Biogeochemical cycling in anoxic sediments

Consortia of bacteria are needed to degrade
Complex organic mater

Waste products of one bacteria serve as the substrate for another

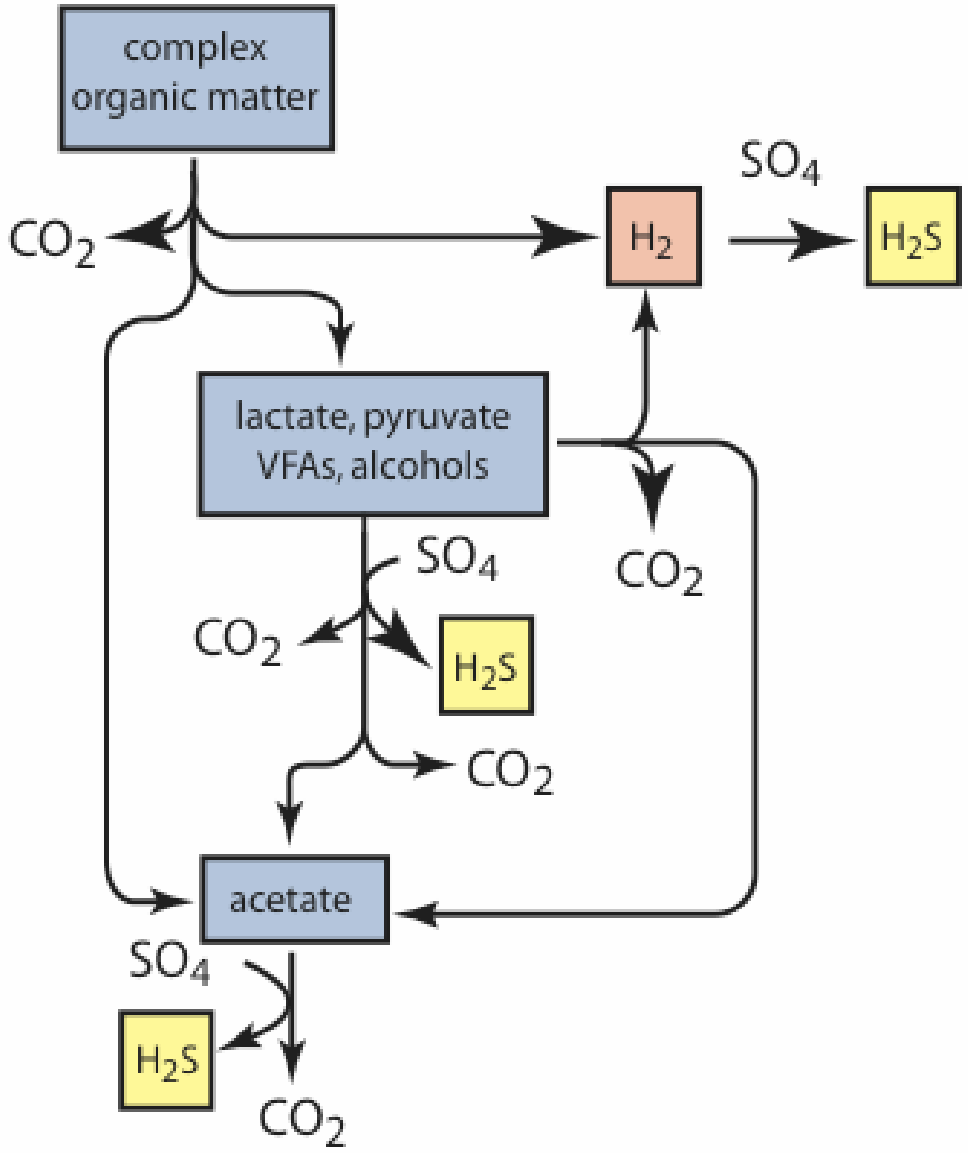
Major reactions are fermetation, sulfate reduction, and methanogenesis

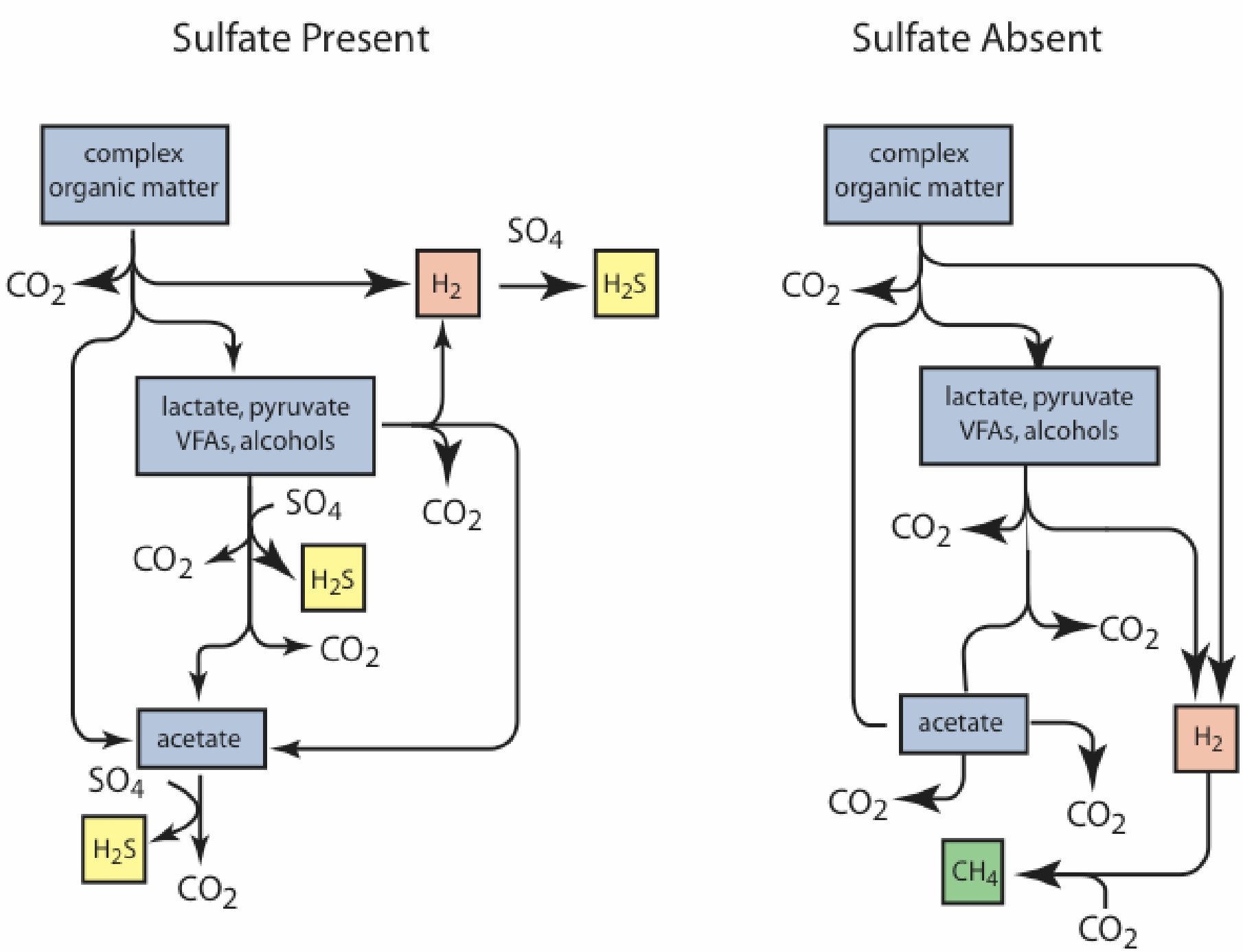
Biogeochemical zonation occurs due to differences in free energy of TEA yields

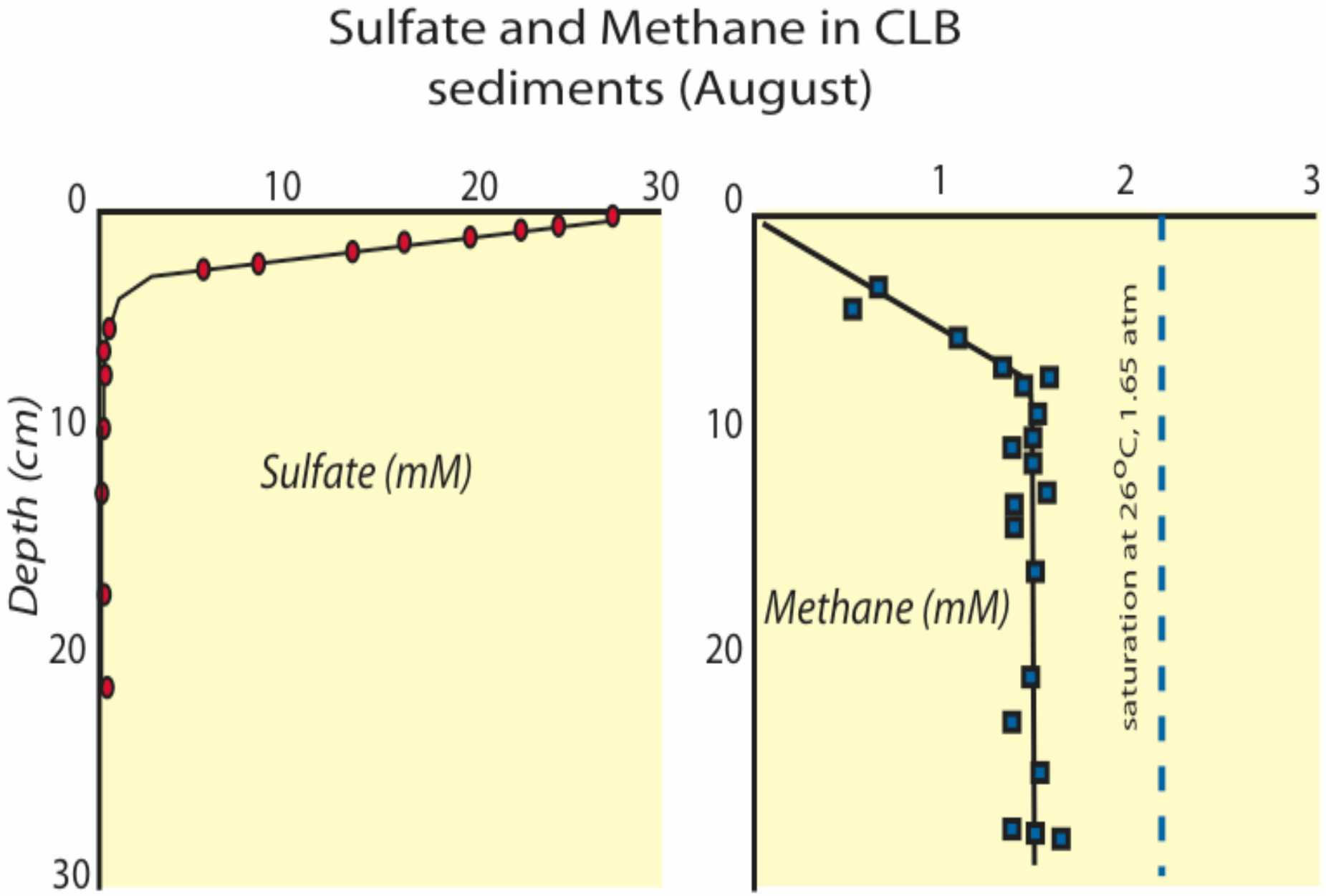
C oxidation in CLB sediments show fluxes and processes are
In balance, suggesting all major pathways are accounted for.

Natural system closely resembles that expected
from pure culture work.

Sulfate Present




Sulfate Present
complex organic matter
CO2
H2
SO4
H2S
lactate, pyruvate VFAs, alcohols
CO2
SO4
CO2
H2S
CO2
acetate
SO4
H2S
CO2
Sulfate Absent
complex organic matter
CO2
lactate, pyruvate VFAs, alcohols
CO2
CO2
acetate
H2
CO2
CO2
CH4
CO2


Sulfate and Methane in CLB sediments (August)
0
10
20
30
Depth (cm)
Sulfate (mM)
0
1
2
3
Methane (mM)
saturation at 26°C, 1.65 atm

Molecular hydrogen as a control on organic matter oxidation in anoxic sediments

Is C oxidation in anoxic sediments under thermodynamic or kinetic control?

$$(CH_2O)n + nH_2O \rightarrow nCO_2 + 2nH_2$$

$$2nH_2 + mX_{ox} \rightarrow mX_{red} + zH_2O$$

(e.g. $X_{ox} = SO_4^{2-}$ $X_{red} = S^{2-}$)

$$\Delta G_{rxn} = \Delta G_{(T)}^{o} + RT \ln \left(\{X_{red}\}^m / \{X_{ox}\}^m (P_{H2})^{2n} \right)$$

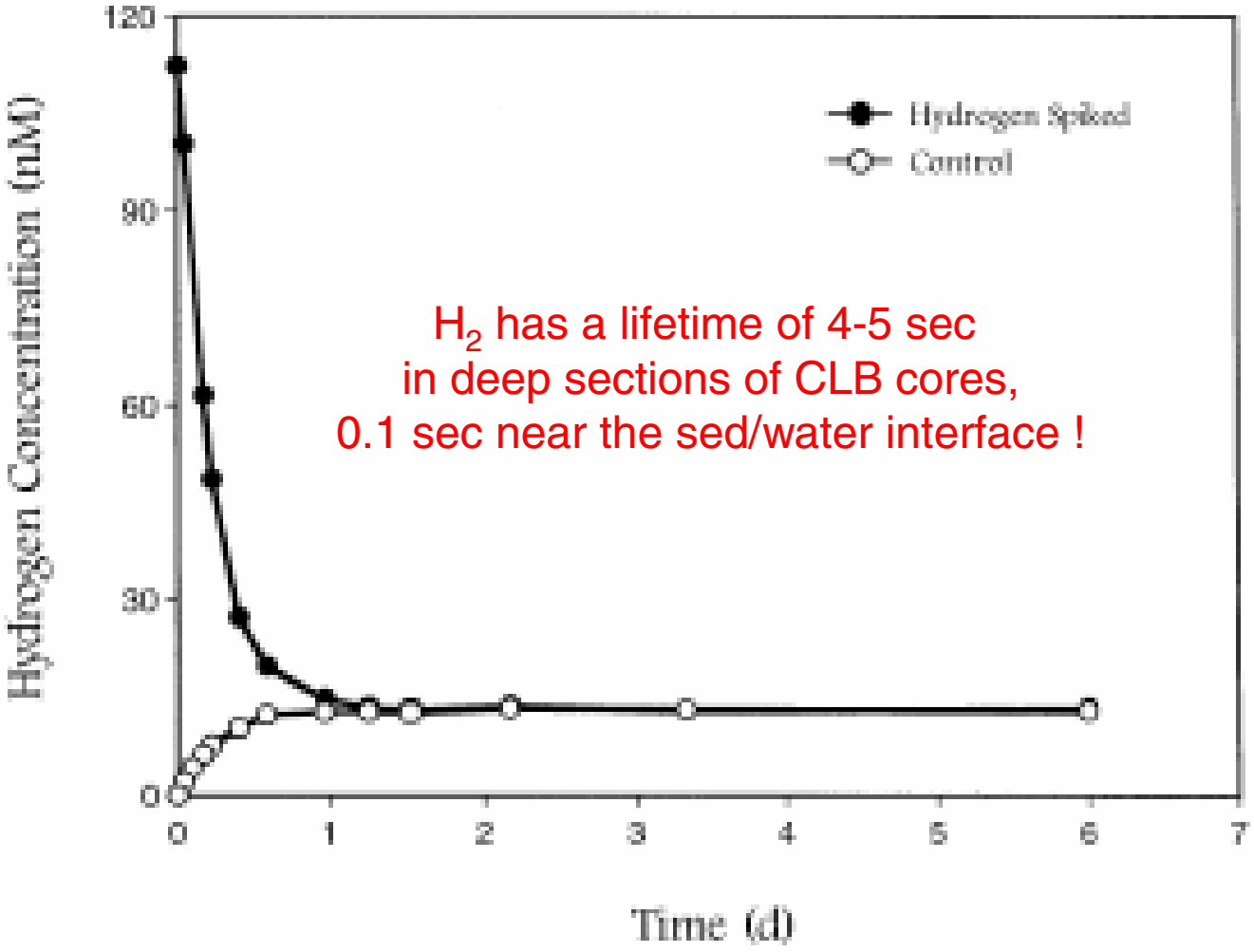
and…

$$P_{H2} = \left(\{X_{red}\}^m / \{X_{ox}\}^m \, e(\Delta G_{rxn} - \Delta G_{(t)}^{o}/RT) \right)^{1/2n}$$

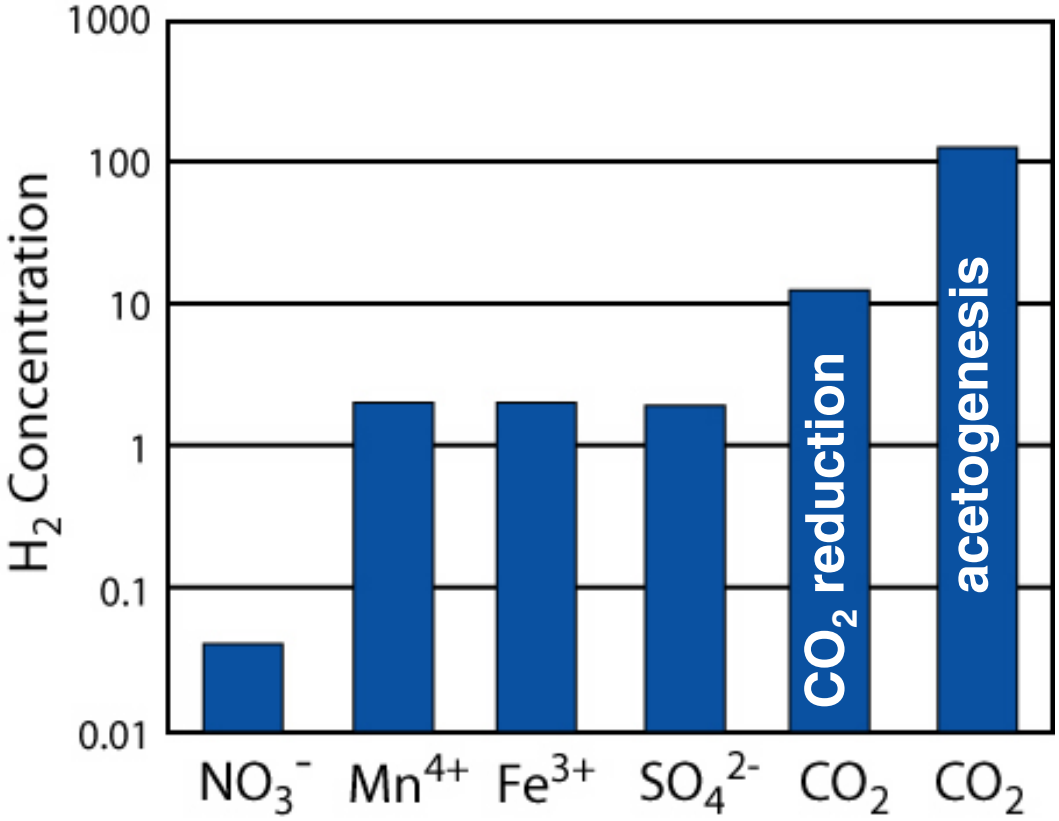
Oxidation of organic matter in marine sediments

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

Rapid cycling of H_2 in anoxic sediments

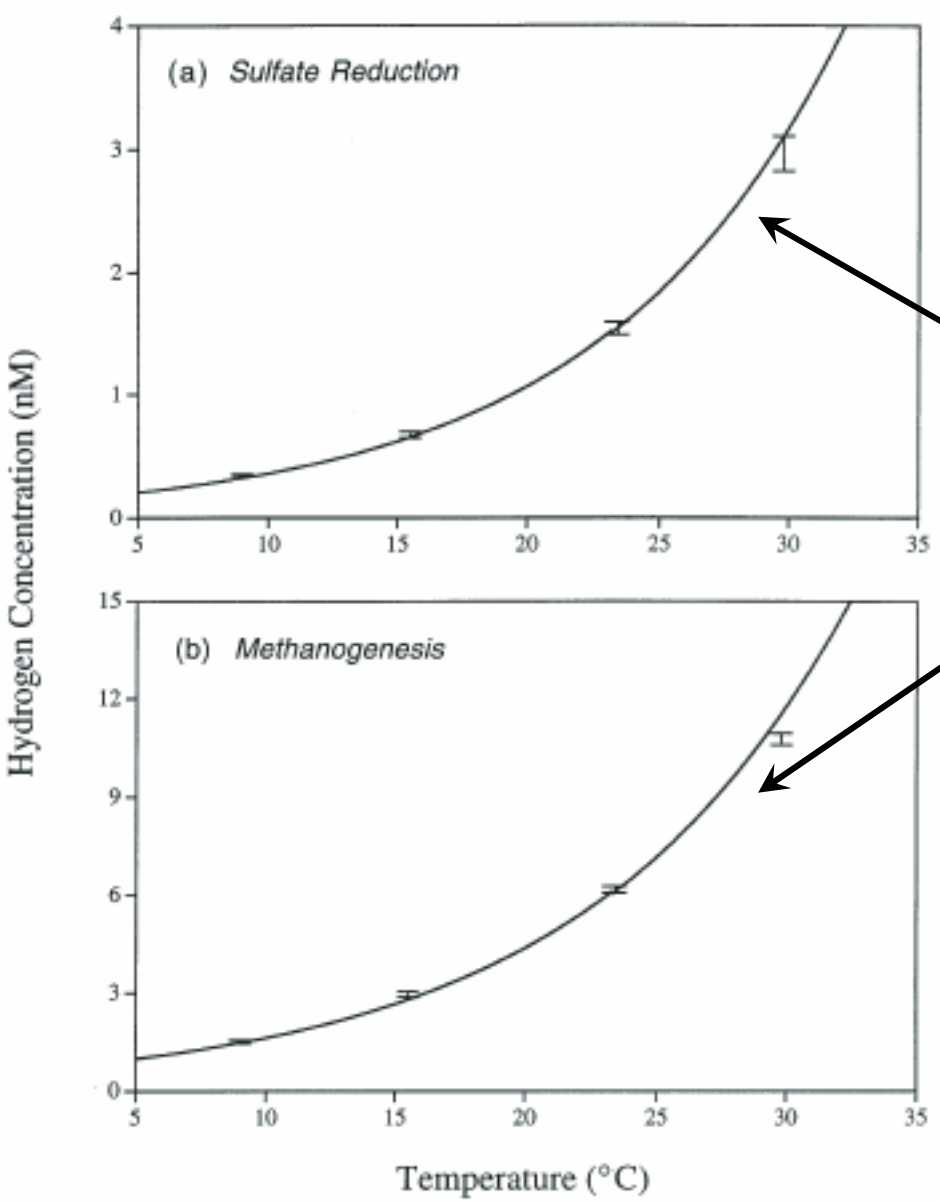


Effect of TEA on H_2 concentrations



TEAP	$[H_2]$ (nM)	ΔG(kJ mol^{-1})
Nitrate redn	0.031	<-180
Sulfate redn	1.64	-23
Methanogenesis	13.0	-20
Acetogenesis	133	-18

Effect of temperature on H_2 concentrations



ΔT from 10 to 30°C
Will affect ΔG_{rxn} by
+15 $kJmol^{-1}$

Theoretical
effect

Dependence of $[H_2]$ on $[SO_4^{2-}]$

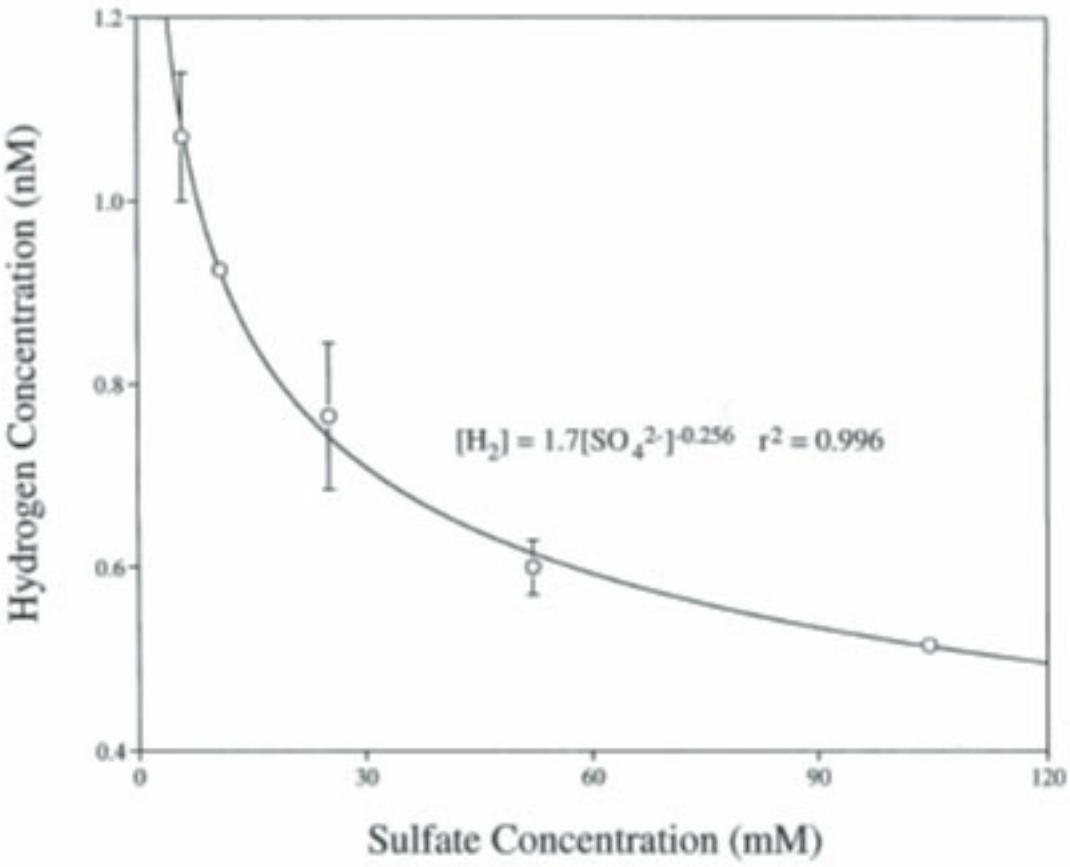
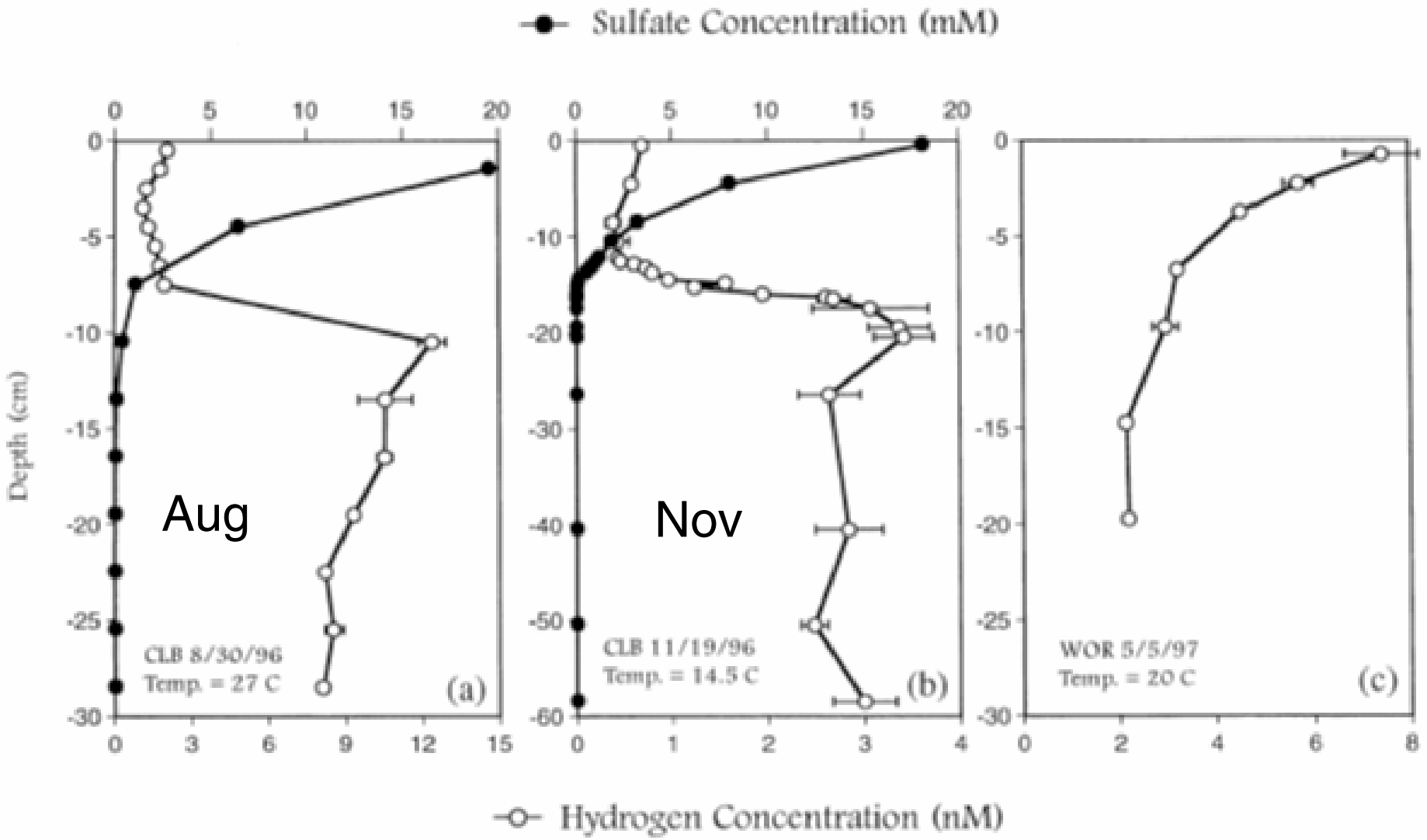
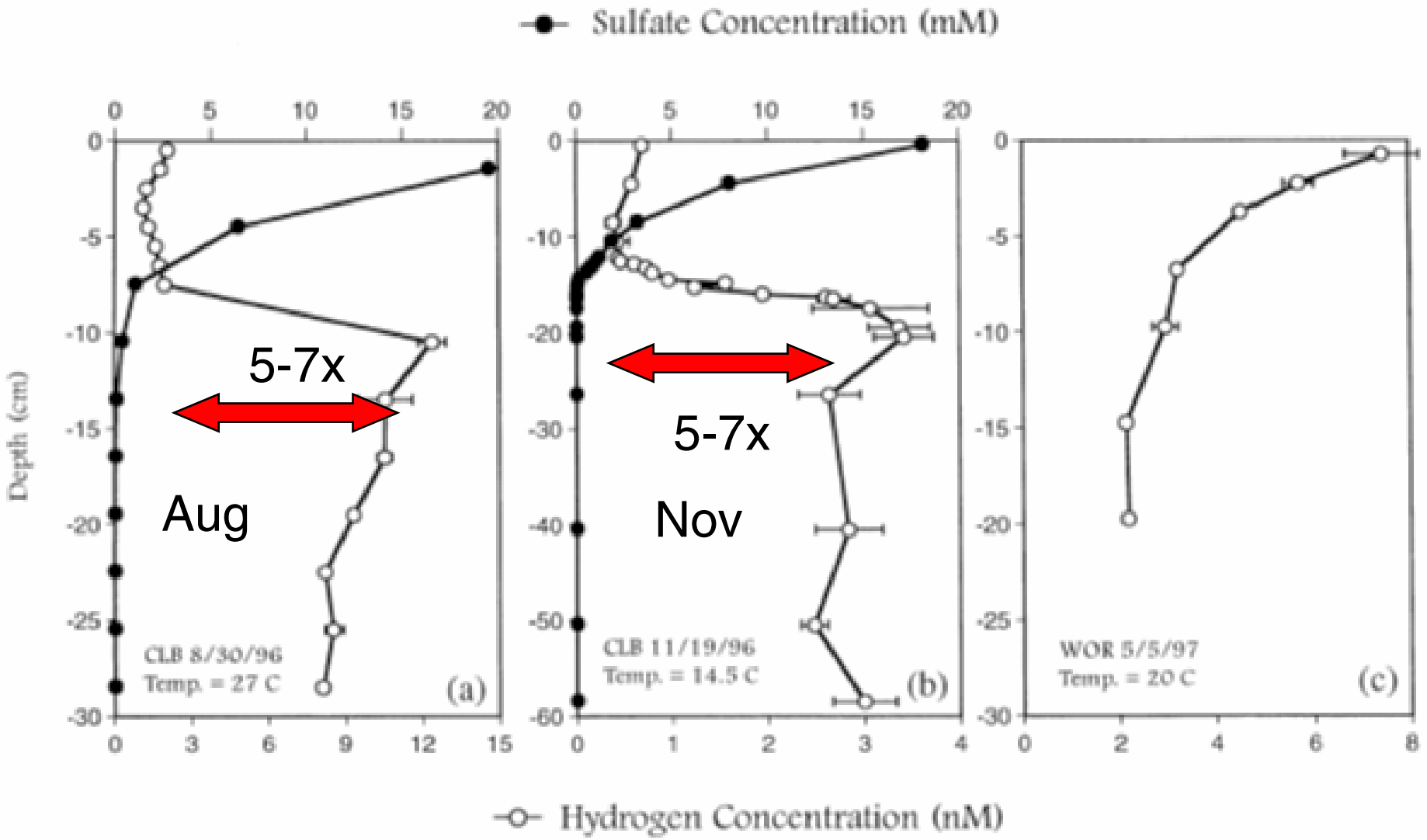


Fig. 5. Response of hydrogen concentrations to variations in porewater sulfate concentration. Error bars represent one standard deviation about the mean of triplicate sediment samples. A power function fit to the data indicates that hydrogen has an exponential dependence of -0.26 ± 0.01 on sulfate (compare to theoretical value of -0.25).

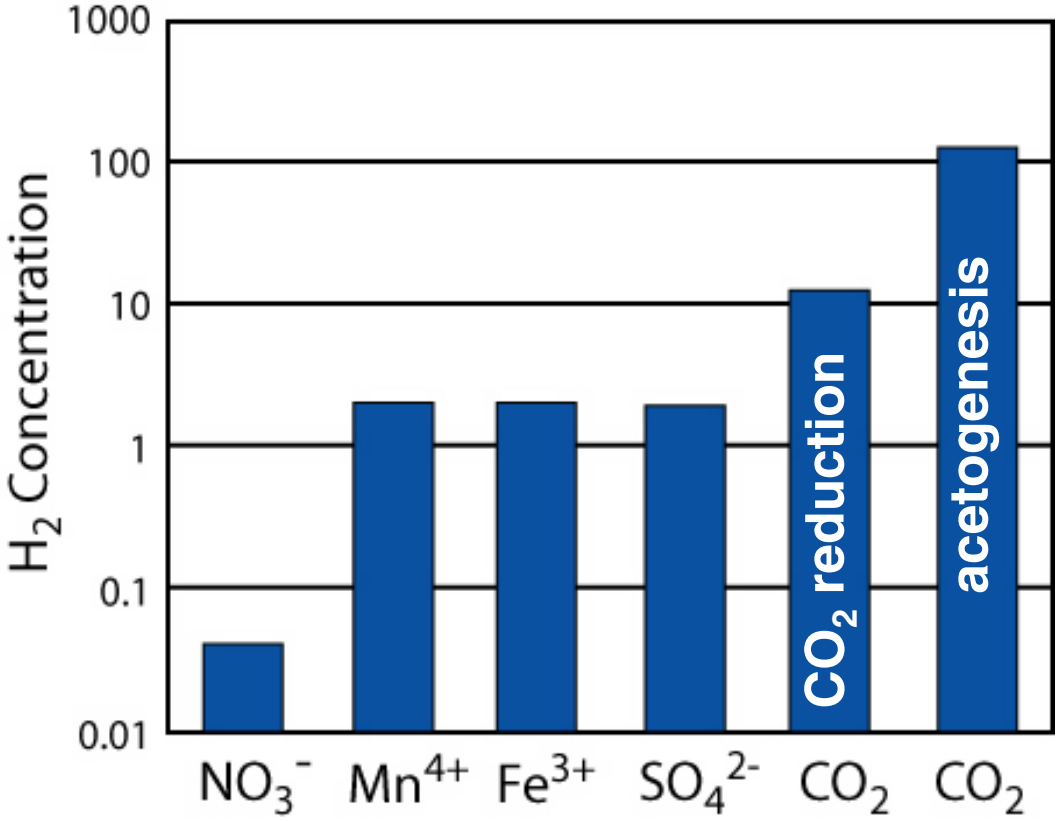
Profiles of hydrogen and sulfate in CLB and WOR sediments



Profiles of hydrogen and sulfate in CLB and WOR sediments



Effect of TEA on H_2 concentrations



TEAP	$[H_2]$ (nM)	ΔG(kJ mol^{-1})
Nitrate redn	0.031	<-180
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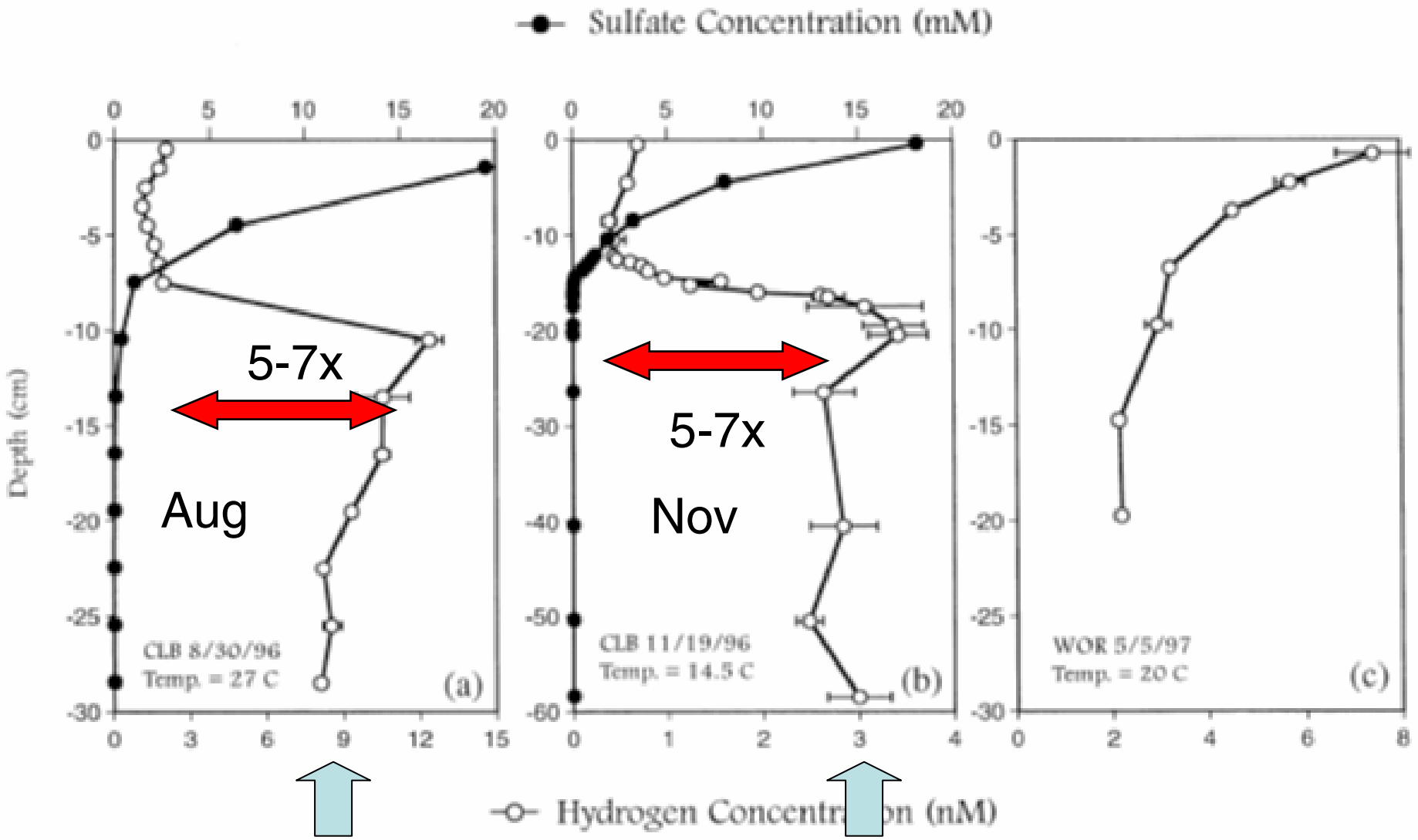
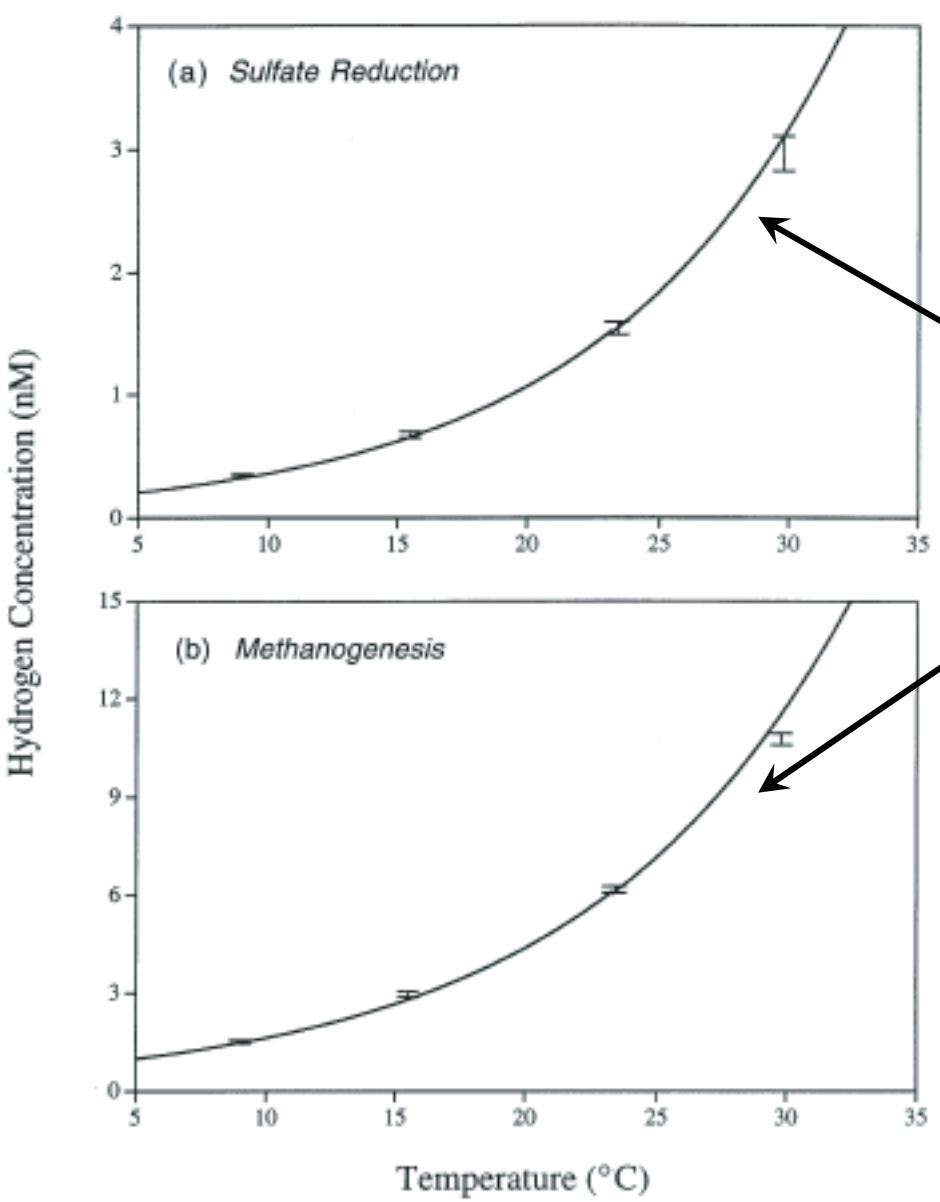
Acetogenesis	133	-18

Profiles of hydrogen and sulfate in CLB and WOR sediments



2.8x meas vs 2.7x predicted

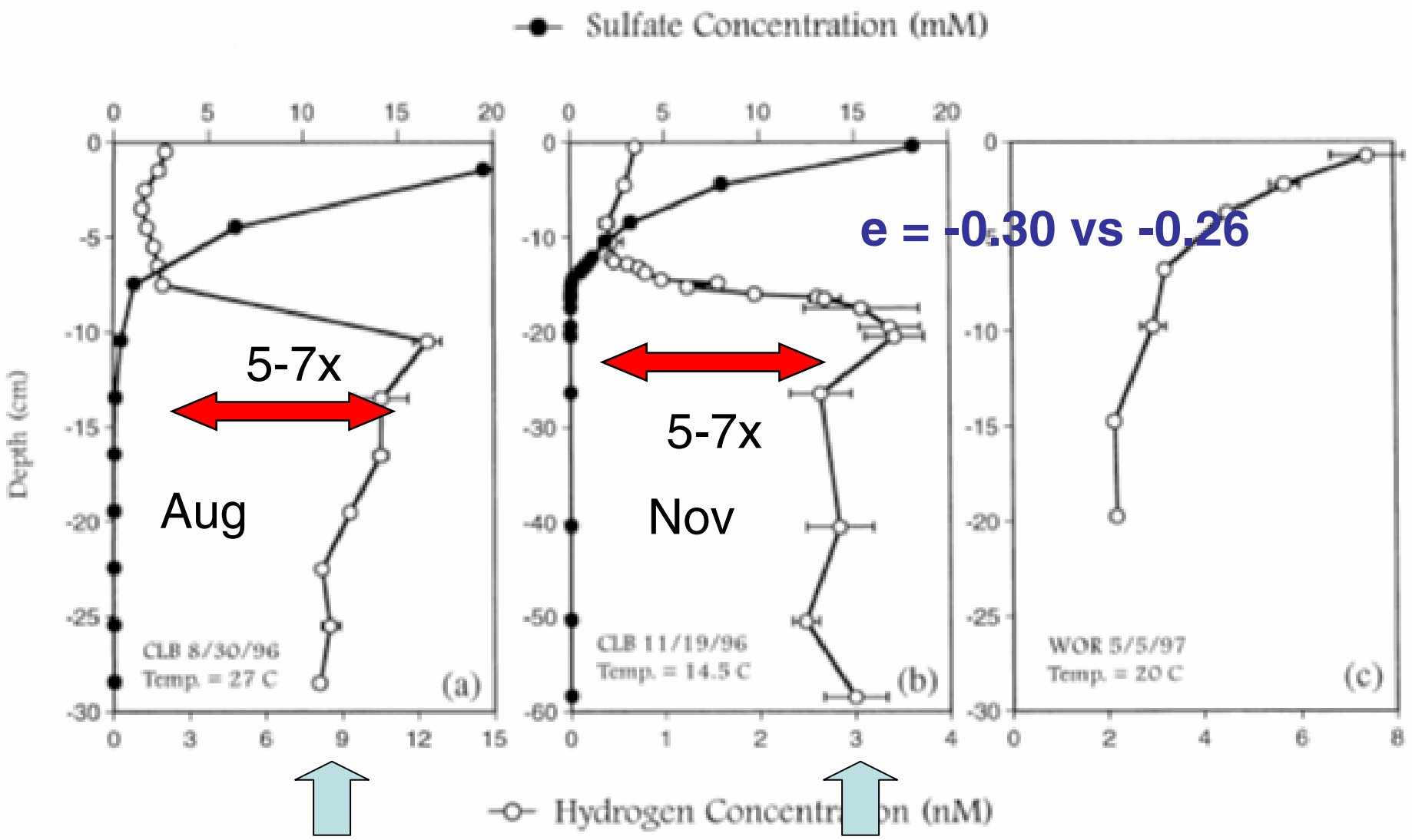
Effect of temperature on H_2 concentrations



ΔT from 10 to 30°C
Will affect ΔG_{rxn} by
+15 $kJmol^{-1}$

Theoretical
effect

Profiles of hydrogen and sulfate in CLB and WOR sediments



e = -0.30 vs -0.26

2.8x meas vs 2.7x predicted

Effect of sulfate on H_2 in CLB sediments

1.6 mM

10µM

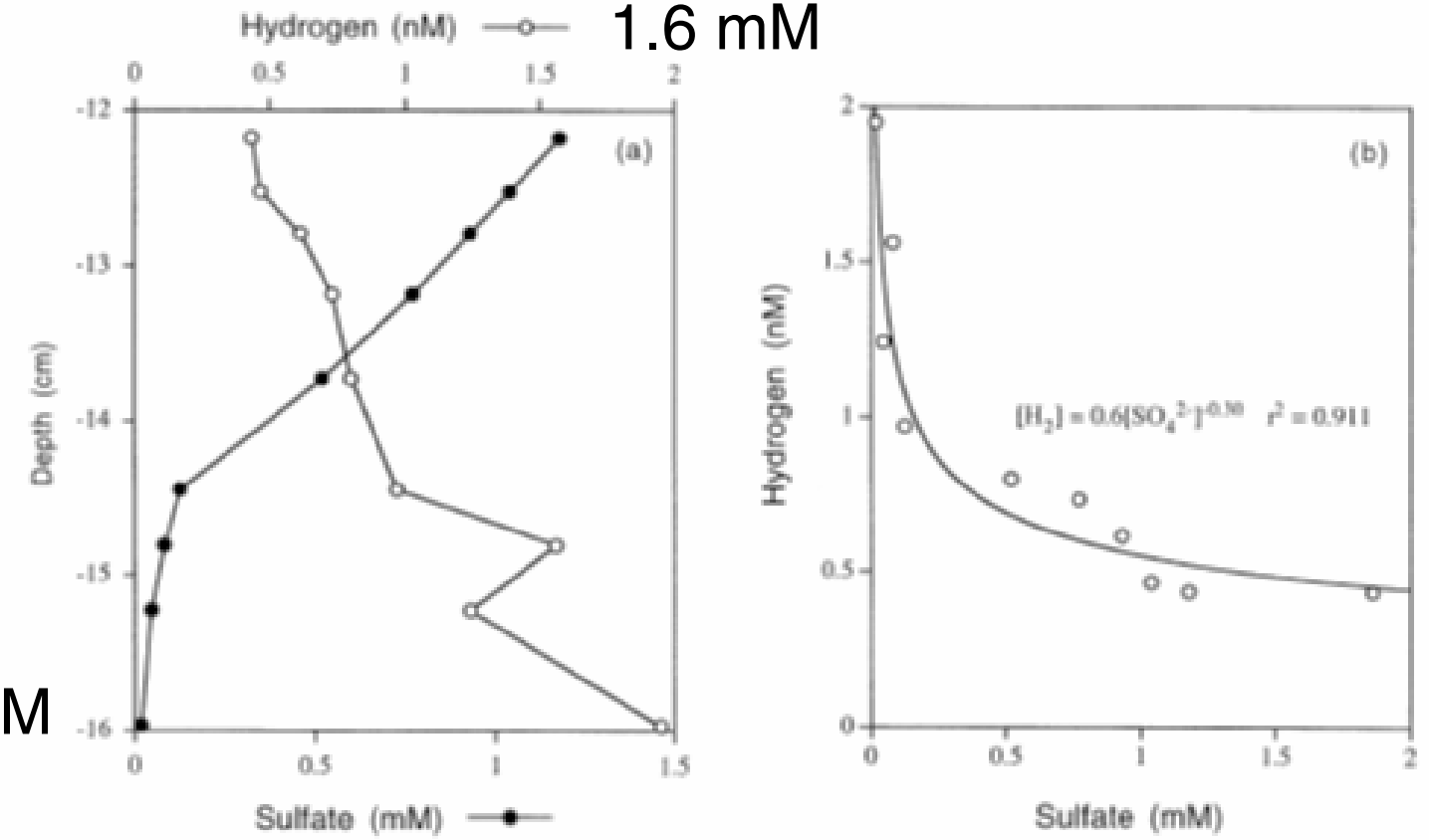
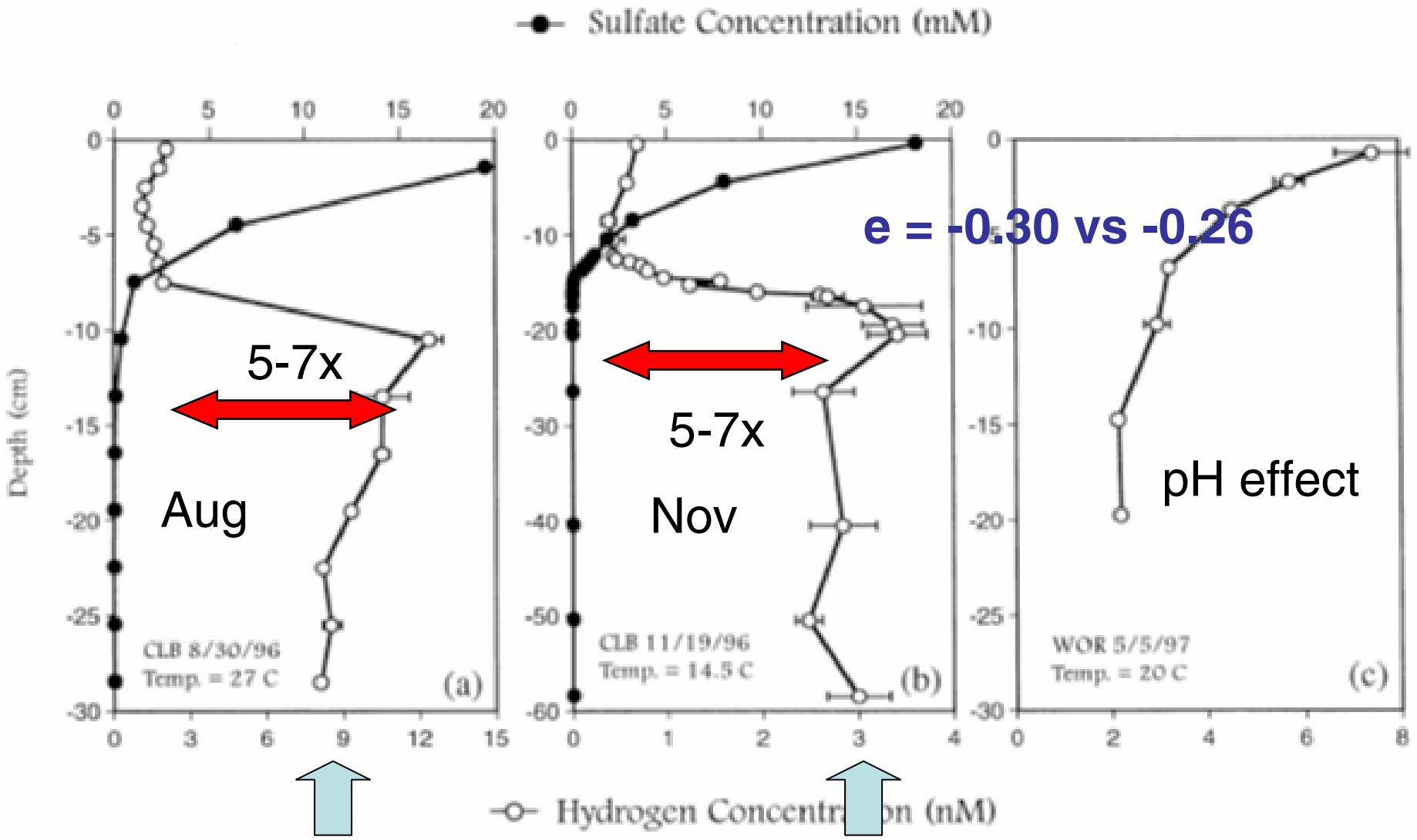


Fig. 8. The dependence of hydrogen concentrations on sulfate concentrations in the November core from Cape Lookout Bight (Fig. 7b). (a) blow-up of the 12–16 cm depth interval. Note that sulfate concentrations only reach threshold values below 16 cm; (b) plot of hydrogen concentration vs. sulfate concentration over the 12–16 cm interval. A power function fit to the data indicates that hydrogen has an exponential dependence of 0.30 ± 0.04 on sulfate (compared to a lab value of 0.26 ± 0.01 and a theoretical value of 0.25).

Profiles of hydrogen and sulfate in CLB and WOR sediments



e = -0.30 vs -0.26

pH effect

2.8x meas vs 2.7x predicted

Hydrogen as a control on organic matter oxidation In anoxic sediments (fresh and marine)

Hydrogen is a by-product of fermentation and is essential for sulfate reduction and methanogenesis.

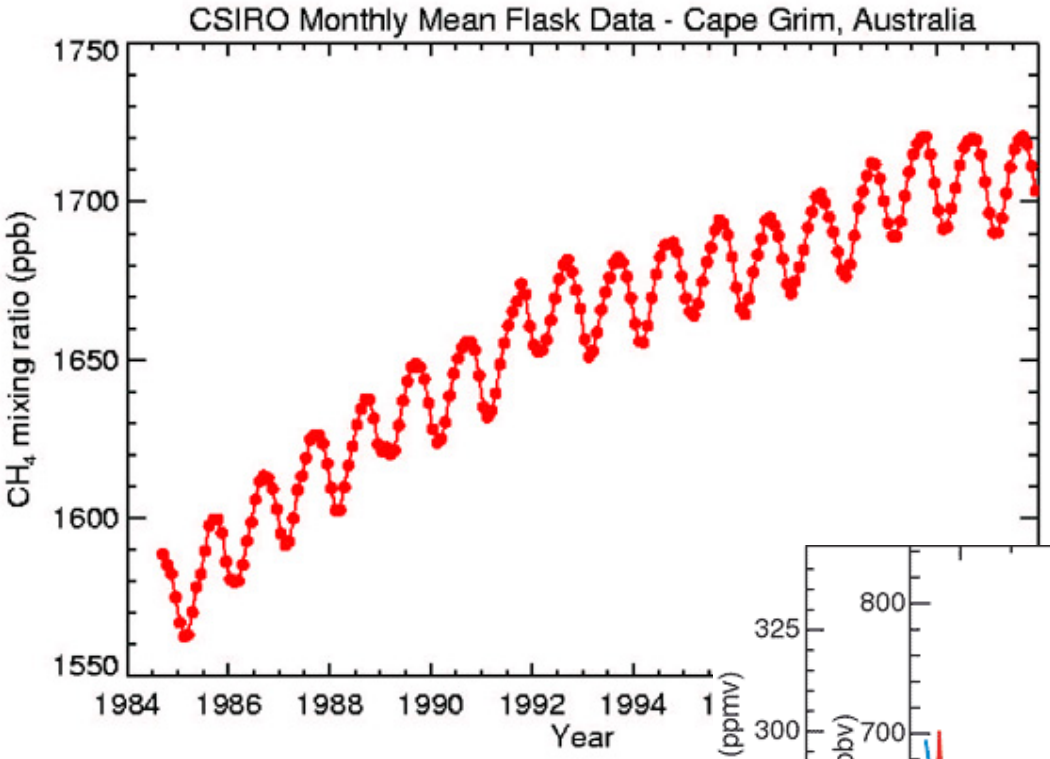
Hydrogen concentrations respond to T, [X], pH. Laboratory changes correspond well to field observations.

Variations in H_2 suggest maintenance of constant ΔG values of -10 to -15 kJ mol^{-1} .

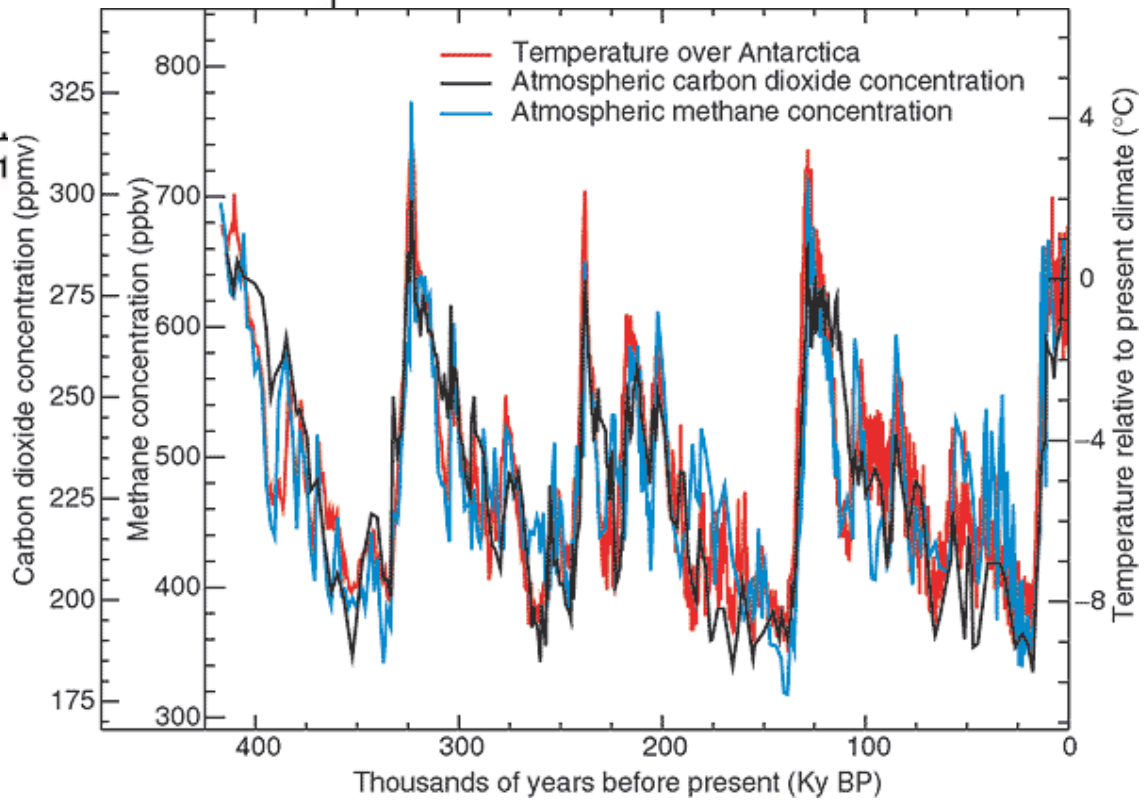
H2 has a very short lifetime in sediments- makes an Excellent E regulator. Small changes in H2 concentration Results in large changes in ΔG.

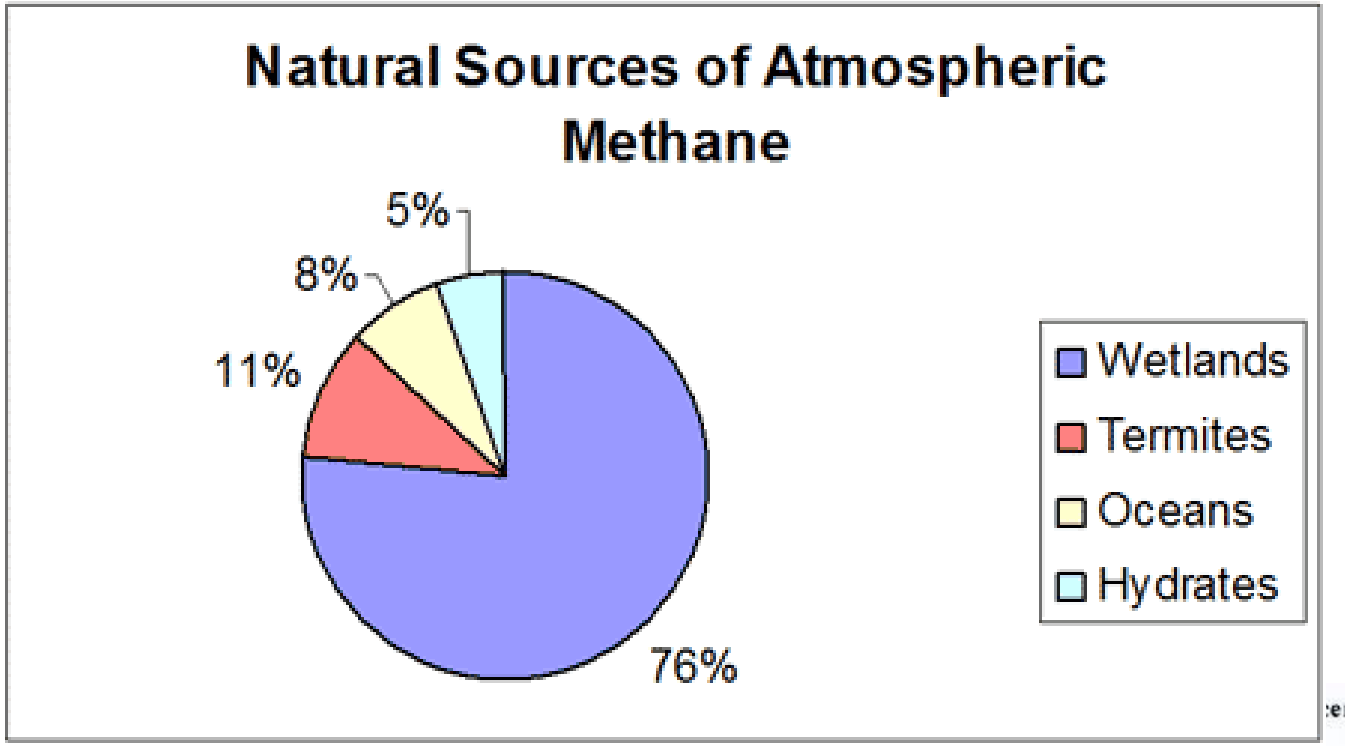
Intense competition by bacteria regulate [H_2]

Methane and the Global greenhouse

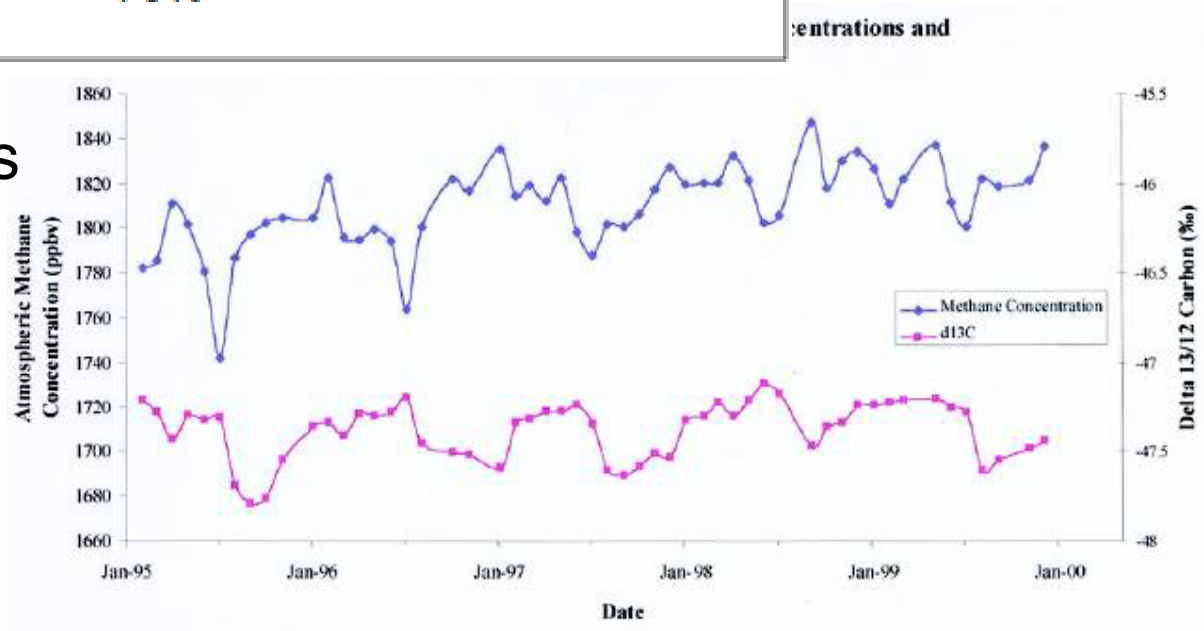


atms. Methane is increasing in concentration by about 1-2% per year.

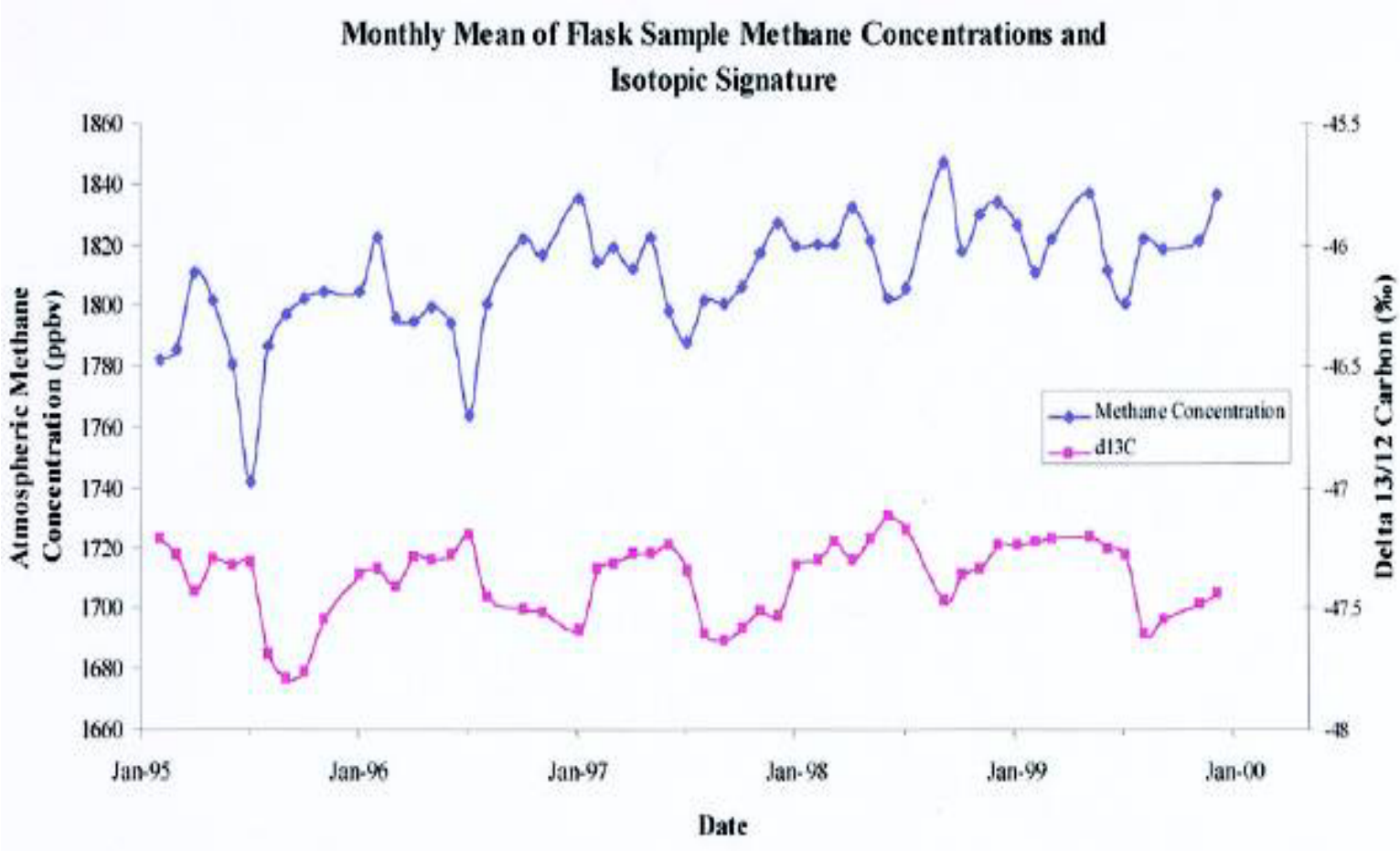




C isotopic changes in atms methane



C isotopic changes in atmospheric methane

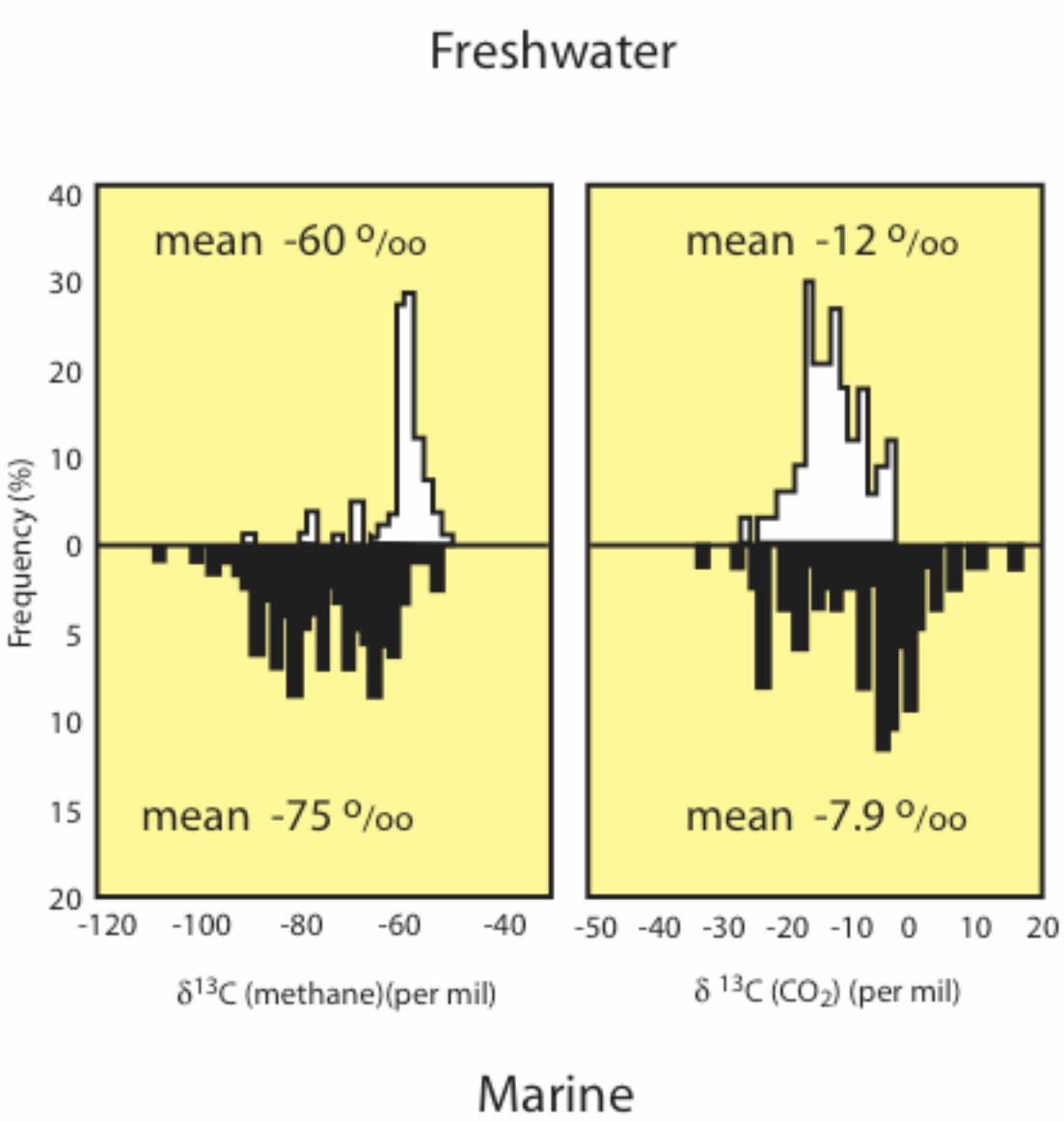


How do we explain the increase in atmospheric ?

Why is there a seasonal cycle in methane concentration?

Why is there a seasonal cycle in methane C isotopes?

(can C isotopes be used to understand and
Quantify processes that lead to atms increase?)


Freshwater
mean -60 °/oo
mean -12 °/oo
mean -75 °/oo
mean -7.9 °/oo
Frequency (%)
40
30
20
10
0
5
10
15
20
-120 -100 -80 -60 -40
-50 -40 -30 -20 -10 0 10 20
δ13C (methane)(per mil)
δ 13C (CO2) (per mil)
Marine

There are two pathways that yield methane:

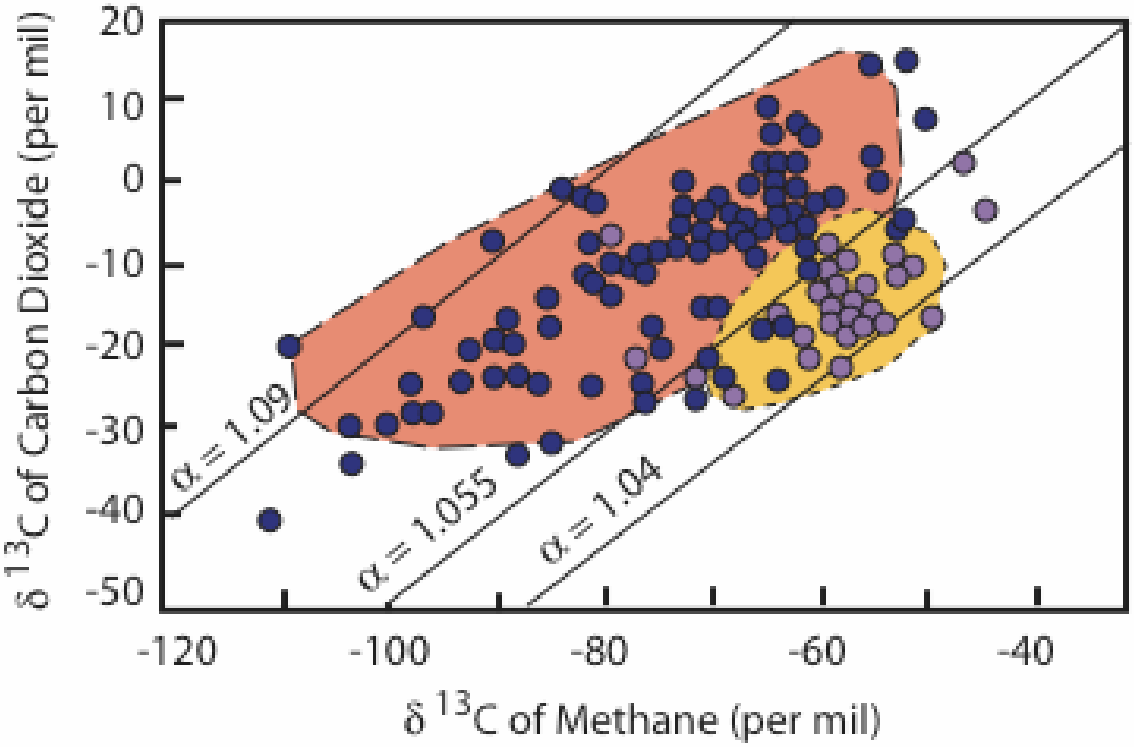
Freshwater

$$CH_3COOH \rightarrow CH_4 + CO_2$$

Marine

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

Isotope fractionation and methanogenesis



Carbon isotope fractionation with methanogenesis

Freshwater

$$CH_3COOH \rightarrow CH_4 + CO_2$$

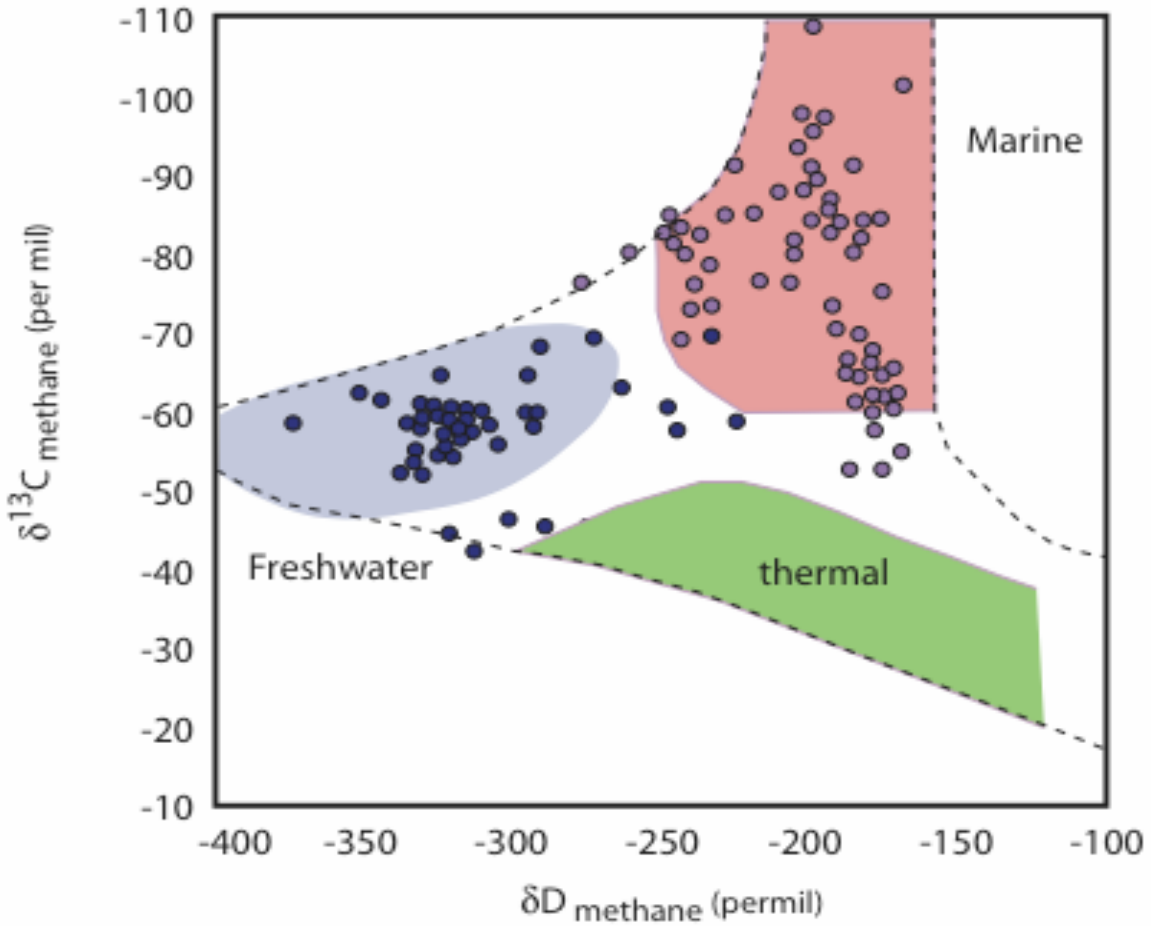
$$\alpha = -48‰$$

Marine

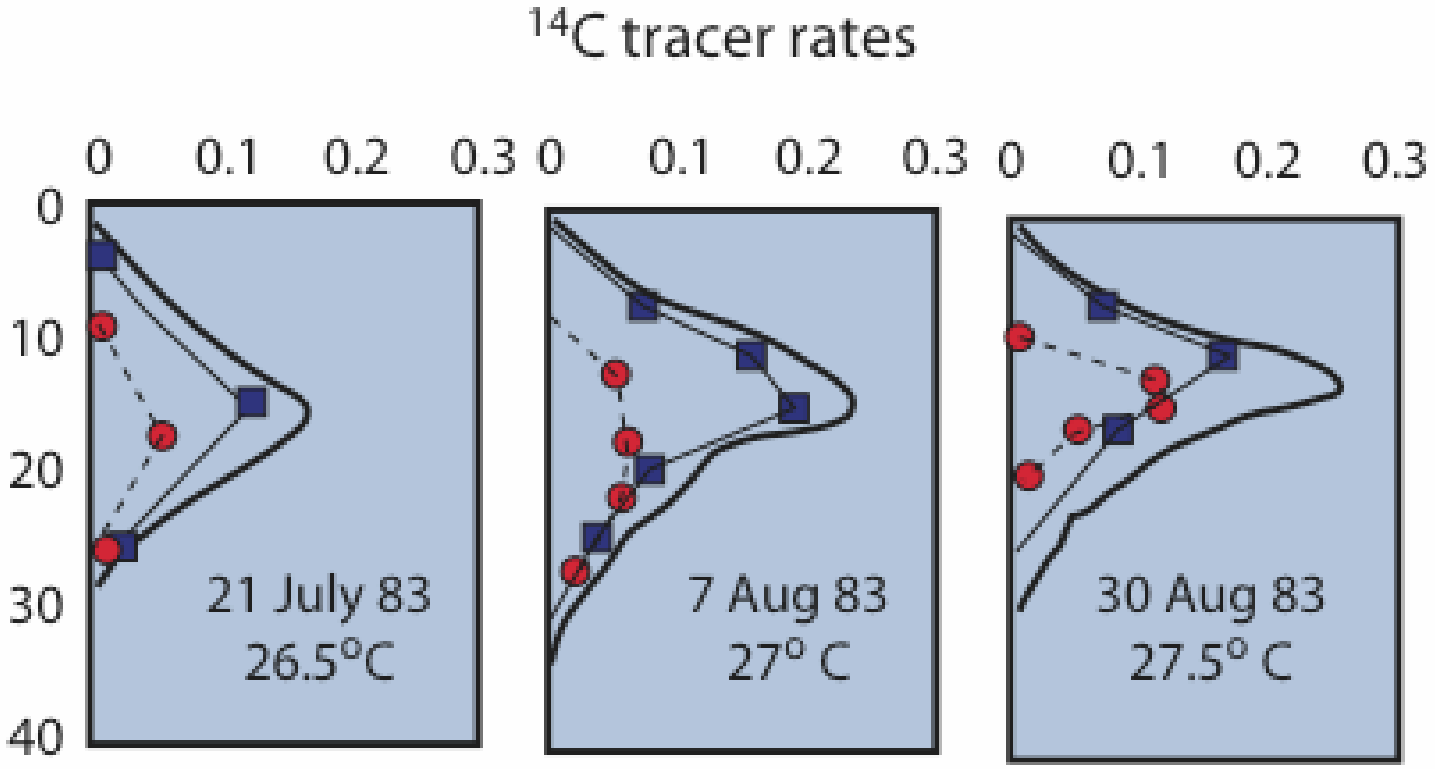
$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$$

$$\alpha = -70‰$$

Carbon and Hydrogen isotopes fractionation with methanogenesis



Production of methane from acetate and CO_2 in CLB sediments. ^{14}C tracer studies.

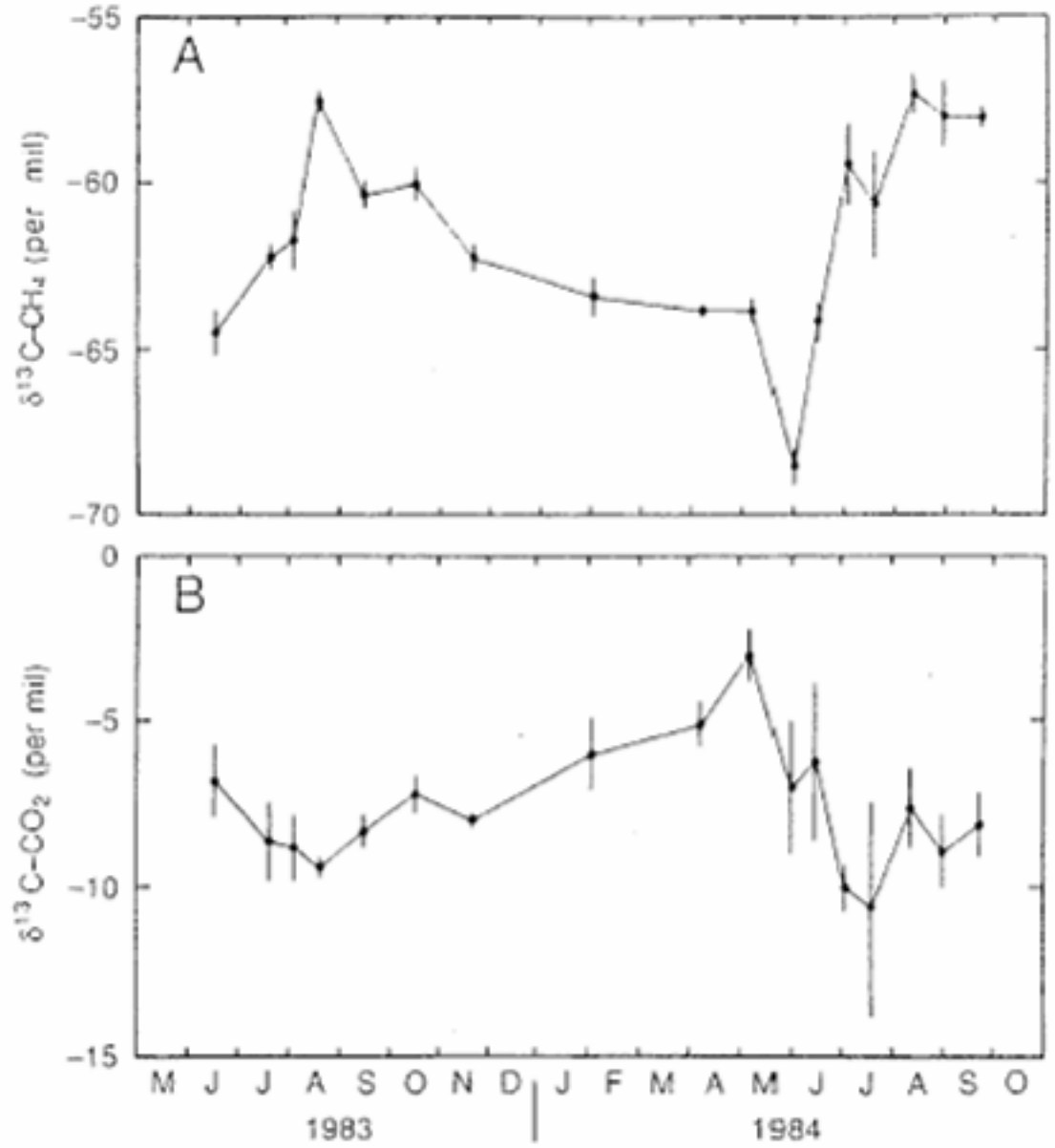


Seasonal changes in ^{13}C for methane and CO_2

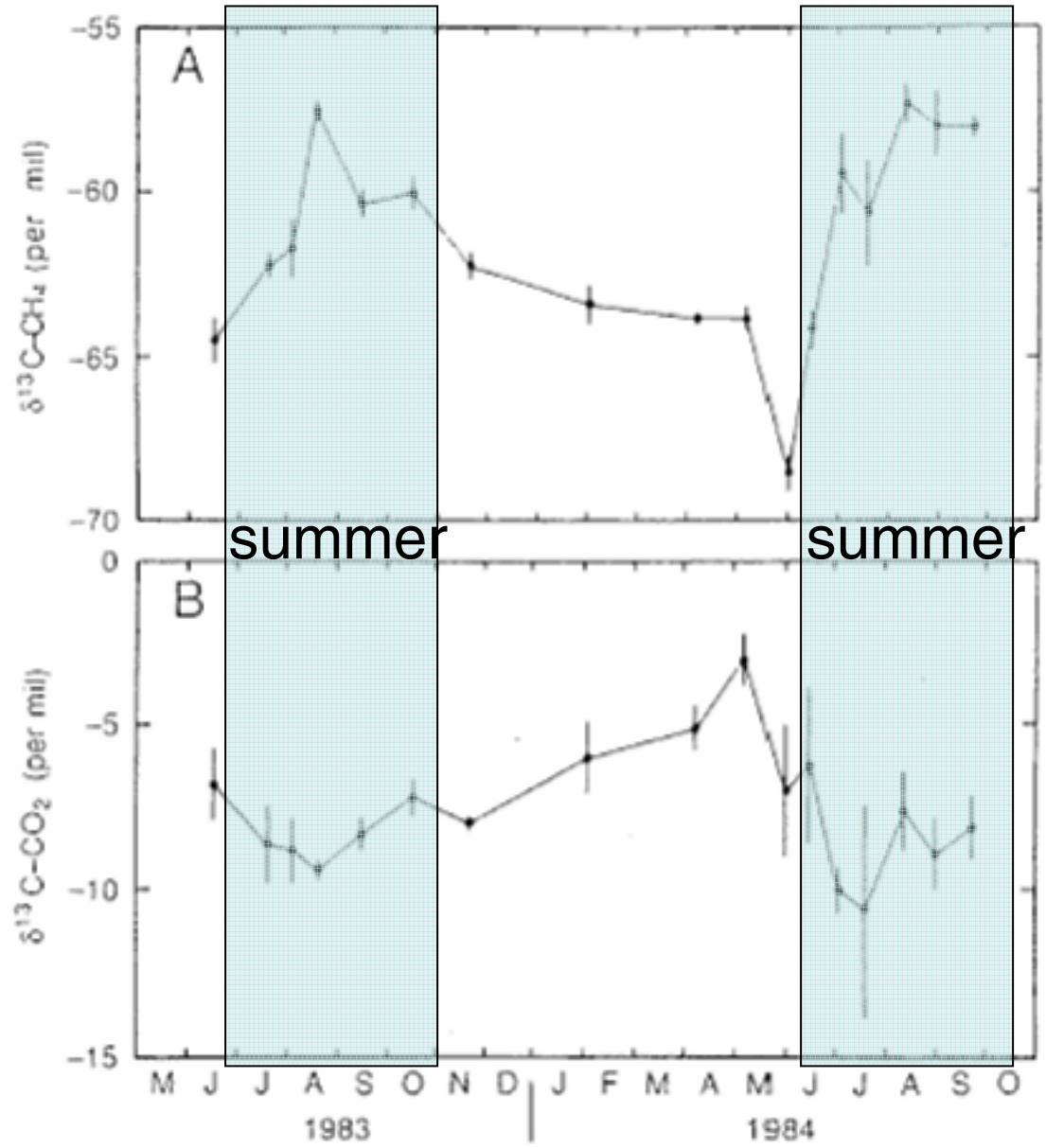
Table 1. Cape Lookout Bight sediment gas bubble composition and $\delta^{13}C$ data. Values listed are means ± SD for the number of sample bottles listed. Superscripts indicate the number of samples for which compositional data were obtained when different from the number of sample bottles listed.

Date	Methane sample bottles (no.)	Methane content (%)	$\delta^{13}C$-CH_4 (per mil)	Carbon dioxide sample bottles (no.)	Carbon dioxide content (%)	$\delta^{13}C$-CO_2 (per mil)
6 June 1983	5	97 ± 2	−64.5 ± 0.7	5	2.5 ± 0.1	−6.8 ± 1.1
19 July 1983	6	95 ± 4	−62.2 ± 0.4	6	3.4 ± 0.2^3	−8.6 ± 1.2
3 August 1983	5	96 ± 4	−61.7 ± 0.9	5	2.4 ± 0.3	−8.8 ± 1.0
19 August 1983	5	94 ± 2	−57.5 ± 0.3	4	2.4 ± 0.2	−9.4 ± 0.3
15 September 1983	5	97 ± 2	−60.3 ± 0.4	5	2.5 ± 0.1	−8.3 ± 0.5
16 October 1983	6	95 ± 3	−60.0 ± 0.5	5	2.4 ± 0.5^4	−7.2 ± 0.6
20 November 1983	4	93 ± 2	−62.2 ± 0.4	4	2.4 ± 0.6	−8.0 ± 0.2
2 February 1984	4	98 ± 3	−63.4 ± 0.6	4	1.6 ± 0.5^3	−6.0 ± 1.2
7 April 1984	4	94 ± 3^3	−63.8 ± 0.2	4	1.0 ± 0.2^3	−5.1 ± 0.7
6 May 1984	4	90 ± 6	−63.8 ± 0.4	3	1.5 ± 0.2	−3.0 ± 0.8
31 May 1984	5	94 ± 5	−68.5 ± 0.7	3	1.8 ± 0.6	−7.0 ± 2.0
14 June 1984	5	94 ± 3	−64.1 ± 0.6	4	2.9 ± 1.0	−6.2 ± 2.4
2 July 1984	4	97 ± 4^2	−59.4 ± 1.2	2	2.1 ± 0.1	−10.0 ± 0.7
18 July 1984	4	98 ± 2^2	−60.6 ± 1.6	2	2.2 ± 0.2	−10.6 ± 3.2
11 August 1984	5	98 ± 3^4	−57.3 ± 0.6	5	2.3 ± 0.2	−7.6 ± 1.2
30 August 1984	4	94 ± 1	−57.9 ± 1.0	3	3.8 ± 1.1	−8.9 ± 1.1
22 September 1984	5	99 ± 0^2	−58.0 ± 0.3	5	2.4 ± 1.3	−8.1 ± 1.0

Changes in C-13 in CLB methane



Changes in C-13 in CLB methane



Monthly flux and isotope data for methane flux from CLB

Month	Monthly methane bubble flux* (mmol m^{-2})	Annual flux† (%)	$\delta^{13}C$-CH_4‡ (per mil)
January	0	0	
February	0	0	−63.4 ± 0.6
March	0	0	
April	0	0	−63.8 ± 0.2
May	38	0.8	−66.4 ± 2.5
June	350	7.2	−64.3 ± 0.7
July	1270	26.2	−61.0 ± 1.6
August	1643	33.9	−58.7 ± 2.0
September	1095	22.6	−59.1 ± 1.4
October	409	8.4	−60.0 ± 0.5
November	47	1.0	−62.2 ± 0.4
December	0	0	
Full year	4582 ± 1277	100.0	−60.0 ± 1.0 WA§

Anaerobic methane oxidation…where has all the methane gone?

Oceans have a huge reservoir of methane in sediments, but Contribute only 2% of the global atmospheric flux of methane.

Several lines of evidence suggest methane is being efficiently Oxidized before it reaches the sediment water interface:

curvature in methane profiles

radiotracer experiments

isotopic fractionation between methane and CO_2

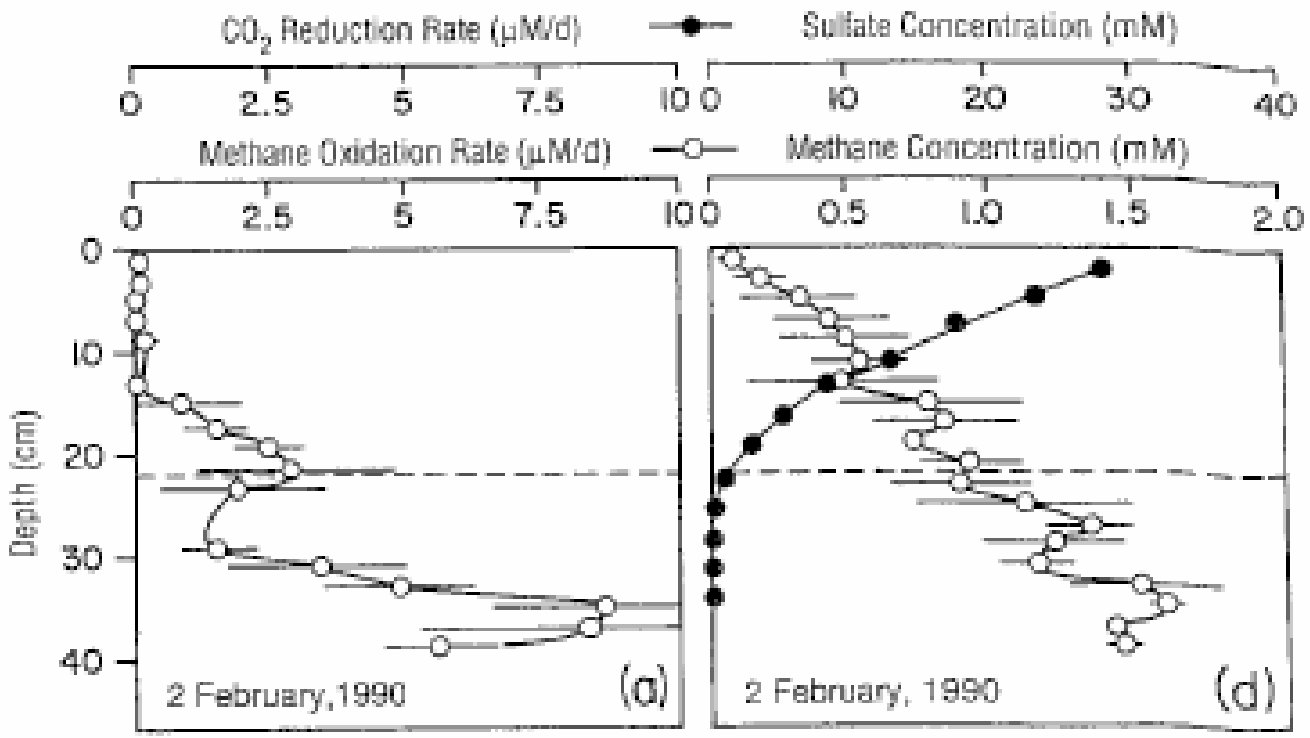
measured rates of methane oxidation in sulfate reduction zone.

$$CH_4 + SO_4^{2-} \text{ --->> } HCO_3^- + HS^- + H_2O$$

Energetically favorable, but ratio of SRR/MOR is very high (>99.99).

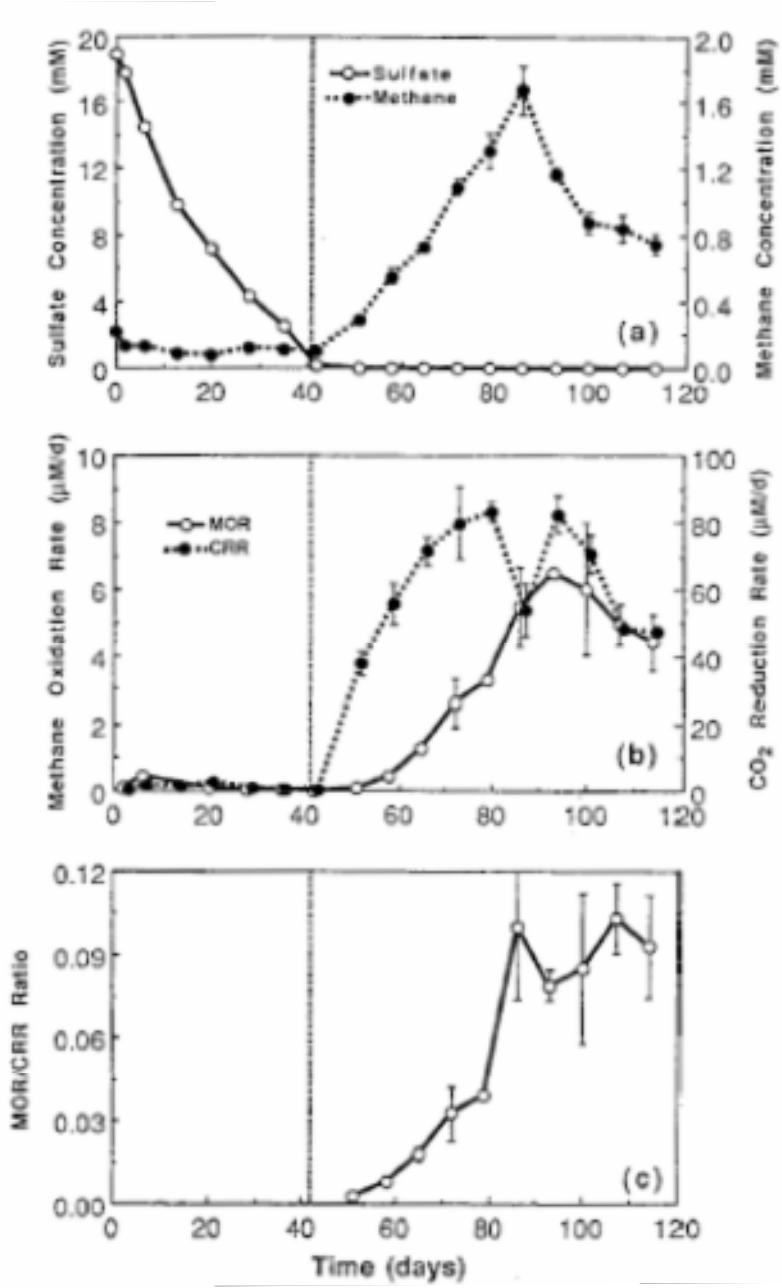
Anaerobic methane oxidation probably occurs as a consortia between SRB and MOB

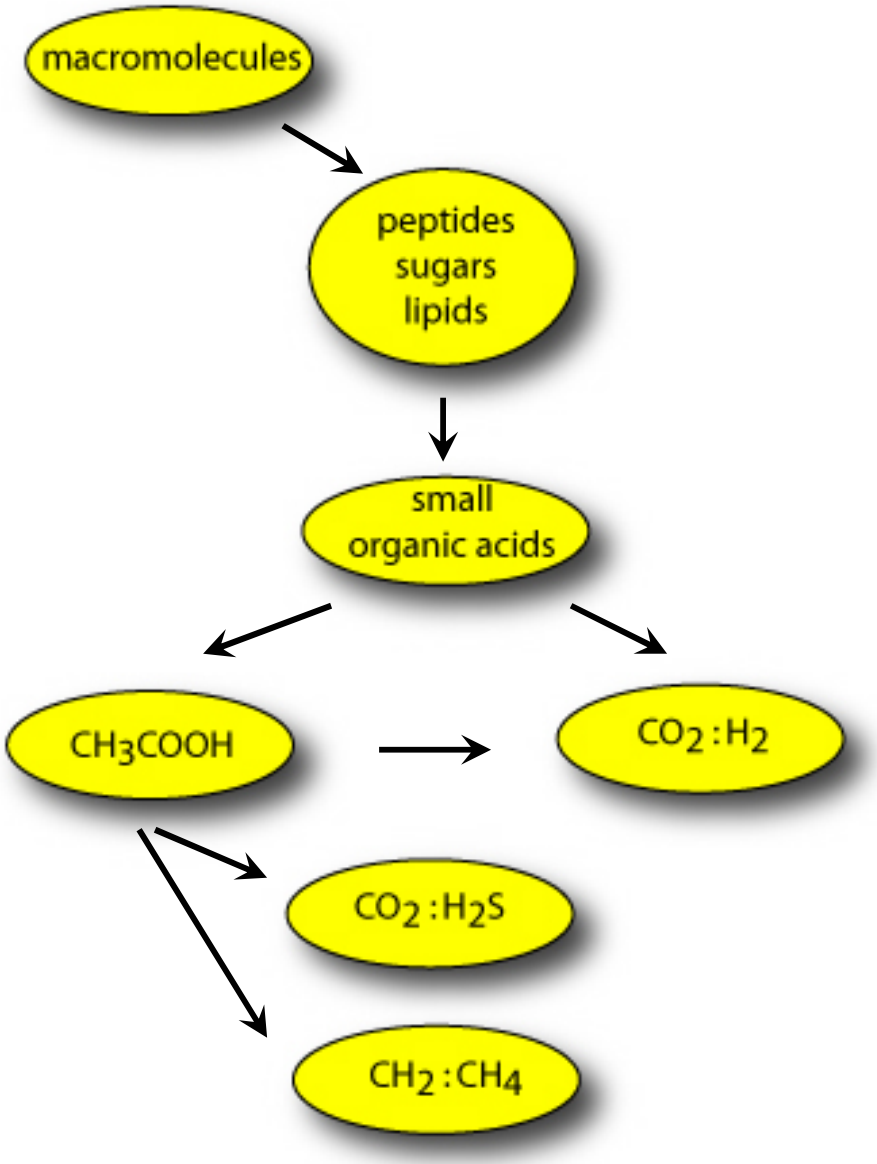
Coupled methane oxidation and sulfate reduction in CLB sediments



Methane oxidation and CO_2 reduction to methane in CLB sediments

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




macromolecules
peptides
sugars
lipids
small
organic acids
CH_3COOH
$CO_2 : H_2$
$CO_2 : H_2S$
$CH_2 : CH_4$