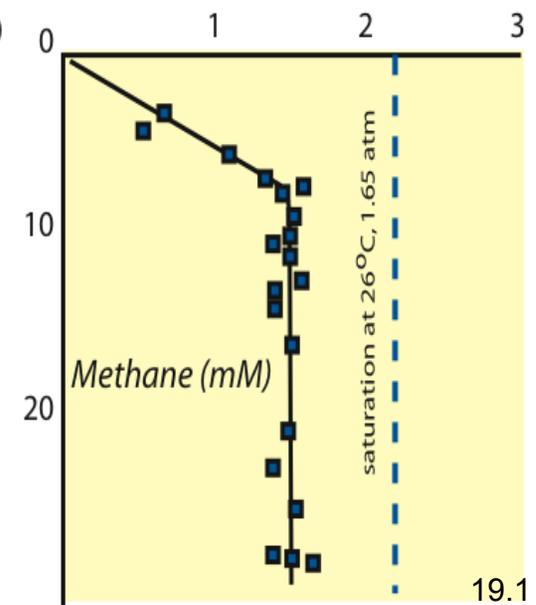
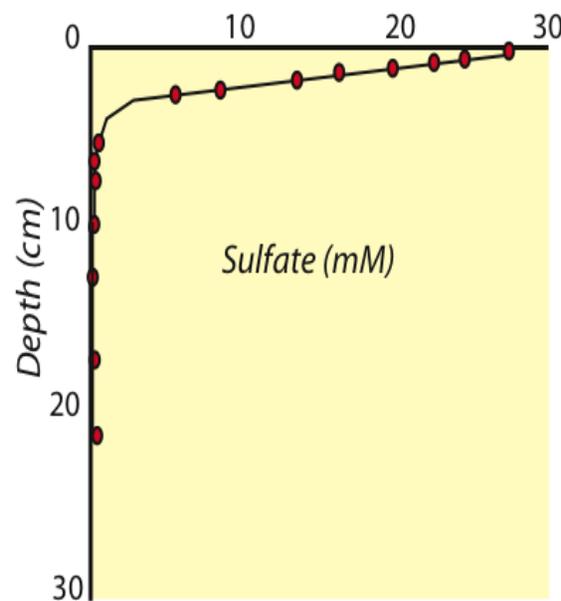
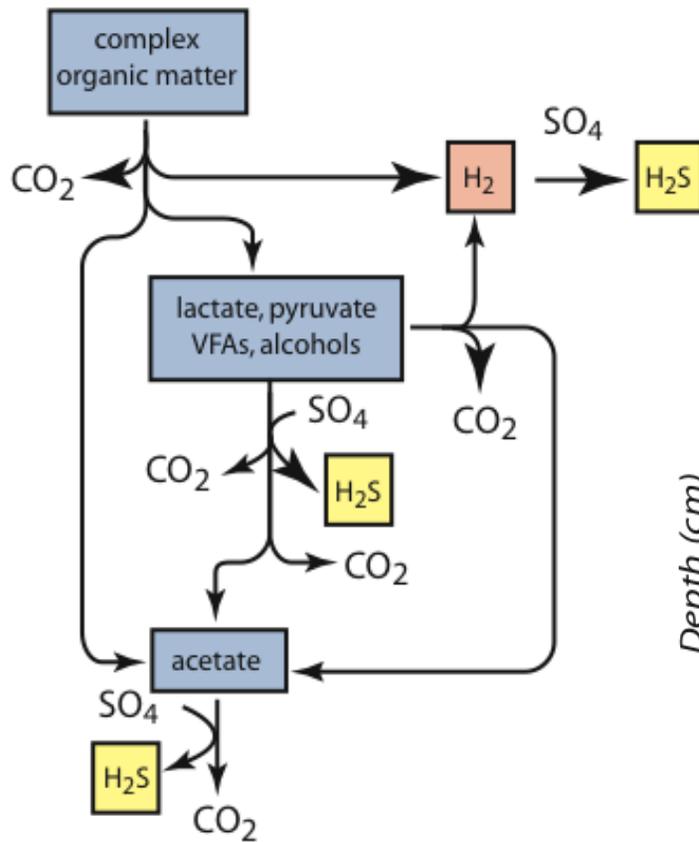


Organic carbon oxidation is an
Energy yielding process

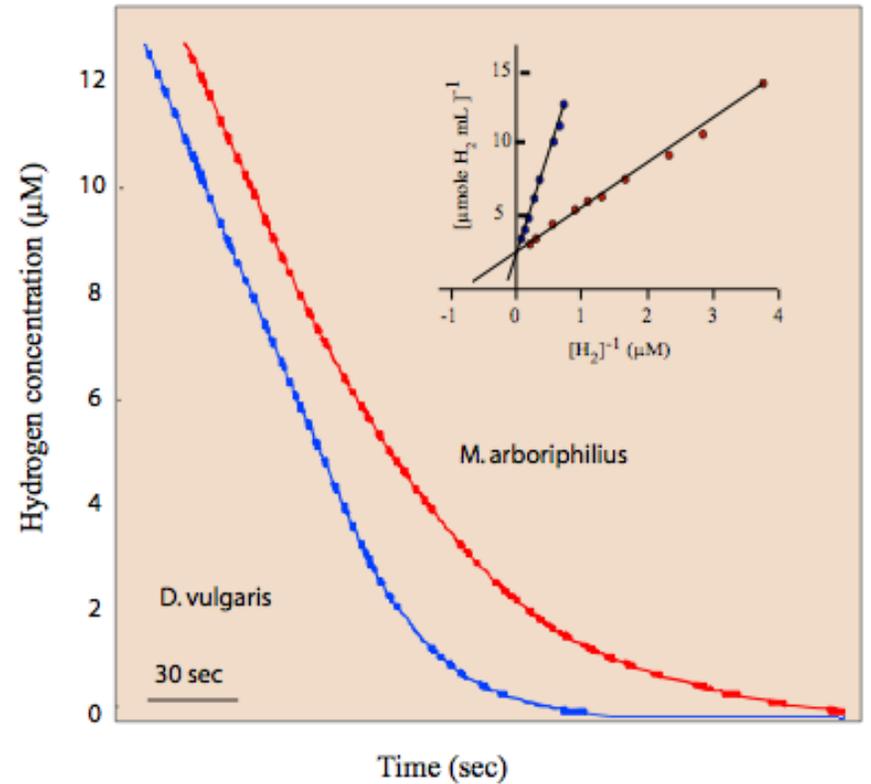
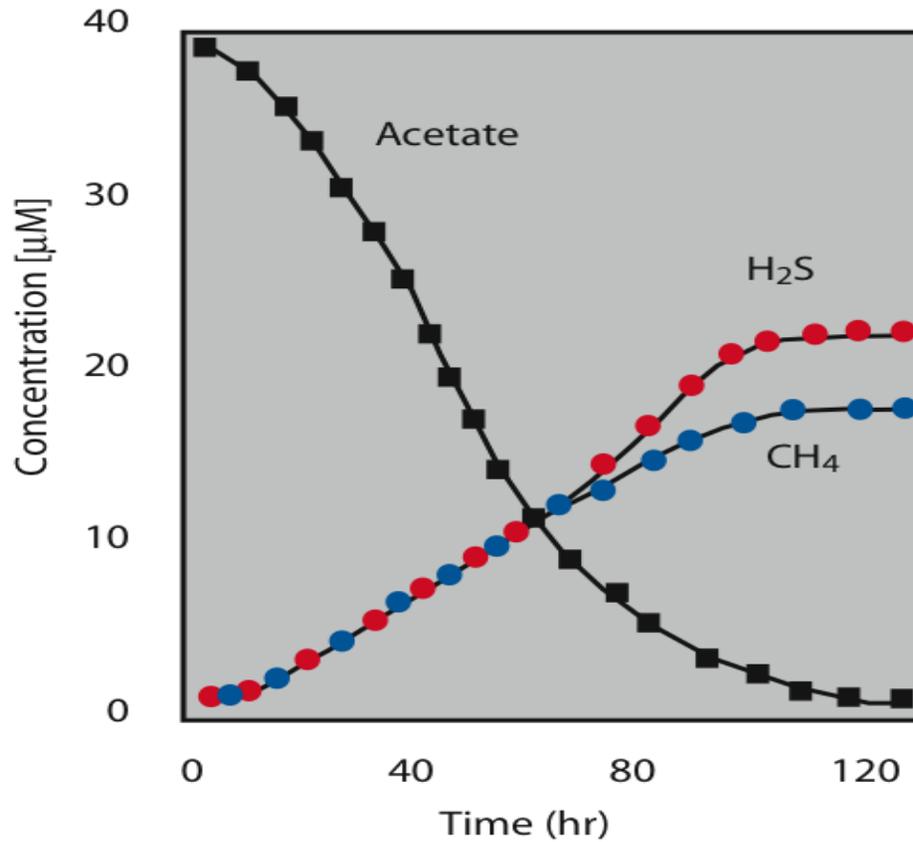


$$\Delta G = \Delta G_0 + RT \ln (X_{red}/X_{ox})$$

$$\Delta G > -40 \text{ Kcal/mole C}$$

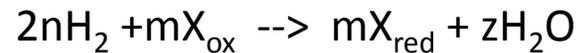
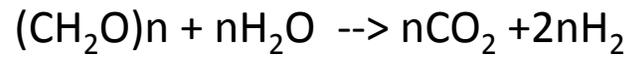


Competition for acetate and hydrogen between
Desulfobacter postgatei and *Methanosarcina bakerii*



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

Is C oxidation in anoxic sediments under thermodynamic regulation?



(e.g. $\text{X}_{\text{ox}} = \text{SO}_4^{2-}$ $\text{X}_{\text{red}} = \text{S}^{2-}$)

$$\Delta G_{\text{rxn}} = \Delta G_{(T)}^{\circ} + RT \ln \left(\frac{\{\text{X}_{\text{red}}\}^m}{\{\text{X}_{\text{ox}}\}^m (P_{\text{H}_2})^{2n}} \right)$$

and...

$$P_{\text{H}_2} = \left(\frac{\{\text{X}_{\text{red}}\}^m}{\{\text{X}_{\text{ox}}\}^m} e^{(\Delta G_{\text{rxn}} - \Delta G_{(t)}^{\circ})/RT} \right)^{1/2n}$$

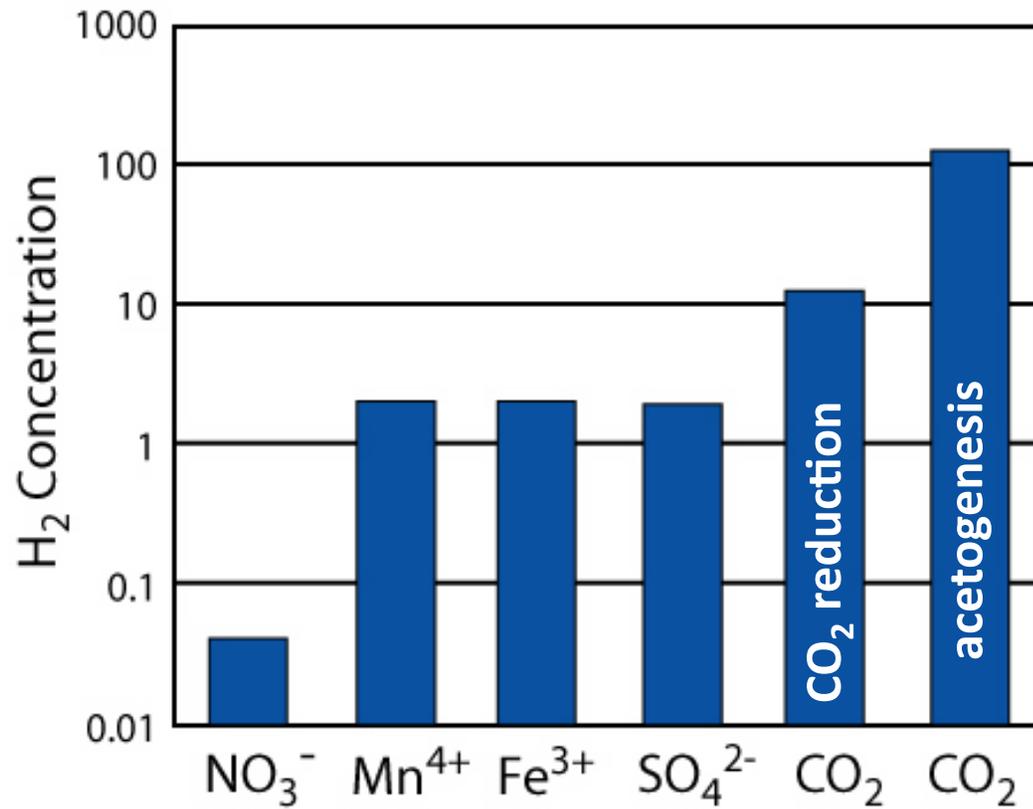
Hoehler et al. (and others...) developed a headspace analysis
 To measure hydrogen in cores. Cores were manipulated
 By adding a TEA or ΔT , ΔpH , $\Delta[\text{TEA}]$, etc. and measured
 Steady state concentration of hydrogen

$$P_{\text{H}_2} = \left(\frac{\{X_{\text{red}}\}^m}{\{X_{\text{ox}}\}^m} e^{(\Delta G_{\text{rxn}} - \Delta G(t)_0 / RT)} \right)^{1/2n}$$

ΔG (KJ/mol)

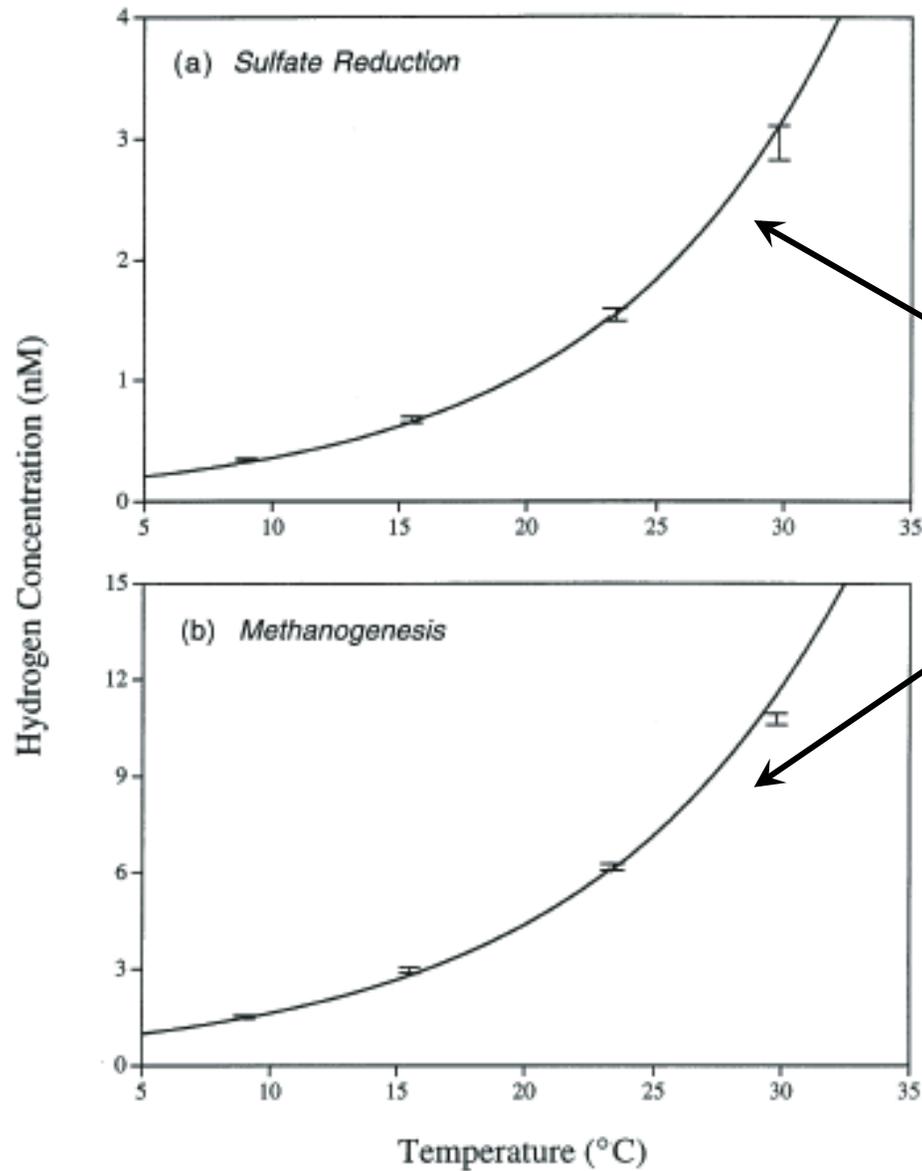
NO_3^-	\longrightarrow	N_2	-448
Mn(IV)	\longrightarrow	Mn(II)	-349
Fe(III)	\longrightarrow	Fe(II)	-114
SO_4^{2-}	\longrightarrow	S^{2-}	-77
CO_2	\longrightarrow	CH_4	-58

Effect of TEA on H₂ concentrations



TEA	[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 H₂ concentrations



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

Theoretical
effect

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



$$P_{H_2} = (\{X_{red}\}^m / \{X_{ox}\}^m e^{(\Delta G_{rxn} - \Delta G_{(t)}^0 / RT)})^{1/2n}$$

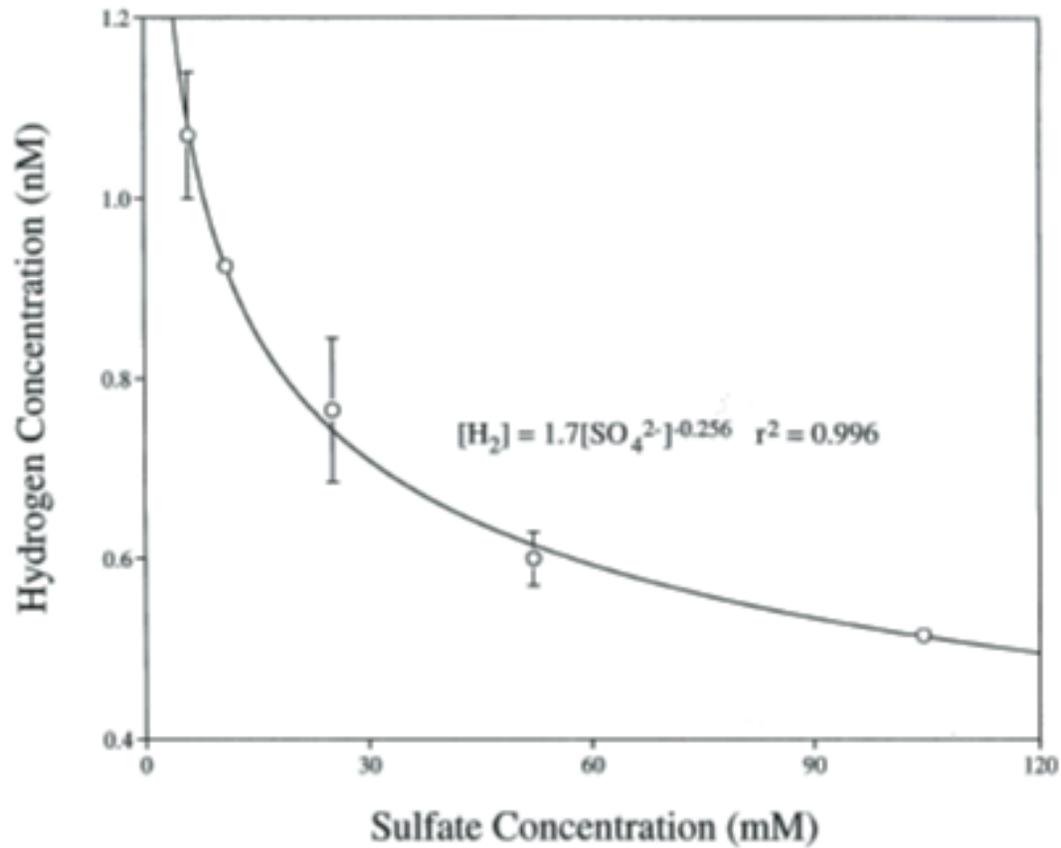
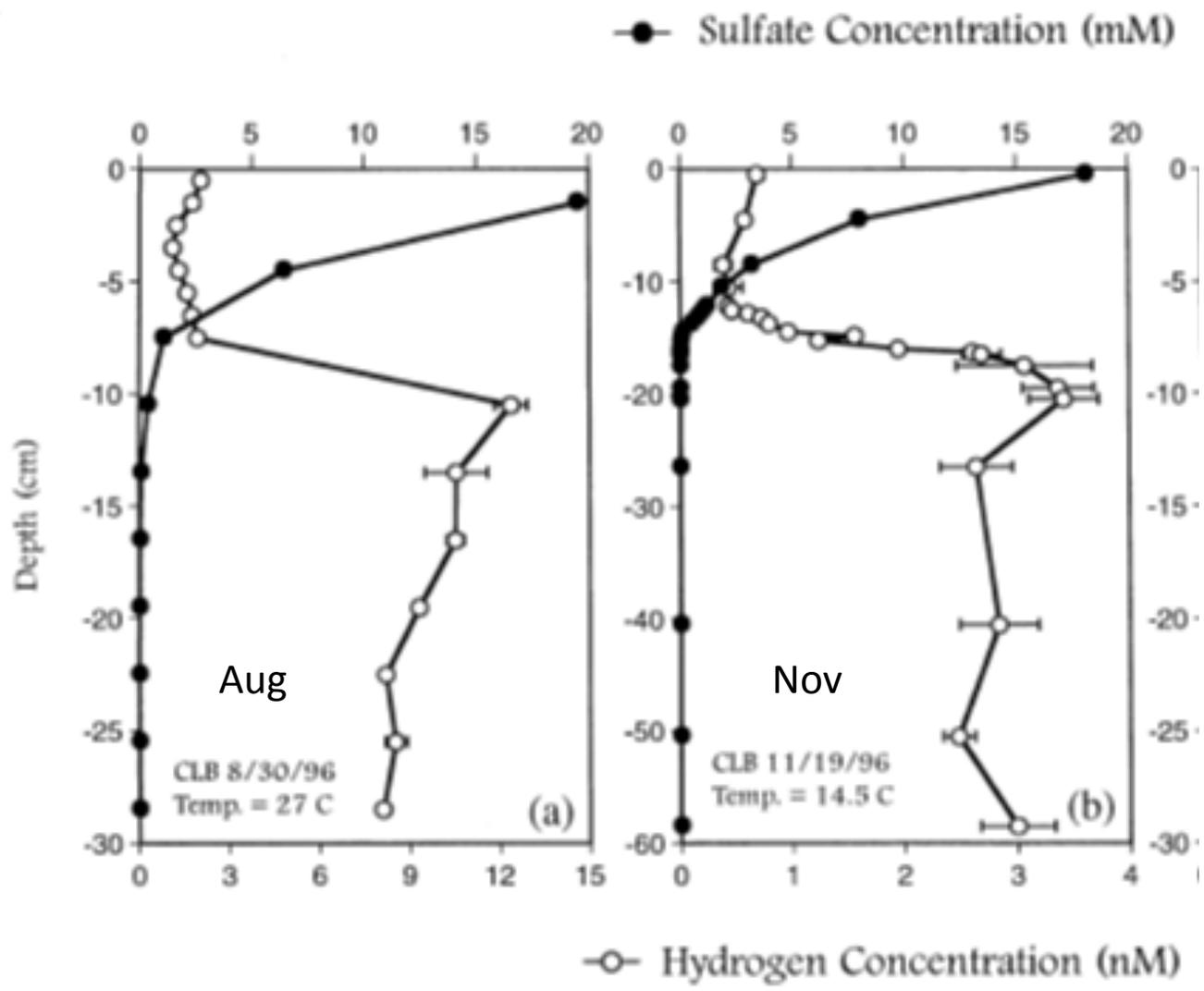
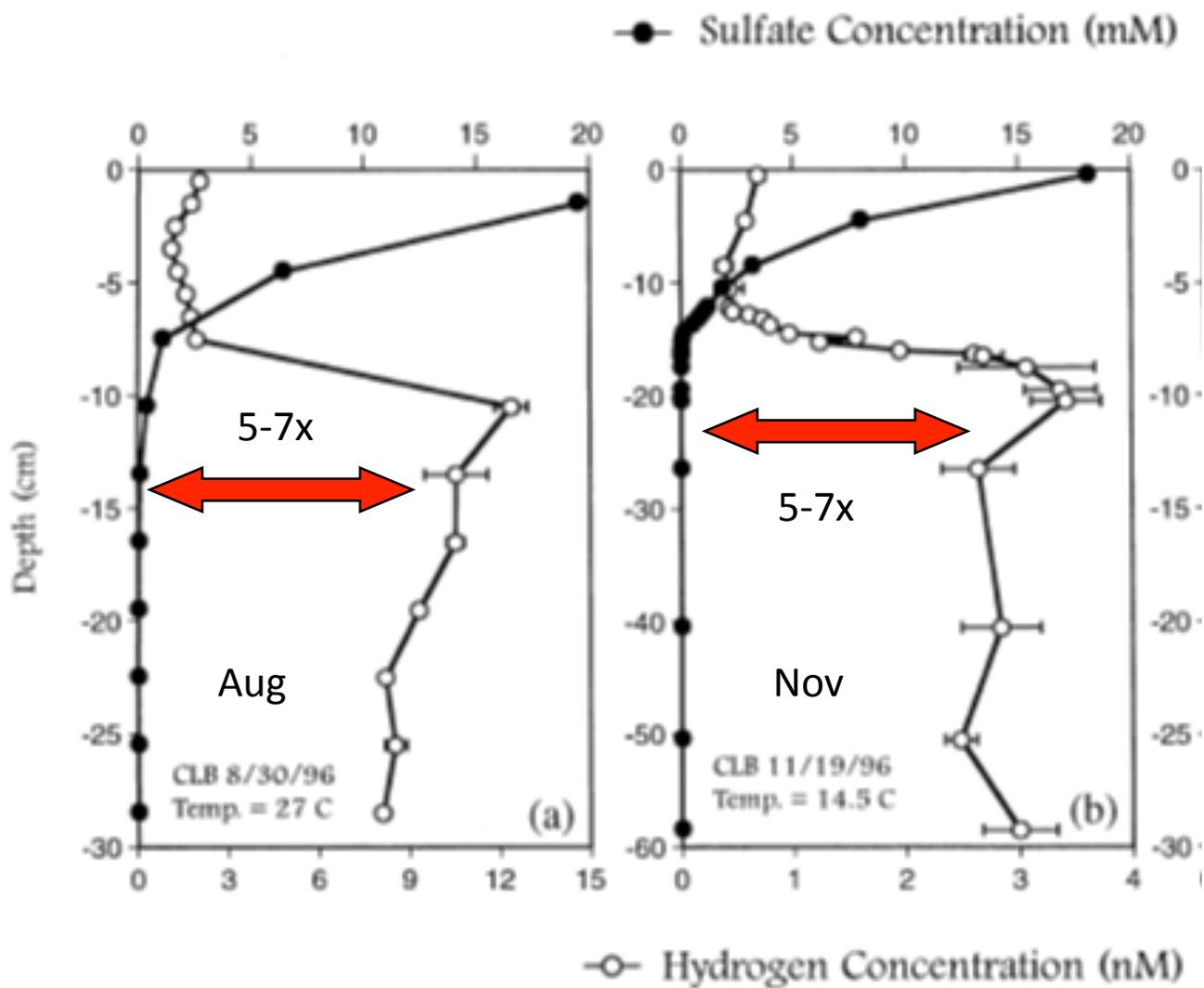


Fig. 5. Response of hydrogen concentrations to variations in porewater sulfate concentration. Error bars represent one standard deviation about the mean of triplicate sediment samples. A power function fit to the data indicates that hydrogen has an exponential dependence of -0.26 ± 0.01 on sulfate (compare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

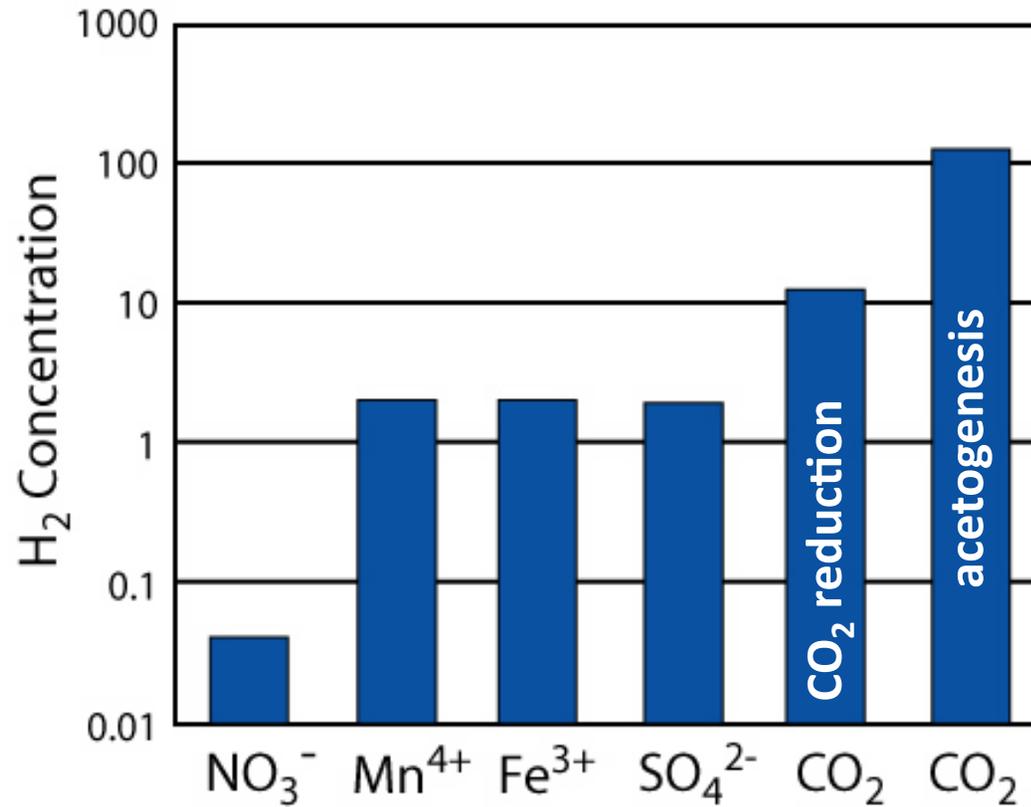
Profiles of hydrogen and sulfate in CLB sediments



Profiles of hydrogen and sulfate in CLB sediments

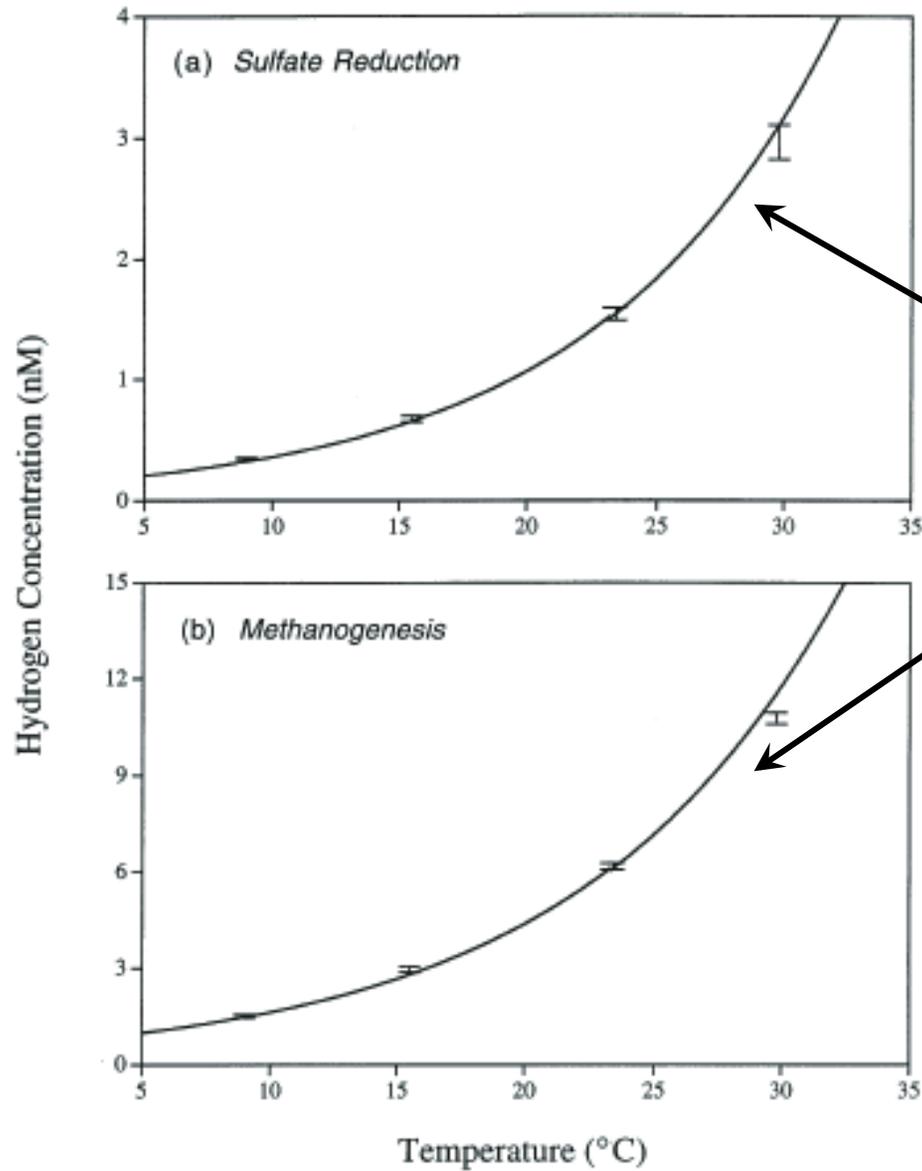


Effect of TEA on H₂ concentrations



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

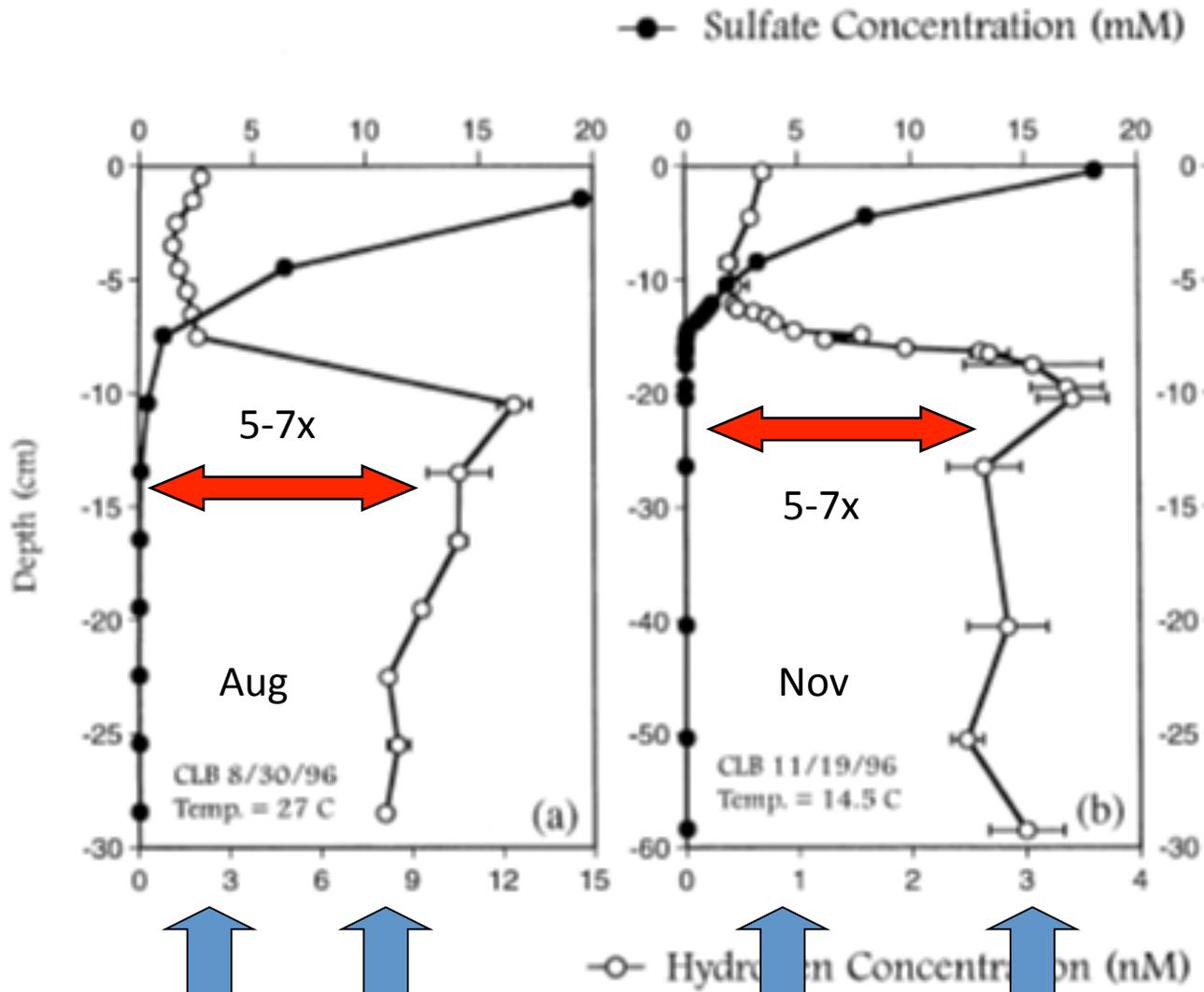
Effect of temperature on H₂ concentrations



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

Theoretical
effect

Profiles of hydrogen and sulfate in CLB sediments



2.8x meas vs 2.7x predicted

Effect of sulfate on H₂ in CLB sediments

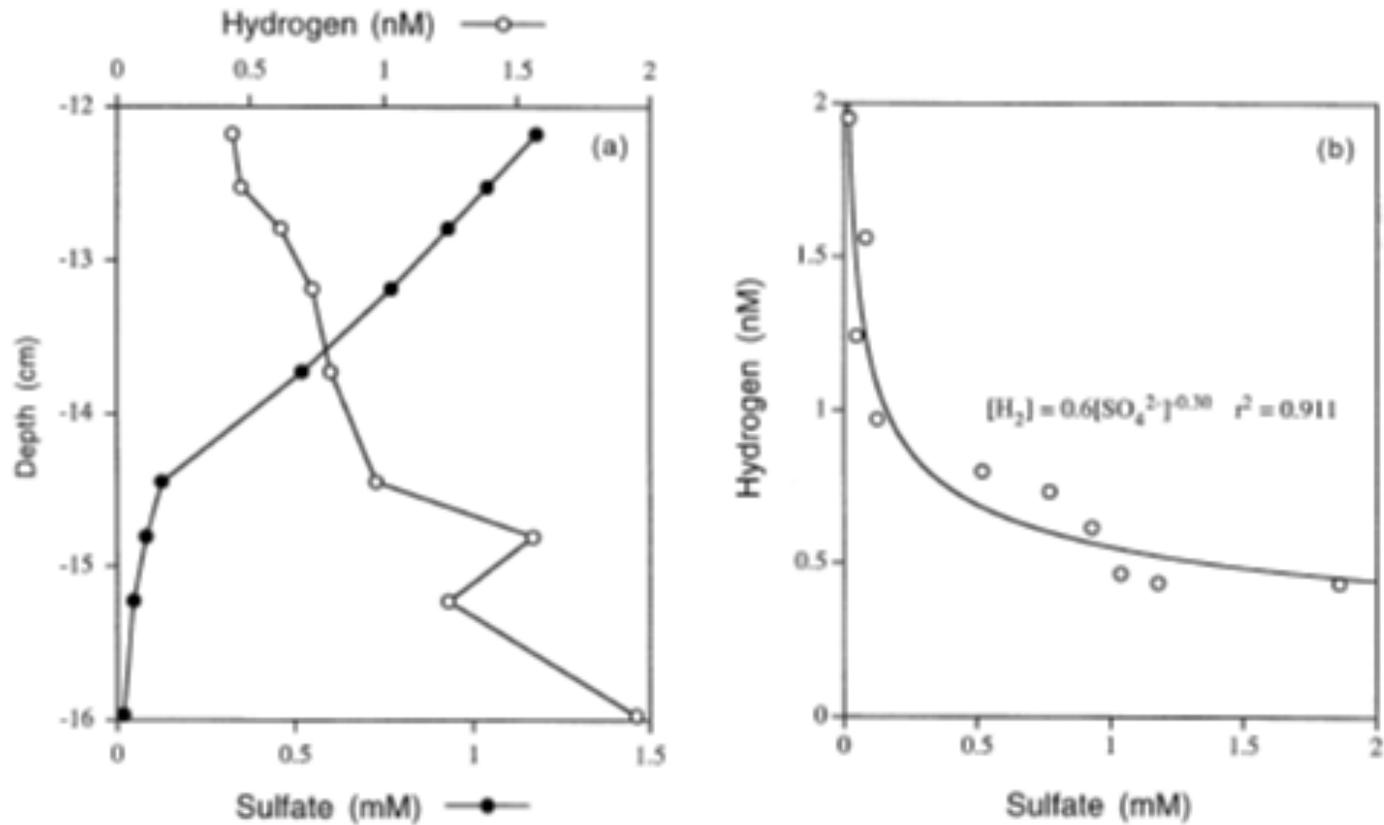
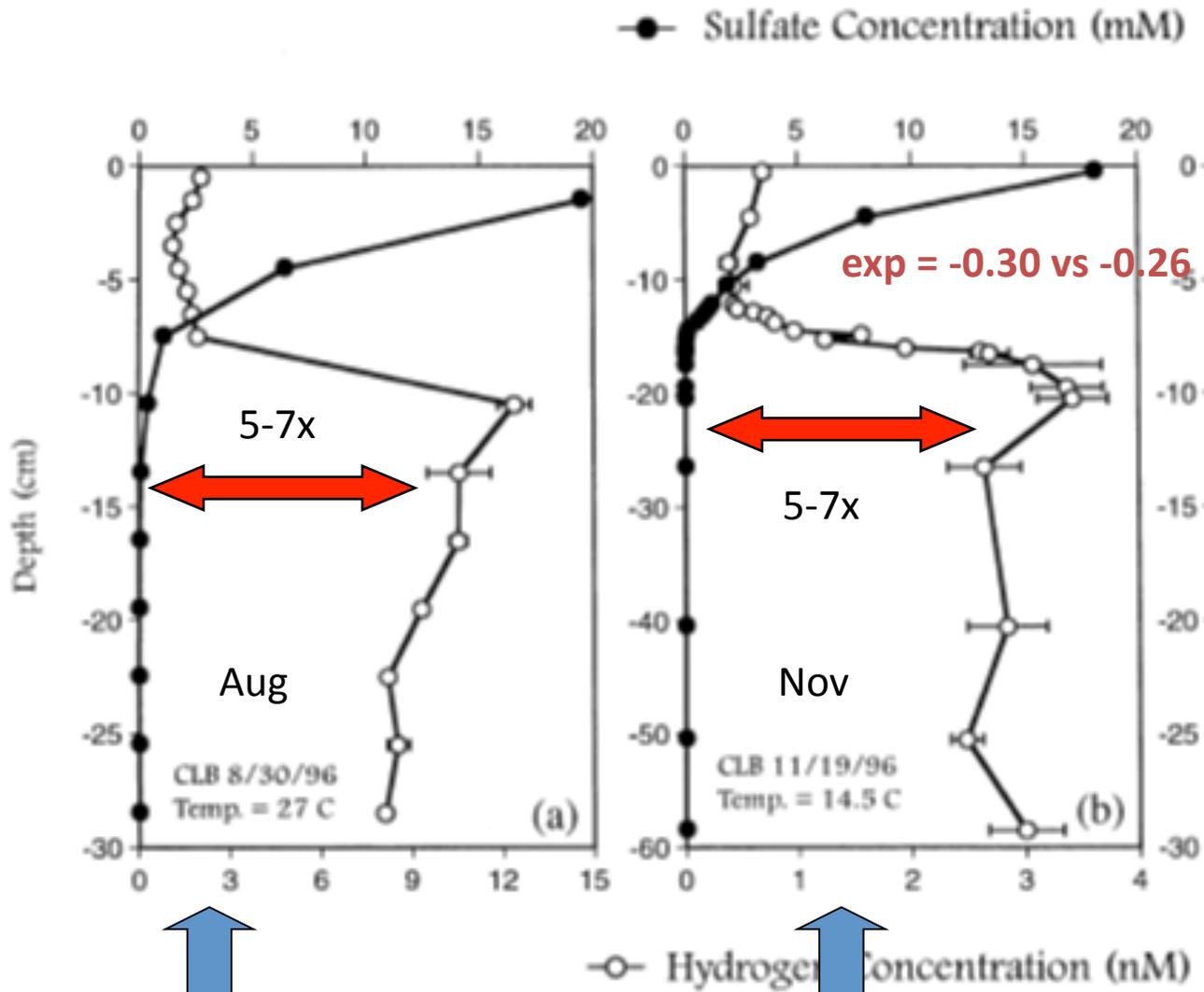


Fig. 8. The dependence of hydrogen concentrations on sulfate concentrations in the November core from Cape Lookout Bight (Fig. 7b). (a) blow-up of the 12–16 cm depth interval. Note that sulfate concentrations only reach threshold values below 16 cm; (b) plot of hydrogen concentration vs. sulfate concentration 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 sediments



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.

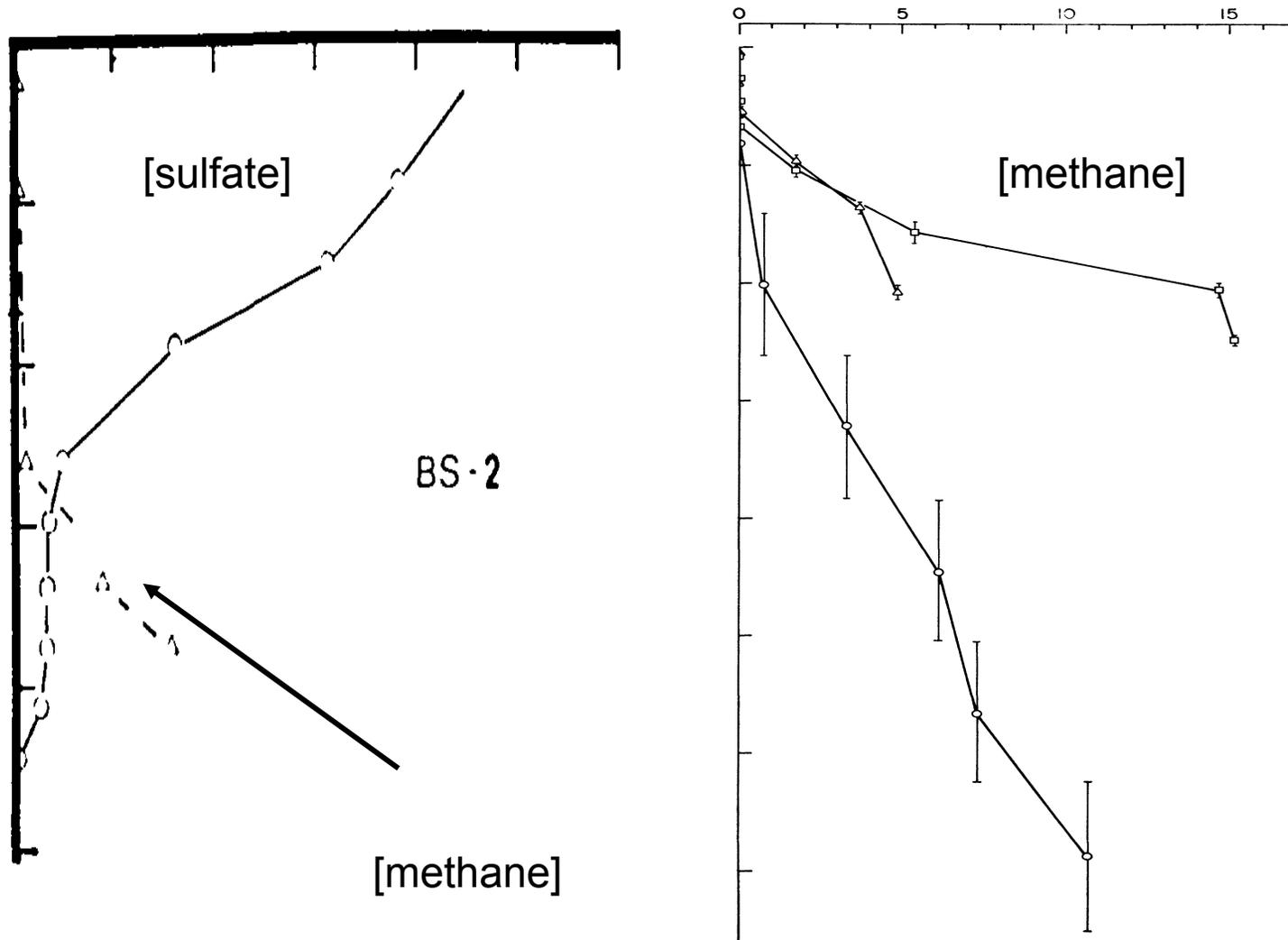
Hydrogen concentrations respond to T, [X], pH.
laboratory changes correspond well to field observations.

Variations in H₂ 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/archaea regulate [H₂]

It was also recognized very soon after sedimentary methane profiles were compiled that methane consumption appeared to be occurring in marine systems



Anaerobic methane oxidation...where has all
the methane gone?

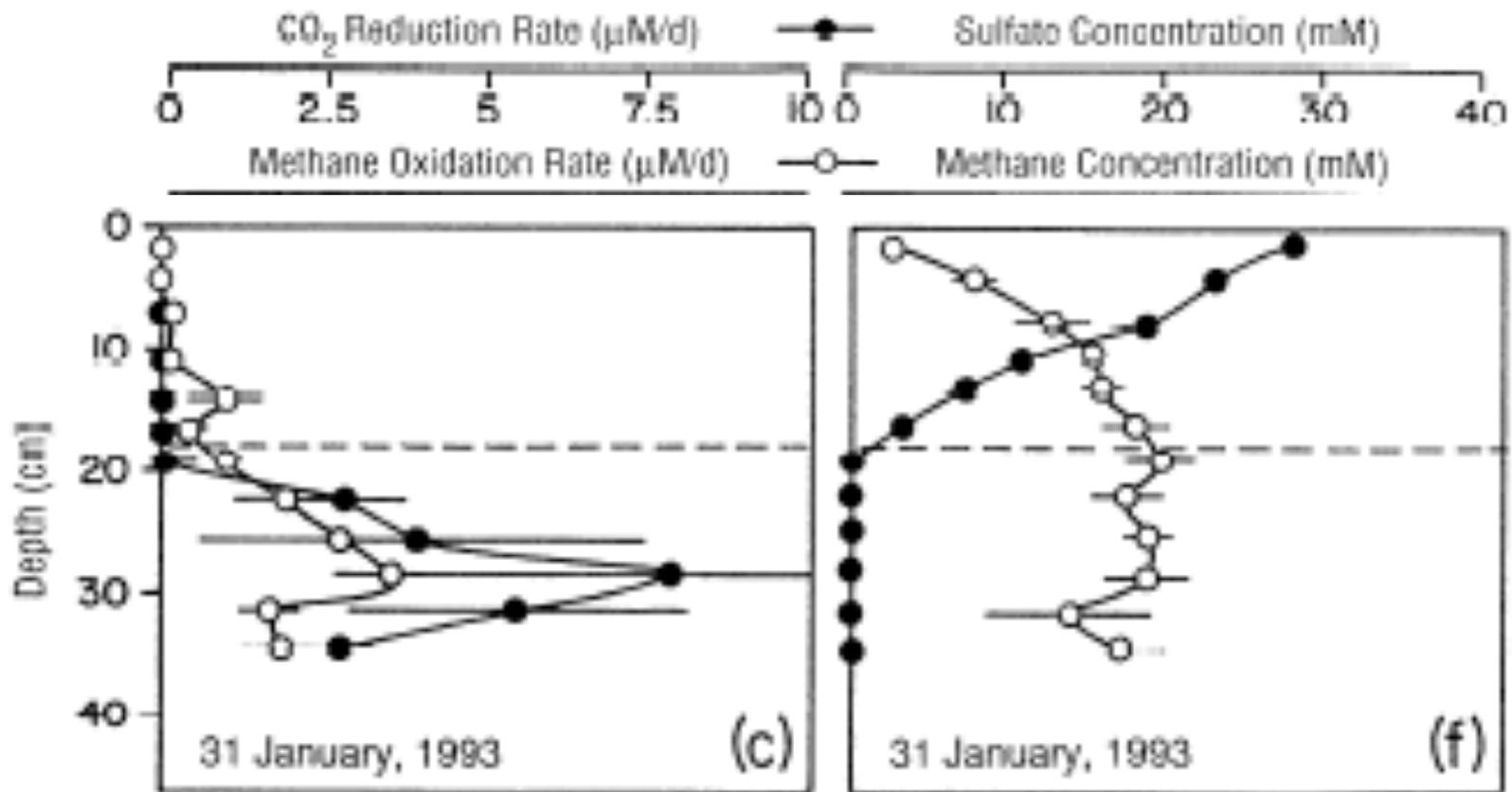
Oceans have a huge reservoir of methane in sediments, but
Contribute only 2% of the global atmospheric flux of methane.



Energetically favorable, but depends critically on the
concentration of hydrogen. Only favorable in CLB
sediments when $[\text{H}_2] < 0.29 \text{ nM!}$

Anaerobic methane oxidation probably occurs
as a consortia between SRB and MO Archea

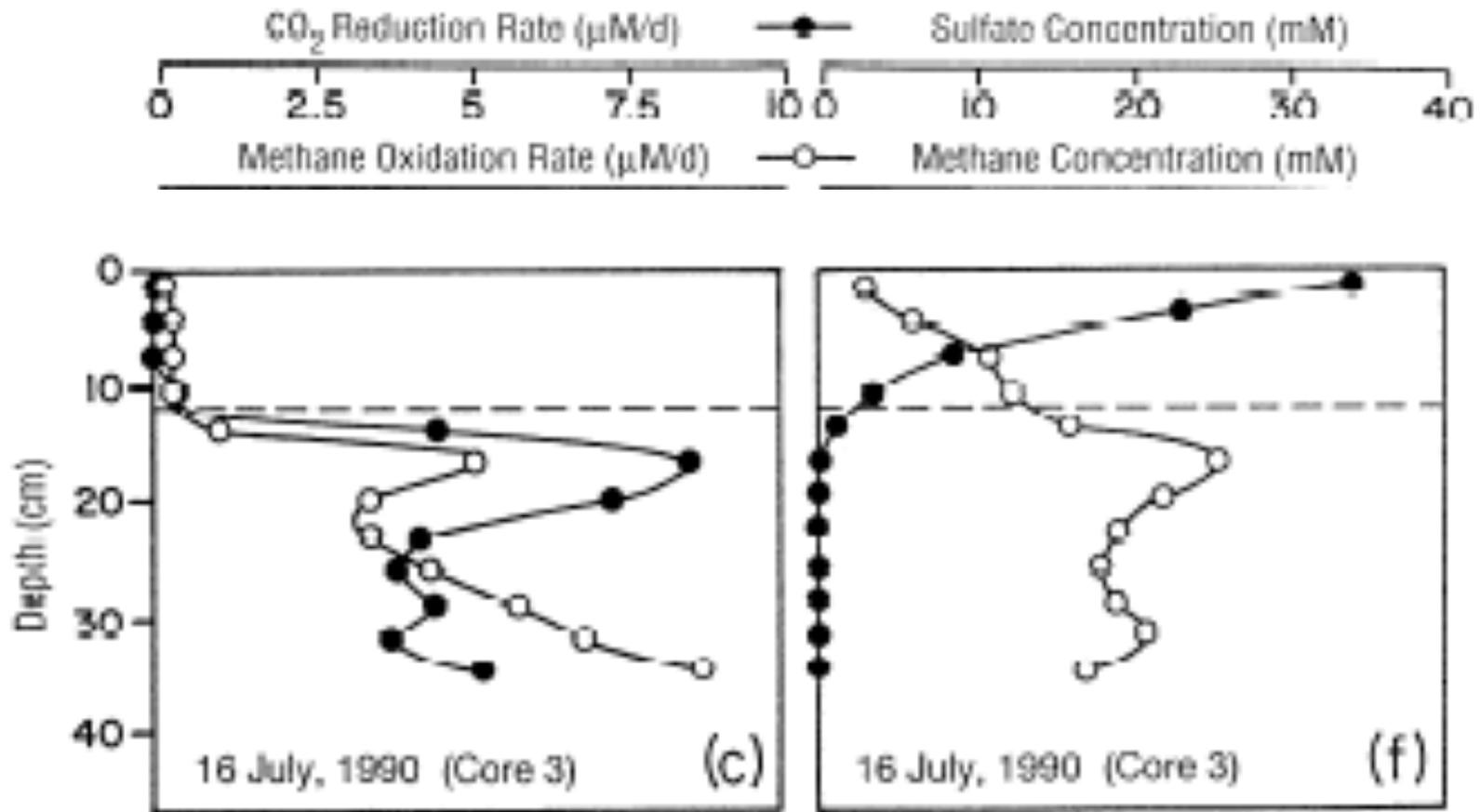
Coupled methane oxidation and sulfate reduction in
CLB sediments



Hydrogen concentrations are < nM

Coupled methane oxidation and sulfate reduction in CLB sediments

summertime



Hydrogen concentrations are a few nM

We can use molecular probes to identify sulfate reducing bacteria (green) and methane oxidizing Archea (red) to visually examine the consortia

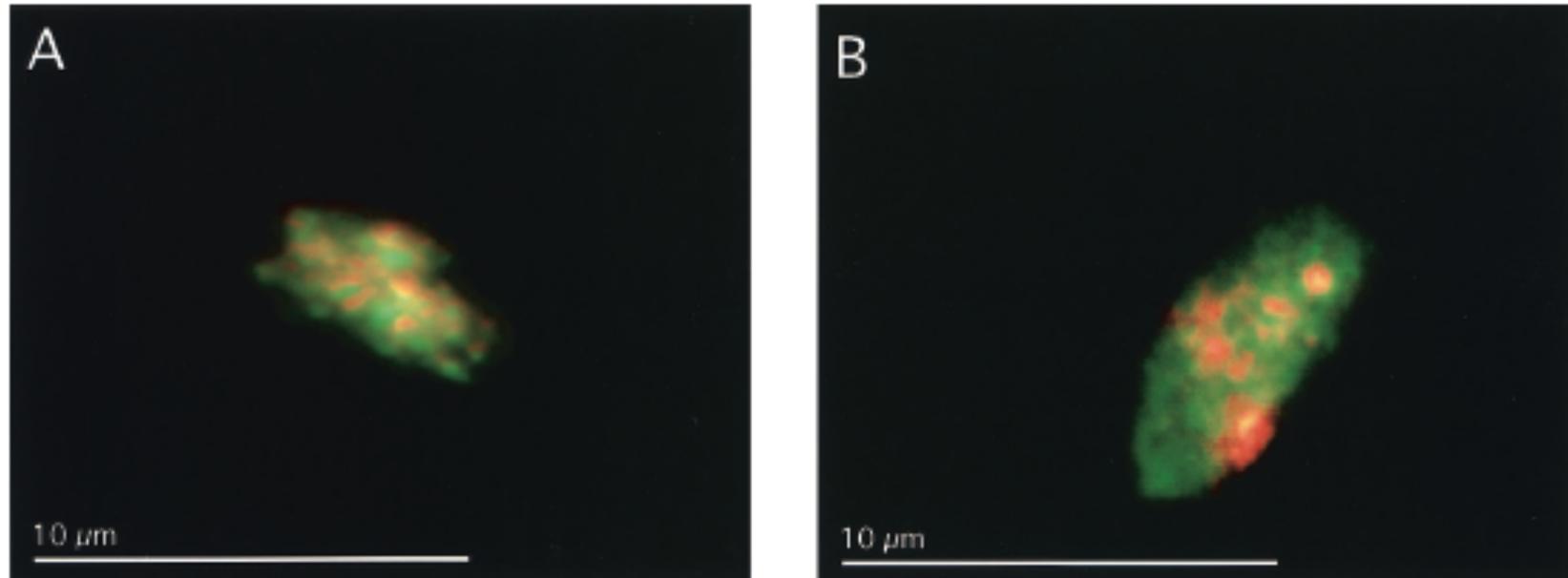
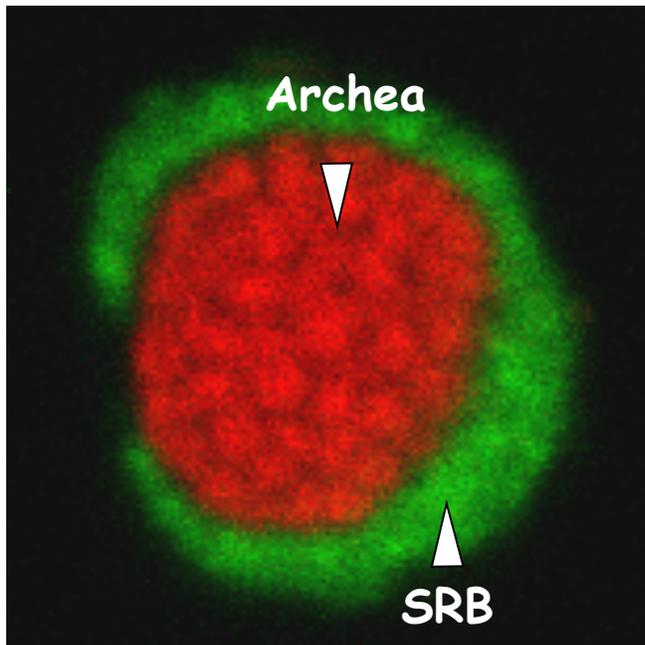


FIG. 5. Whole-cell fluorescent in situ hybridization of methane-oxidizing consortia found in Monterey Canyon seep sediments (A) and in Monterey Canyon nonseep sediments after incubation on AMIS (B). Sediments were fixed in 4% formalin and transferred into a 1:1 ethanol-phosphate-buffered saline solution for storage. Green-stained cells correspond to *Desulfosarcina-Desulfococcus* bacteria (DSS658), and red-stained cells correspond to the archaeal ANME-2 group (EelMSMX932). Separate images were overlaid to represent the structure of the aggregate. Scale bar, 10 μm . No consortia were detectable in Monterey Canyon nonseep sediments before incubation on the AMIS.

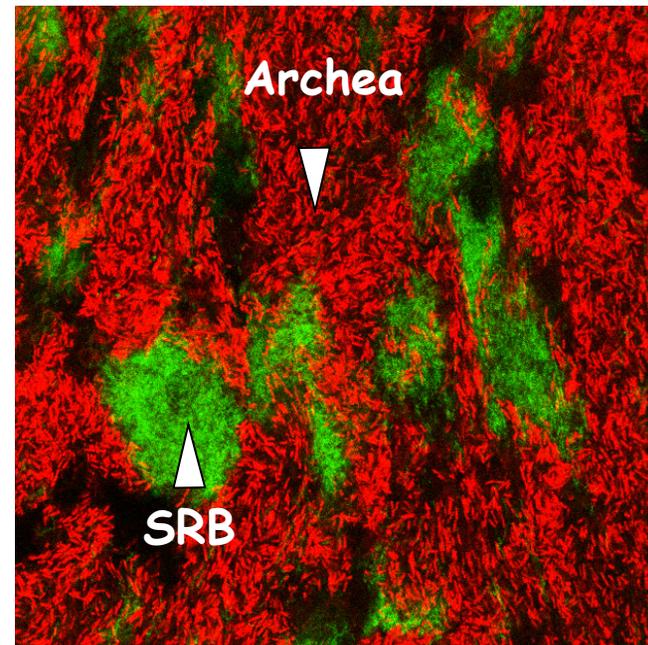
AOM consortia of different shapes

aggregate-structure



AOM consortium above gas hydrates at Hydrate Ridge, Cascadia Margin.

"tissue"-structure



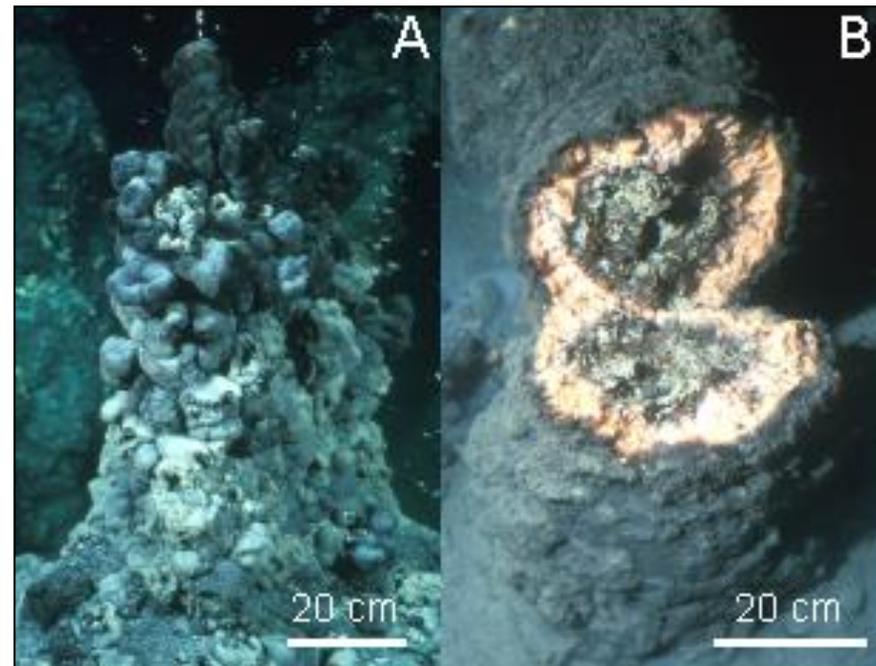
AOM consortium above gas seeps in the anoxic Black Sea.

by A. Boetius, K. Knittel & A. Gieseke



The History of AOM

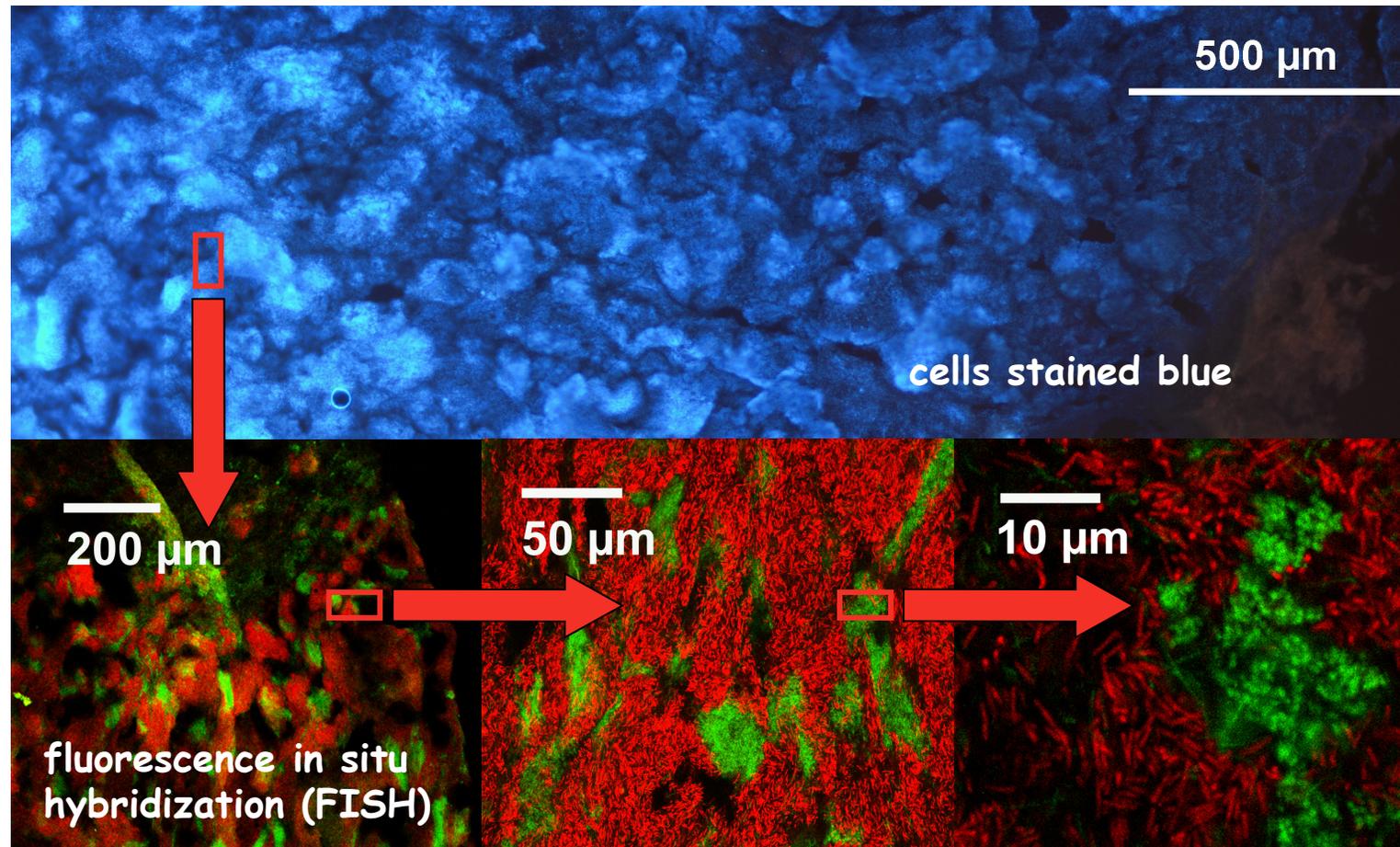
In 2001 Walter Michaelis et al. found out, that such AOM-consortia are able to build up a **huge biomass** above methane seeps in the anoxic part of the Black Sea. These reef-like structures are up to 1 m in diameter and 4 m high.



photos: GHOSTDABS, Jago-Team



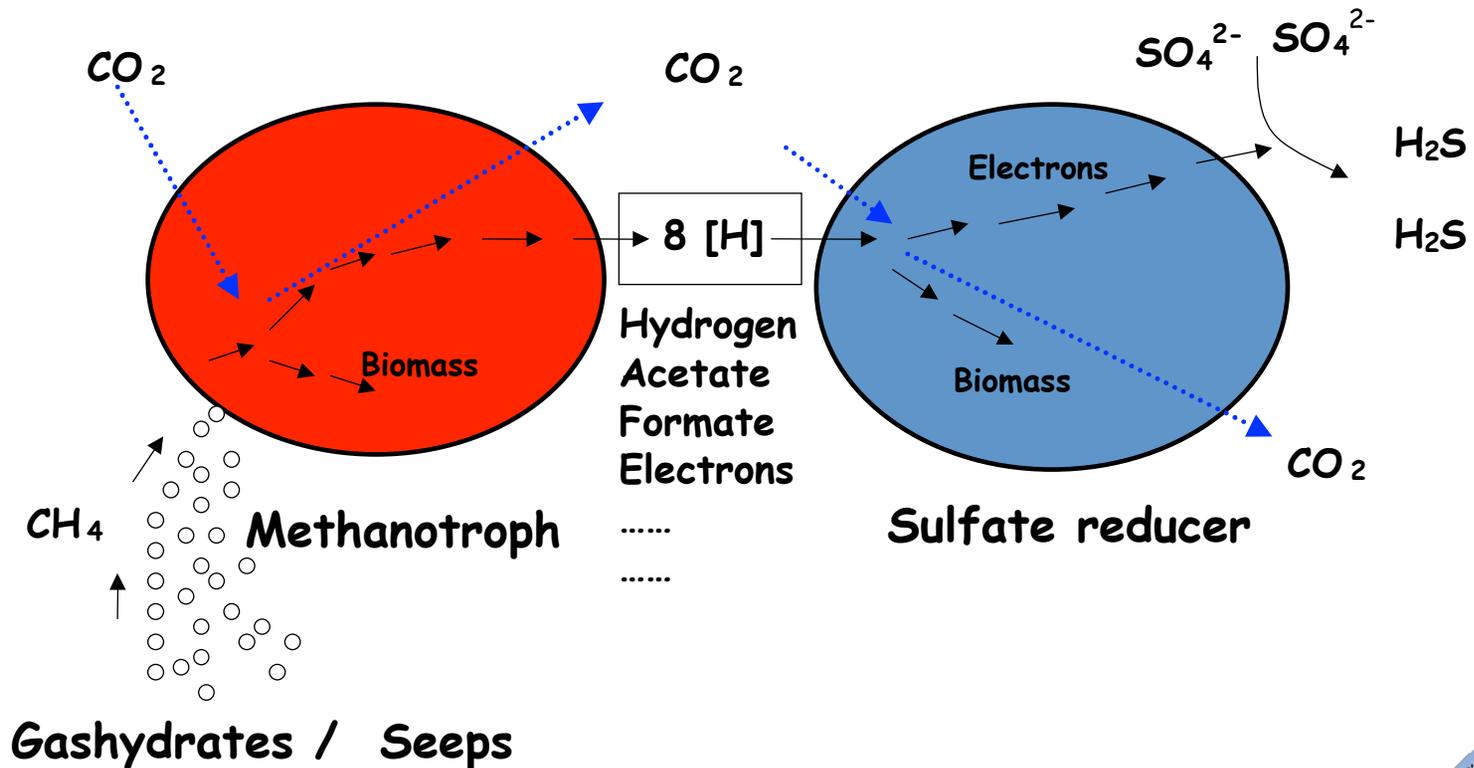
Molecular identification reveal that a microbial consortium is responsible for AOM in the reef



by K. Knittel & A. Gieseke



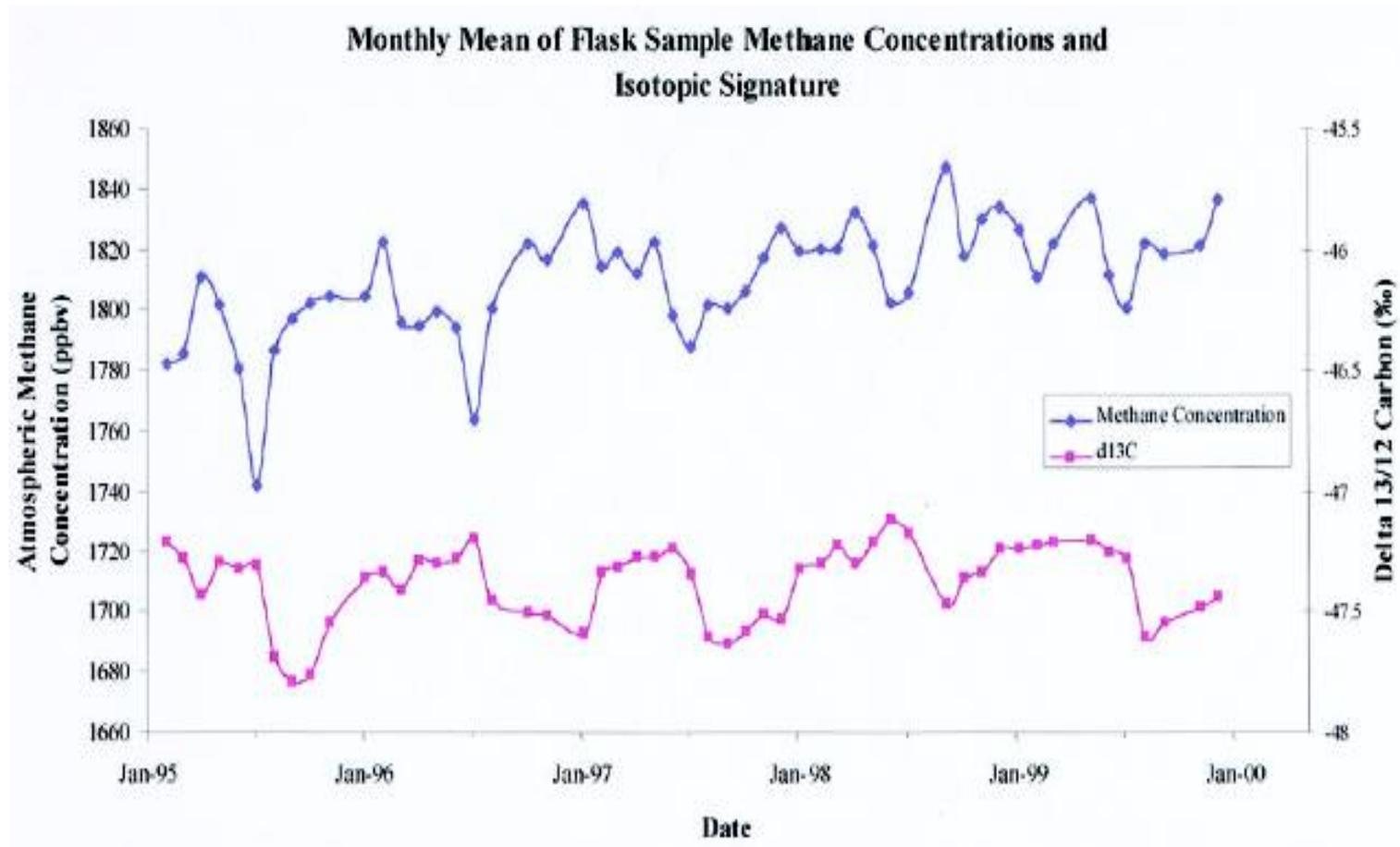
The AOM symbiosis



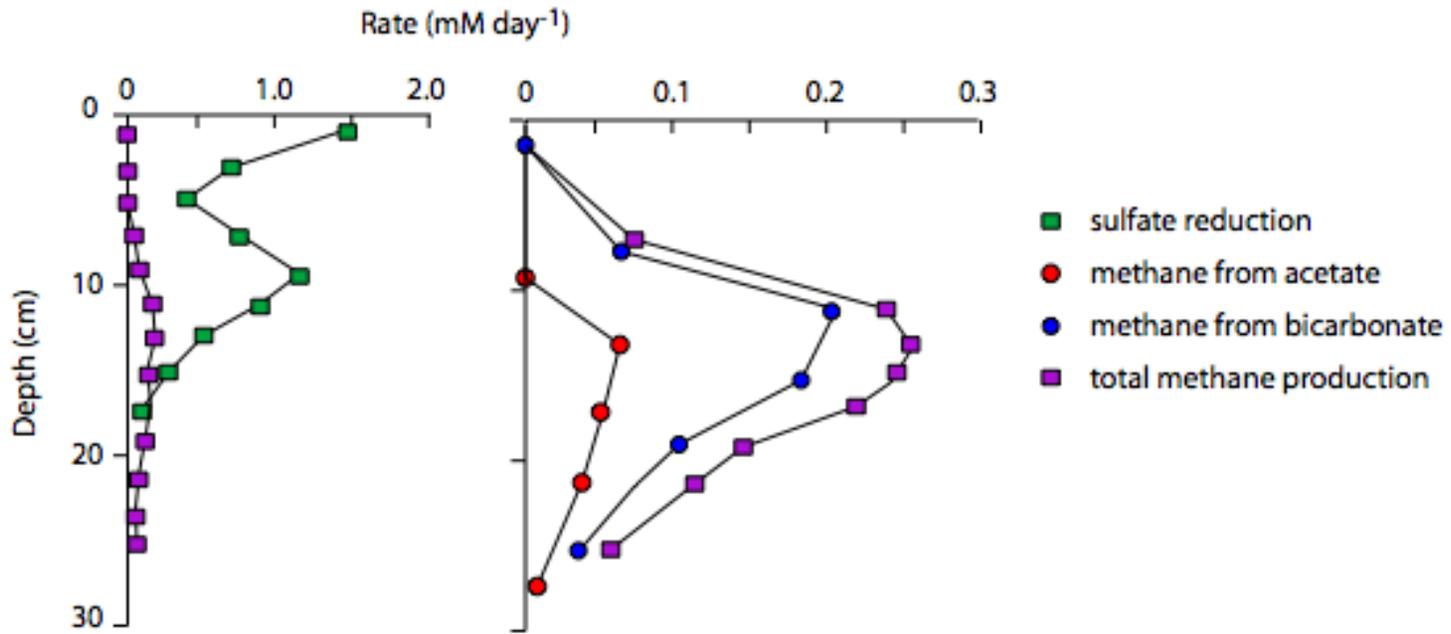
scheme by K. Nauhaus



Carbon isotopic changes in atmospheric methane



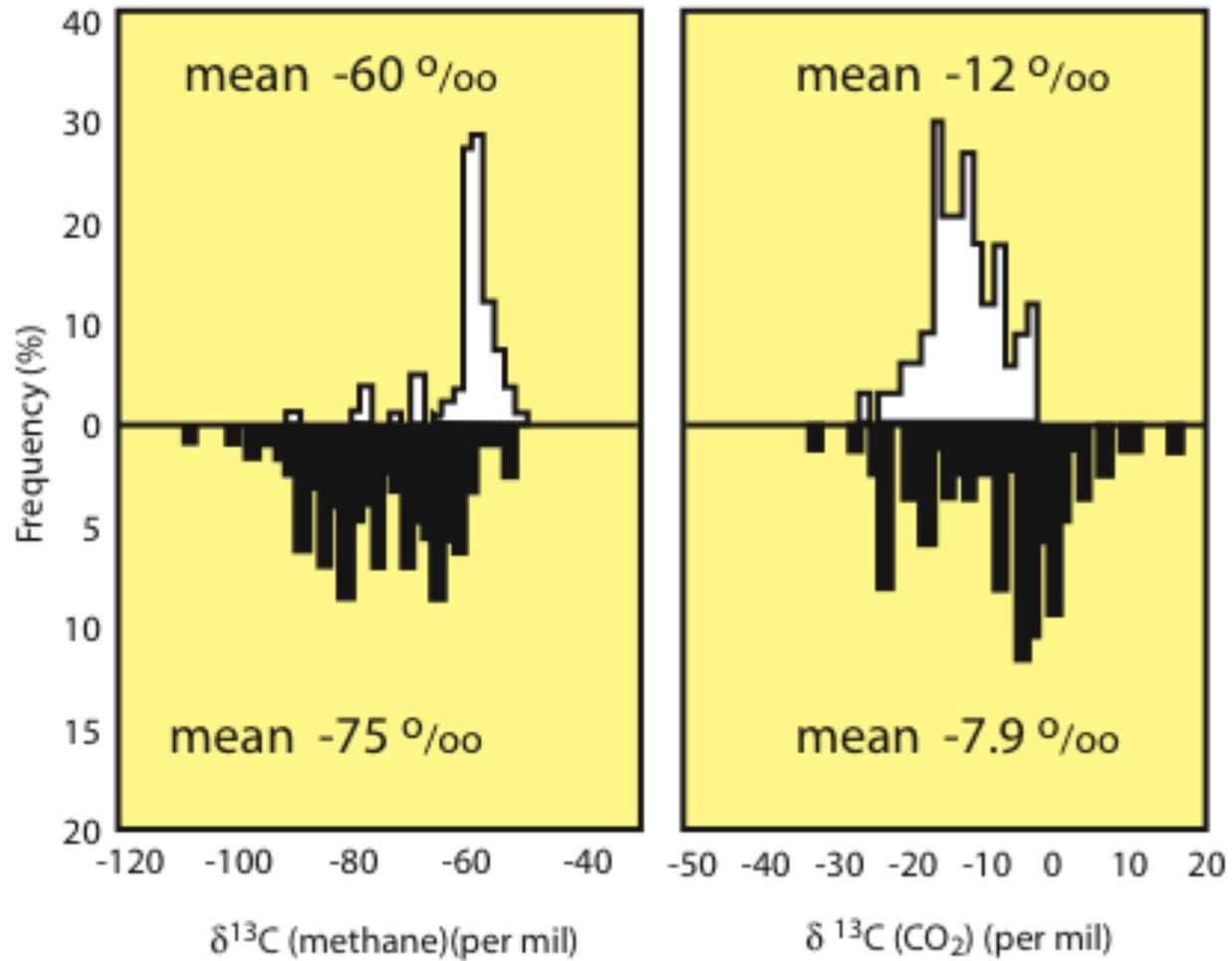
Methane production rate profiles



Date	Temp	CO ₂	acetate	bicarbonate	total	%total production
7/21/83	26.5	0.70	0.18	0.00	0.88	20
8/7/83	27	1.02	0.33	0.00	1.35	24
8/29/83	27.5	1.10	0.46	0.00	1.56	29

Differences in carbon isotope fractionation between freshwater and marine systems

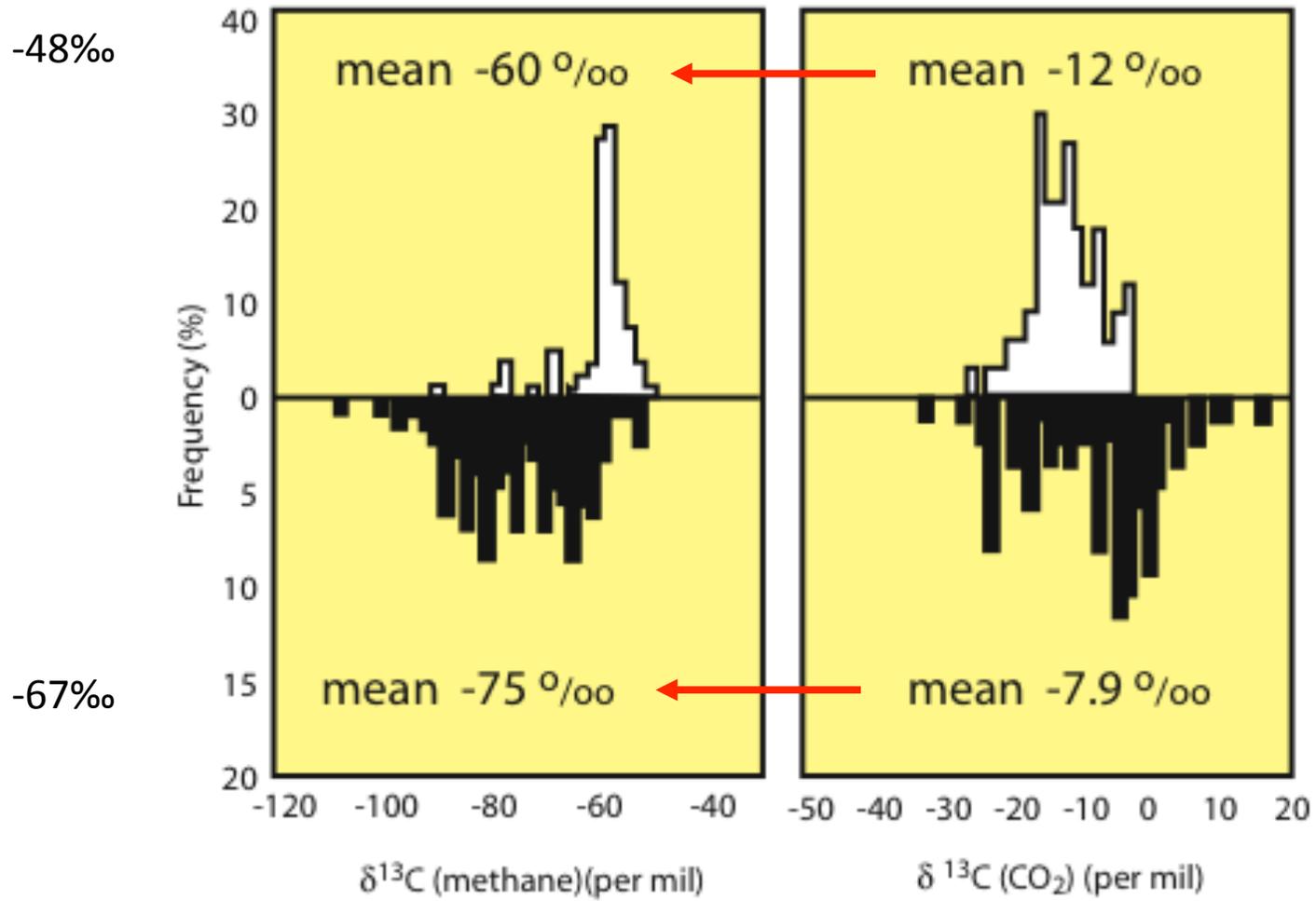
Freshwater



Marine

Differences in carbon isotope fractionation between freshwater and marine systems

Freshwater

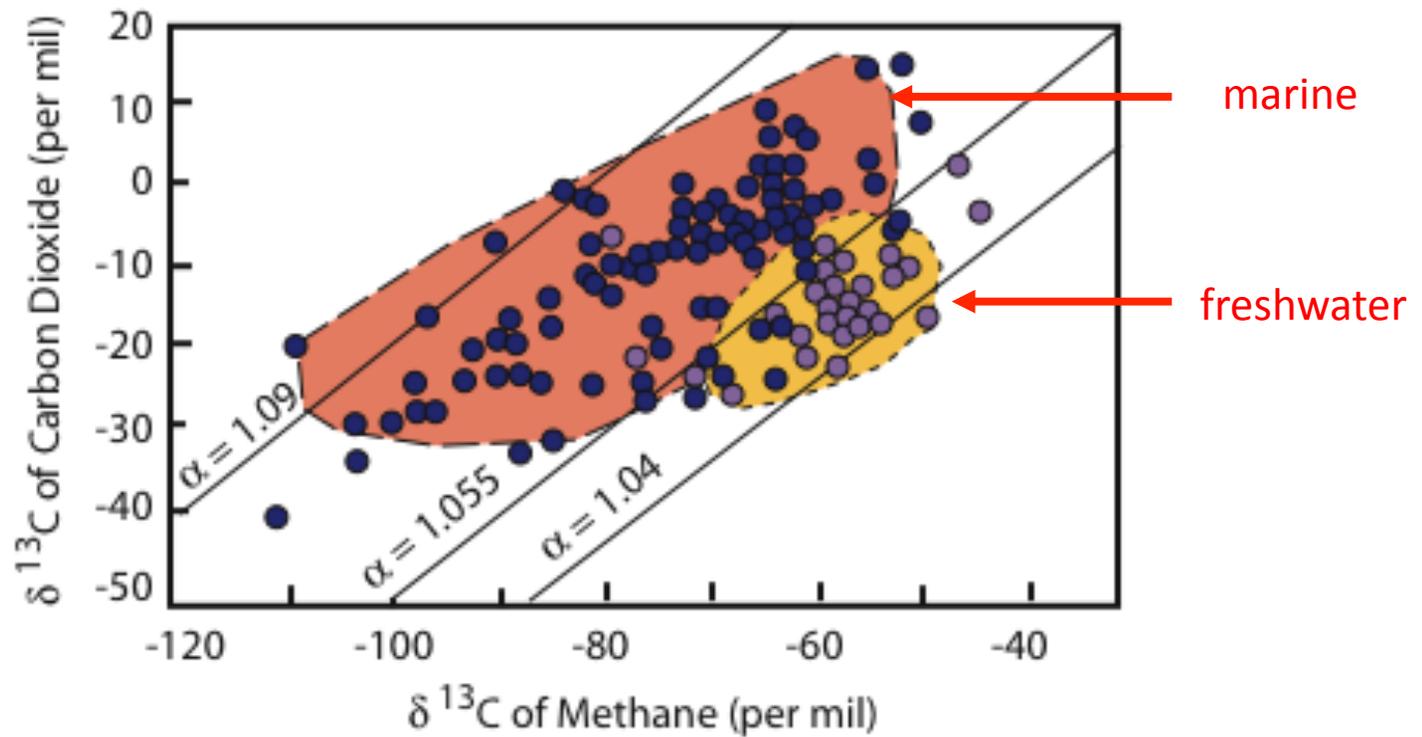


-48‰

-67‰

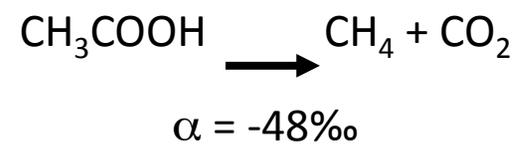
Marine

Isotope fractionation and methanogenesis

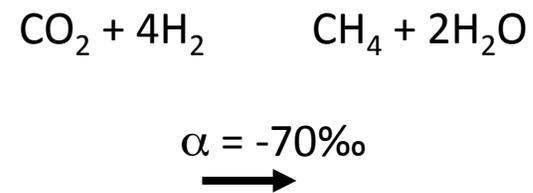


Carbon isotope fractionation with methanogenesis

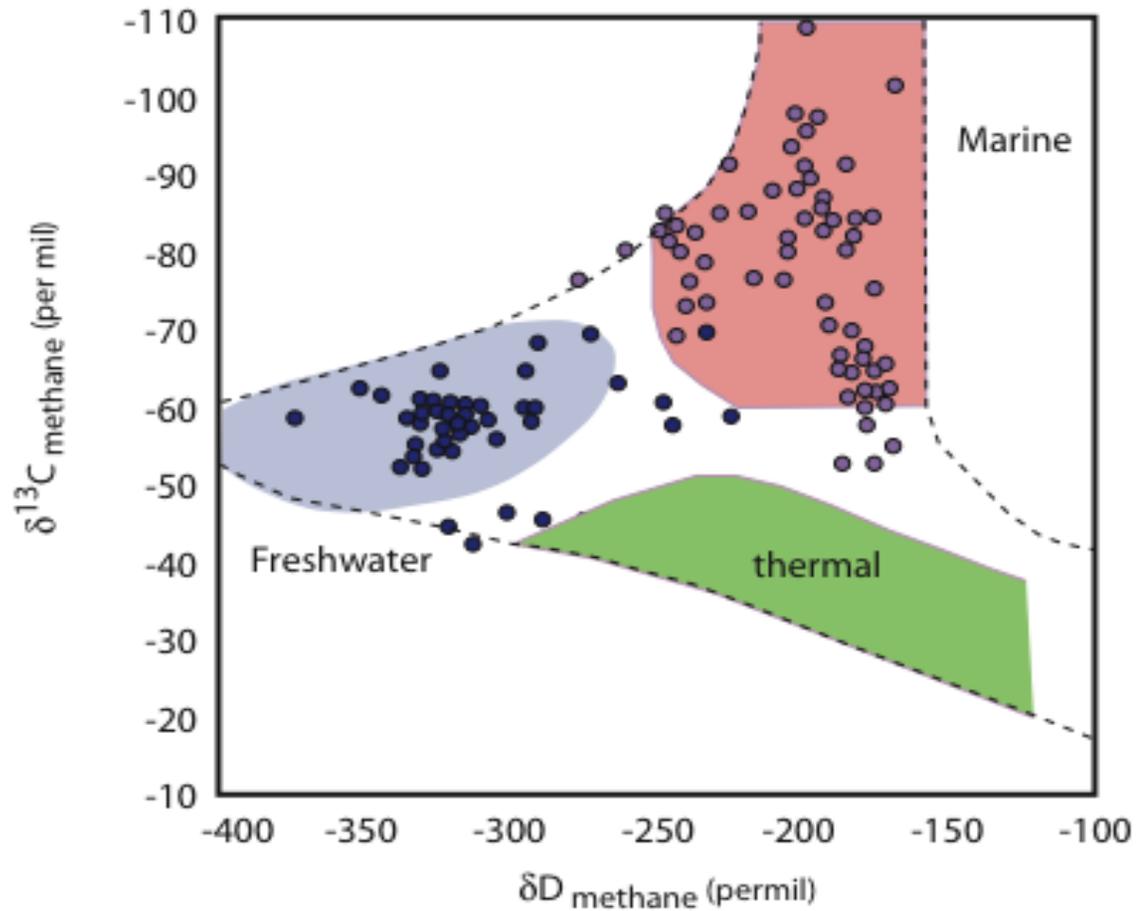
Freshwater



Marine

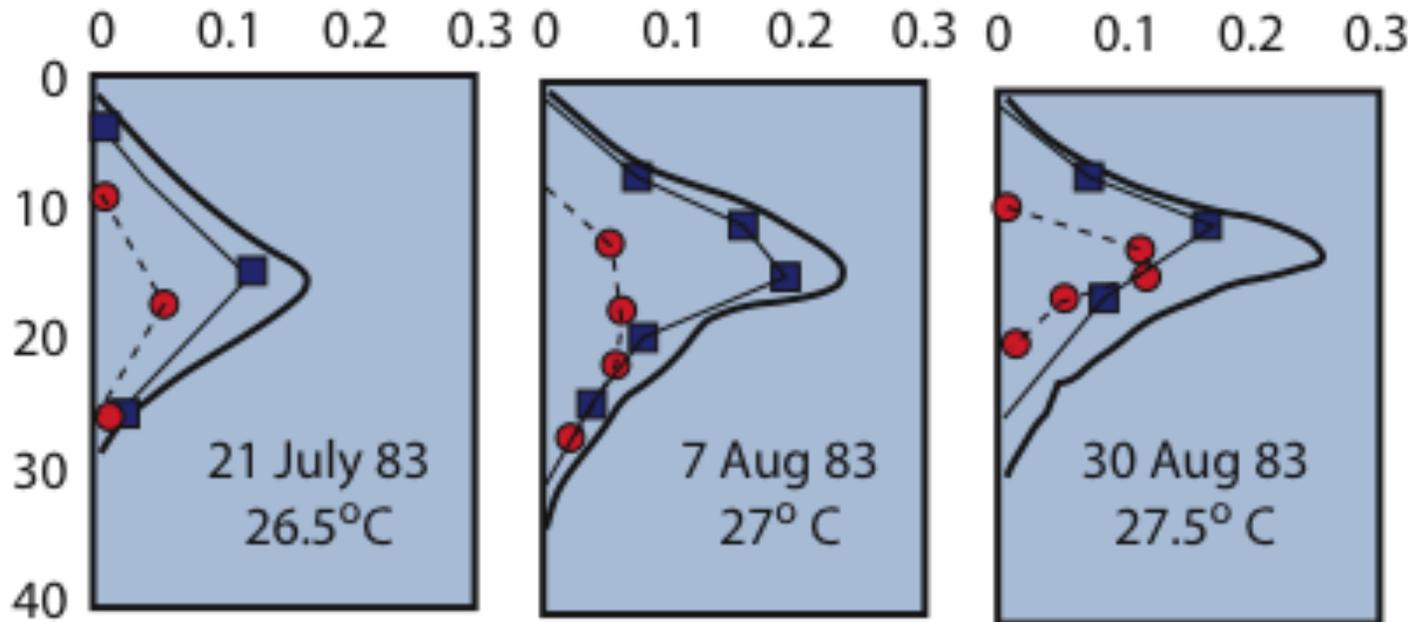


Carbon and Hydrogen isotopes fractionation with methanogenesis



Production of methane from acetate and CO₂
in CLB sediments. ¹⁴C tracer studies.

¹⁴C tracer rates

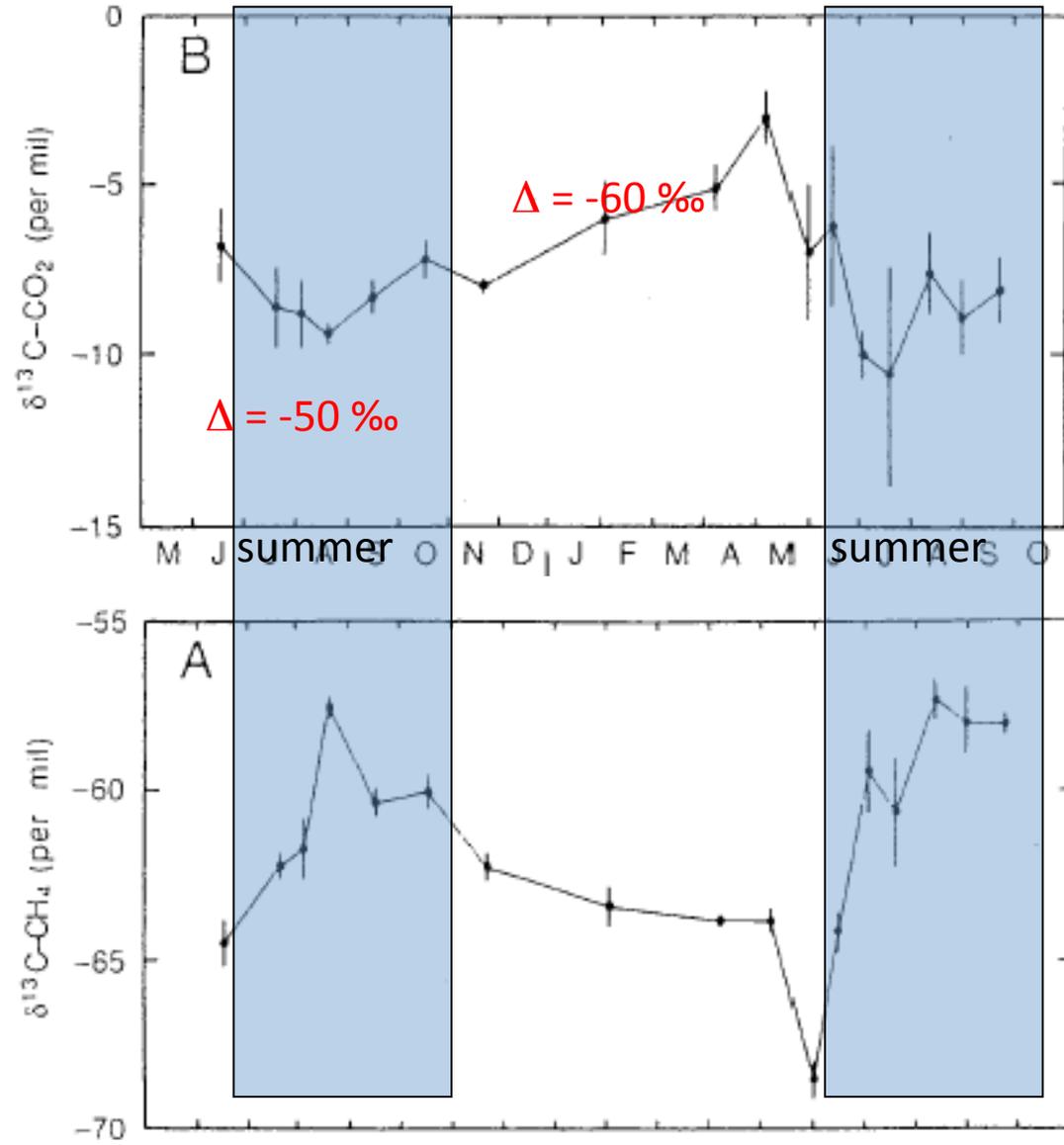


Seasonal changes in ^{13}C for methane and CO_2

Table 1. Cape Lookout Bight sediment gas bubble composition and $\delta^{13}\text{C}$ data. Values listed are means \pm 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 (%)	$\delta^{13}\text{C}\text{-CH}_4$ (per mil)	Carbon dioxide sample bottles (no.)	Carbon dioxide content (%)	$\delta^{13}\text{C}\text{-CO}_2$ (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 $\Delta^{13}\text{C}$ in CLB methane



Changes in $\Delta^{13}\text{C}$ in CLB methane

