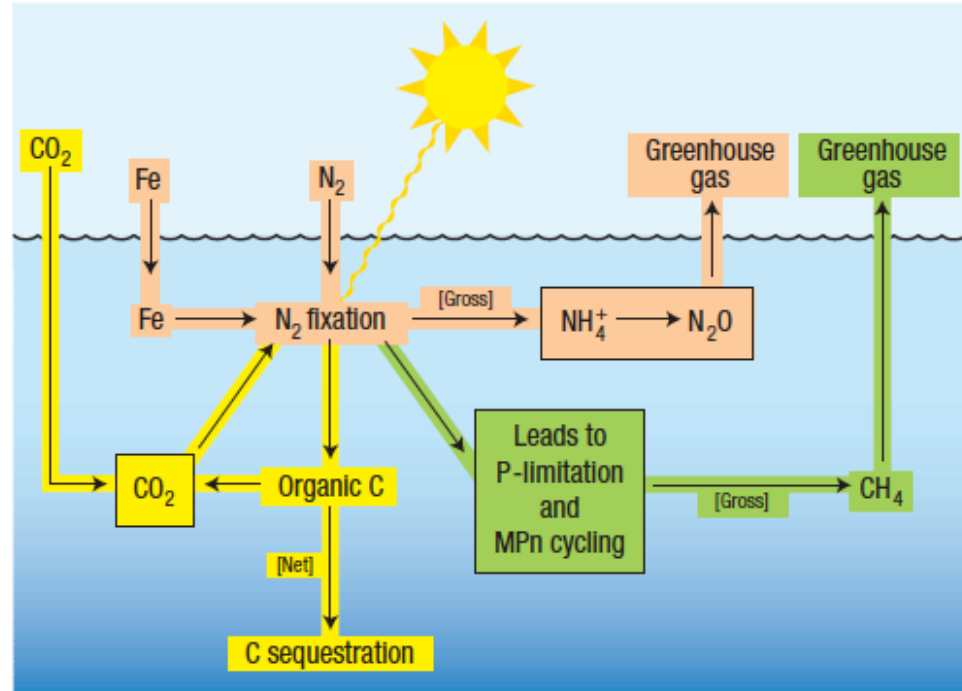
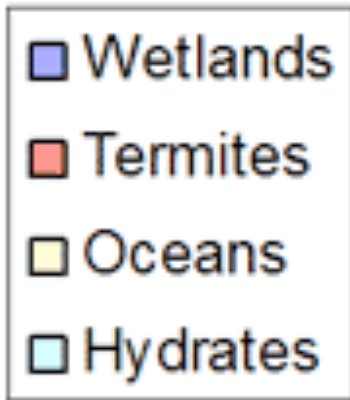
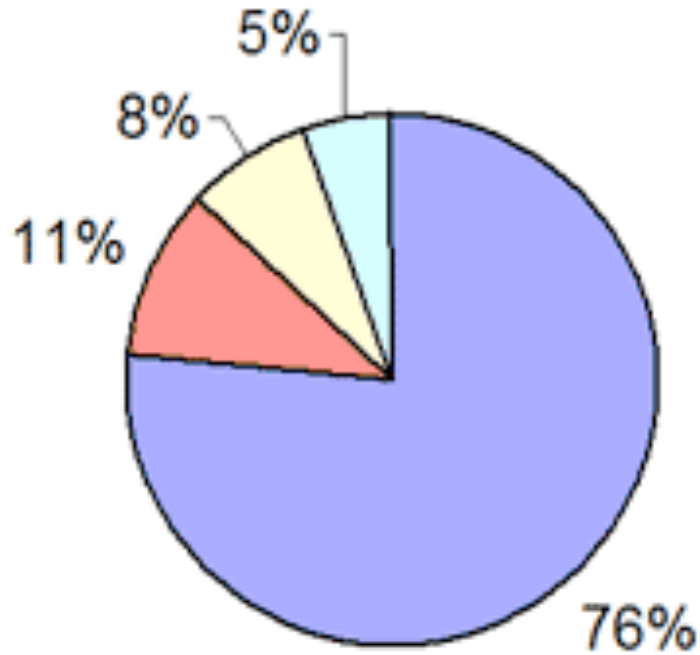
Methane and the Global greenhouse



Atms. Methane is increasing in concentration by about 1-2% per year.



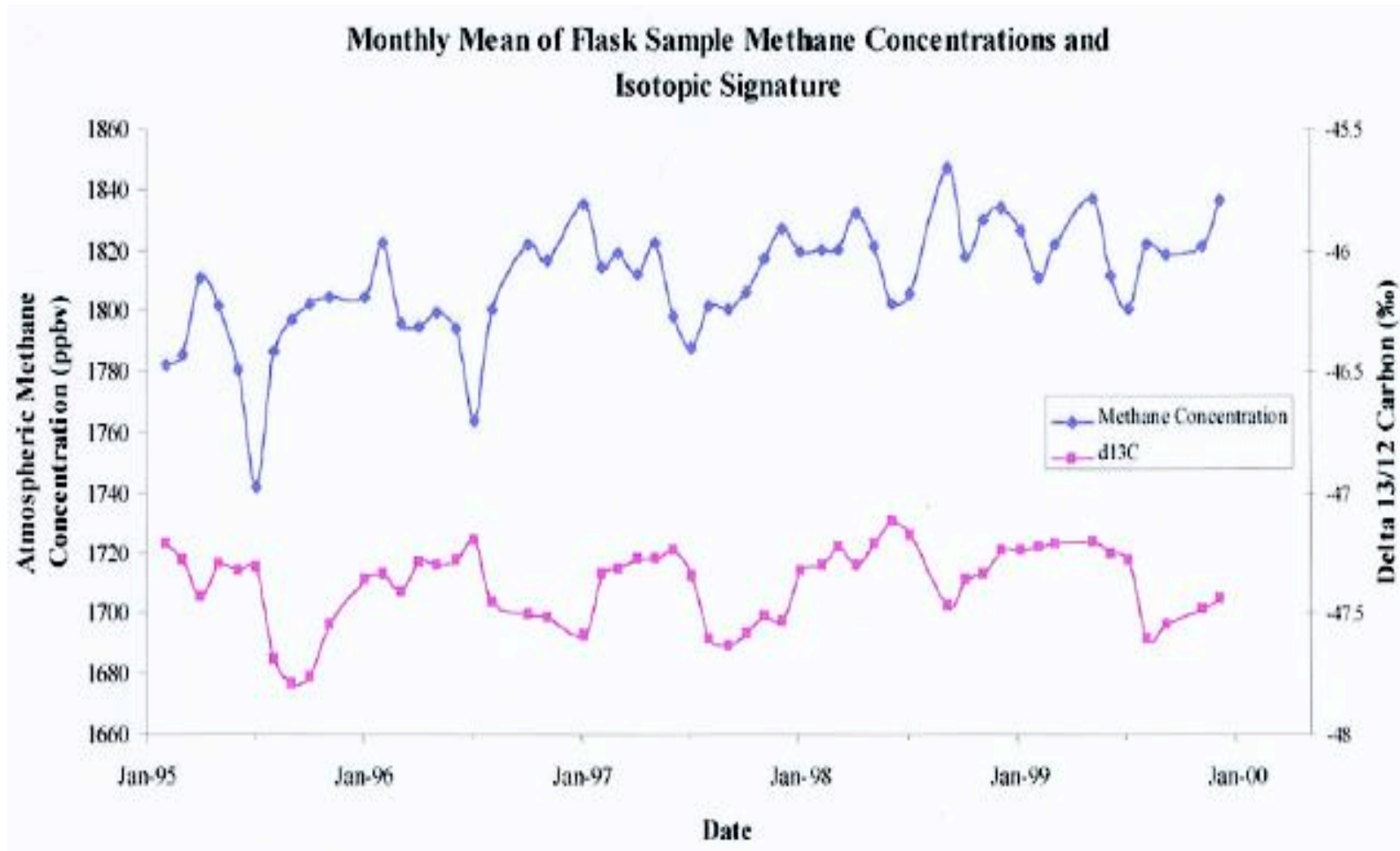
Wetlands are by far the largest source of methane to the Atms-includes coastal Wetlands at ocean/continental margins

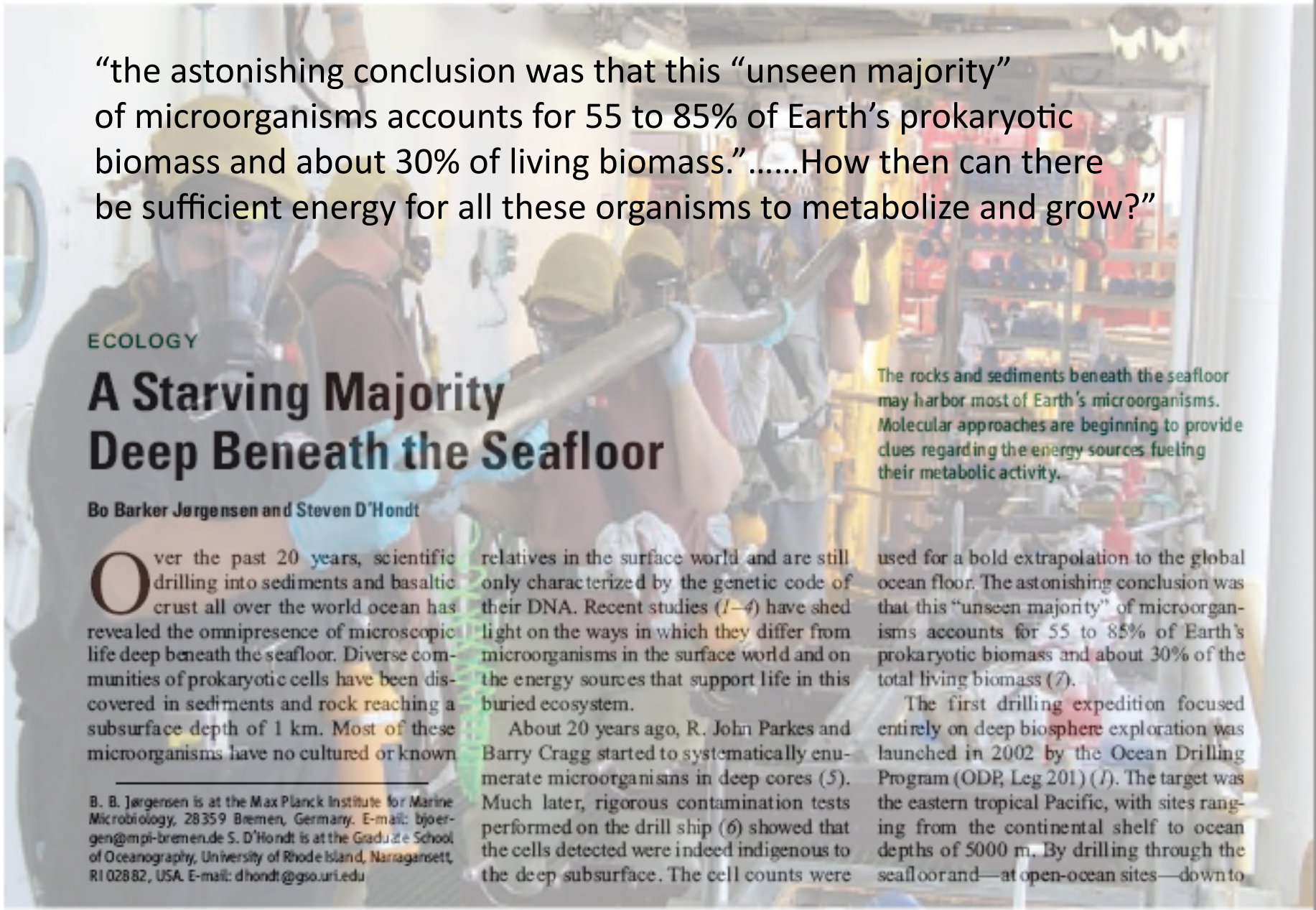


Aerobic production of methane in the sea

DAVID M. KARL^{1*}, LUCAS BEVERSDORF¹, KARIN M. BJÖRKMAN¹,
MATTHEW J. CHURCH¹, ASUNCION MARTINEZ² AND EDWARD F. DELONG²

C isotopic changes in atmospheric methane





“the astonishing conclusion was that this “unseen majority” of microorganisms accounts for 55 to 85% of Earth’s prokaryotic biomass and about 30% of living biomass.”.....How then can there be sufficient energy for all these organisms to metabolize and grow?”

ECOLOGY

A Starving Majority Deep Beneath the Seafloor

Bo Barker Jørgensen and Steven D’Hondt

Over the past 20 years, scientific drilling into sediments and basaltic crust all over the world ocean has revealed the omnipresence of microscopic life deep beneath the seafloor. Diverse communities of prokaryotic cells have been discovered in sediments and rock reaching a subsurface depth of 1 km. Most of these microorganisms have no cultured or known

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relatives in the surface world and are still only characterized by the genetic code of their DNA. Recent studies (1–4) have shed light on the ways in which they differ from microorganisms in the surface world and on the energy sources that support life in this buried ecosystem.

About 20 years ago, R. John Parkes and Barry Cragg started to systematically enumerate microorganisms in deep cores (5). Much later, rigorous contamination tests performed on the drill ship (6) showed that the cells detected were indeed indigenous to the deep subsurface. The cell counts were

The rocks and sediments beneath the seafloor may harbor most of Earth’s microorganisms. Molecular approaches are beginning to provide clues regarding the energy sources fueling their metabolic activity.

used for a bold extrapolation to the global ocean floor. The astonishing conclusion was that this “unseen majority” of microorganisms accounts for 55 to 85% of Earth’s prokaryotic biomass and about 30% of the total living biomass (7).

The first drilling expedition focused entirely on deep biosphere exploration was launched in 2002 by the Ocean Drilling Program (ODP, Leg 201) (1). The target was the eastern tropical Pacific, with sites ranging from the continental shelf to ocean depths of 5000 m. By drilling through the seafloor and—at open-ocean sites—down to

Organic matter cycling in anoxic (no oxygen) Marine sediments



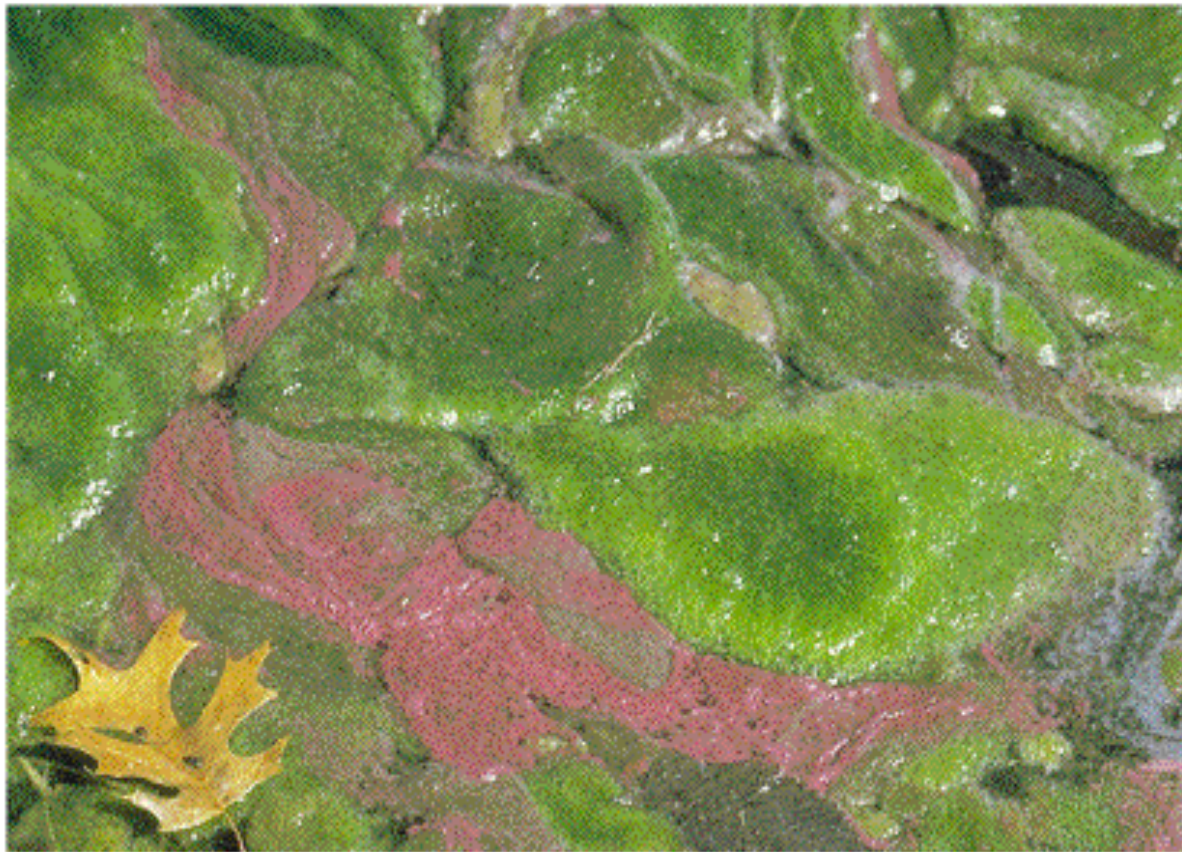
How is organic matter oxidized without oxygen?

What biological communities can exist in anoxic sediments and how do they function?

How does biogeochemical cycling in anoxic marine sediments affect global C:N:S cycles?

What is the origin of petroleum source rocks?

Bacterial communities are much more metabolically specialized than higher heterotrophs. The communities are strictly segregated according to the environmental conditions. This leads to biogeochemical zoning of microbes and chemical species (nutrients, carbon dioxide, methane, etc.).



T. D. Brock

These communities are widespread in the Great Sippewissett Marsh in West Falmouth.

Oxidation of organic matter in marine sediments

Reaction	ΔE (kJ/mole)	Capacity (mmol/L sediment)
$O_2 \longrightarrow CO_2$	-475	0.85
$NO_3^- \longrightarrow N_2 + CO_2$	-448	0.05
$Mn(IV) \longrightarrow Mn(II)$	-349	2 - 22
$Fe(III) \longrightarrow Fe(II)$	-114	14 - 28
$SO_4^{2-} \longrightarrow S^{2-}$	-77	56
$CO_2 \longrightarrow CH_4$	-58	

Organic matter cycling in anaerobic sediments

After oxygen is depleted, organic matter is degraded only by microbes, which degrade complex organic substrates through consortial interactions

Fermentation:



Sulfate reduction:



Methanogenesis:



Organic Matter

proteins 50% C, 80% N (soluble/structural)
polysaccharides 20-30% C, 10% N (soluble/structural)
nucleic acids 10% C, 5% N, 50% P
lipids 10% C, few % N

oxic degradation
nitrate reduction



soluble constituents
 $\text{CO}_2, \text{NO}_3^-, \text{HPO}_3^-$

proteins (structural), peptides
polysaccharides (structural), oligosaccharides,
sugars, nucleic acids, lipids

extracellular hydrolysis
fermentation



$\text{CO}_2, \text{NH}_3, \text{HPO}_3^-, \text{H}_2$

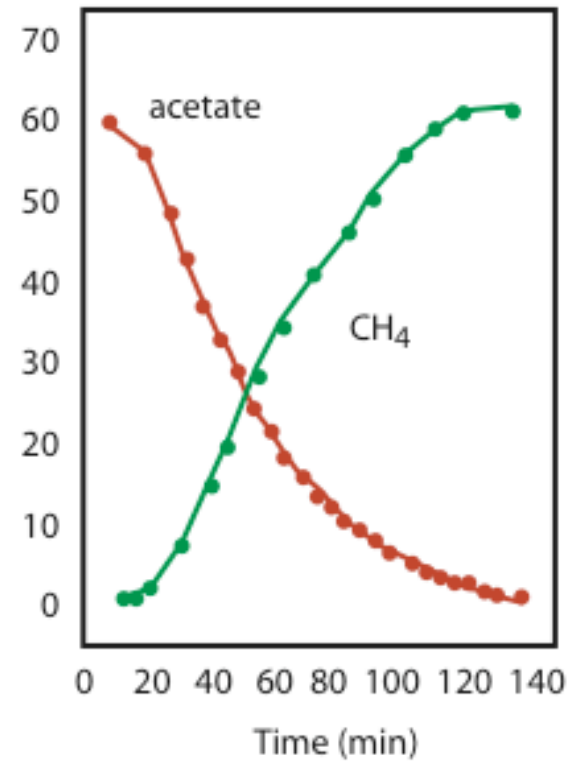
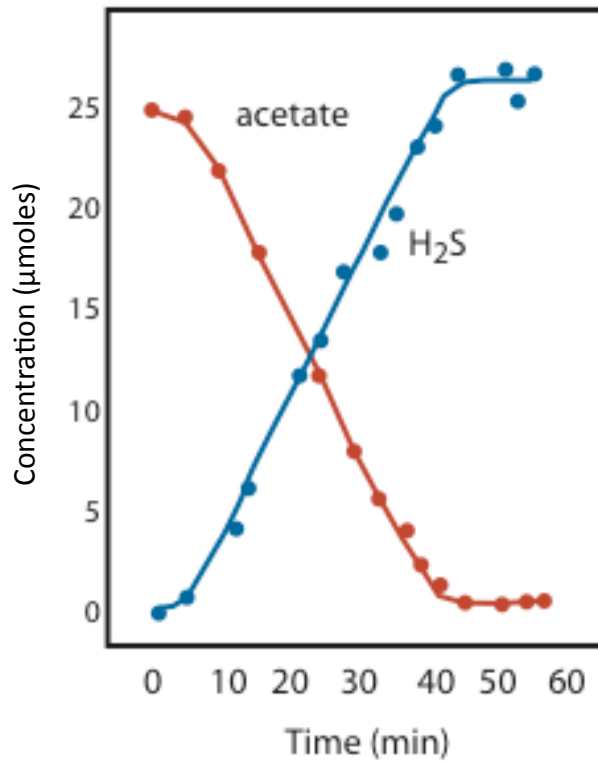
volatile fatty acids

sulfate reduction
methanogenesis



$\text{CO}_2, \text{CH}_4, \text{NH}_3, \text{HPO}_3^-, \text{H}_2\text{S}$

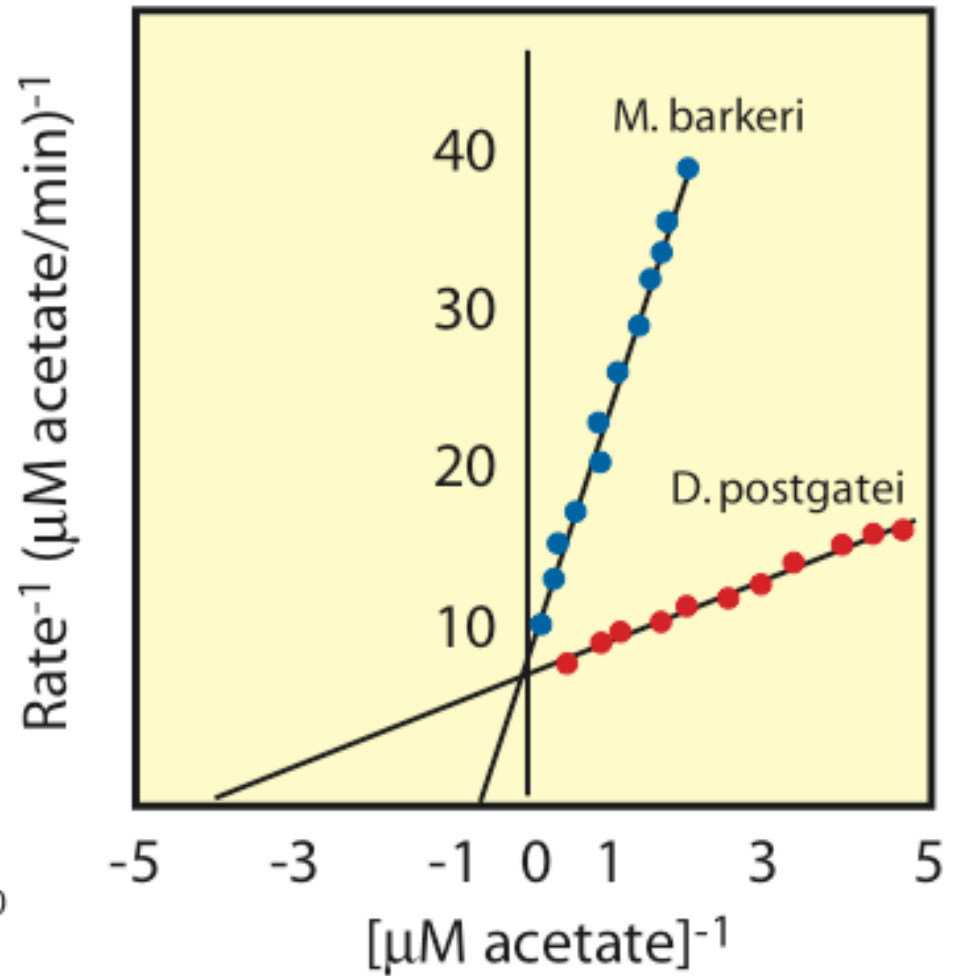
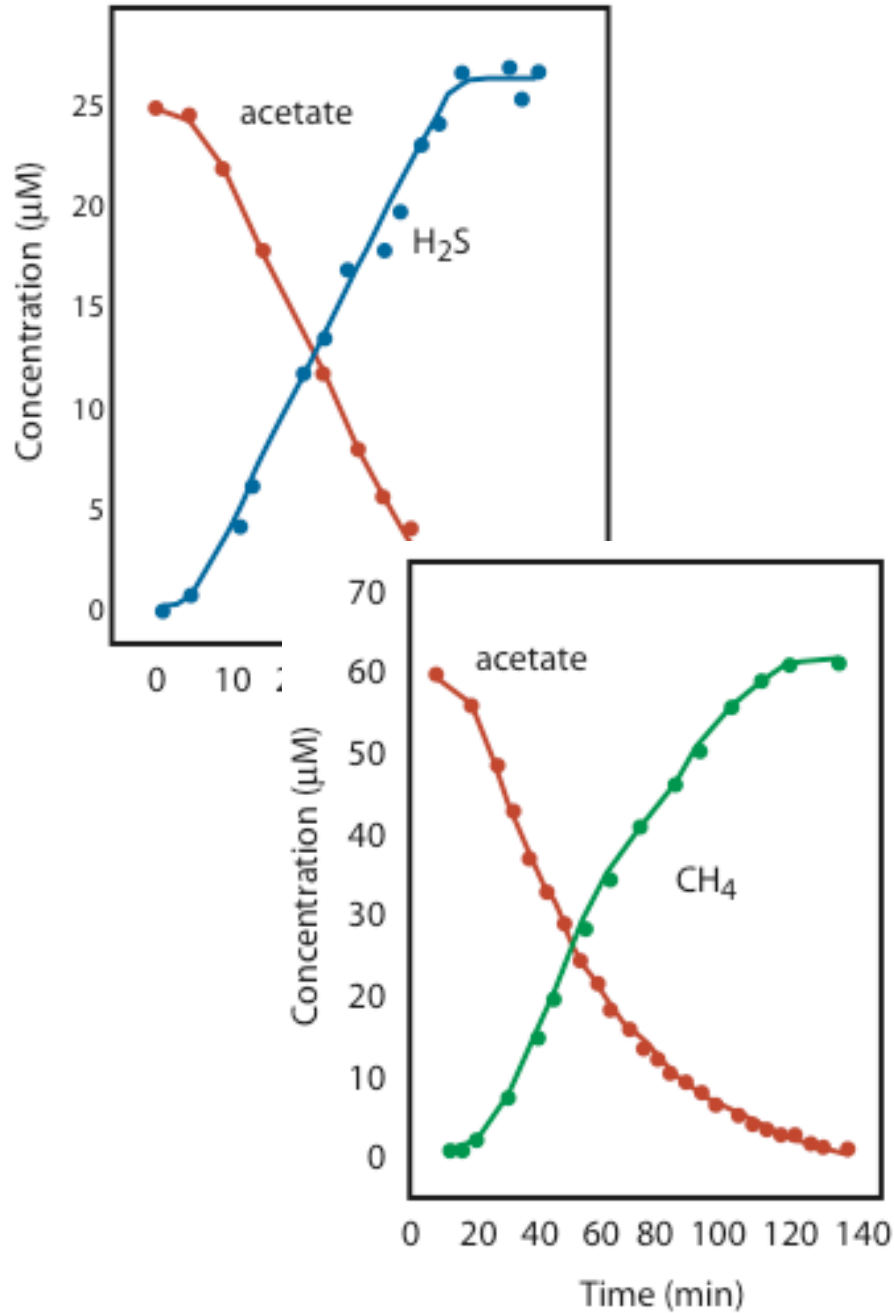
Sulfate reducing and methanogenic bacteria use only a small, specific set of substrates as terminal electron acceptors- and there is competition for these substrates that yields biogeochemical stratification or zonation in sediments



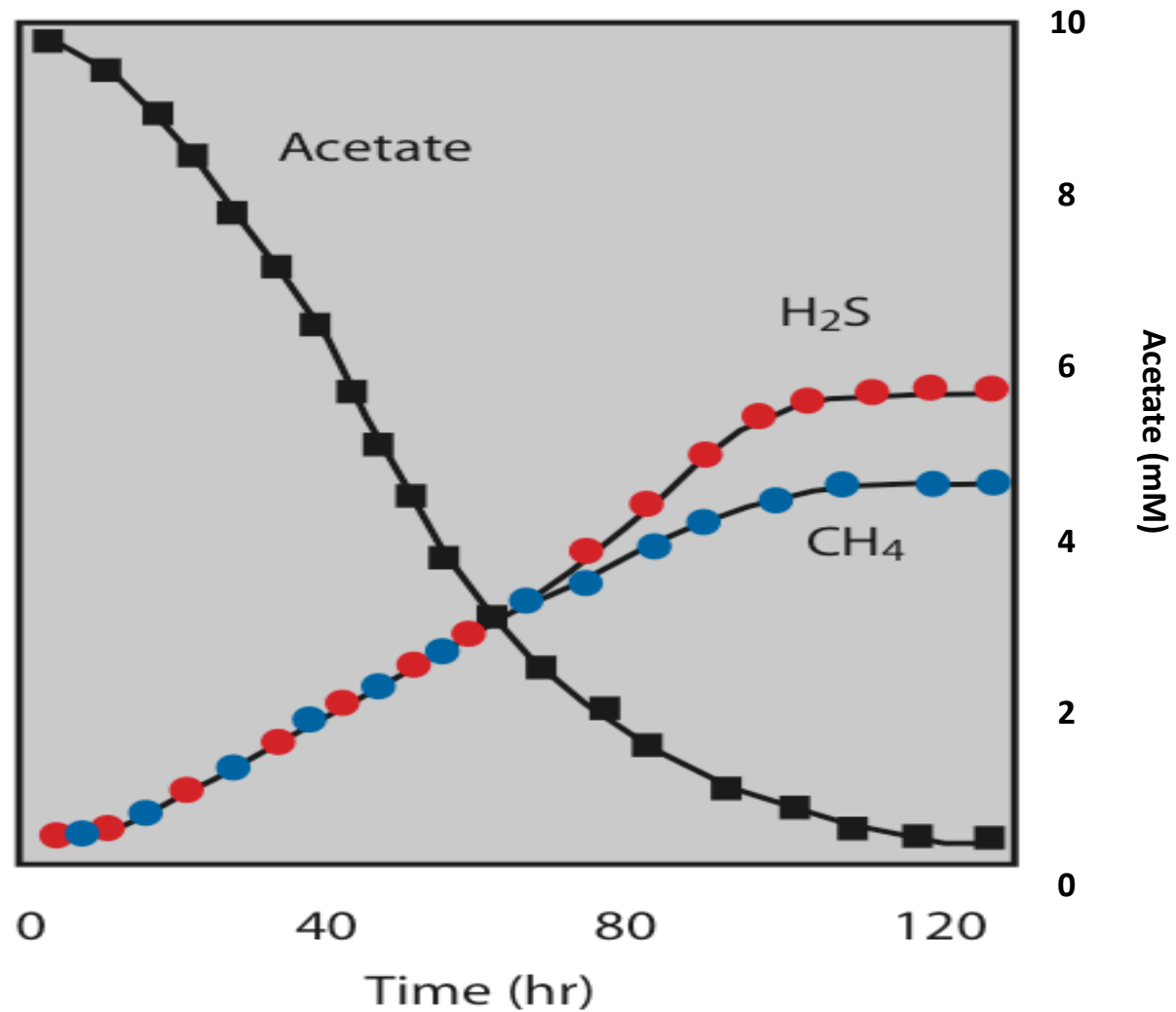
Acetate = CH_3COOH
Volatile Fatty Acid (VFA) = CH_3RCOOH

Double reciprocal plot of rate vs Acetate concentration

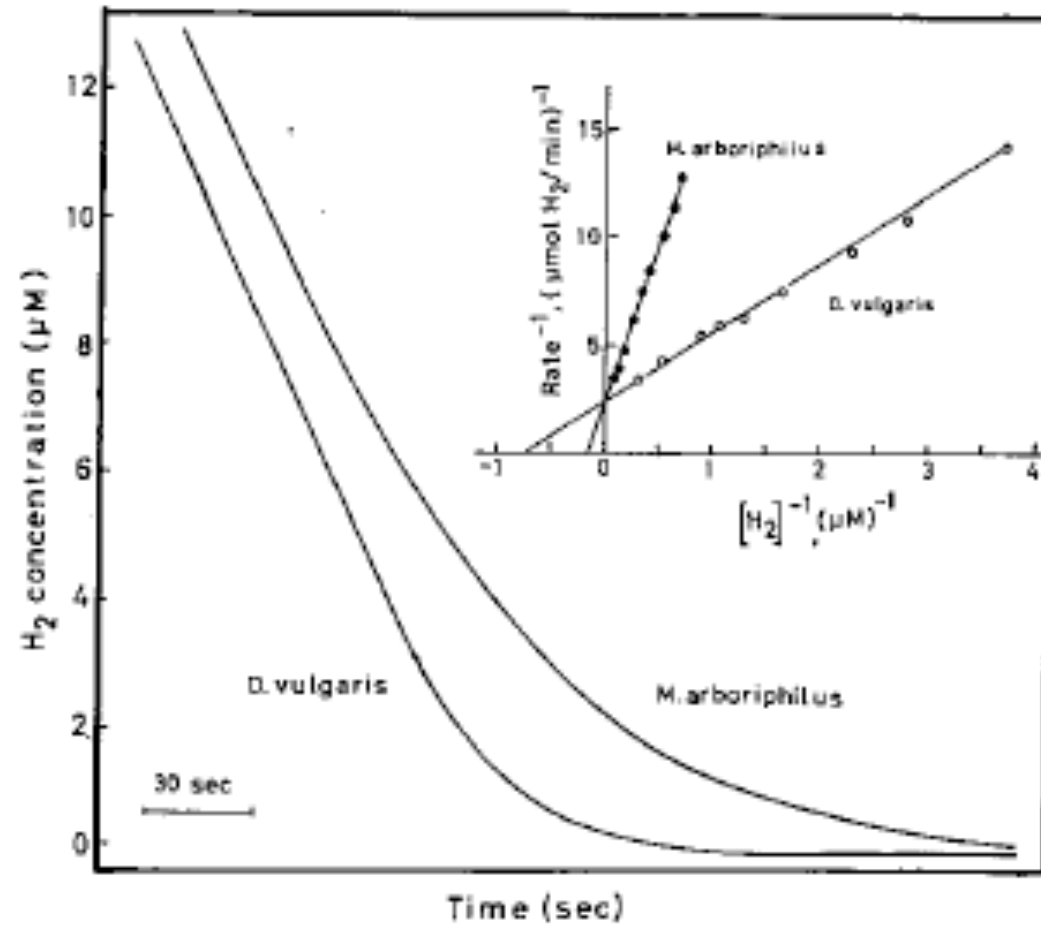
$$1/\text{rate} = 1/R_m + K_s/R_m (1/[\text{acetate}])$$



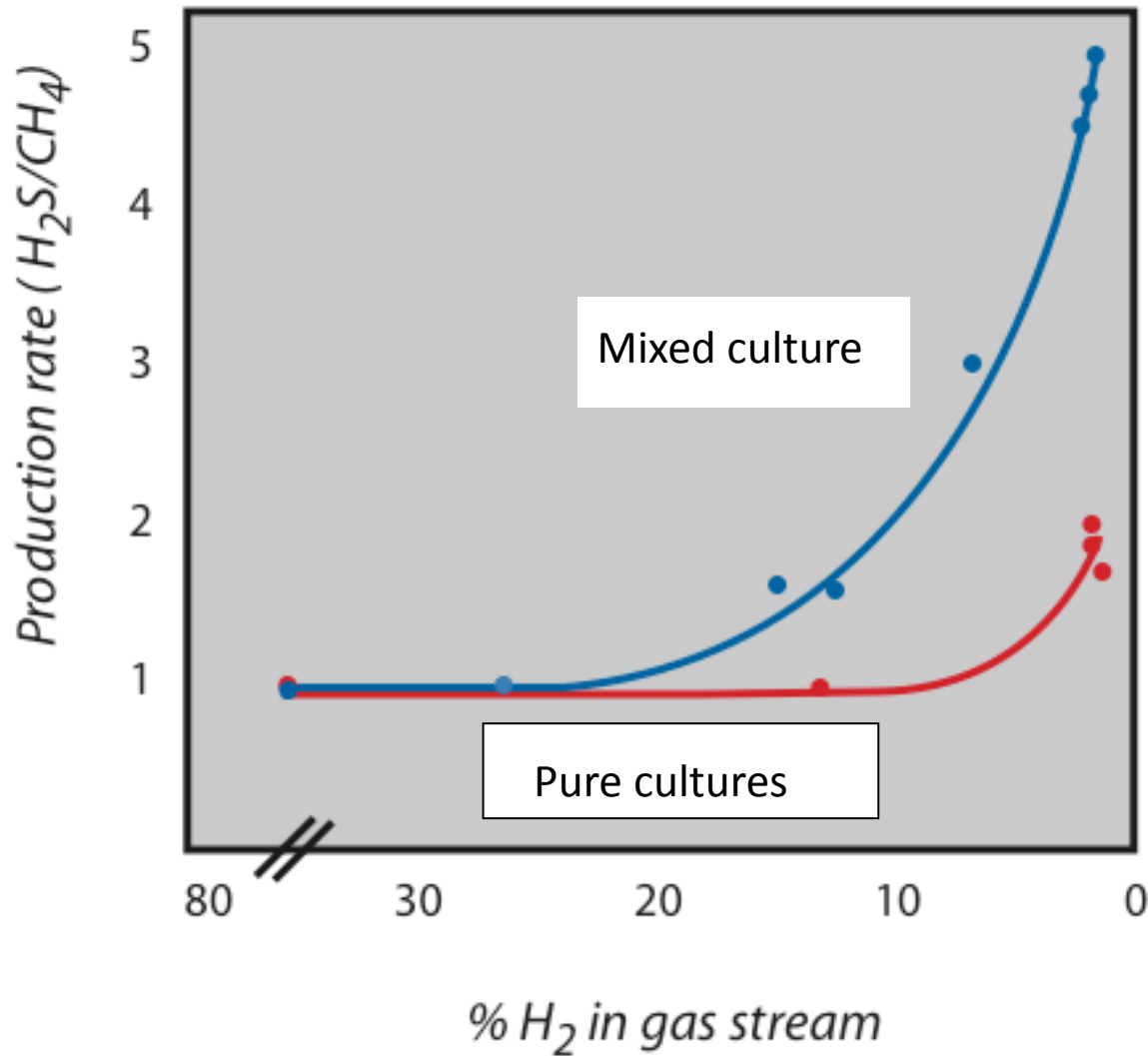
Competition for acetate between
Desulfobacter postgatei and *Methanosarcina bakerii*



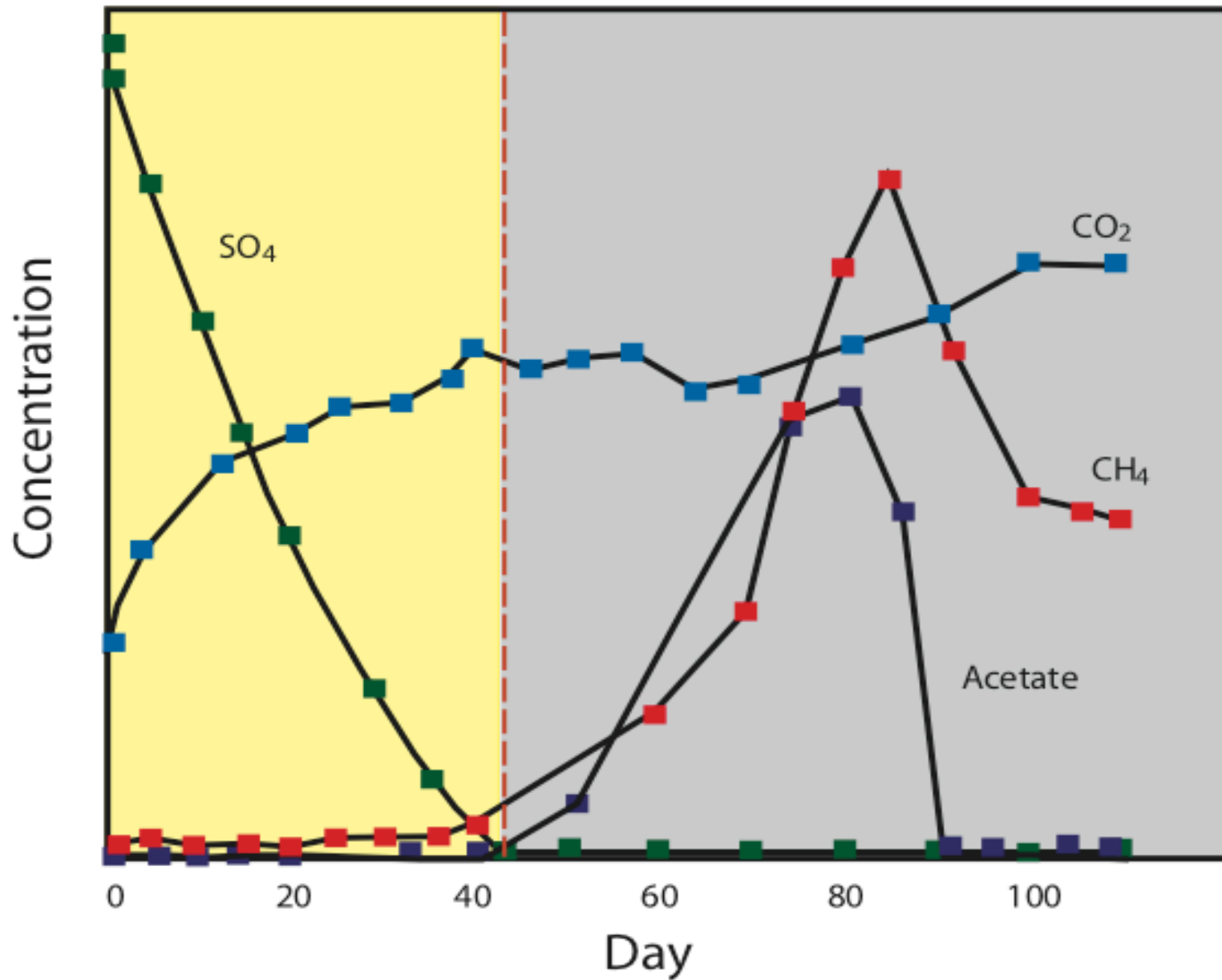
Uptake of hydrogen gas by SRB and Methanogens



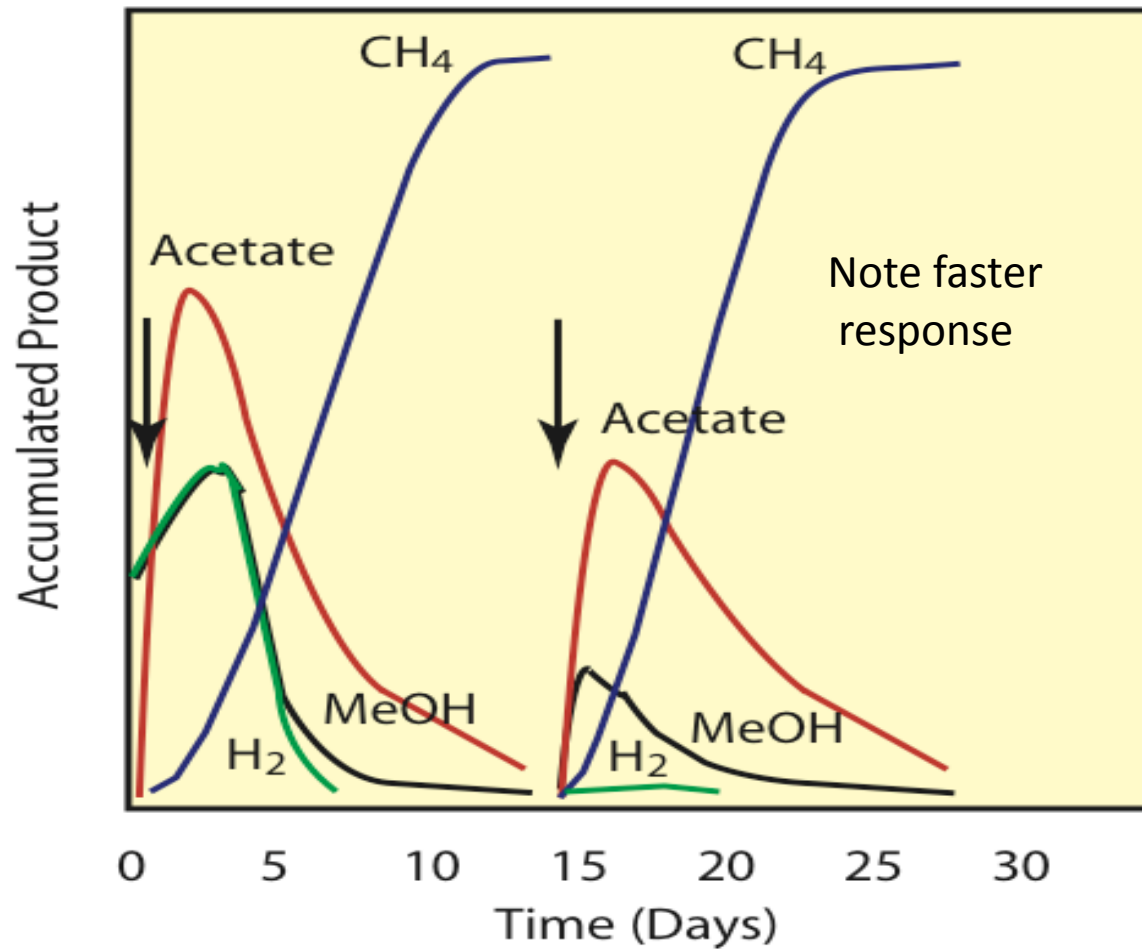
Competition for hydrogen between sulfate reducing and methanogenic bacteria



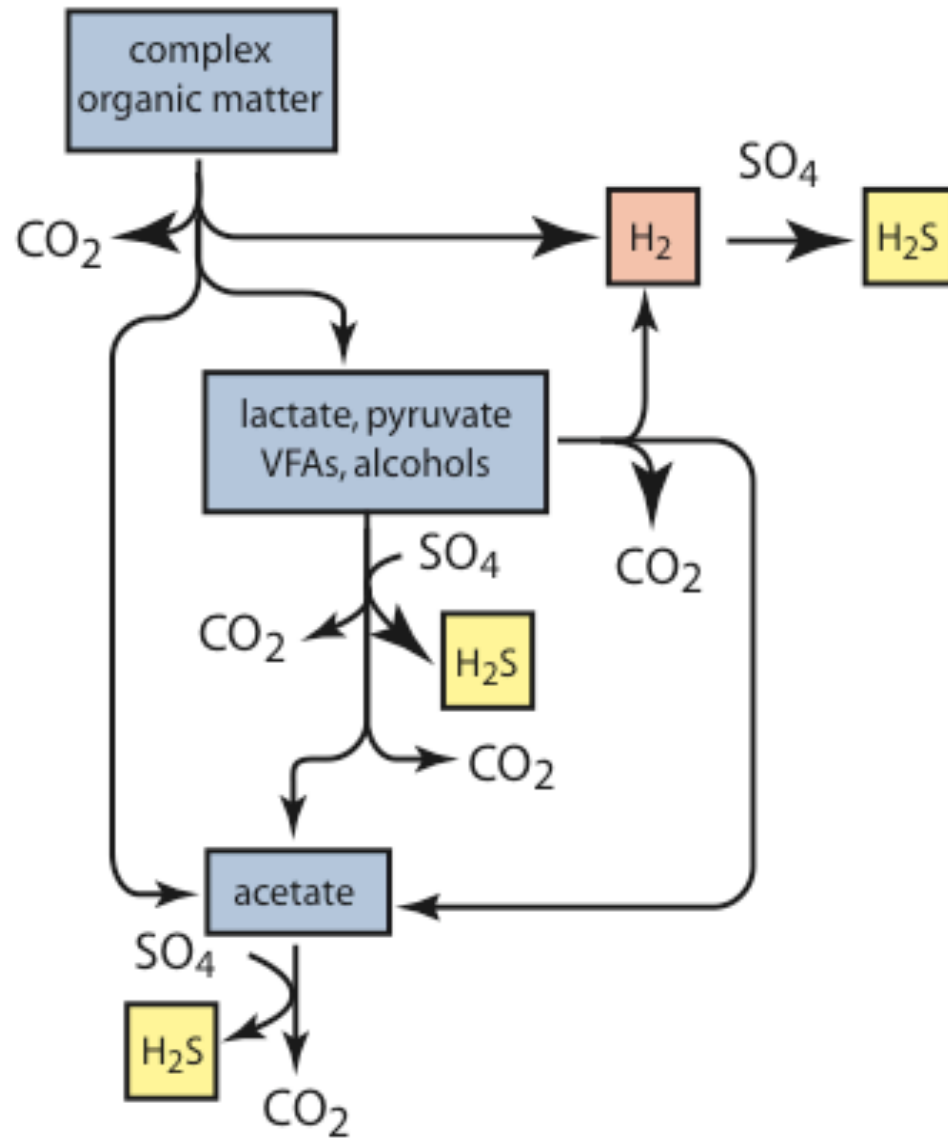
Changes in pore water concentrations during a 114 day incubation



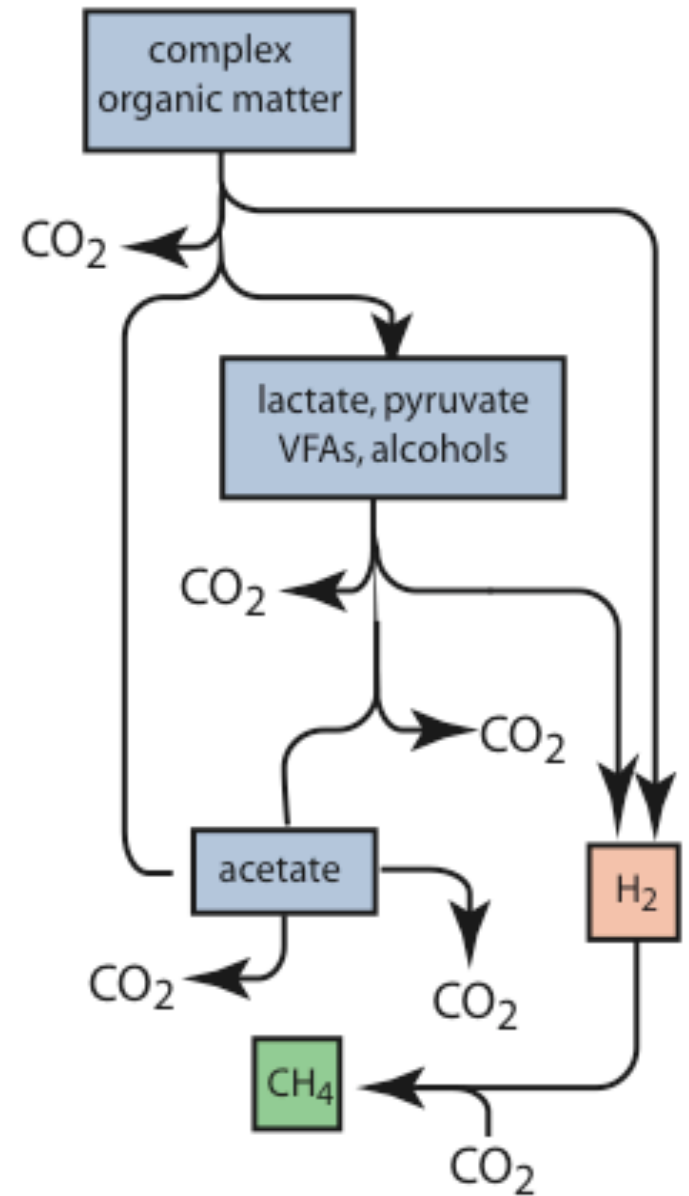
Anaerobic degradation of pectin (plant cell wall methylated sugar)
in a sediment slurry



Sulfate Present



Sulfate Absent



Chemical thermodynamics and pure culture studies of anaerobic micro-organisms show that the oxidizing capacity of sediments is >>> than $[O_2]$.

We predict that sulfate and ultimately carbon dioxide will be used as electron acceptors during organic matter oxidation.

We also predict that sulfate reduction will occur before methanogenesis.

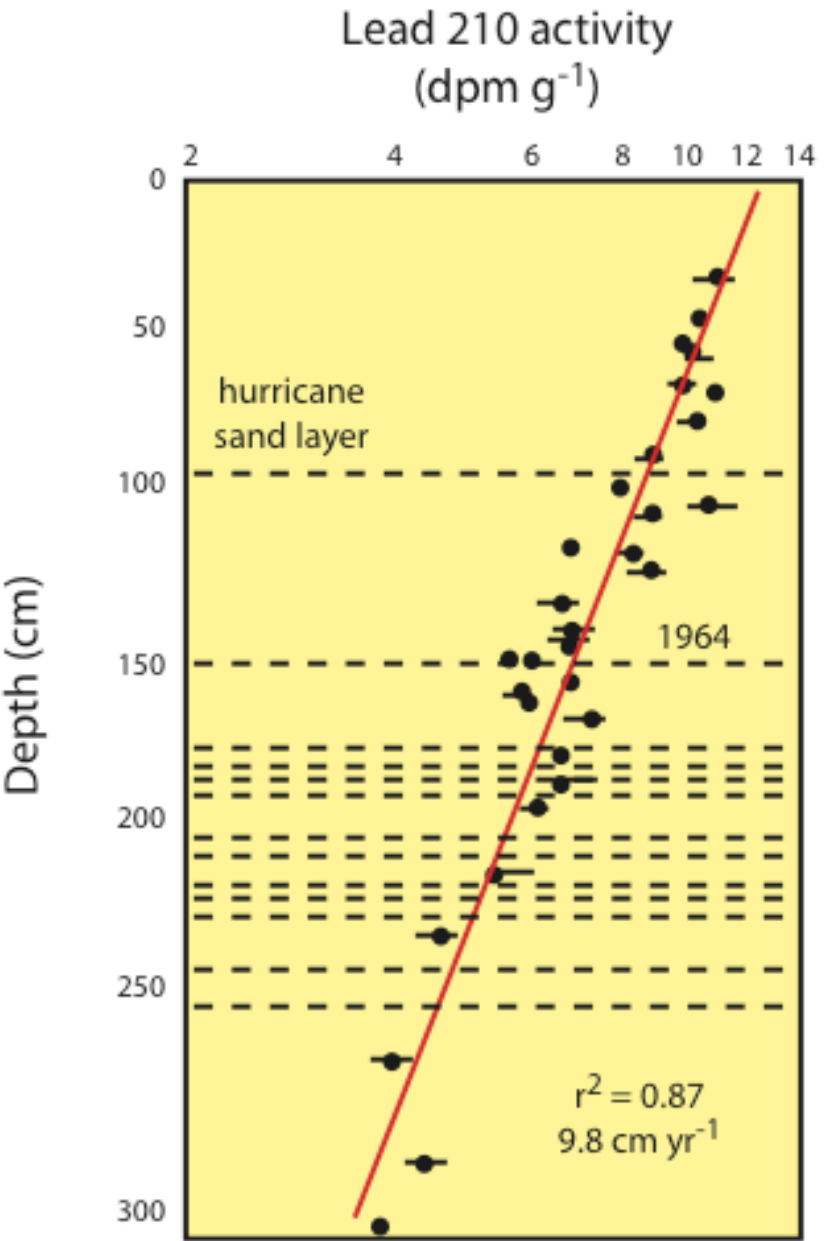
Can we observe the consequences of these factors
And model their impact on organic matter oxidation?

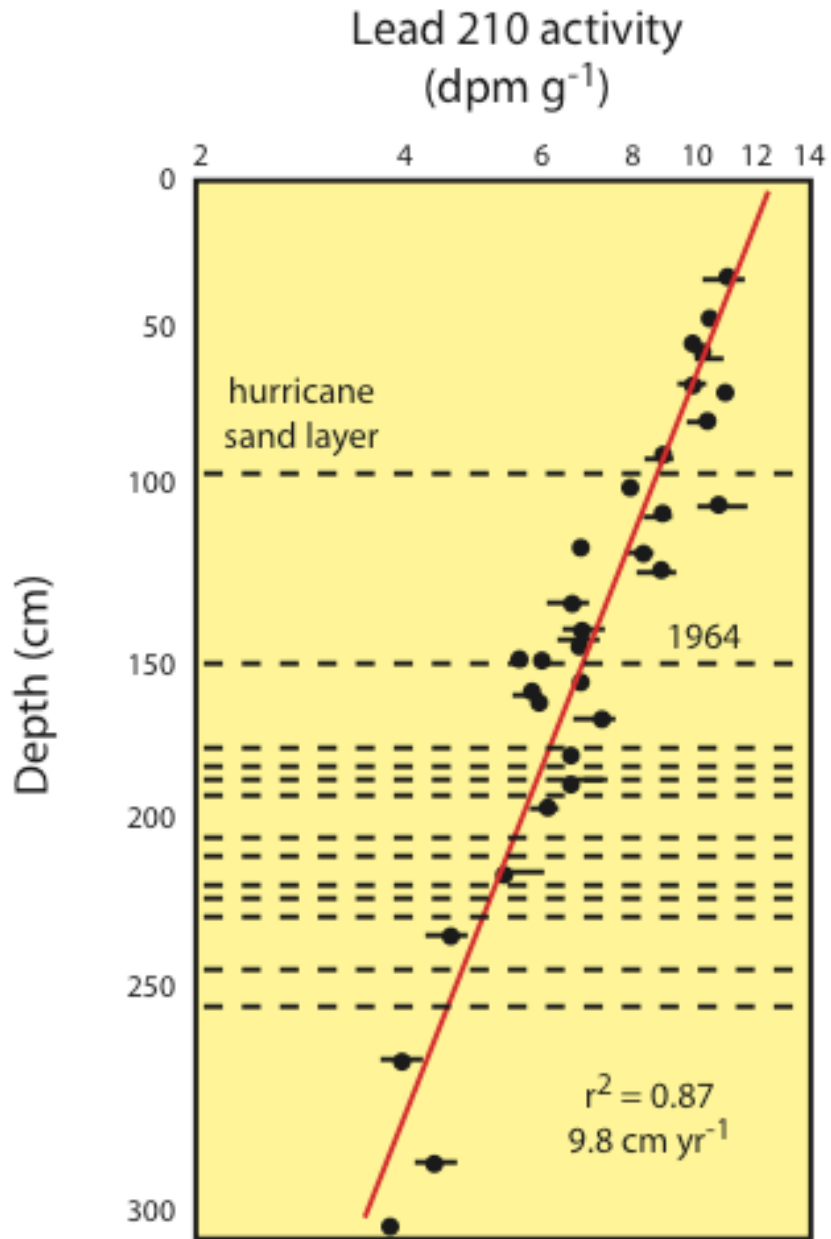
Biogeochemical cycling in Cape Lookout Bight Sediments



The site has been studied by Chris Martens and his group at UNC Chapel Hill for > 30 years.

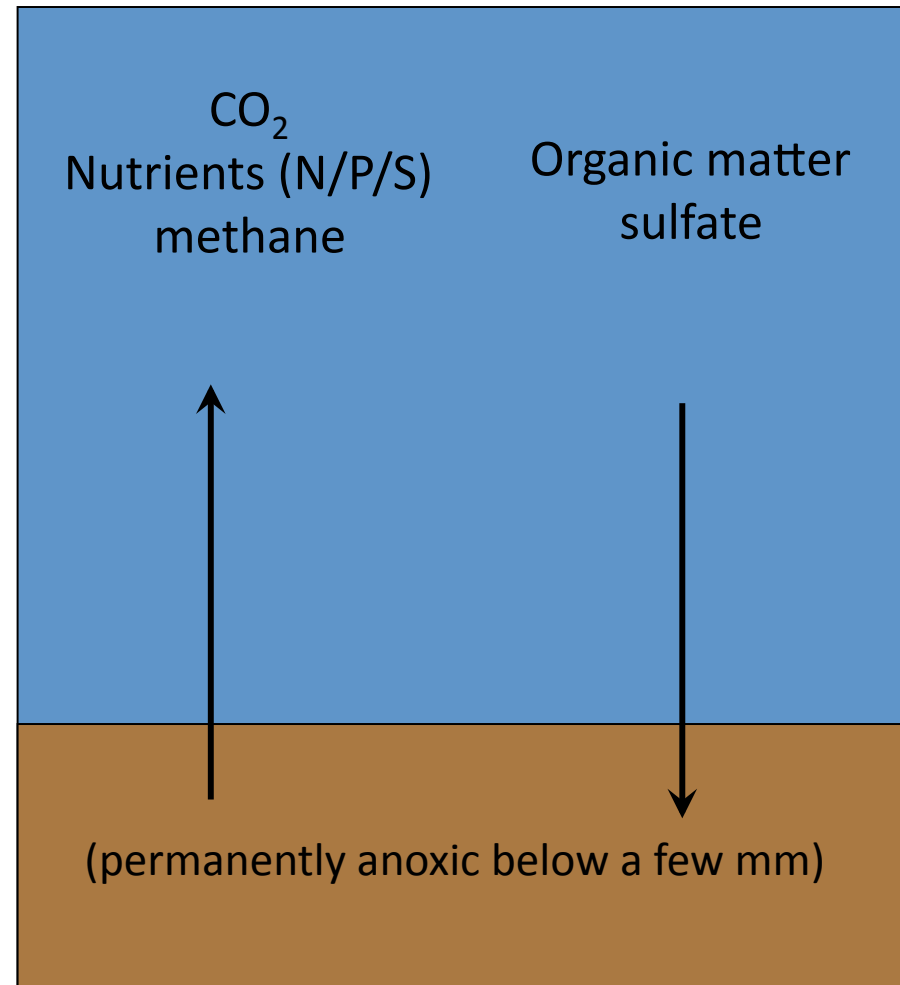
Biogeochemical cycling in Cape Lookout Bight Sediments



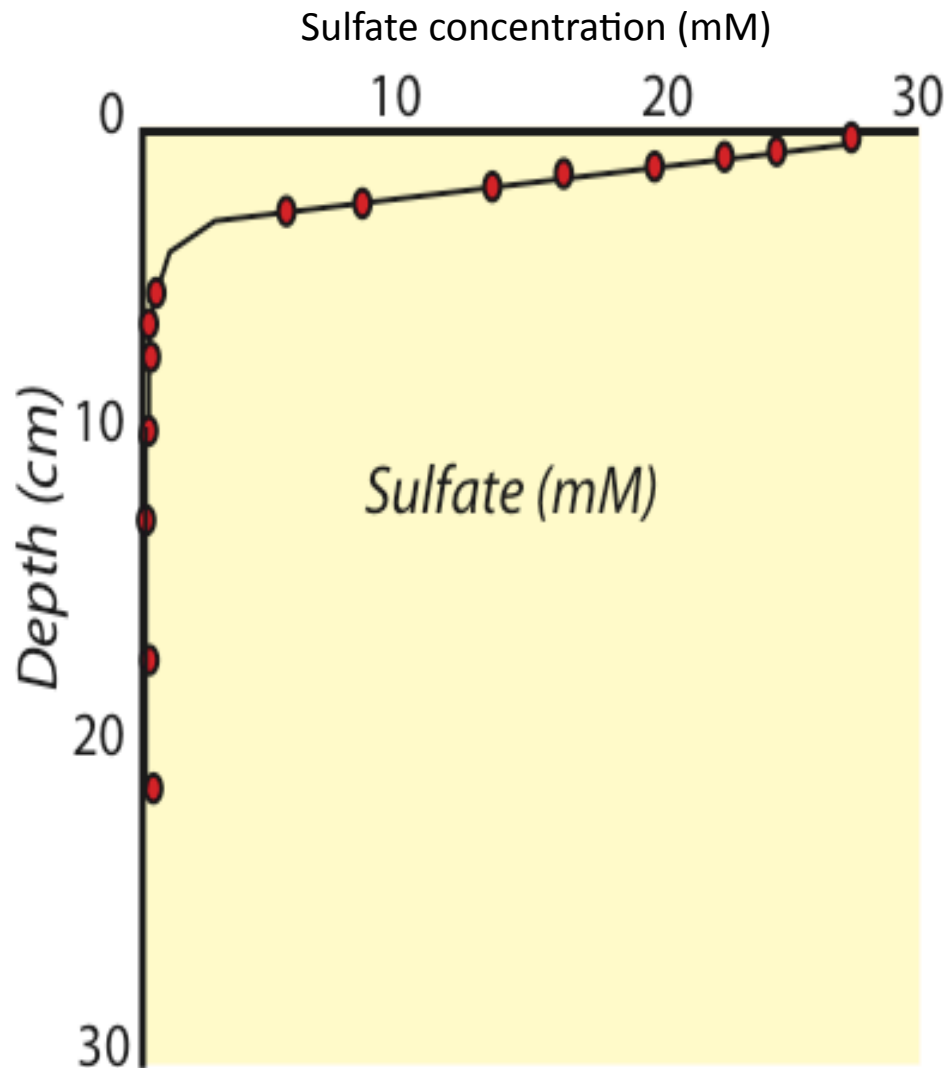


BGC cycling in Cape Lookout
Bight Sediments

Can we achieve mass balance if the
system is at steady state?



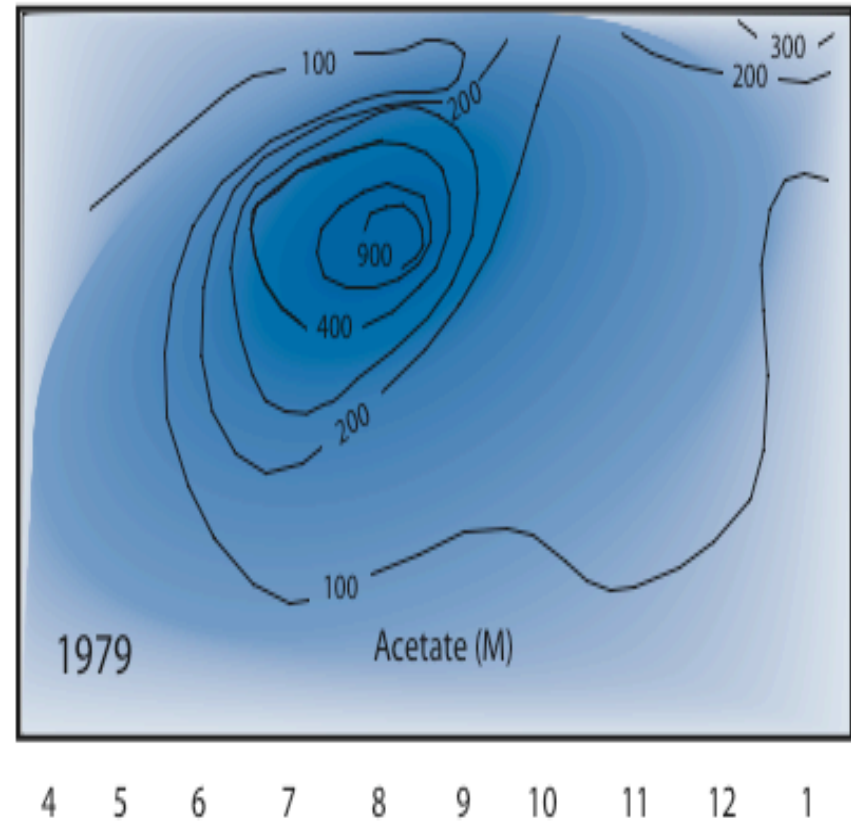
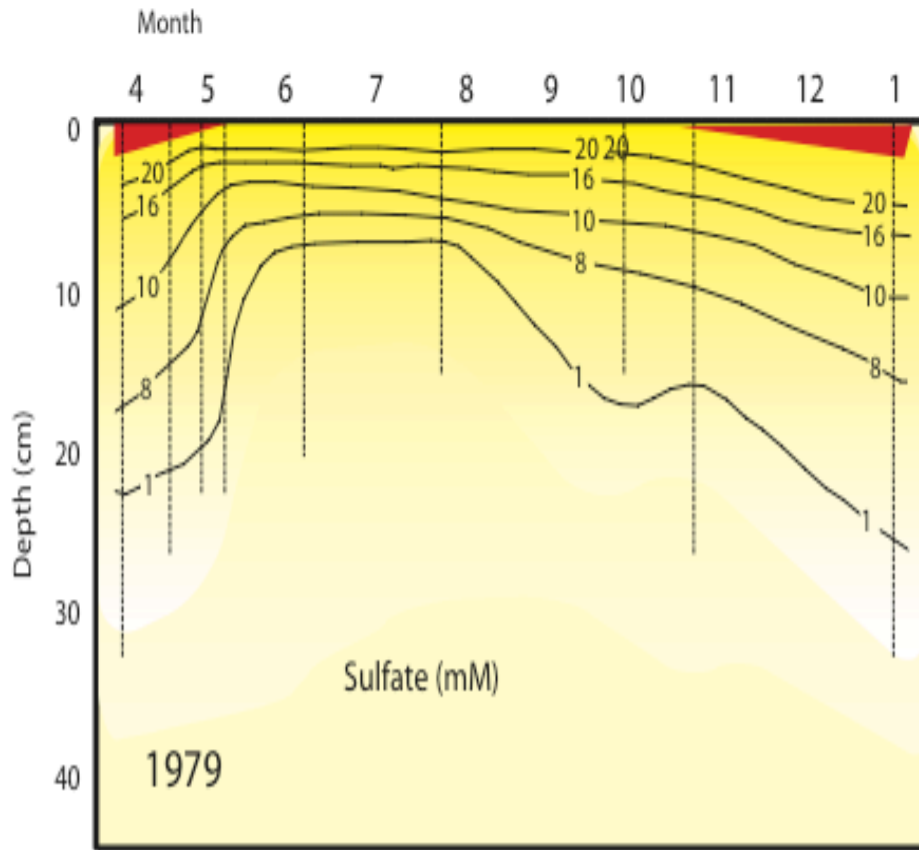
Summertime (August) porewater sulfate concentrations in CLB sediments



$$\text{Flux} = k (\delta C / \delta z)$$

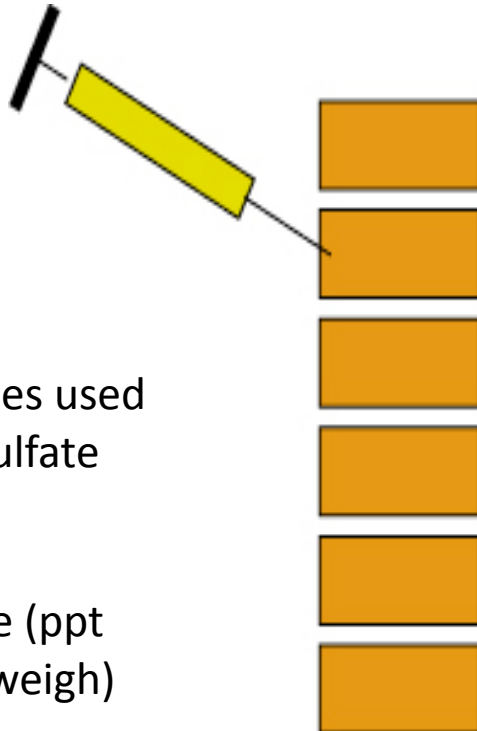
If we have the stoichiometry
correct S loss = 2x CO₂ production

Seasonal distribution of sulfate and acetate In Cape Lookout Bight sediments



Note that sulfate is exhausted closer to the sediment/water interface in summer due to enhanced rate of sulfate reduction. Acetate accumulates only when sulfate reaches low concentrations

Measurement of sulfate oxidation using ^{35}S



Two techniques used to measure sulfate reduction:

Loss of sulfate (ppt with BaSO_4 , weigh)

Radiolabel (production of volatile ^{35}S and ZnS)

Moles of sulfate reduced ($\text{m}^{-2} \text{yr}^{-1}$)

	tube	^{35}S
Jan	8.0	12.2
Feb	7.7	13.3
Mar	11.4	12.7
Apr	15.2	7.4
May	11.8	16.4
Jun	16.8	20.9
July	22.0	25.4
Aug	27.2	30.0
Sept	26.2	23.3
Oct	17.5	16.2
Nov	8.7	10.0
Dec	6.4	11.1
	15.1	16.6



Therefore 32 moles C by sulfate oxidation

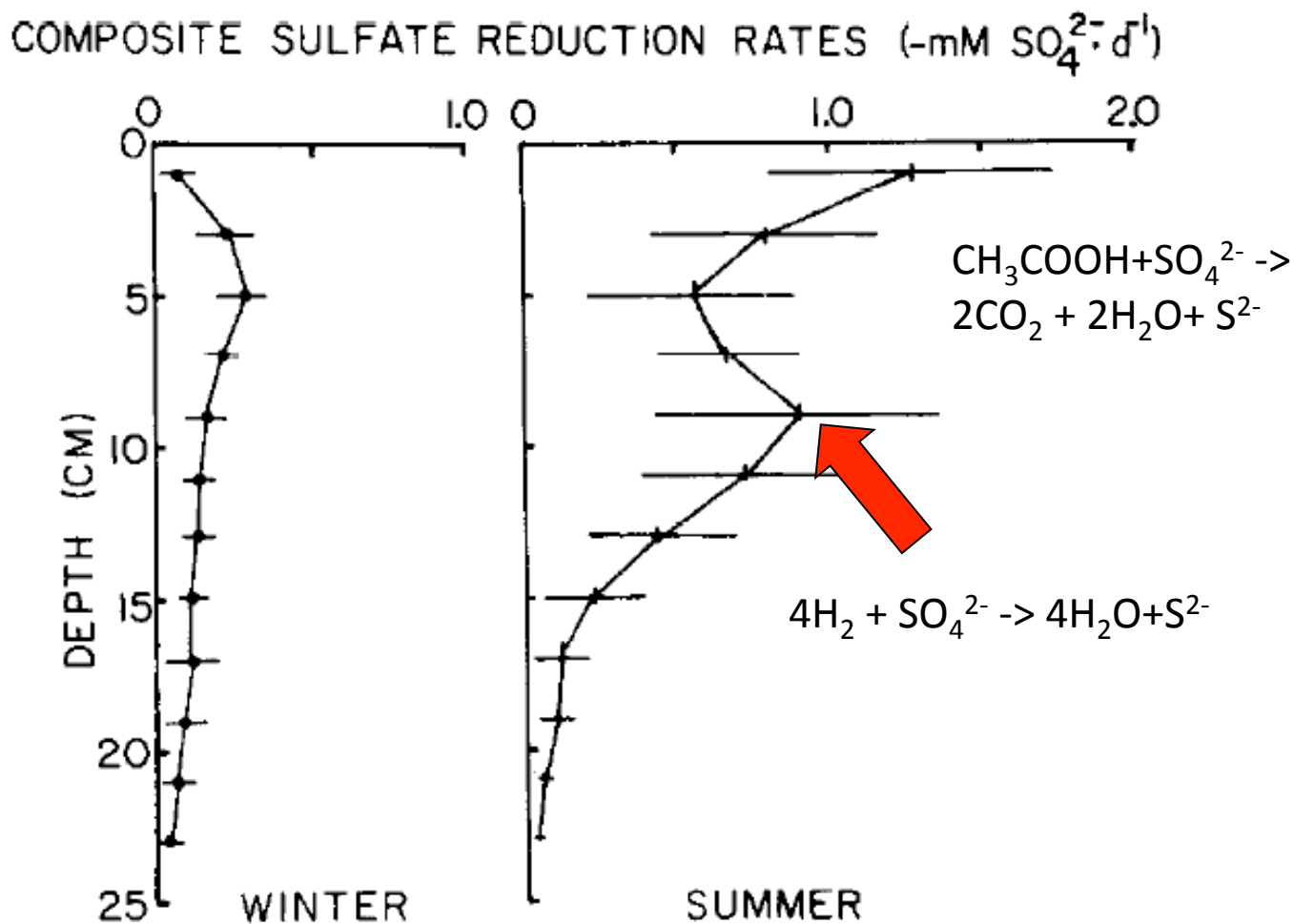
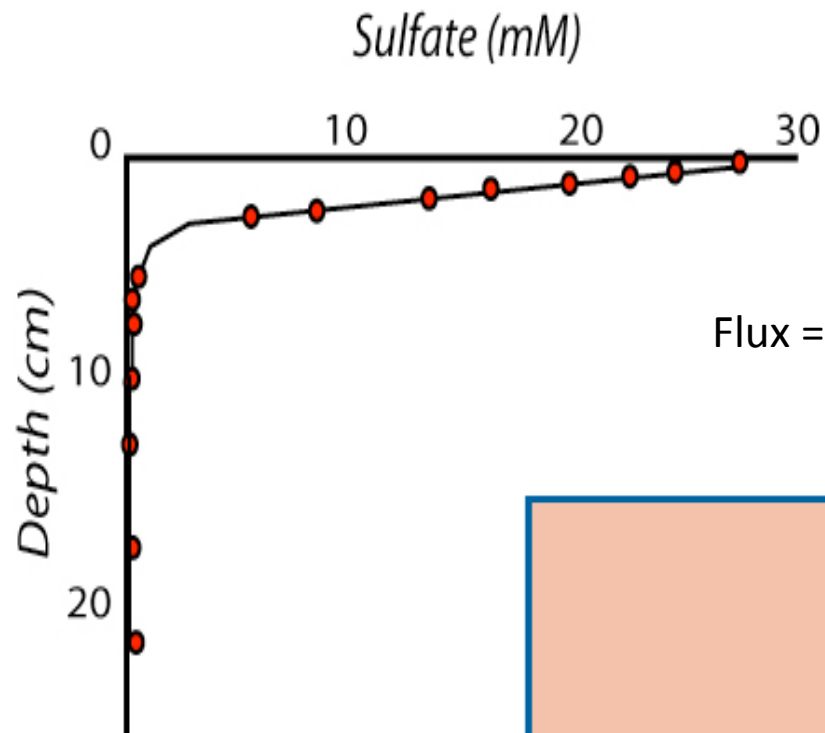


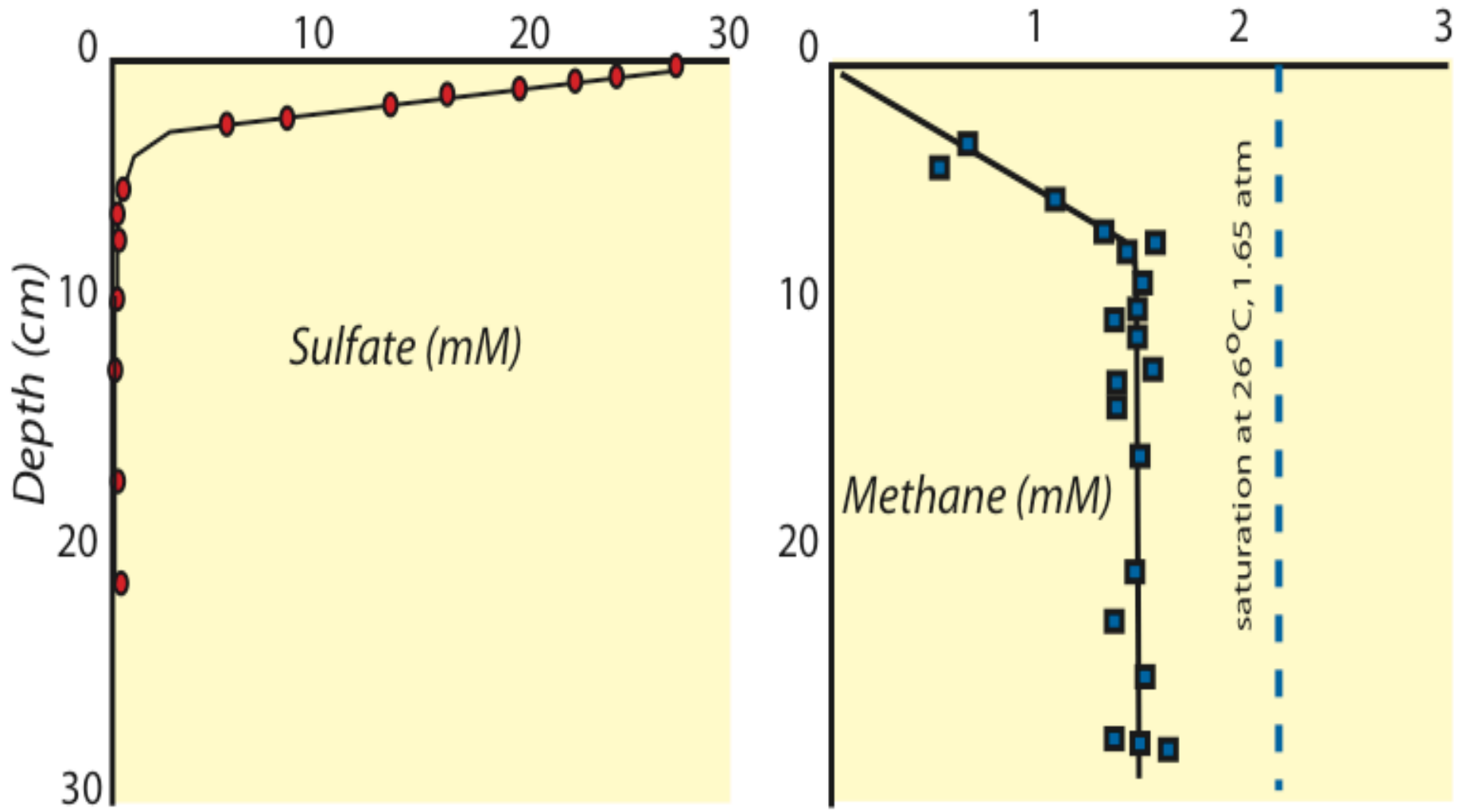
FIG. 5. Composite rates of sulfate reduction vs. depth for winter, non-bubbling (Nov–Apr) sediments and for mid-summer, bubbling sediments (June–Aug). The horizontal lines are the ranges of the rates measured at that depth.



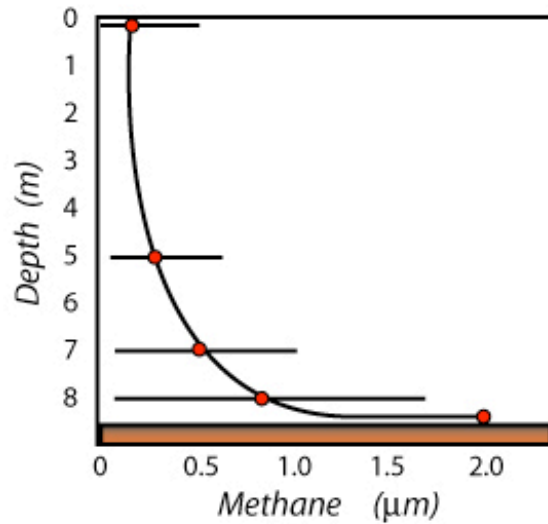
How can we calculate C remineralization from sulfate reduction?

	Sulfate Reduction Rate		
	DS	D'S	measured
Kinetic model	13.1	15.5	
Computer gradient	12.1	16.2	
Linear gradient	12.1		
sediment incubation			15.6
³⁵ S reduction			16.6

Sulfate and Methane in CLB sediments (August)



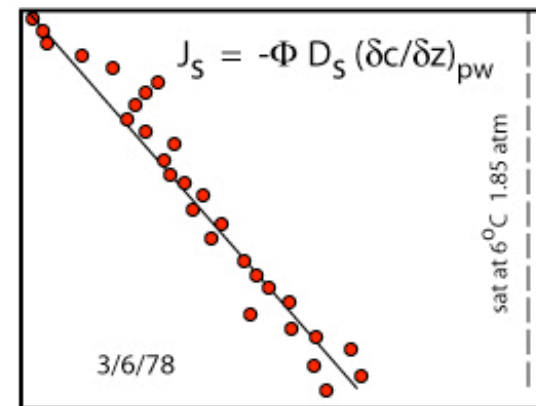
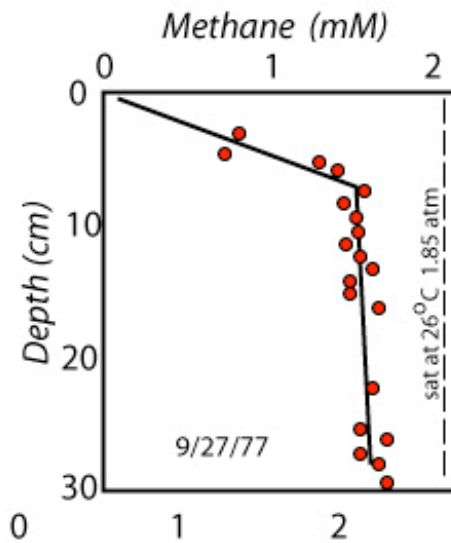
Methane fluxes from CLB sediments



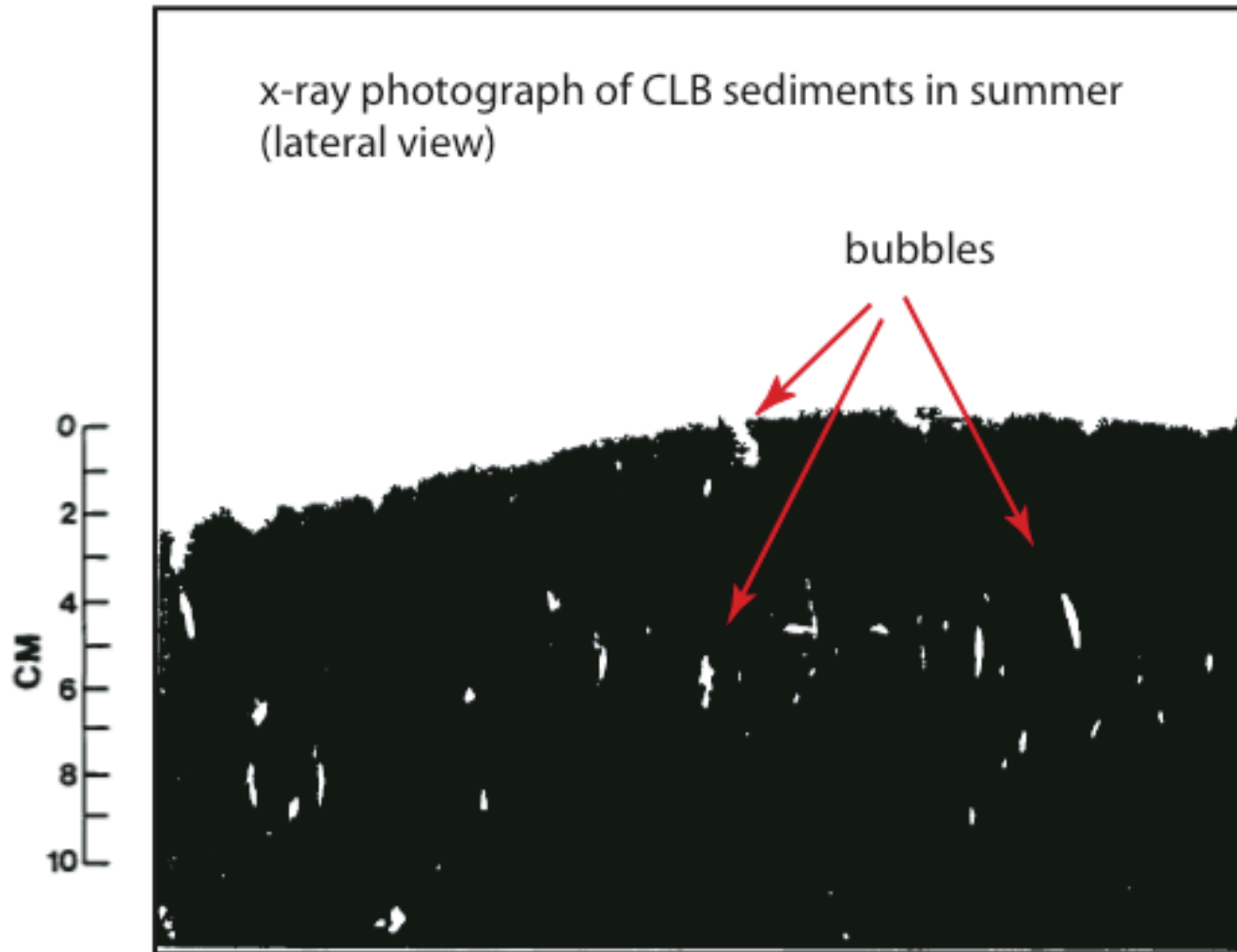
Methane diffusive fluxes

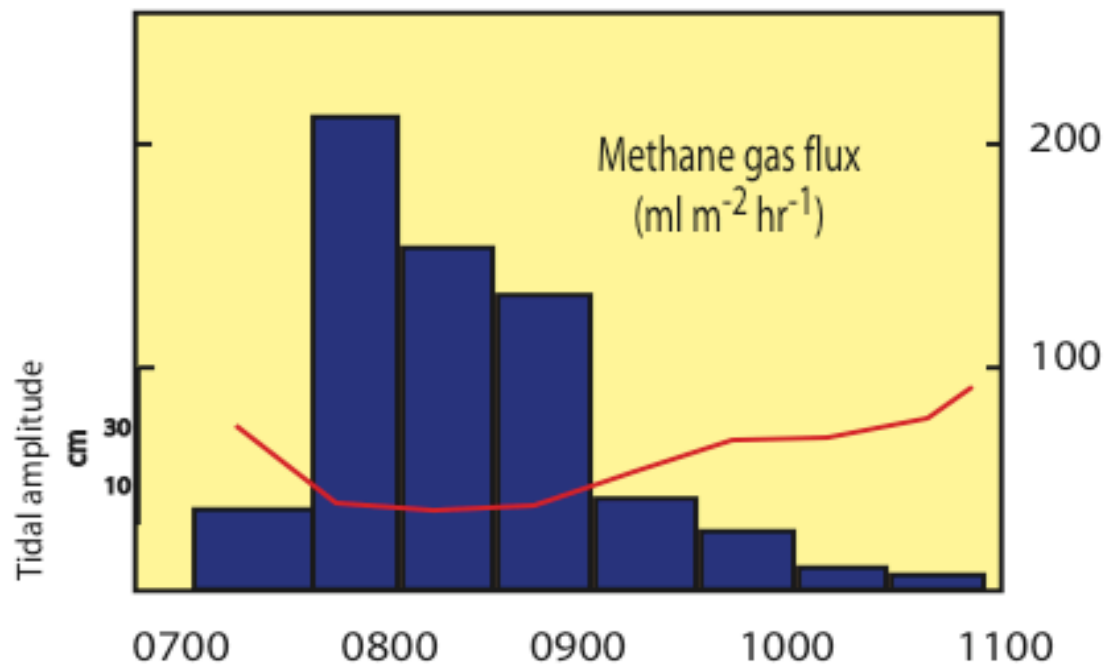
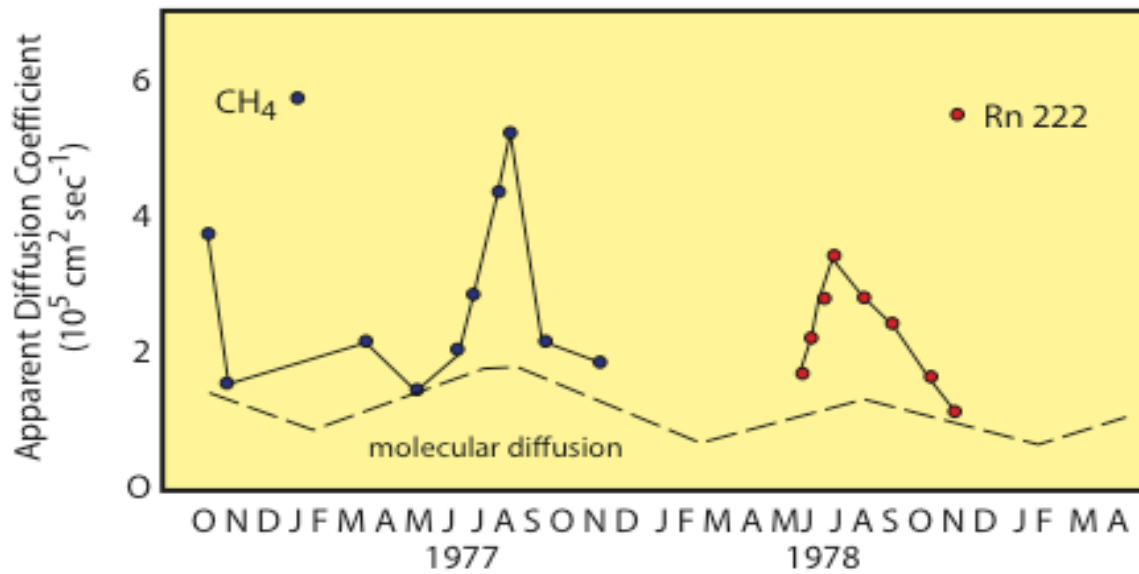
Date	J_s	J_{theor}	J_{excess}
16 October 76	84	31	53
6 November 76	30	26	4
25 March 77	51	27	24
16 May 77	48	50	0
27 June 77	82	69	13
13 July 77	130	78	52
5 August 77	274	115	159
22 August 77	393	129	264
20 September 77	186	160	25
17 November 77	66	46	20

Calculation of Methane flux from CLB sediments



Methane concentrations build up to saturation values and form bubbles that remove CO_2 and methane from sediments





ΣCO_2 fluxes
 $\mu\text{m m}^{-2} \text{hr}^{-1}$

CH_4 fluxes
 $\mu\text{m m}^{-2} \text{hr}^{-1}$

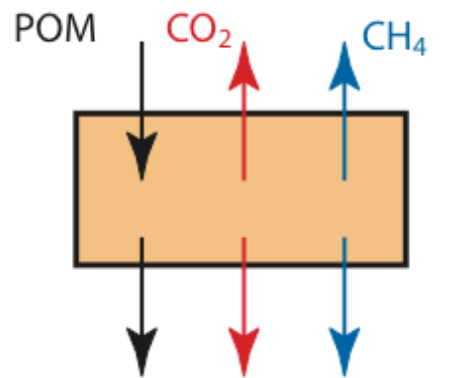
Month	diff	bubble	Total	diff	bubble	Total
Jan	1900	0	1900	50	0	50
Feb	1900	0	1900	50	0	50
March	1900	0	1900	51	0	51
April	1900	0	1900	50	0	50
May	3825	0.6	3826	48	52	100
June	5400	5.6	5406	82	480	562
July	6000	20	6020	130	1740	1870
Aug	6300	26	6326	334	2250	2484
Sept	4900	18	4918	184	1500	1684
Oct	2700	6.5	2707	84	560	644
Nov	2200	0.8	2201	48	65	113
Dec	1900	0	1900	50	0	50

Average 3400 6.5 **3407** 97 544 **651**

mean monthly flux ($\text{mole m}^{-2} \text{yr}^{-1}$)

29.8 0.057 **29.9** 0.85 4.85 **5.70**

Total C remineralization in CLB sediments



remineralization = C flux

	out of top	out of bottom
	$\Sigma\text{CO}_2 = 29.9$	$\Sigma\text{CO}_2 = 5.7$
	$\Sigma\text{CH}_4 = 5.7$	$\Sigma\text{CH}_4 = 0.1$
	<hr/>	<hr/>
	35.6	5.8
	Total C remineralization	
	41.4 moles $\text{m}^{-2} \text{yr}^{-1}$	

If the total methane flux is 5.8 moles $\text{m}^{-2} \text{yr}^{-1}$, then twice this (11.6 moles, or 28% total) of C remineralization must be due to methanogenesis.

The remainder ($41.4 - 11.6 = 29.8$ moles $\text{C m}^{-2} \text{yr}^{-1}$) must be due to sulfate reduction. Measurements suggest that sulfate reduction is 30-36 moles $\text{C m}^{-2} \text{yr}^{-1}$, Which is in excellent agreement !

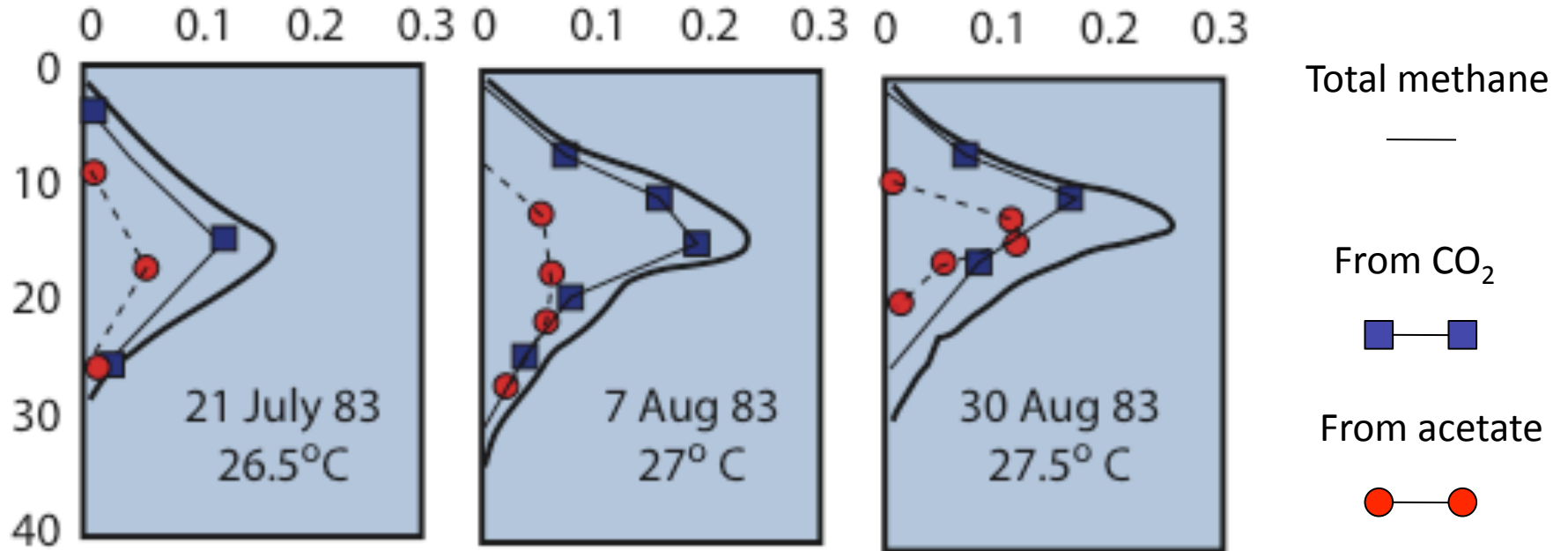
Methanogenesis occurs via two general pathways:



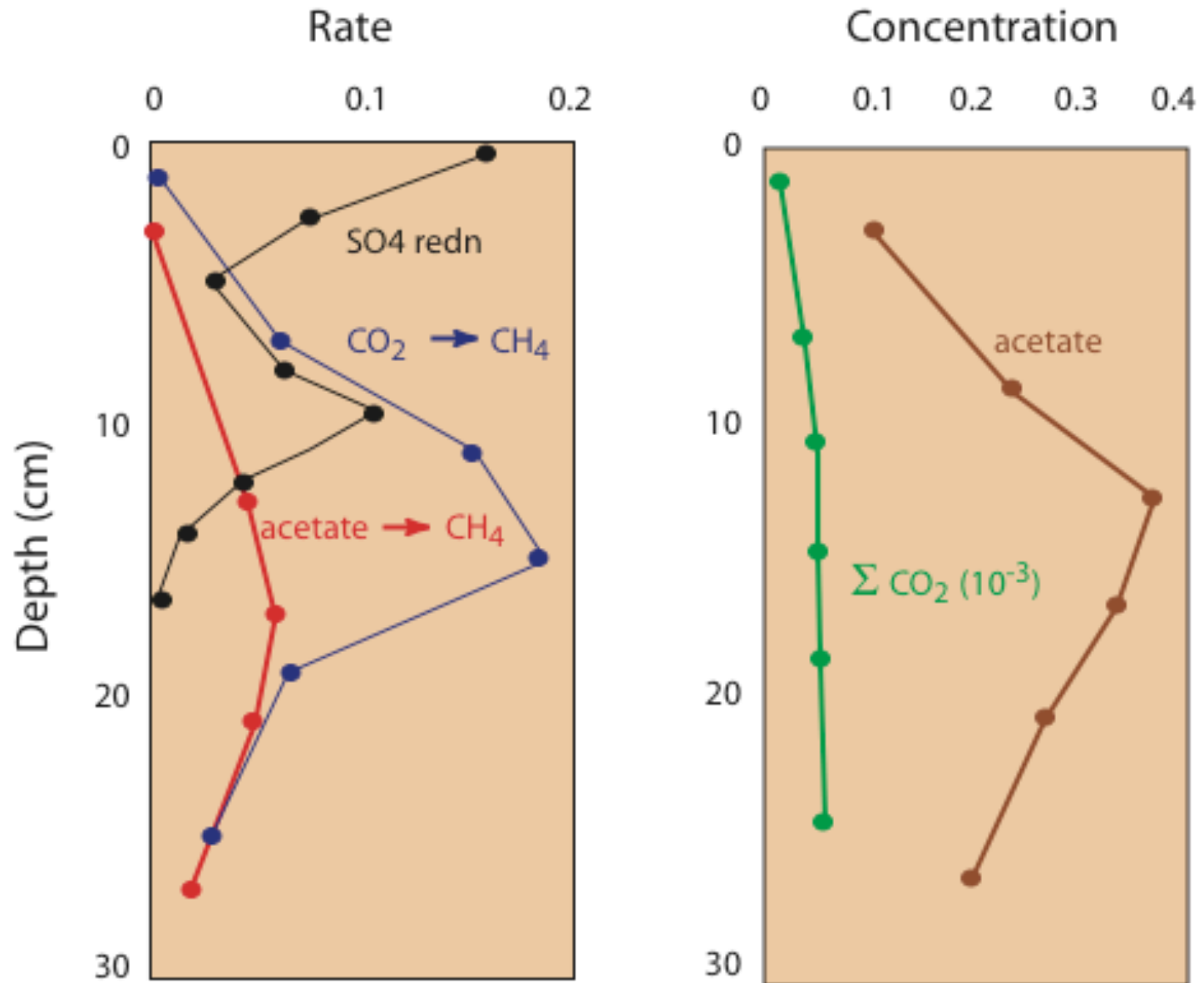
Reduction of CO_2 by hydrogen



Fermentation of acetate



Rates of C remineralization in CLB sediments



Summary:

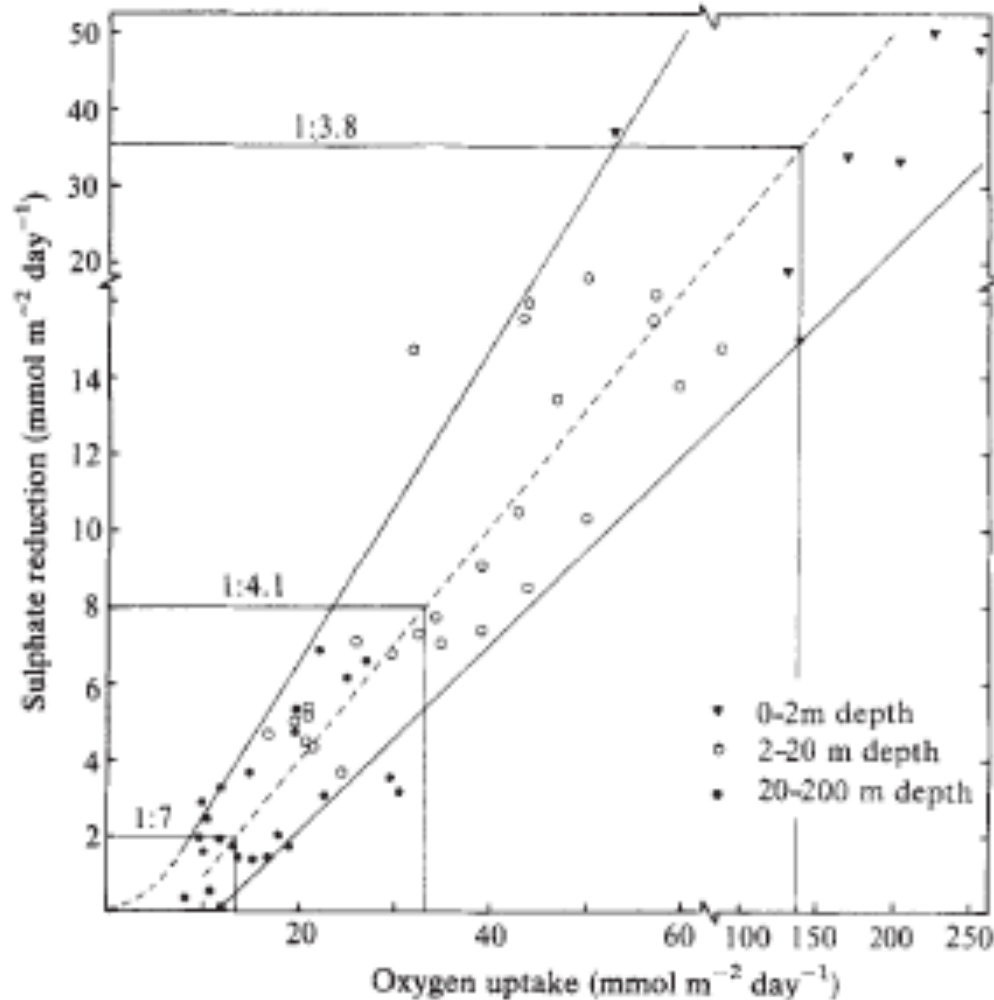
Terminal electron acceptors are used in the order of free E yields (O_2 , Fe/Mn, SO_4 , CO_2)

Anoxic sediments are biogeochemically zoned according to e^- acceptors

Organic matter is oxidized by microbial consortia - no single organism degrades complex organic matter to CO_2 . Instead, fermentation produces VFAs and hydrogen which are oxidized by acetophiles to yield CO_2 and methane.

Methane is produced by two reactions: CO_2 redn with Hydrogen, and disproportionation of acetic acid.

What is the global significance of sulfate reduction?



The ratio of O₂ uptake to S reduction is globally taken to be about 4:1. Since the C:O₂ and C:SO₄ ratios are 1:1 and 2:1 respectively, this means that half of C oxidation in marine sediments occurs via S reduction.

Pyrite formation only consumes 10-20% of sulfide production. The remaining sulfide diffuses through sediments and is oxidized back to sulfate by molecular oxygen.

