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

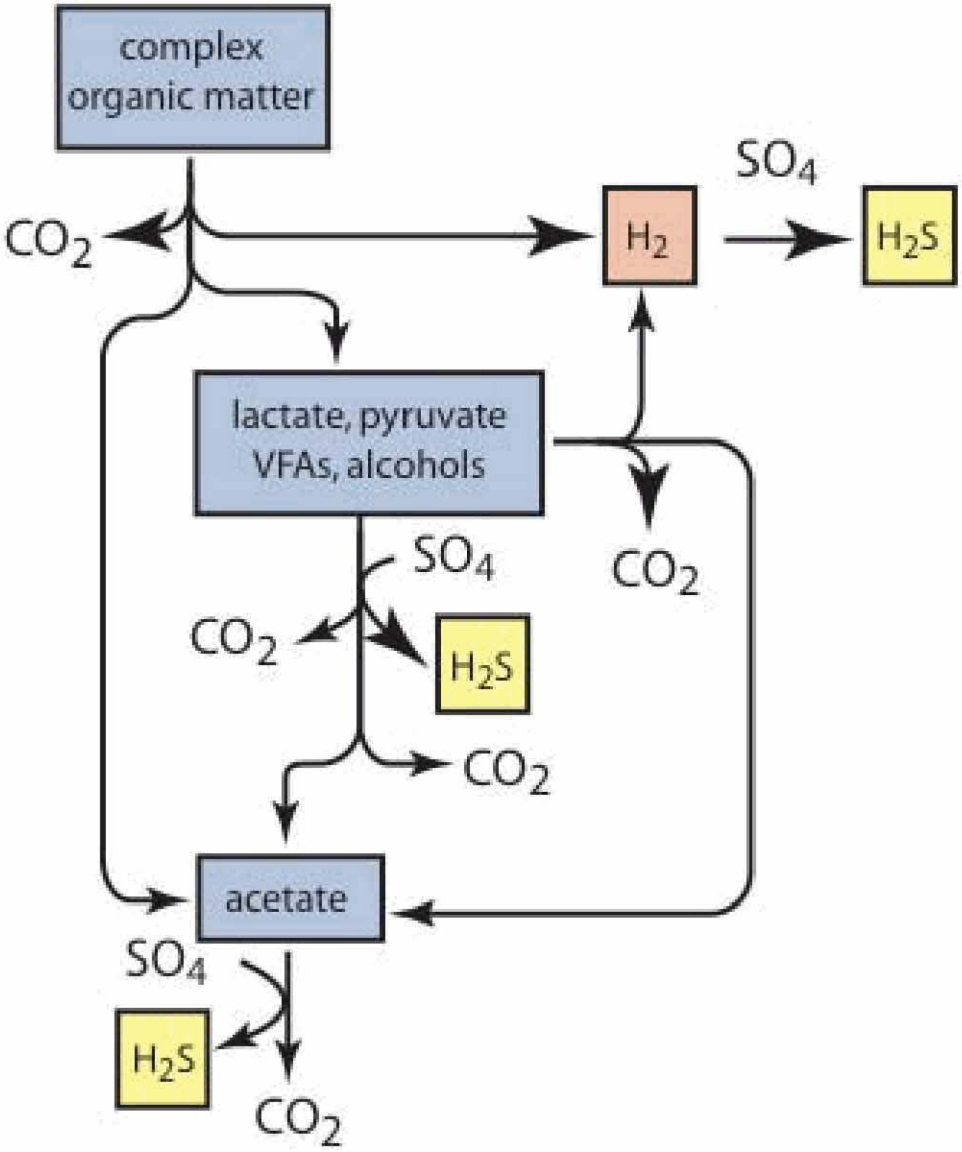
Major reactions are fermetation, sulfate reduction, and methanogenesis

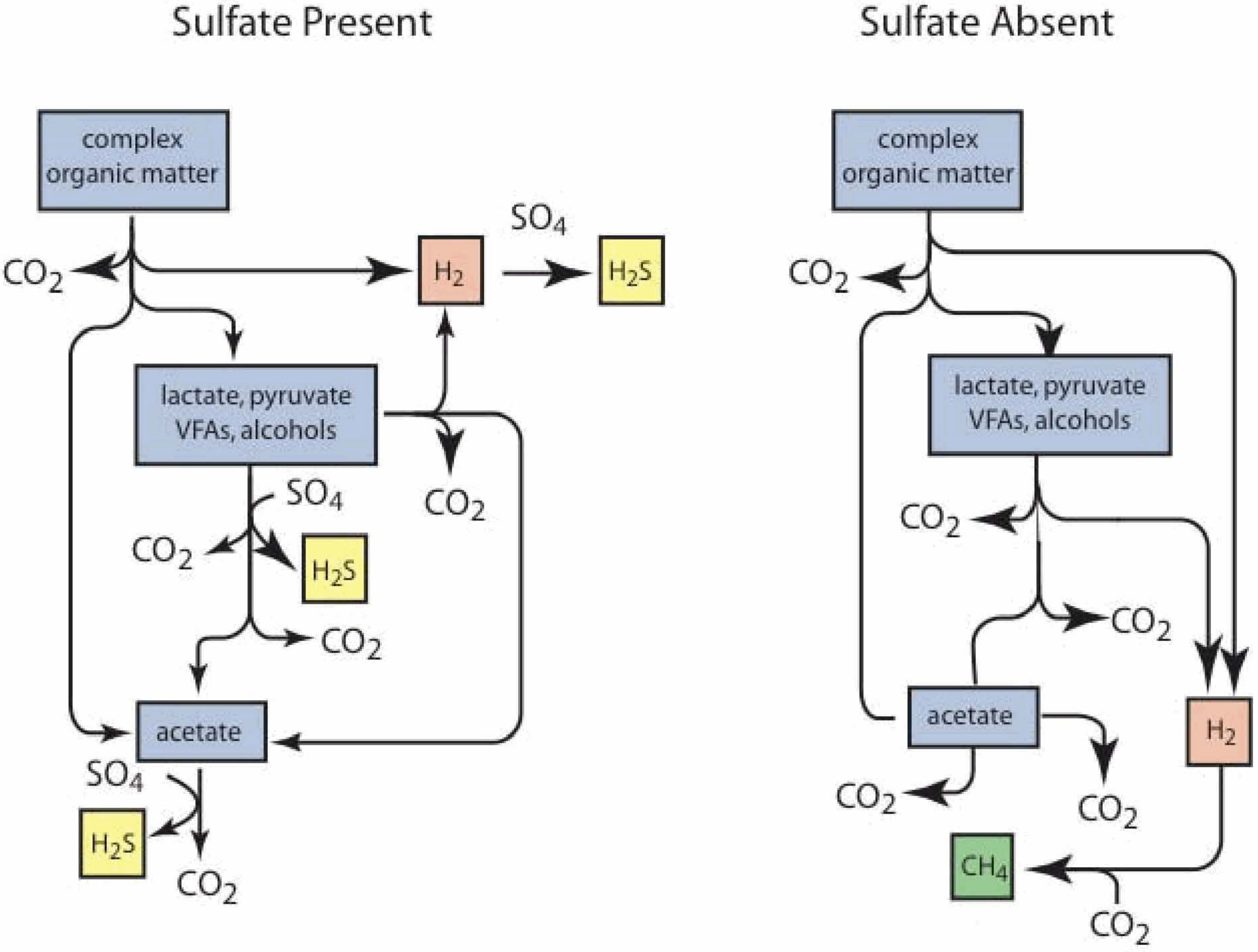
Biogeochemical zonation occurs due to differences in free energy of TEA yields

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

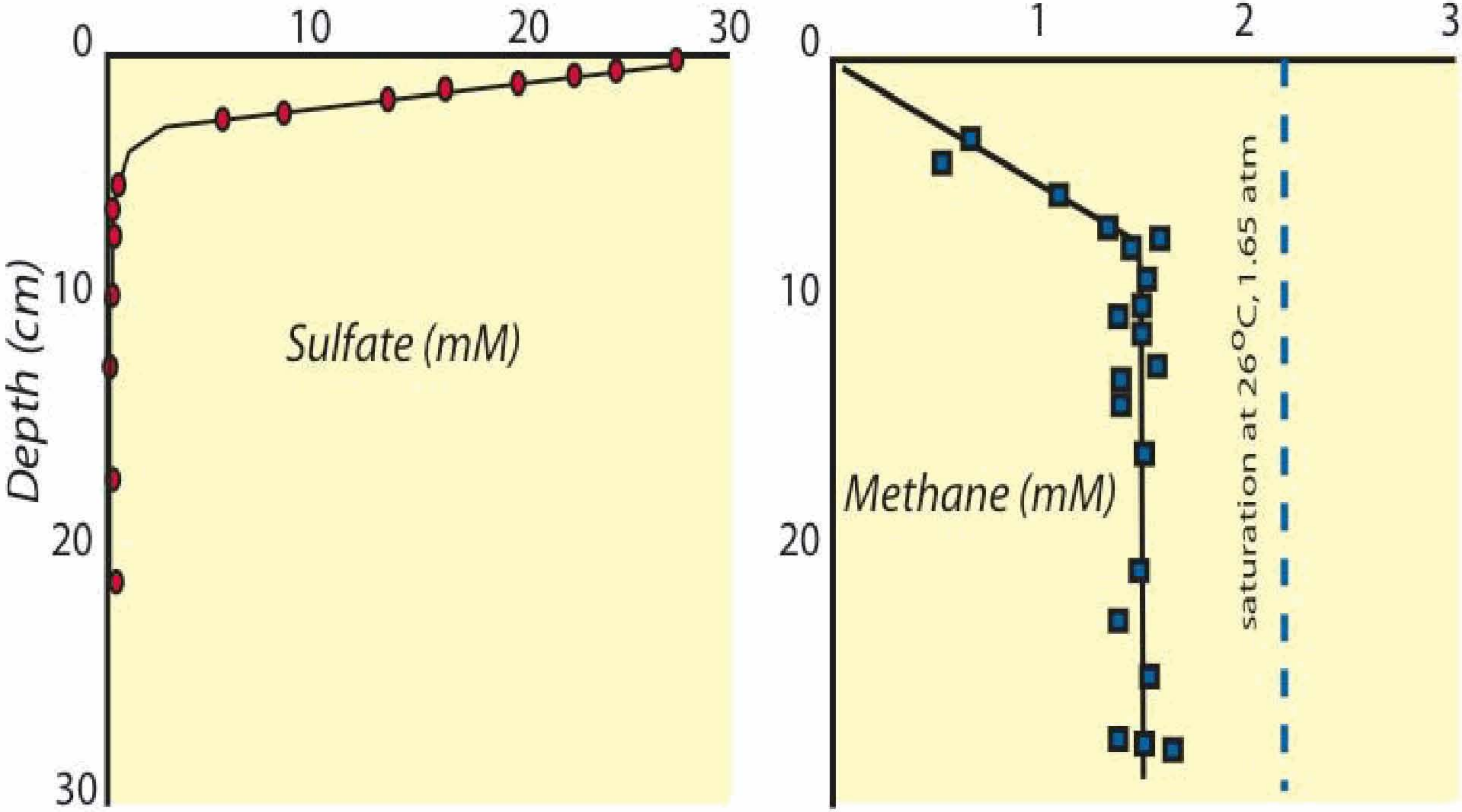
Natural system closely resembles that expected
from pure culture work.

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)



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

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

$$(CH_2O)n + nH_2O \text{ --> } nCO_2 + 2nH_2$$

$$2nH_2 + mX_{ox} \text{ --> } mX_{red} + zH_2O$$

(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)
$O_2 \longrightarrow CO_2$	-475	0.85
$NO_3^- \longrightarrow N_2 + CO_2$	-448	0.05
Mn(IV) ⟶ Mn (II)	-349	2-22
Fe(III) ⟶ Fe (II)	-114	14-28
$SO_4^{2-} \longrightarrow S^{2-}$	-77	56
$CO_2 \longrightarrow CH_4$	-58	

Rapid cycling of H_2 in anoxic sediments

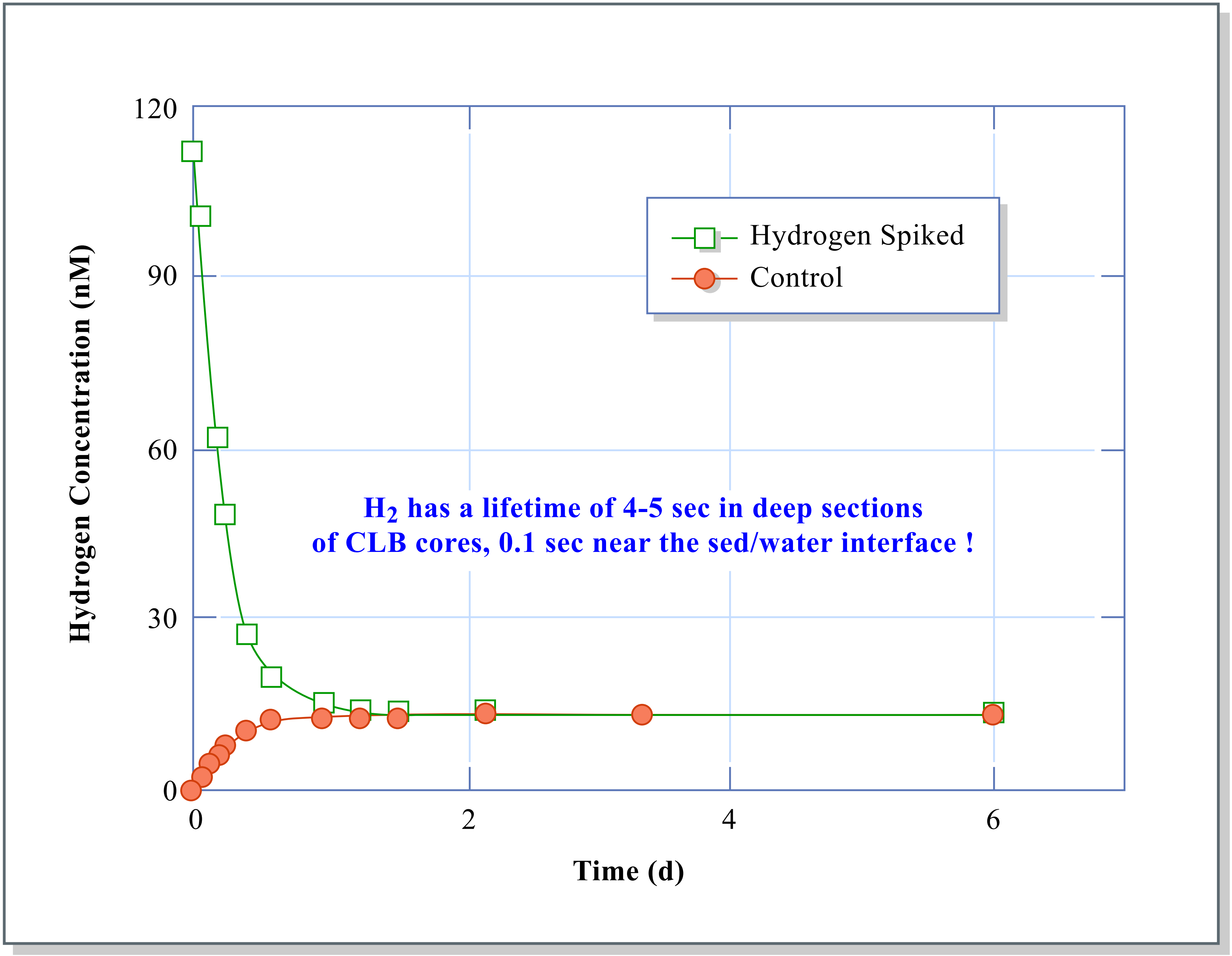
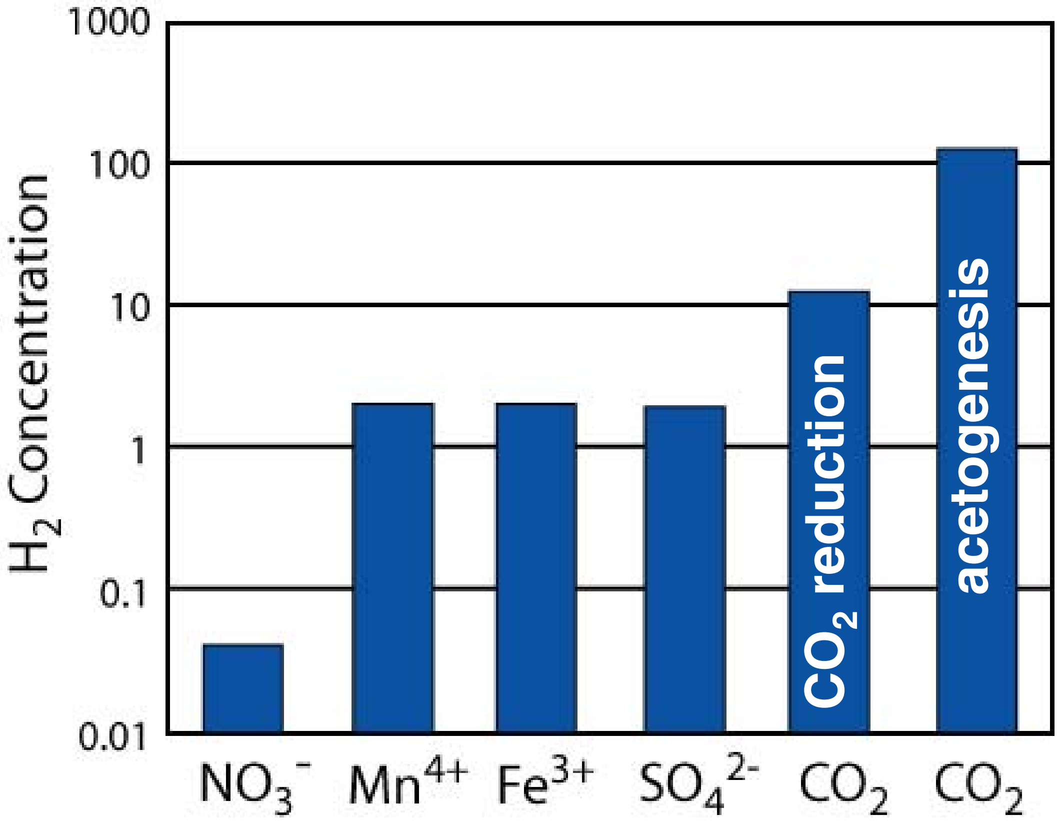


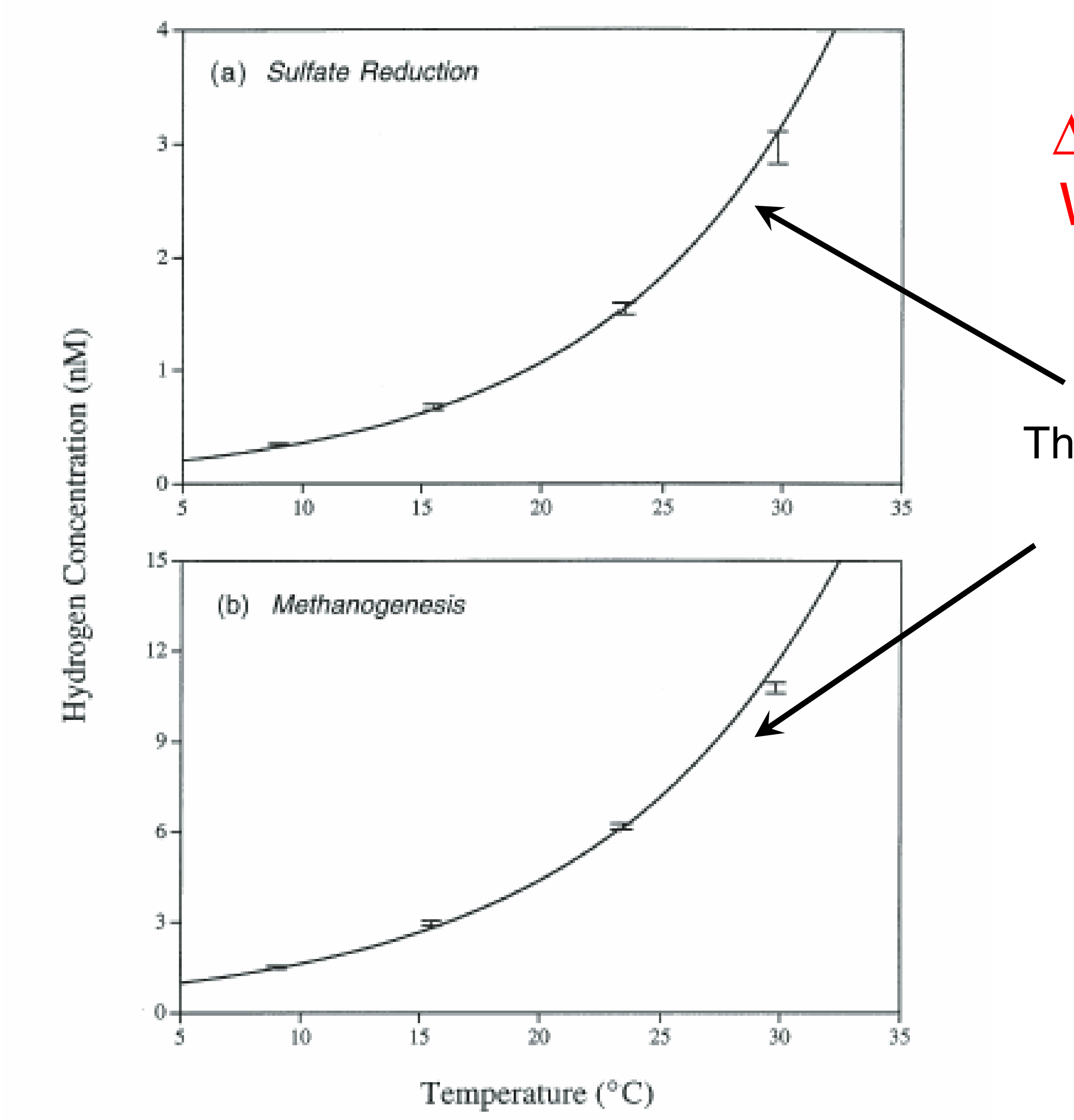
Figure by MIT OCW.

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

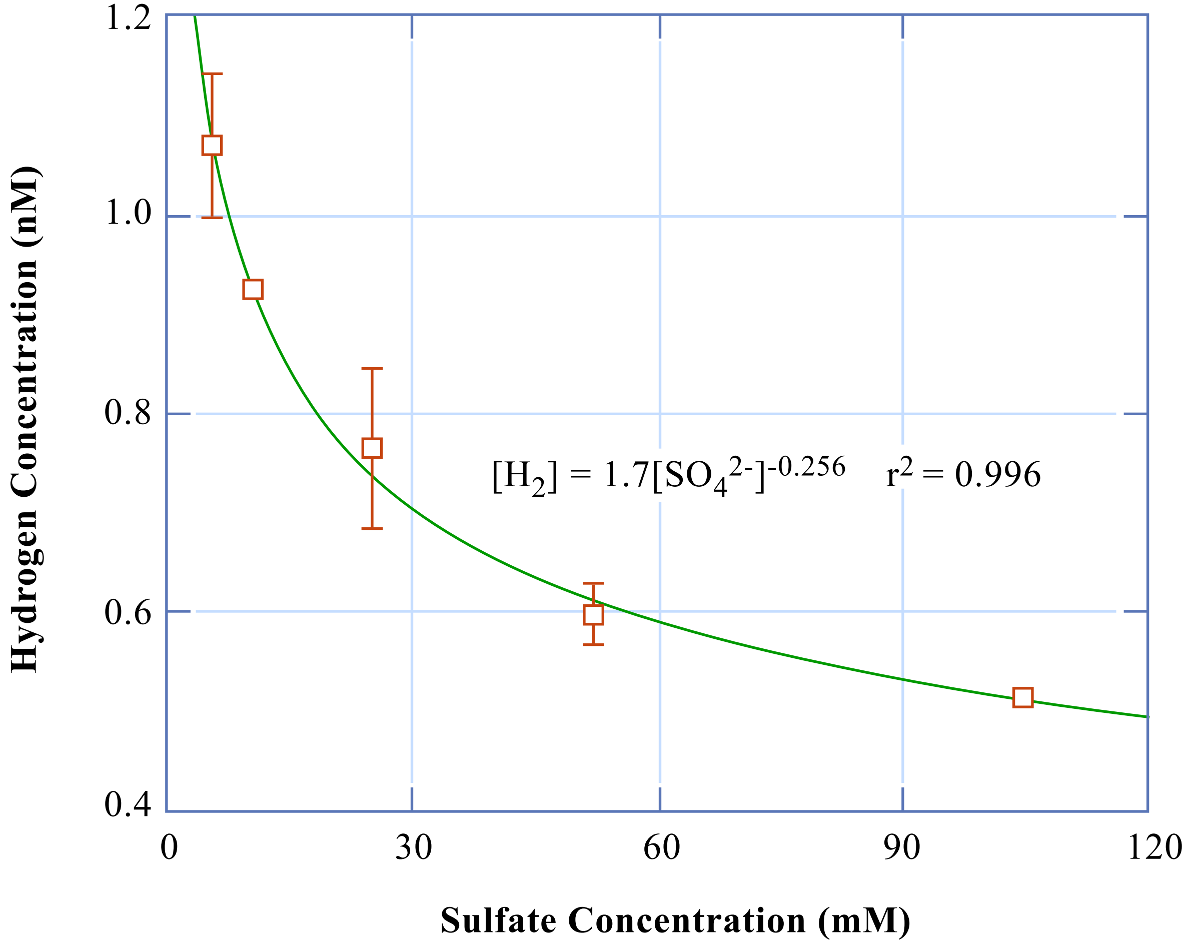
Effect of temperature on H_2 concentrations



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

Theoretical
effect

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



Response of hydrogen concentration 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).

Figure by MIT OCW.

Profiles of hydrogen and sulfate in CLB and WOR sediments

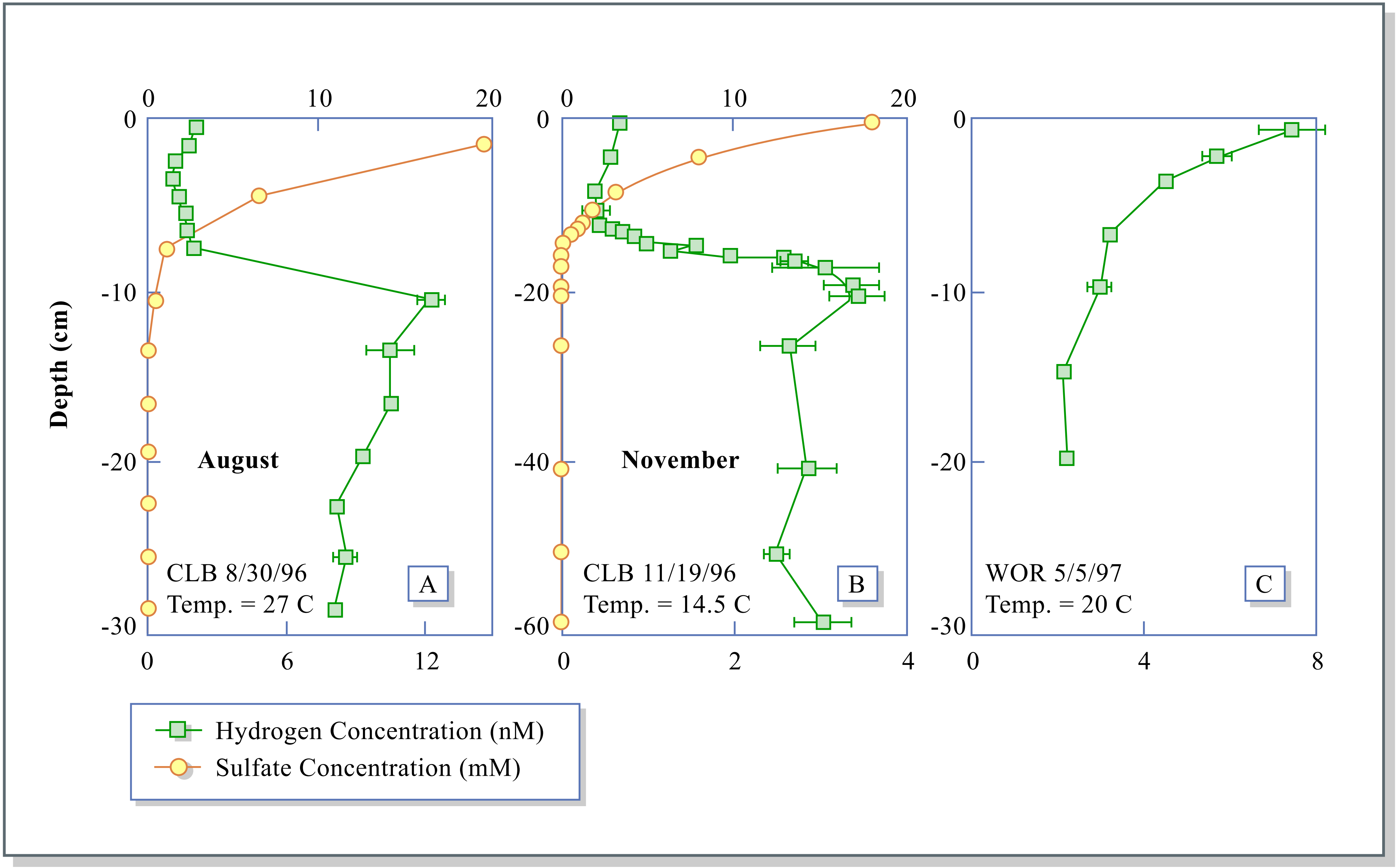


Figure by MIT OCW.

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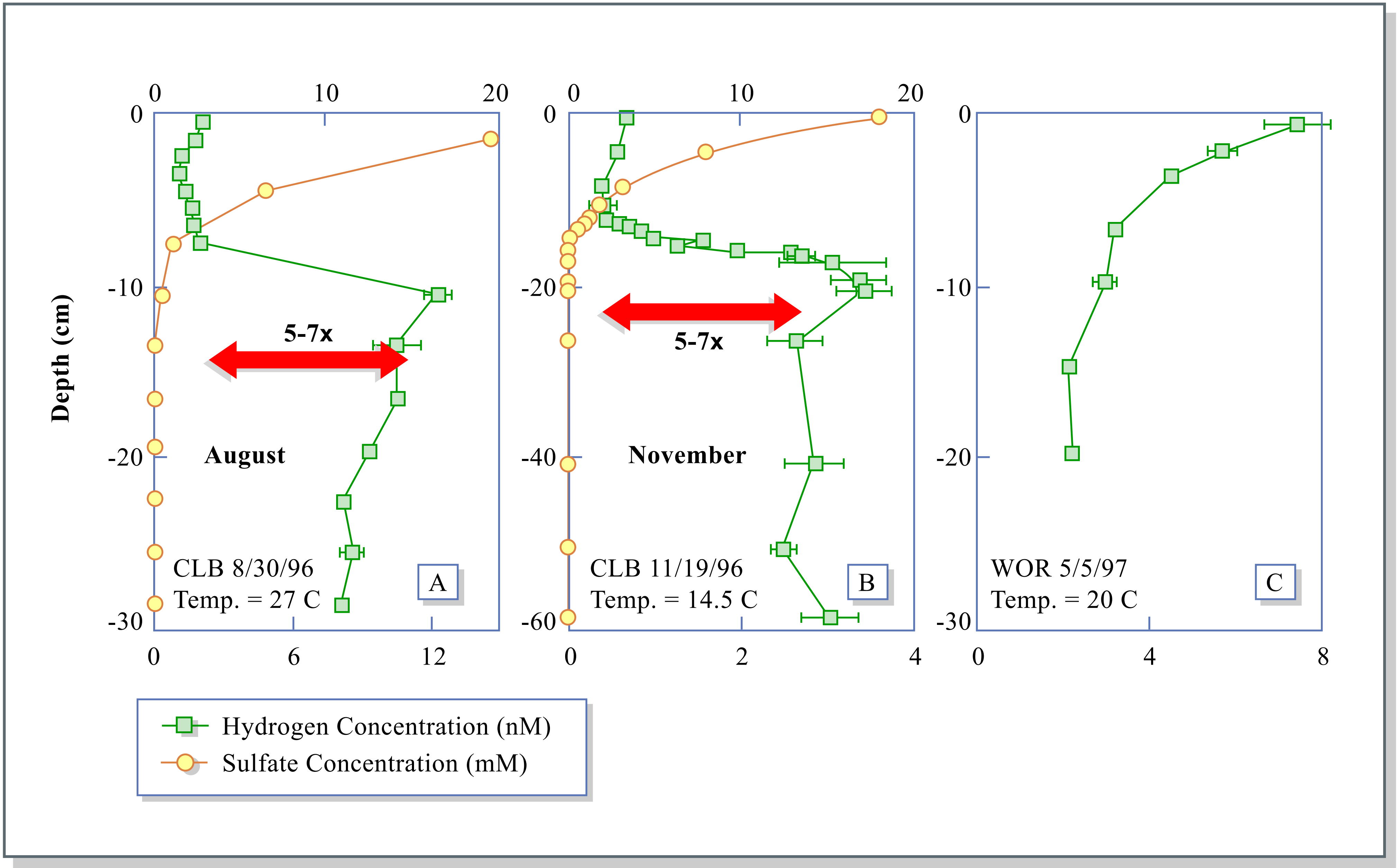

Figure by MIT OCW.

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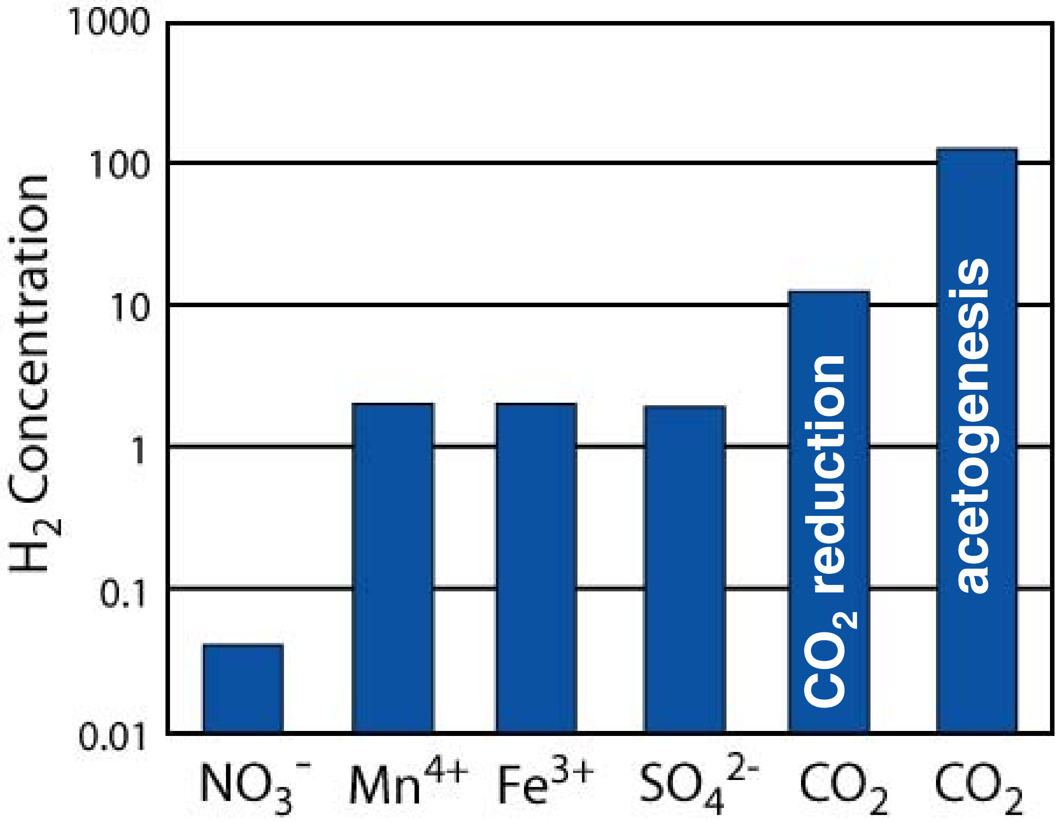

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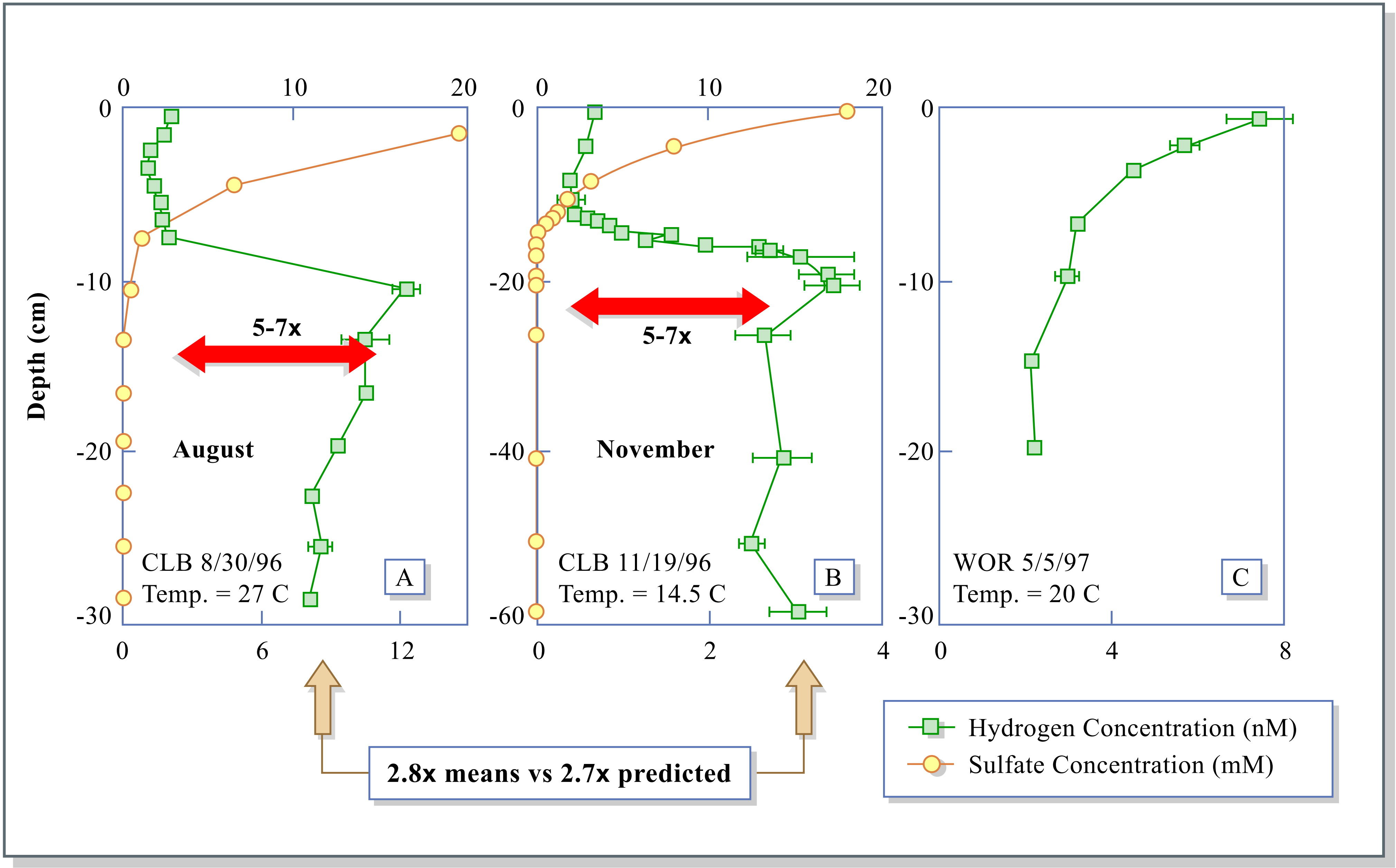
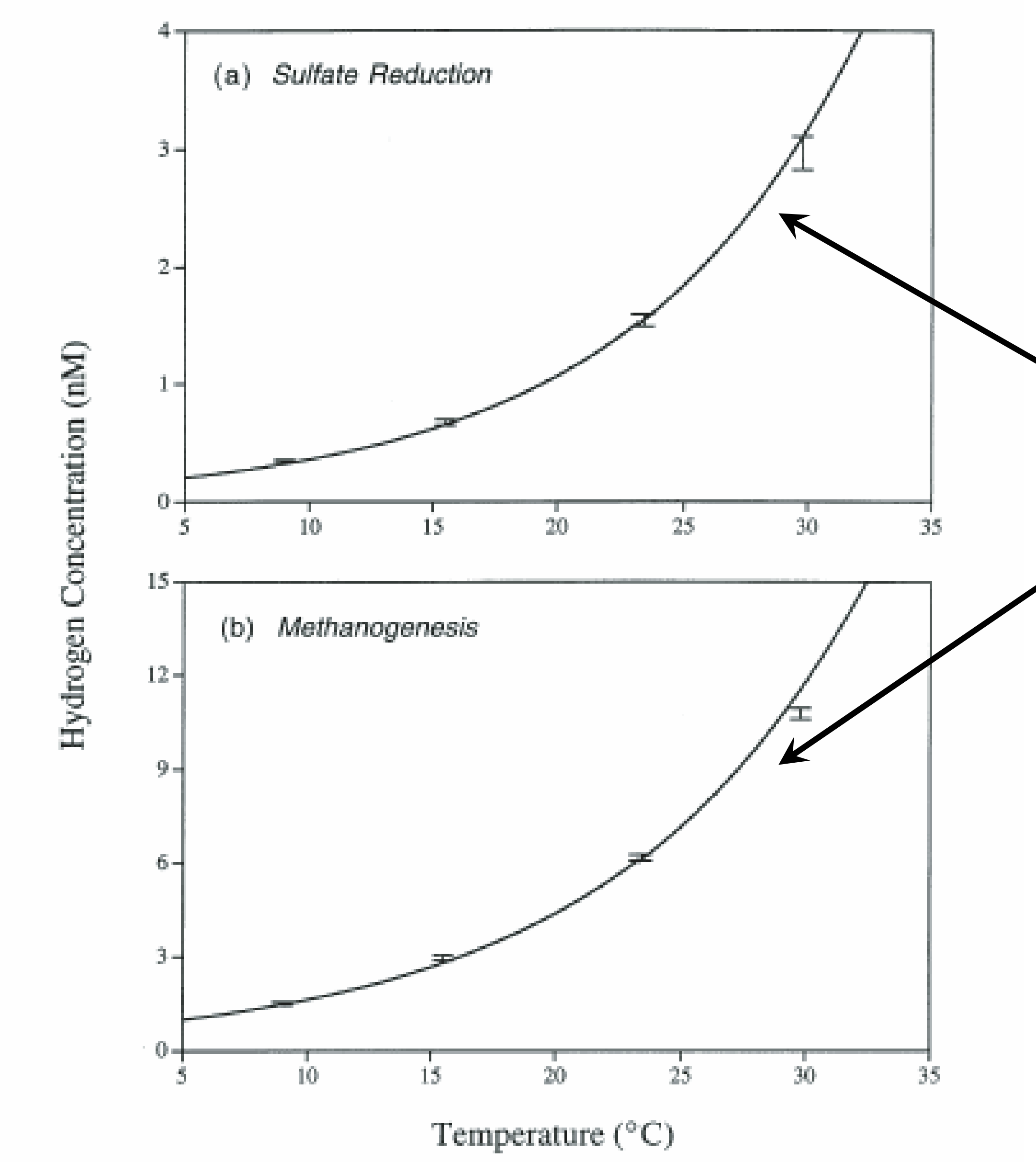


2.8x means vs 2.7x predicted

Figure by MIT OCW.

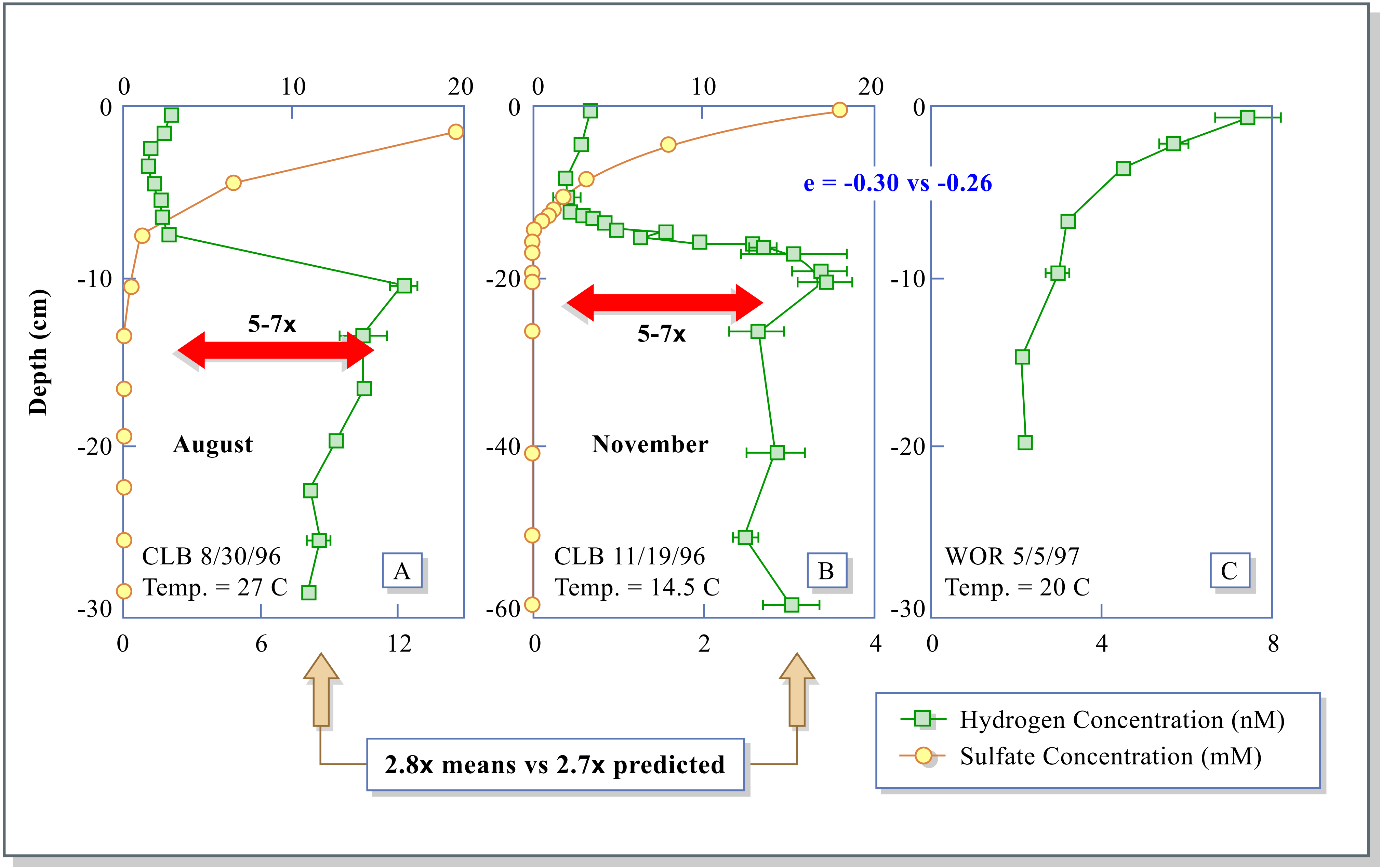
Effect of temperature on H_2 concentrations



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

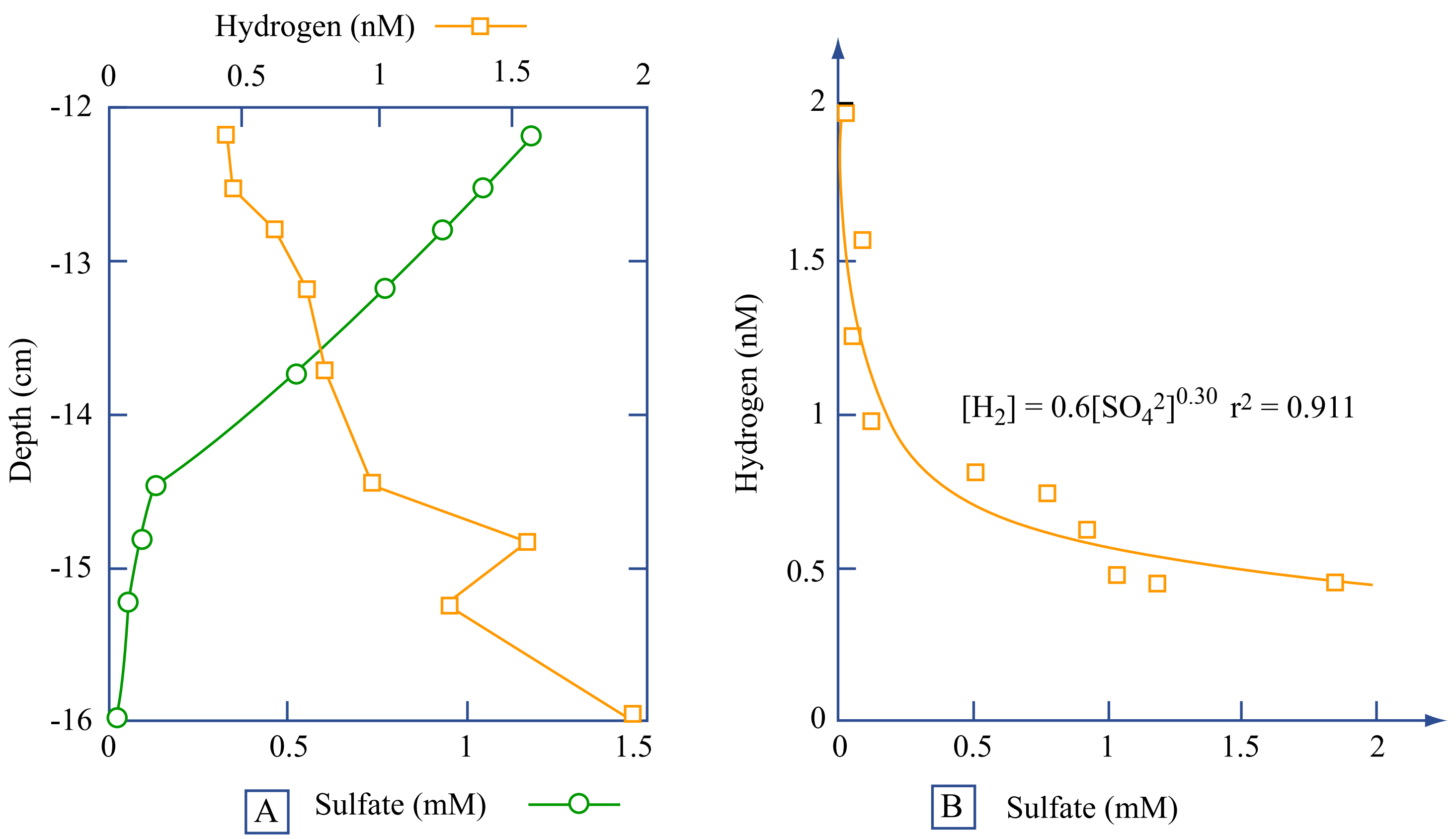


e = -0.30 vs -0.26

2.8x means vs 2.7x predicted

Figure by MIT OCW.

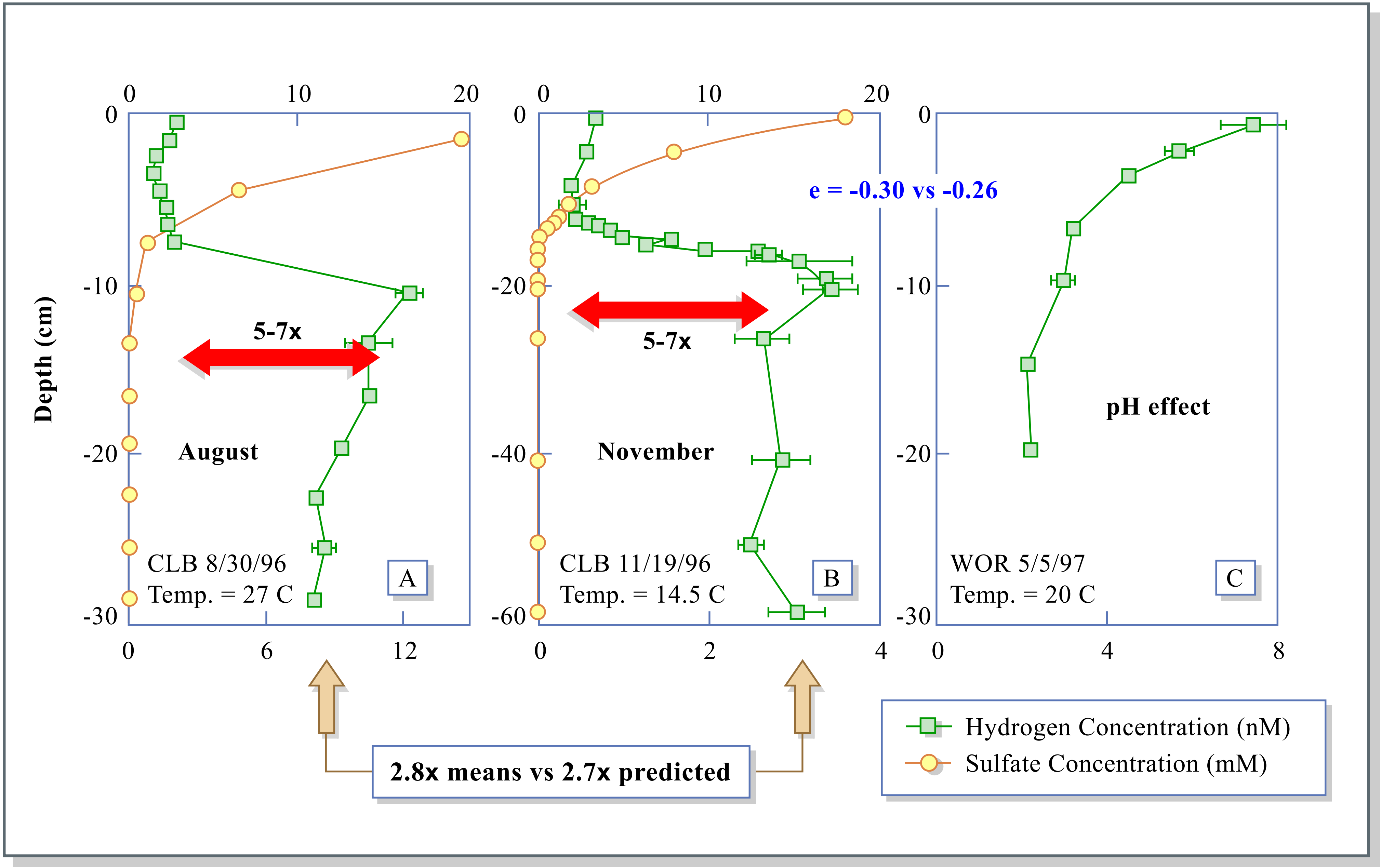
Effect of sulfate on H_2 in CLB sediments



The dependence of hydrogen concentrations on sulfate concentrations in the November core from Cape Lookout Bight . (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).

Figure by MIT OCW.

Profiles of hydrogen and sulfate in CLB and WOR sediments



5-7x

5-7x

e = -0.30 vs -0.26

pH effect

2.8x means vs 2.7x predicted

Figure by MIT OCW.

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.

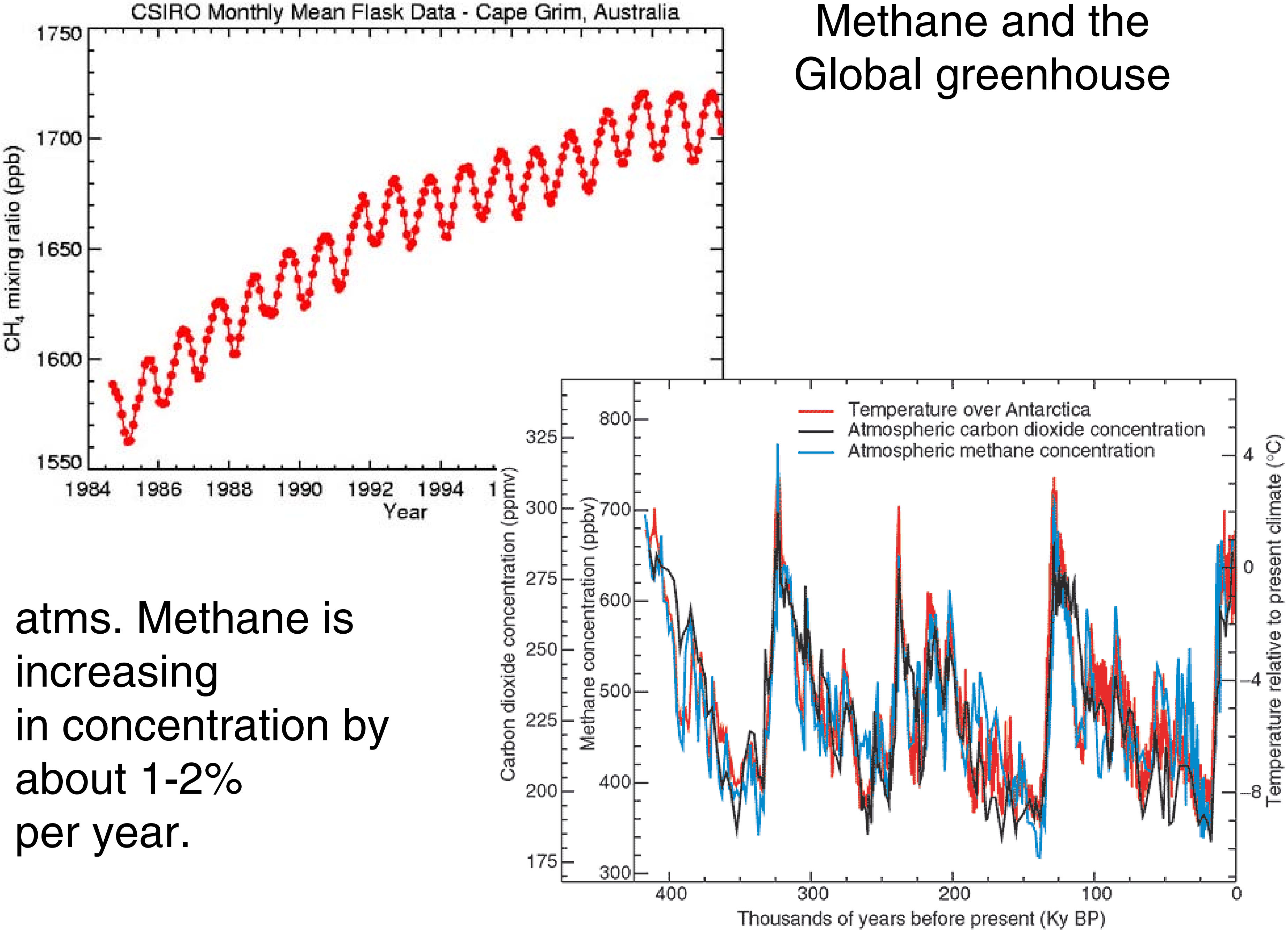
Hydrogen concentrations respond to T, [X], pH.
Laboratory changes correspond well to field observations.

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

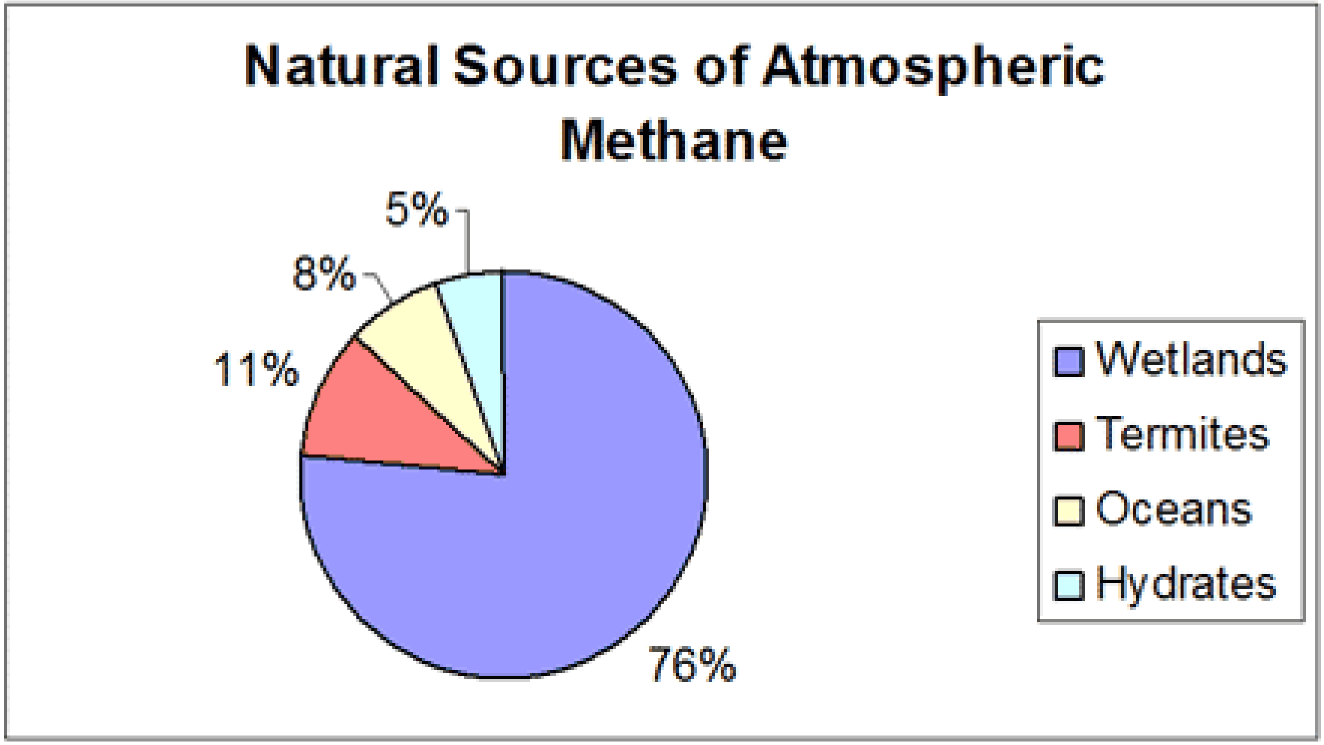
H2 has a very short lifetime in sediments- makes an
Excellent E regulator. Small changes in H2 concentration
Results in large changes in ΔG.

Intense competition by bacteria regulate [H_2]

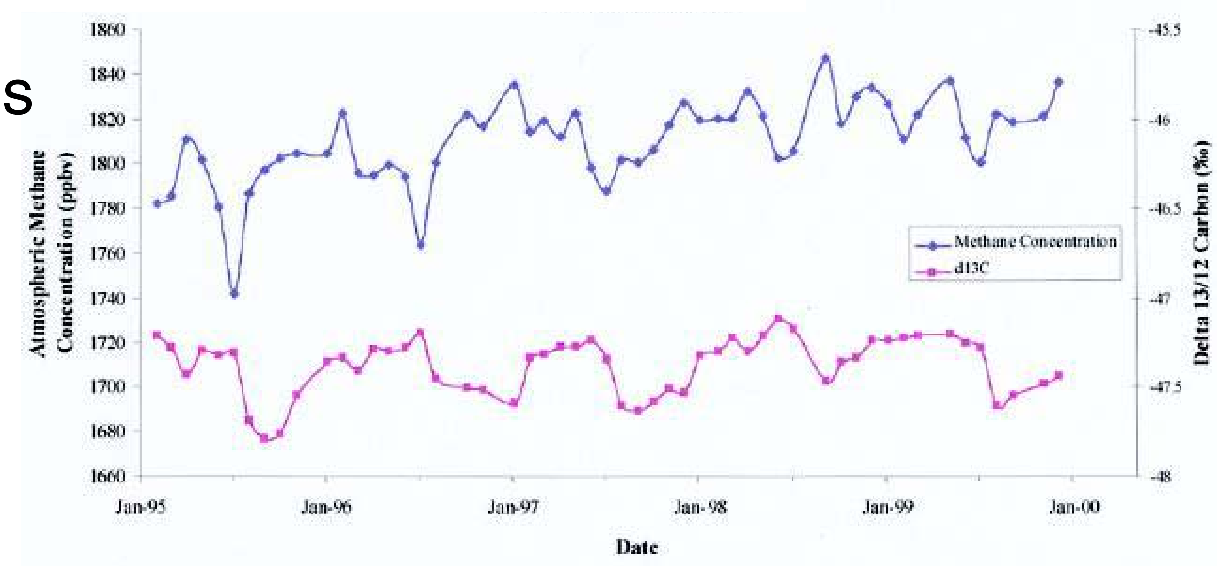
Methane and the Global greenhouse



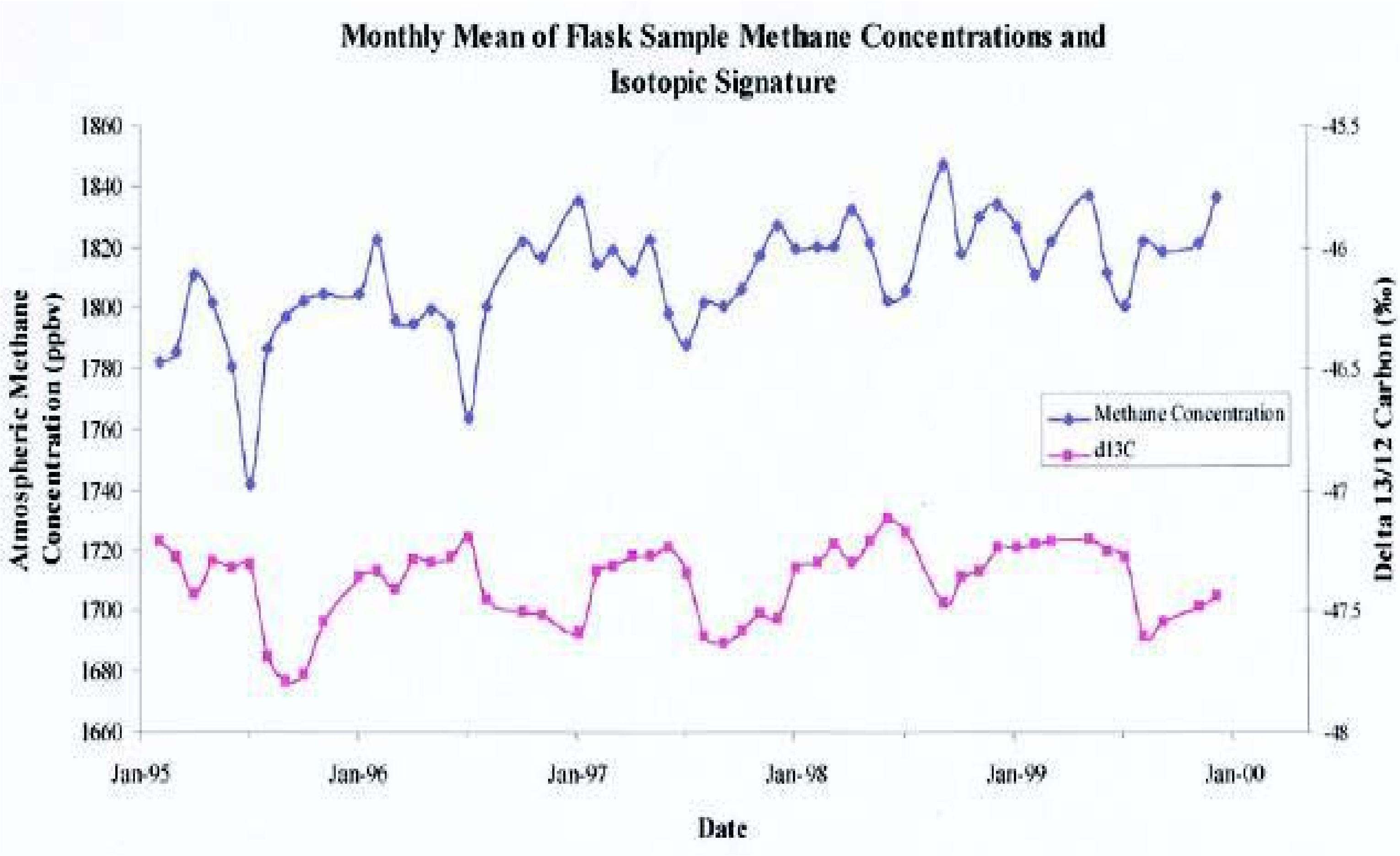
atms. Methane is increasing
in concentration by
about 1-2%
per year.



C isotopic changes in atms methane



C isotopic changes in atmospheric methane



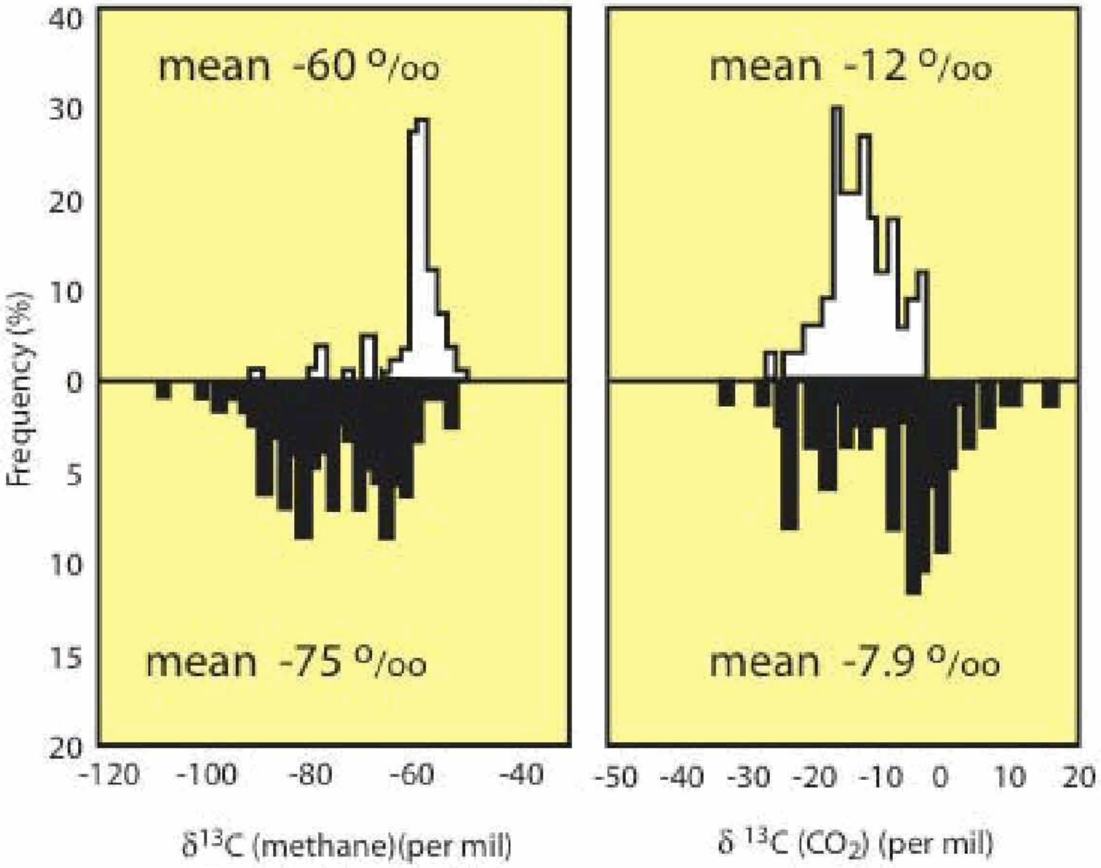
How do we explain the increase in atmospheric ?

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



Marine

There are two pathways that yield methane:

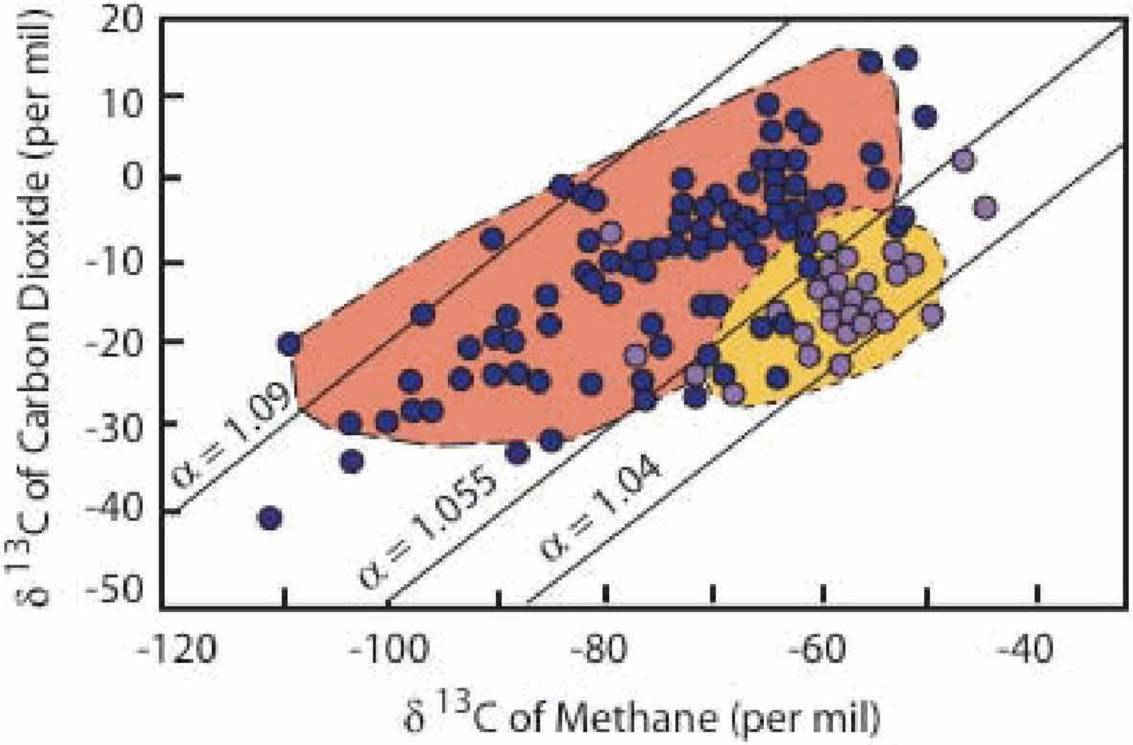
Freshwater

$CH_3COOH \text{ --> } CH_4 + CO_2$

Marine

$CO_2 + 4H_2 \text{ --> } CH_4 + 2H_2O$

Isotope fractionation and methanogenesis



Carbon isotope fractionation with methanogenesis

Freshwater

$CH_3COOH \text{ --> } CH_4 + CO_2$

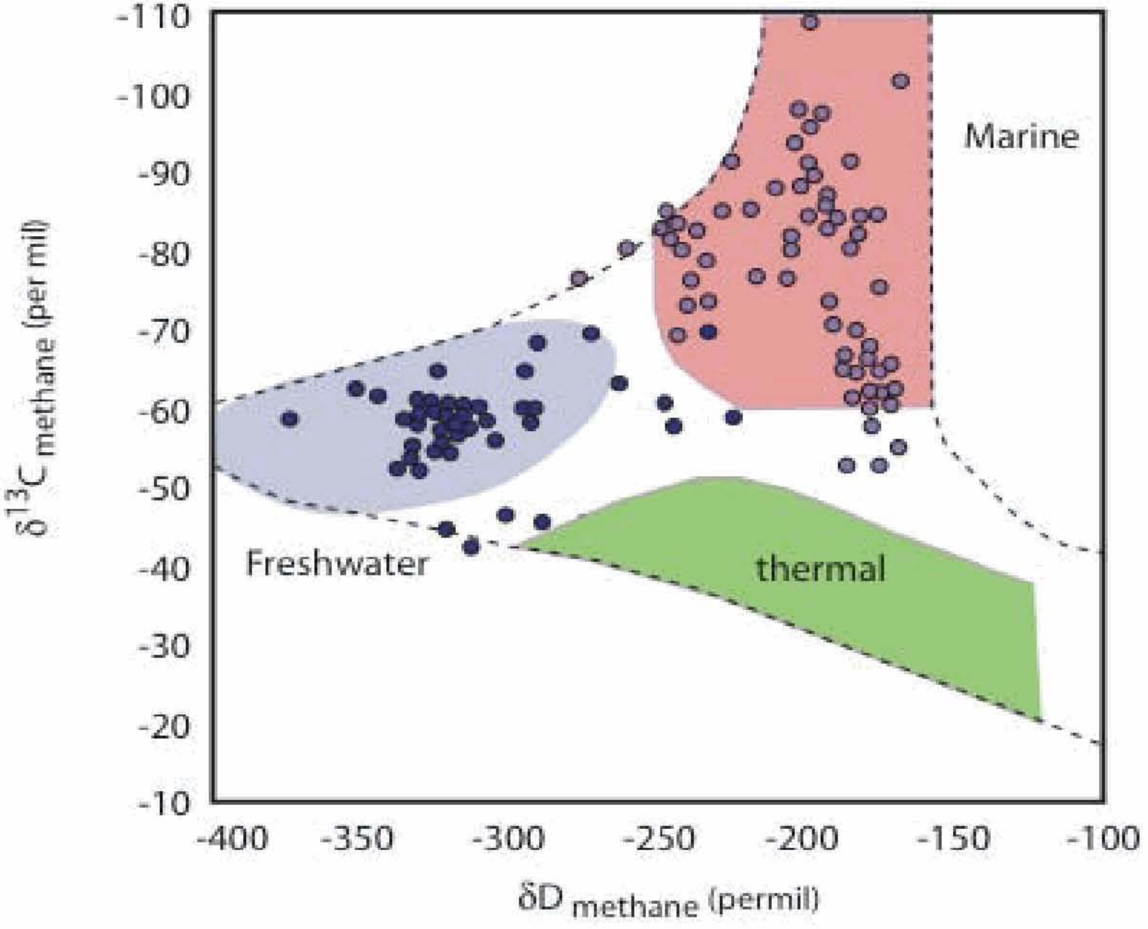
$\alpha = -48‰$

Marine

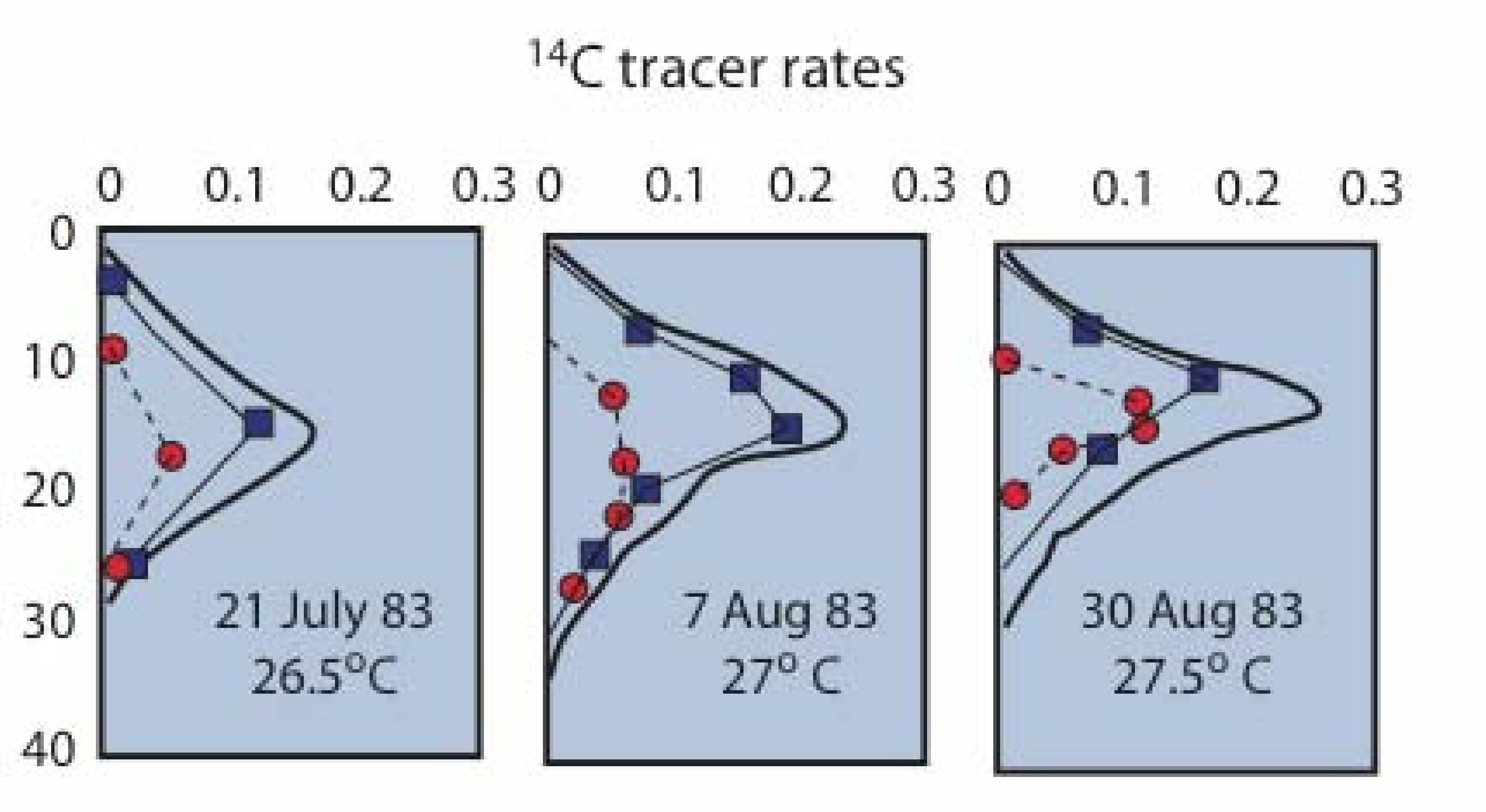
$CO_2 + 4H_2 \text{ --> } CH_4 + 2H_2O$

$\alpha = -70‰$

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$_2$

Cape Lookout Bight sediment gas bubble composition and δ^{13}C data. Values listed are means ± SD for the number of samples bottle listed. Superscript indicate the number of samples for which compositional data wee obtained when different from the number of sample bottle listed.

Date	Methane sample bottles (no.)	Methane content (%)	δ^{13}C-CH$_4$ (per mile)	Carbon dioxide sample bottles (no.)	Carbon dioxide content (%)	δ^{13}C-CO$_2$ (per mil)
6-June-1983	5	97 ± 2	-64.5 ± 7	5	2.5 ± 0.1	-6.8 ± 1.1
19-June-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

Figure by MIT OCW.

Changes in C-13 in CLB methane

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Changes in C-13 in CLB methane

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Monthly flux and isotope data for methane flux from CLB

Month	Monthly methane bubble flux* (mmol m^{-2})	Annual Flux[a] (%)	$\delta^{13}C\text{-}CH_4$‡ (per mil)
January	0	0	
February	0	0	-63.4 ± 0.6
March	0	0	
April	0	0	
May	38	0.8	-63.4 ± 0.2
June	350	7.2	-66.4 ± 2.5
July	1270	26.2	-64.3 ± 0.7
August	1643	33.9	-61.0 ± 1.6
September	1095	22.6	-58.7 ± 2.0
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
			WAS

Figure by MIT OCW.

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.

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

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

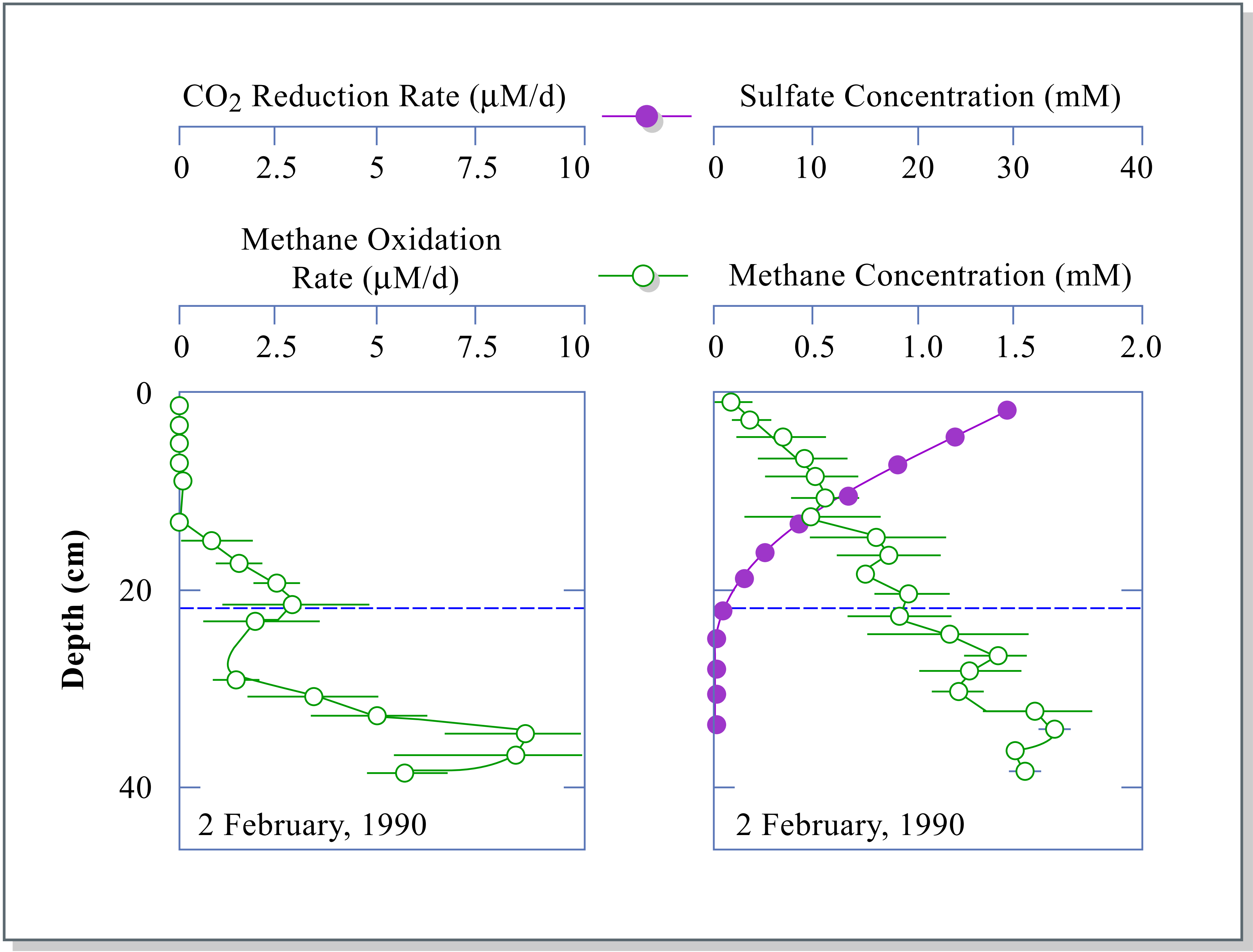
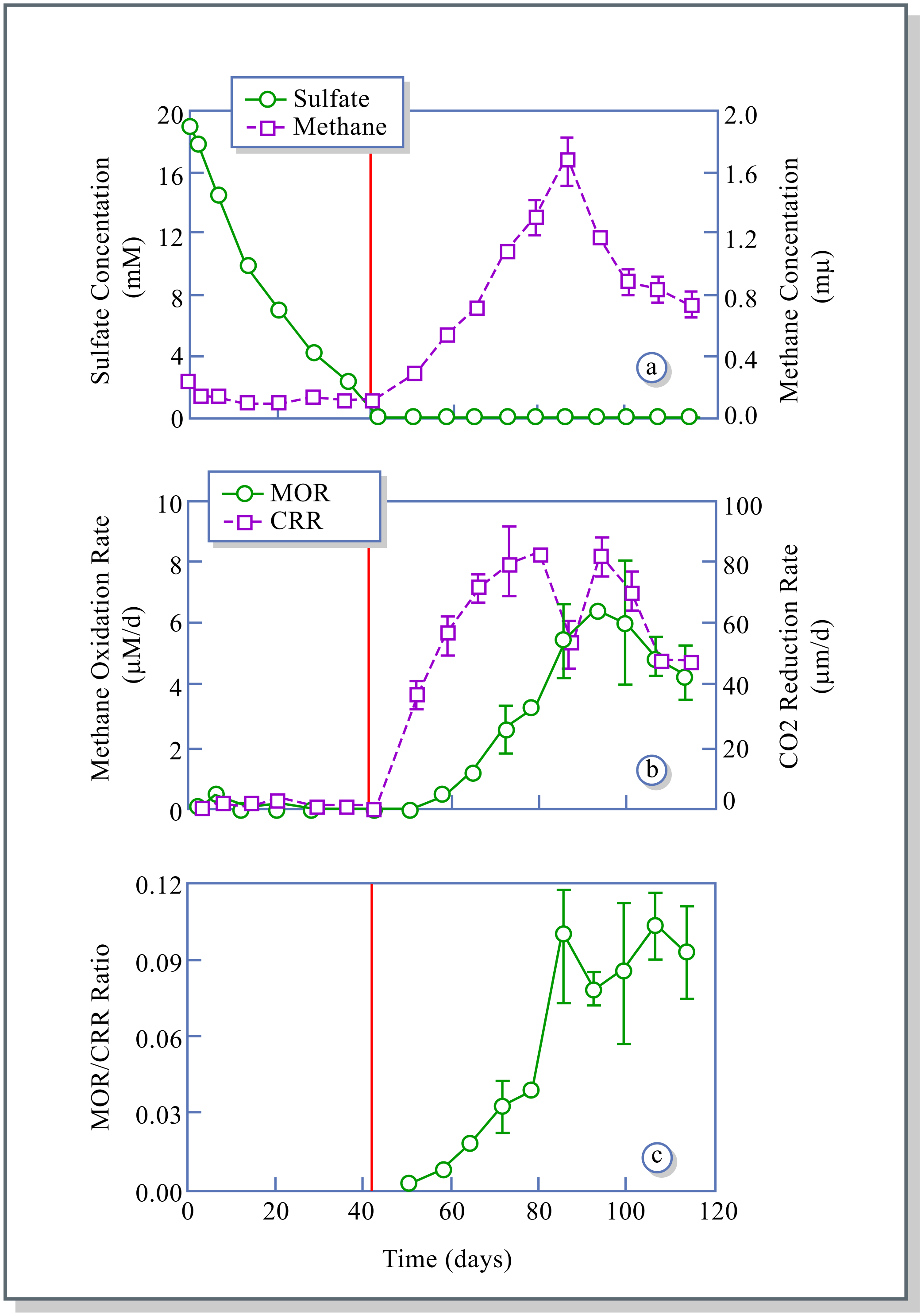


Figure by MIT OCW.

Methane oxidation and CO_2 reduction to methane in CLB sediments

CH_4 +2H_2O --> CO_2 + 4H_2



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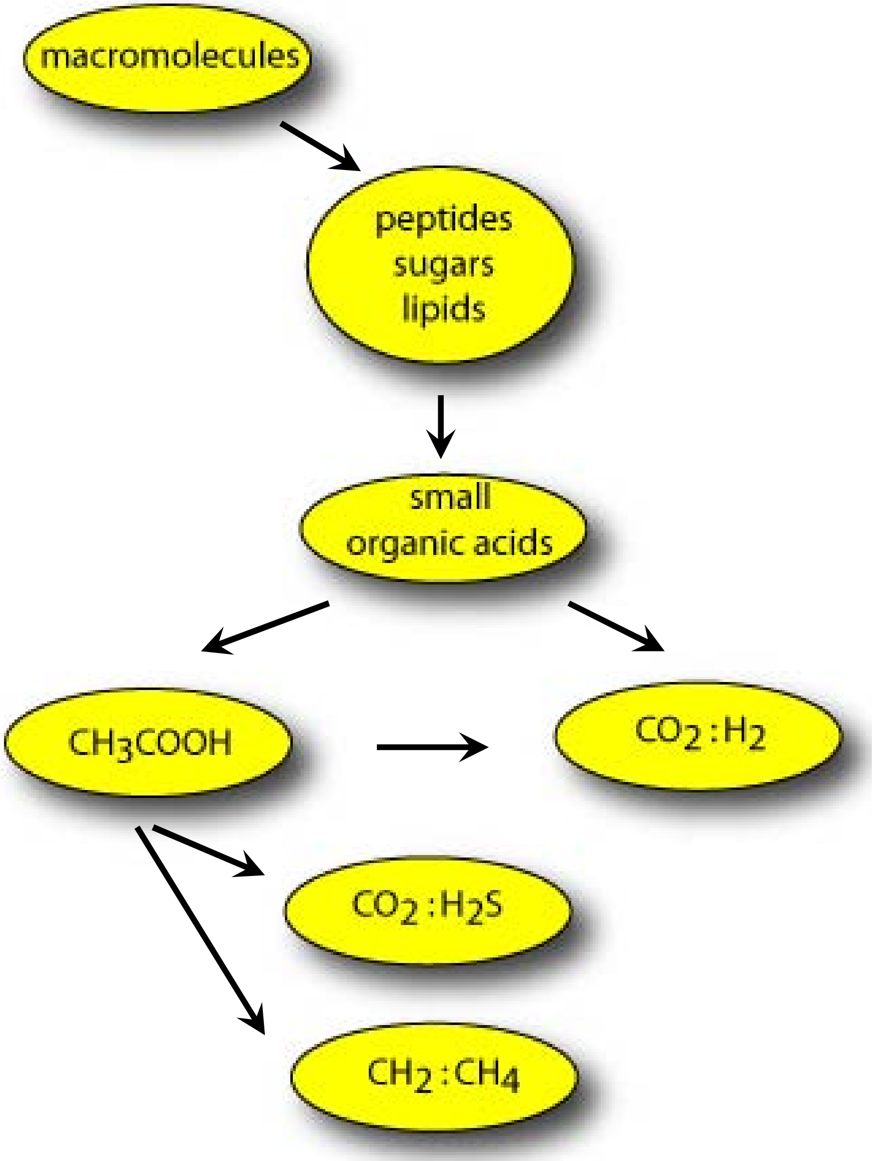

macromolecules

peptides
sugars
lipids

small
organic acids

CH_3COOH

$CO_2 : H_2$

$CO_2 : H_2S$

$CH_2 : CH_4$