Exploring the chemistry of diverse marine environments using *in situ* electrochemistry

Division of Analytical Chemistry, March 16, 2005

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R/V Knorr Crew – Black Sea

Alvin Pilots and R/V Atlantis Crew – vent work

Solid state (micro)electrodes for the analysis of biologically relevant compounds and ions

Chemistry Drives Biology

Rationale for design and use

Fine scale resolution of multiple analytes simultaneously –

mm in sediments; micrometer in biofilms and mats

determine sediment heterogeneity vs. homogeneity

use to prospect for life forms and understand ecosystem health

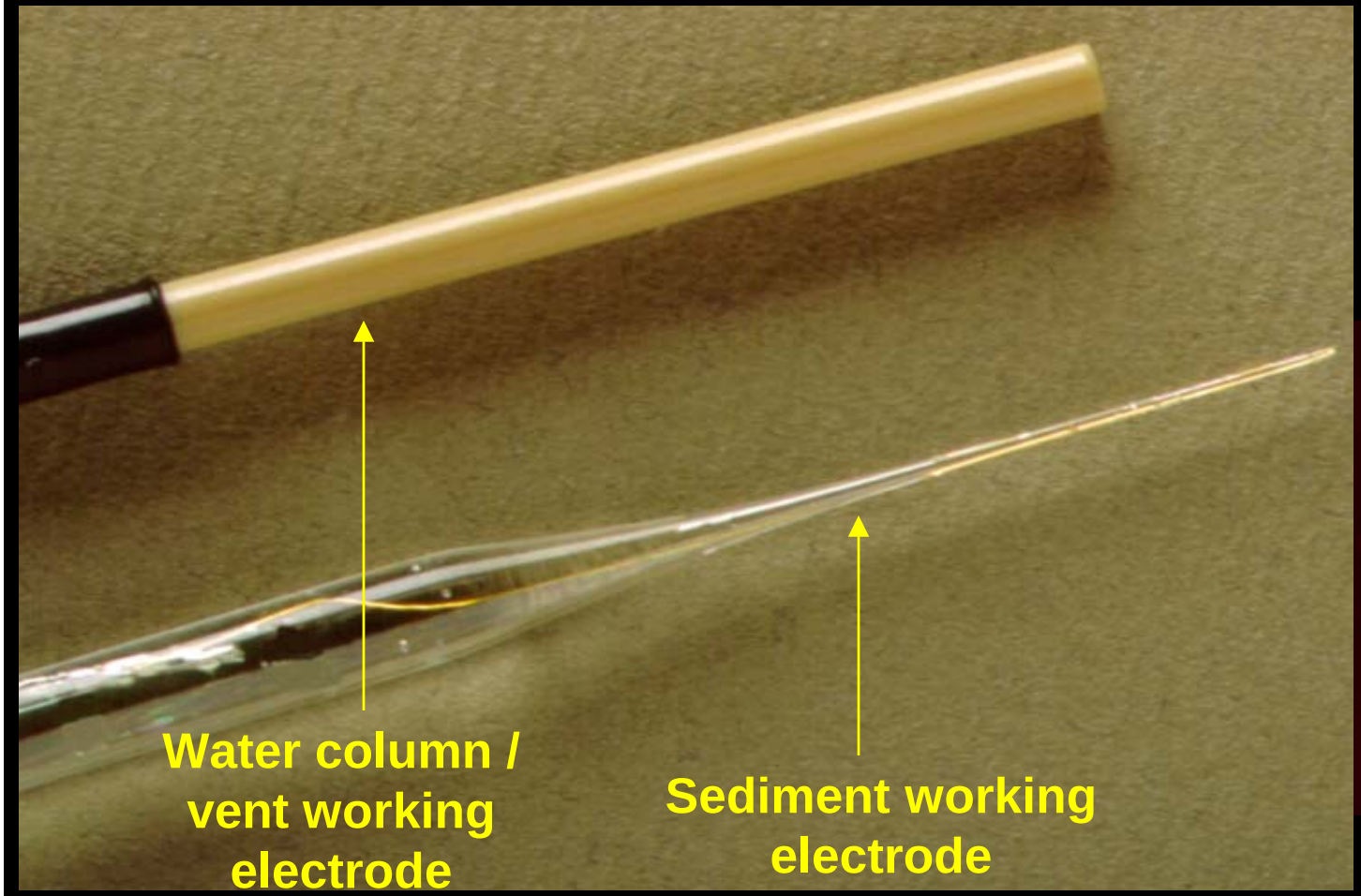
Use in sedimentary porewaters of bays, oceans and lakes

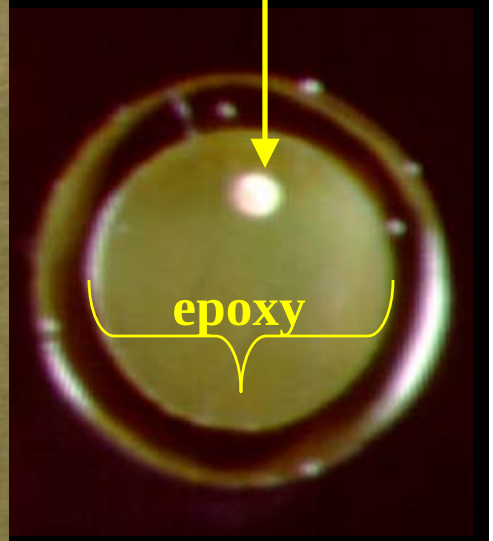
in water column; e.g., Chesapeake Bay, Black Sea

at Hydrothermal Vents, Yellowstone hot springs,

in corrosion studies

PEEK & Glass encased electrodes in marine epoxy





O_2, Fe^{2+}, Mn^{2+}, H_2S, H_2O_2, I^-, S_x^{2-}, $S_2O_3^{2-}$, FeS_{aq}, Fe(III) are all measurable in one scan, if present

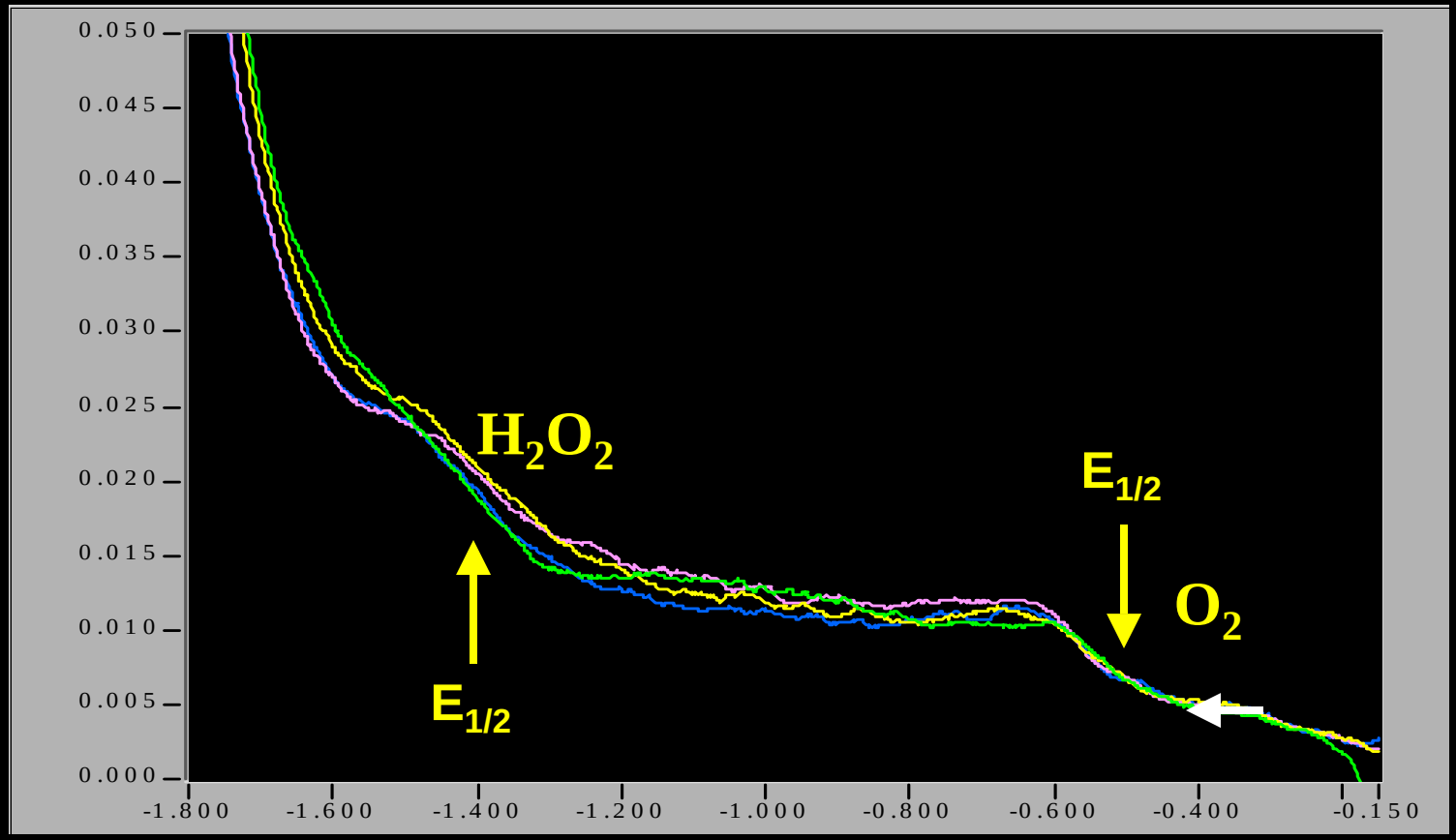
Tested to 2600 m and 120 °C

Au/Hg Electrode Reactions of Interest
Oxygen and sulfur species

Reaction (- scan; 200 mV/s; 25 °C)		Ep (V) vs SCE
1a)	$O_2 + 2\,H^+ + 2\,e^- \rightarrow H_2O_2$	-0.30
1b)	$H_2O_2 + 2\,H^+ + 2\,e^- \rightarrow H_2O$	-1.30
2a)	$HS^- + Hg \rightarrow HgS + H^+ + 2\,e^-$	adsorption onto Hg <-0.62
2b)	$HgS + H^+ + 2\,e^- \leftrightarrow HS^- + Hg$	-0.62
3a)	$S(0) + Hg \rightarrow HgS$	adsorption onto Hg <-0.62
3b)	$HgS + H^+ + 2\,e^- \leftrightarrow HS^- + Hg$	-0.62
4a)	$Hg + S_x^{2-} \rightarrow HgS_x + 2\,e^-$	adsorption onto Hg <-0.62
4b)	$HgS_x + 2\,e^- \leftrightarrow Hg + S_x^{2-}$	-0.62
4c)	$S_x^{2-} + x\,H^+ + (2x-2)\,e^- \rightarrow x\,HS^-$	-0.62 (varies with v)
5)	$2\,RSH + Hg \leftrightarrow Hg(SR)_2 + 2\,H^+ + 2\,e^-$	< -0.62
6)	$2\,S_2O_3^{2-} + Hg \leftrightarrow Hg(S_2O_3)_2^{2-} + 2e^-$	-0.15

VOLTAMMETRY

I vs E plots [similar to A vs λ plots]



In situ **linear sweep voltammograms at 2500 meters below the ocean surface (3 electrode system counter, reference, working); ≥ 1V s^{-1}**

Au/Hg Electrode Metal Reactions of Interest

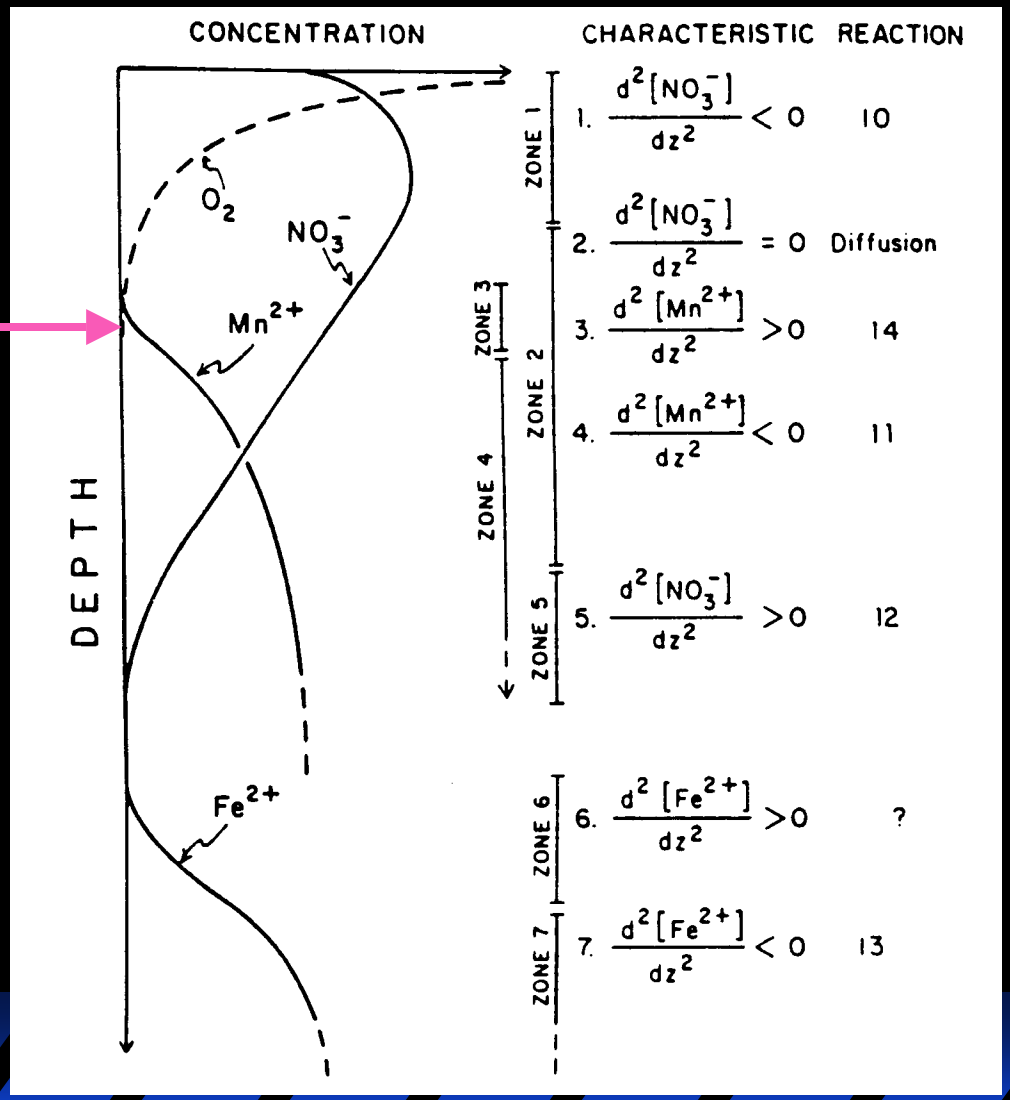
	Reaction (+ scan; 200 mV/s; 25 °C)	Ep (V) vs SCE
	Redox metals measurable	
1)	$FeS + 2\,e^- + H^+ + Hg \rightarrow Fe(Hg) + HS^-$	-1.15
2)	$Fe^{2+} + Hg + 2\,e^- \leftrightarrow Fe(Hg)$	-1.43
3)	$Mn^{2+} + Hg + 2\,e^- \leftrightarrow Mn(Hg)$	-1.55
4)	Fe^{3+}(organic) $+ e^- \rightarrow$ Fe^{2+}(organic)	-0.2 to -0.9
	Trace metals measurable	
5)	$Cu^{2+} + Hg + 2\,e^- \leftrightarrow Cu(Hg)$	-0.18
6)	$Pb^{2+} + Hg + 2\,e^- \leftrightarrow Pb(Hg)$	-0.46
7)	$Cd^{2+} + Hg + 2\,e^- \leftrightarrow Cd(Hg)$	-0.62
8)	$Zn^{2+} + Hg + 2\,e^- \leftrightarrow Zn(Hg)$	-1.05

ELECTRODE STANDARDIZATION

- **Electrodes standardized in seawater for each species.**
- **Current is independent of pH (4-8) for O_2, H_2S, Fe, Mn.**
- **Current is dependent on Temperature for all species; the diffusion coefficient depends on temperature.**
- **Current is independent of Pressure.**
- **Current depends on [flow rate]$^{1/2}$. Above 2 ml/min, there is NO flow rate dependence on 100 μm diameter electrodes.**
- **Validation *via* discrete samples and *in situ* Clark O_2 electrodes.**

Schematic representation of trends in pore water profiles with depth and concentration axes in arbitrary units

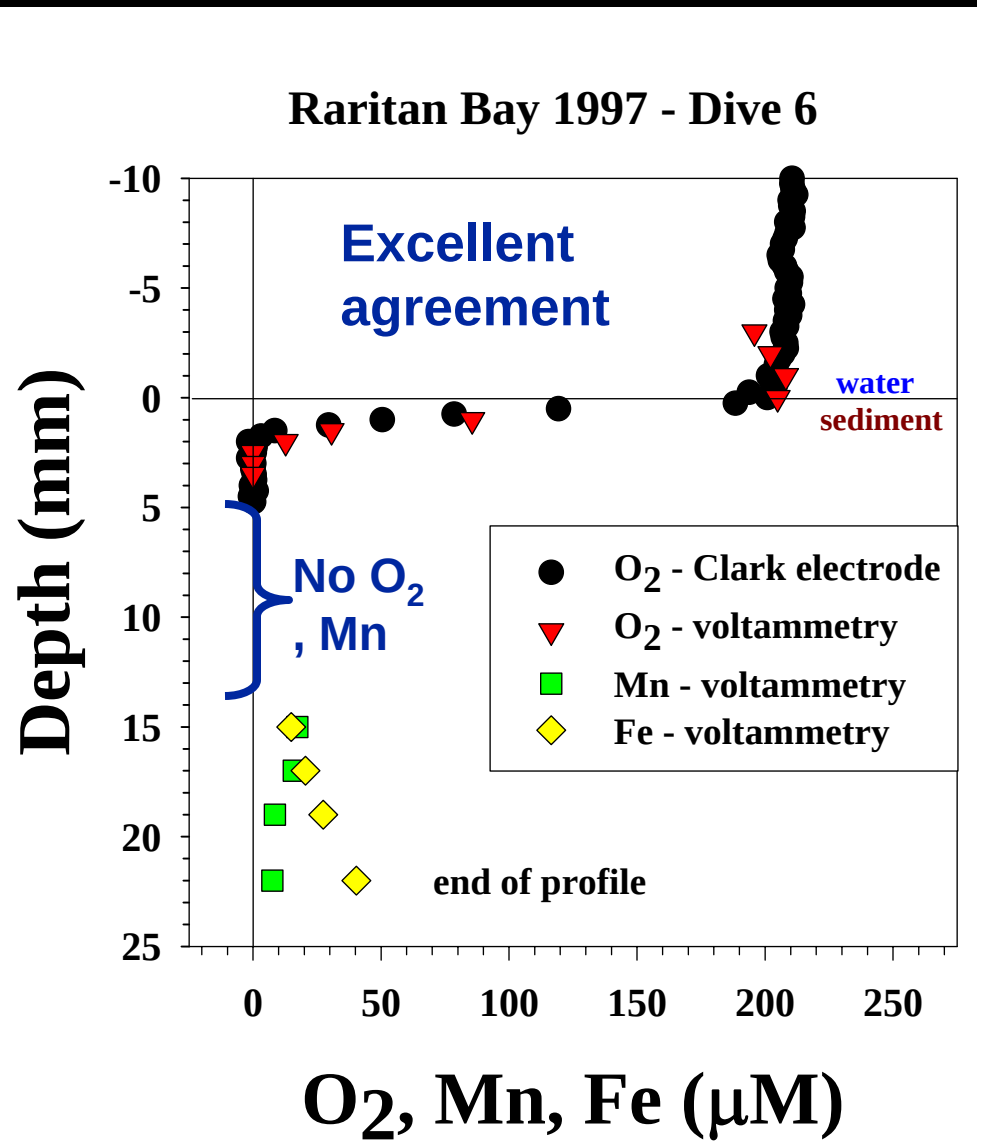
O_2 expected to overlap with dissolved Mn^{2+}



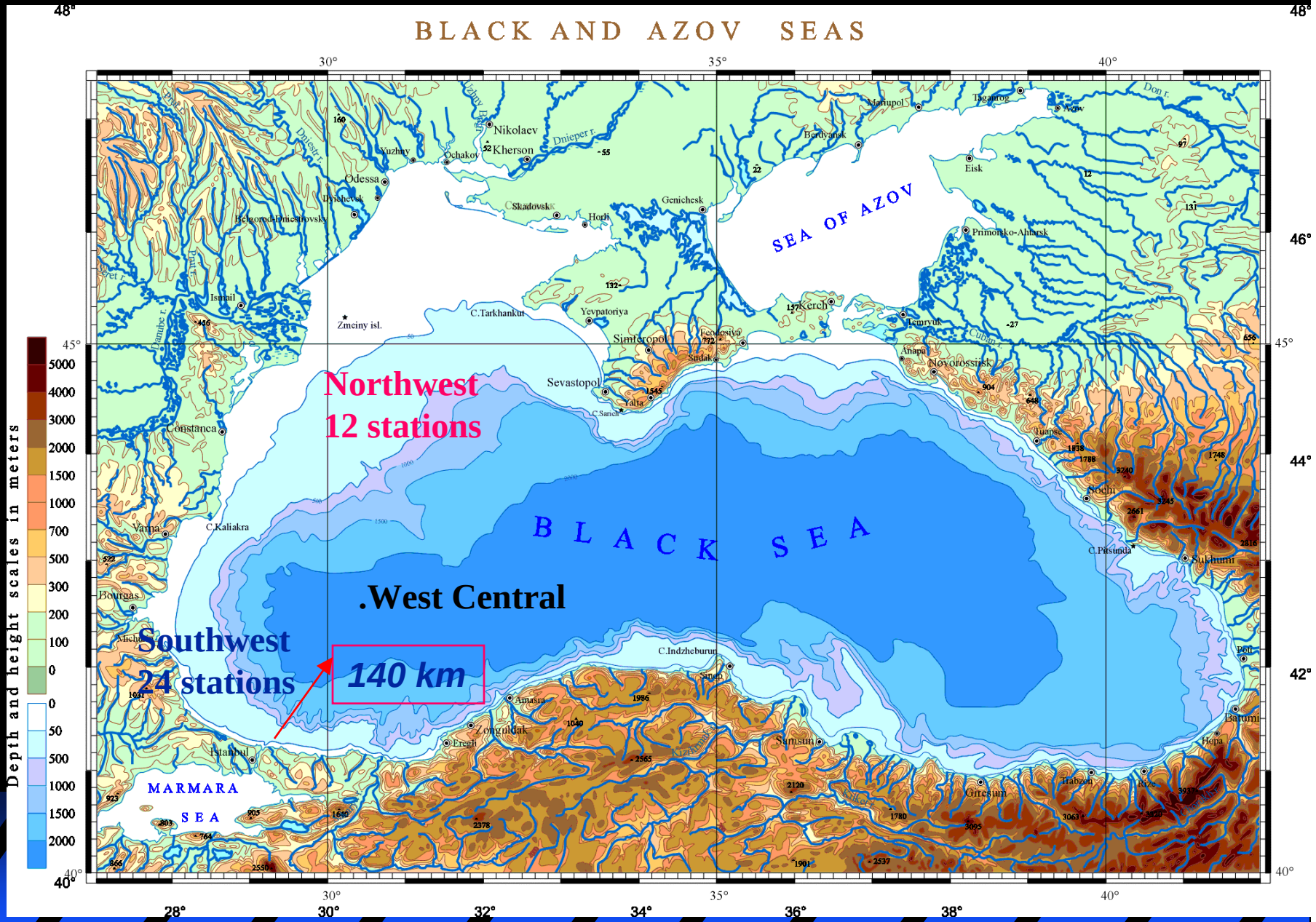
Profiles expected based on the thermodynamics of organic matter decomposition with electron acceptors (O_2, NO_3^-, MnO_2, FeOOH, SO_4^{2-})

In situ comparison of O_2 Clark vs voltammetric Au/Hg in sediments from a ROV

Real time voltammetry of porewaters



May 23 – June 9, 2001 cruise



IN SITU instrumentation

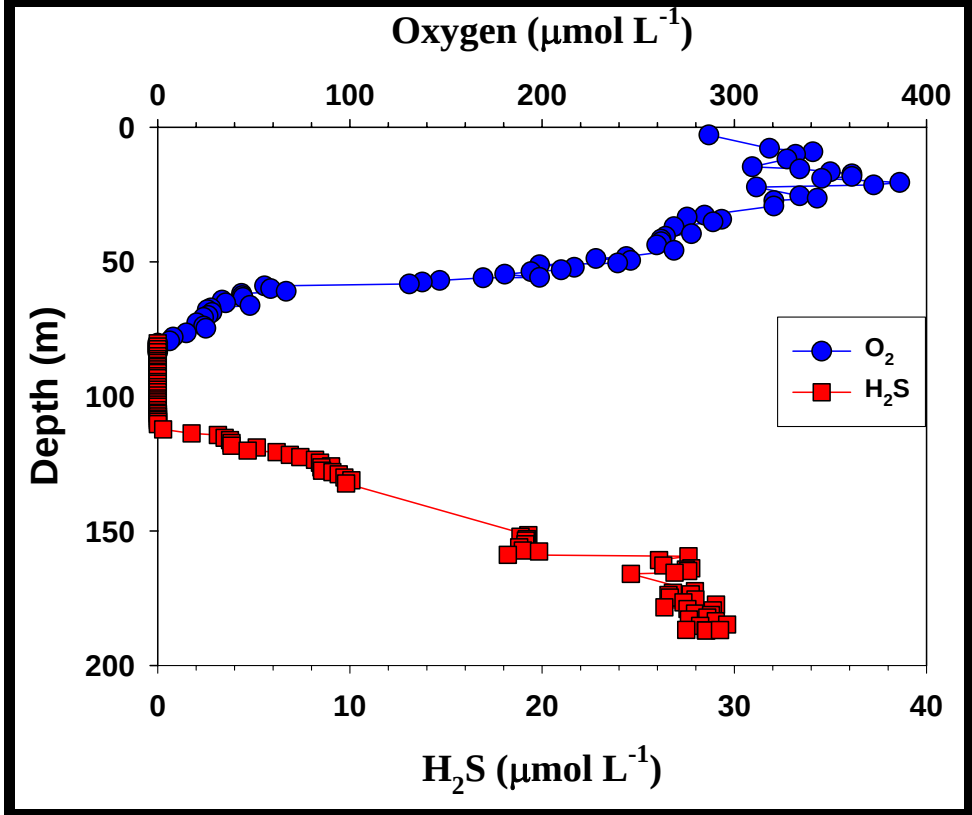
AIS/UD Electrochemical analyzer (O_2 , H_2S)

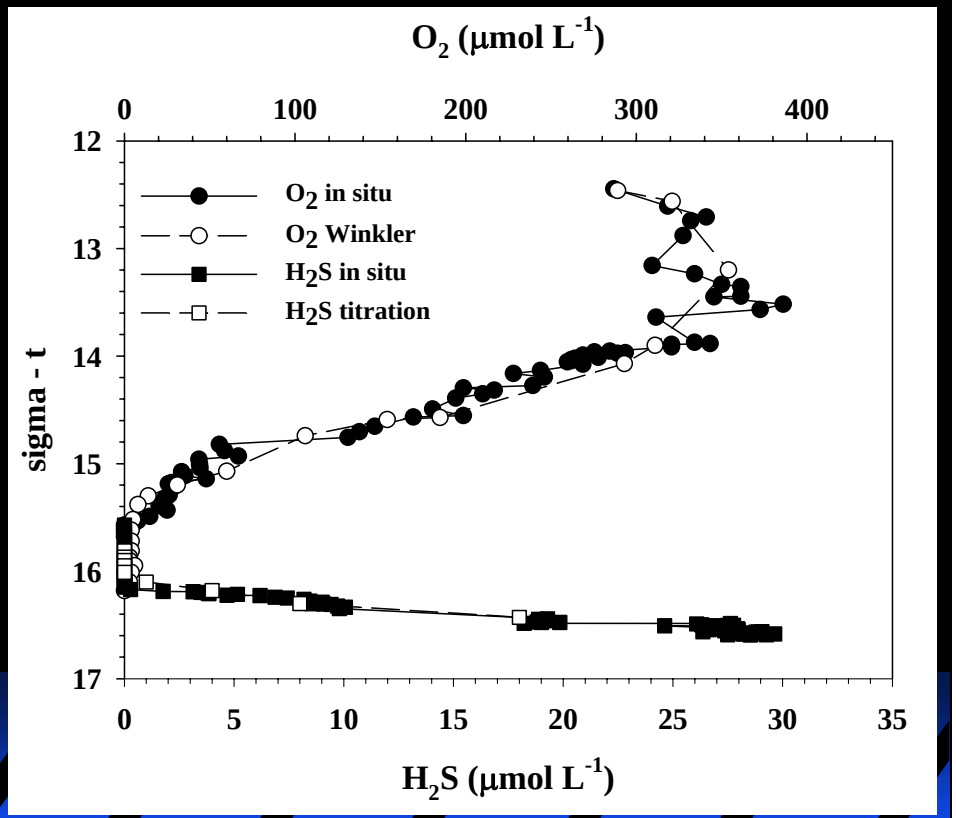
MBARI CTD

Mount for UD electrodes

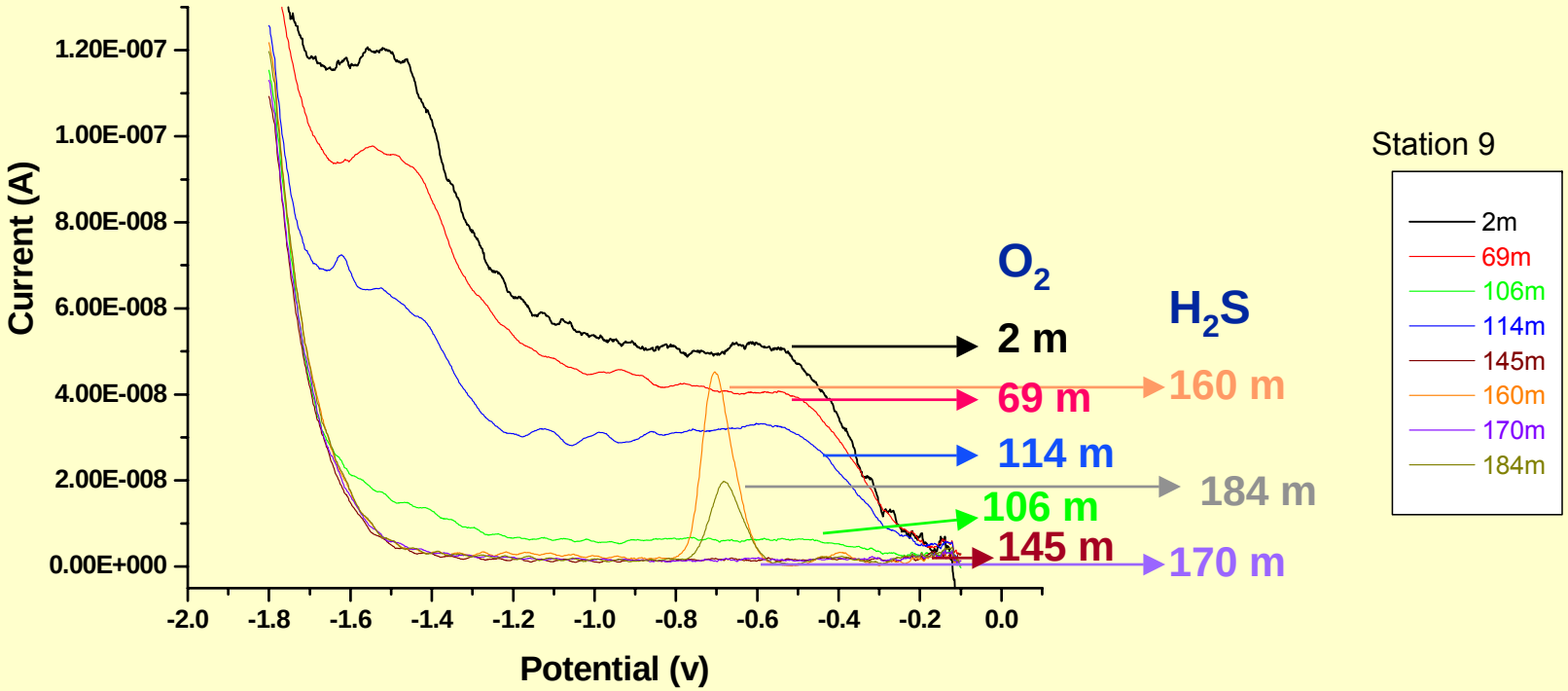
MBARI Pump profiler

Central Black Sea

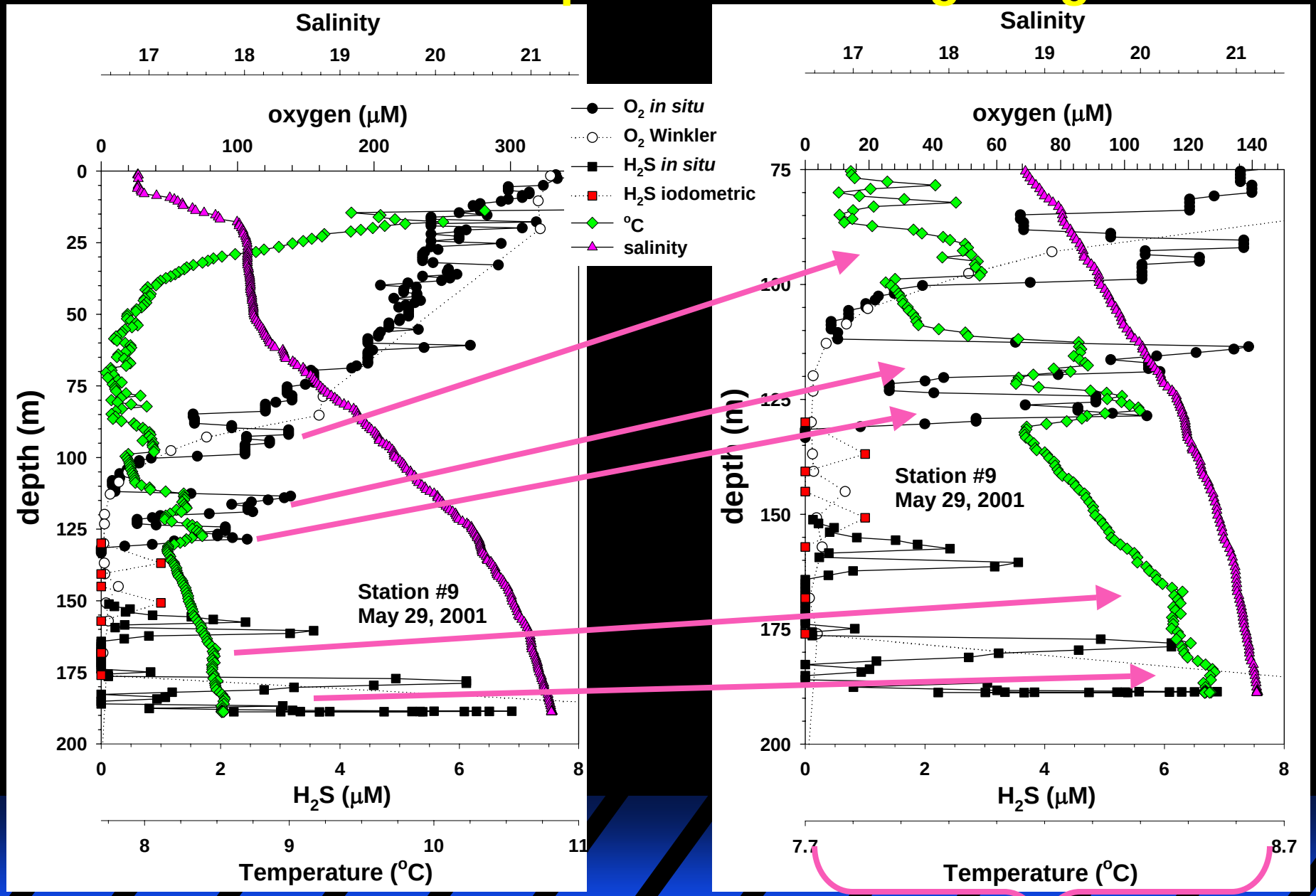




IN SITU voltammograms for O_2 and H_2S over depth at station 9 (Southwest Black Sea) in 2001

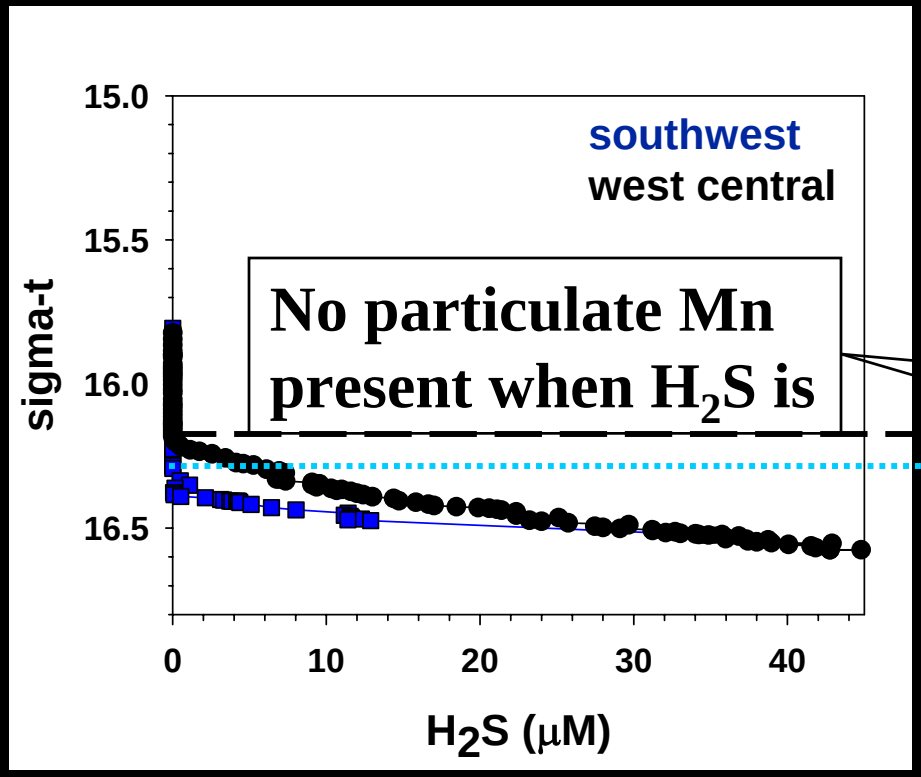


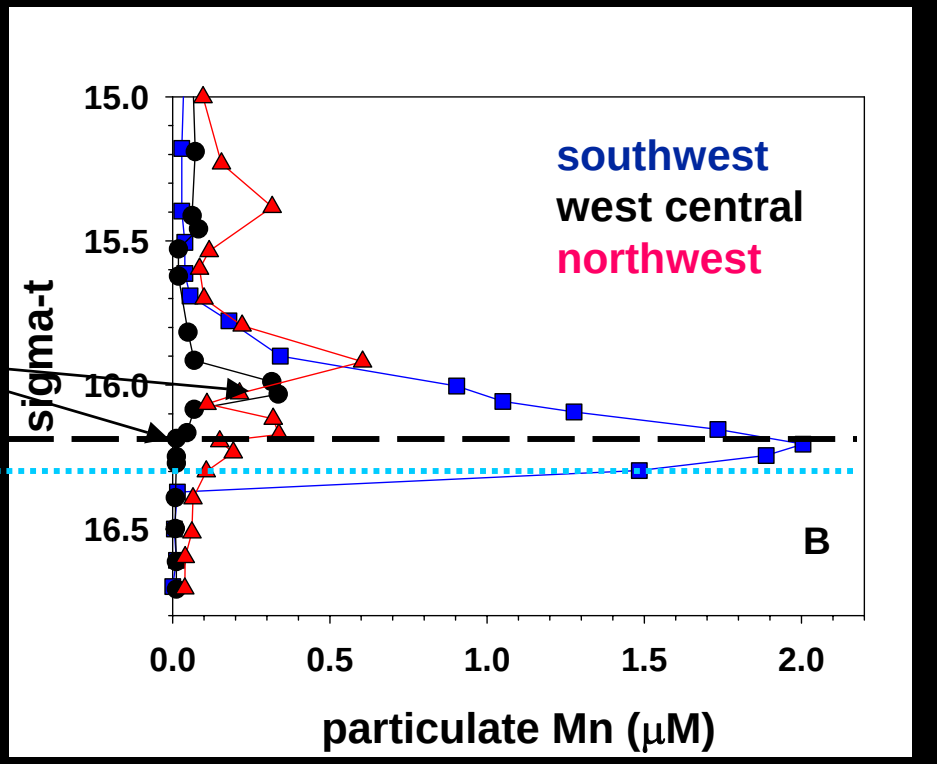
Profiles vs depth shows “fingering”



Increase T, inc. O_2 or decrease H_2S

O_2 forms particulate MnO_2 that overlaps into H_2S zone





Southwest area is enriched in particulate Mn because of O_2 from Bosporus inflow

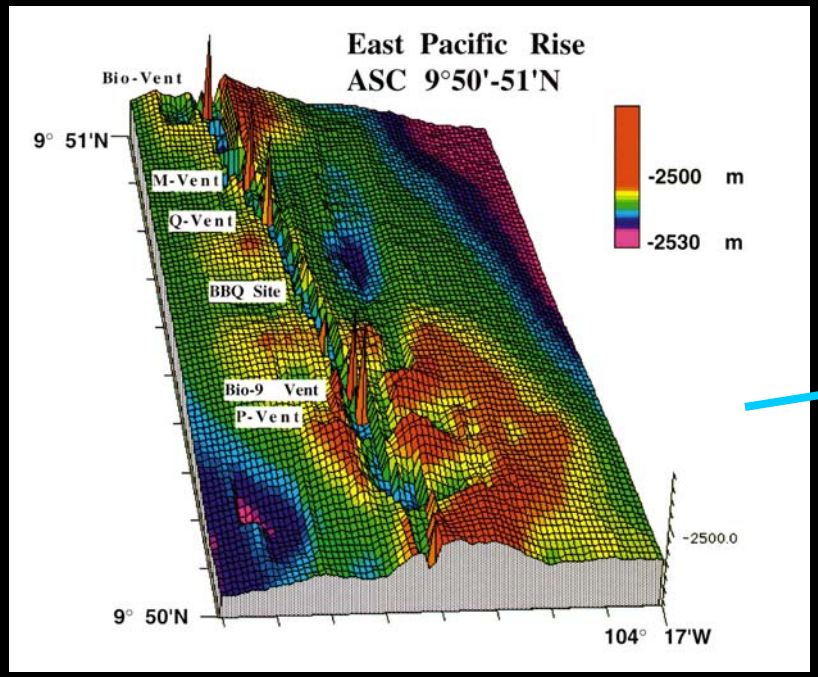
Mn catalytic cycle

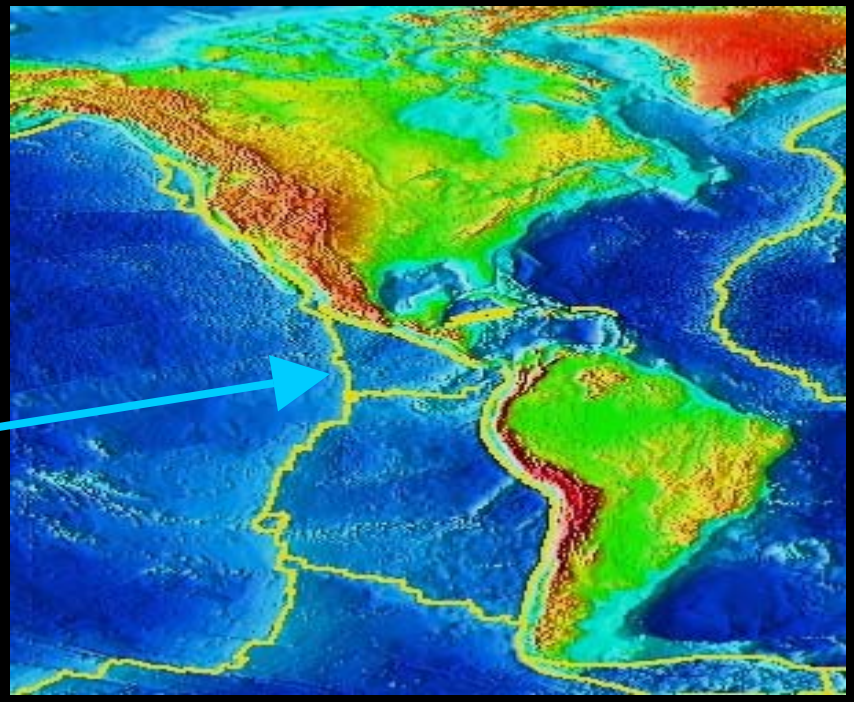
$Mn^{2+} + ½\ O_2 + H_2O \rightarrow MnO_2 + 2\ H^+$ microbial process

$MnO_2 + HS^- + 3\ H^+ \rightarrow Mn^{2+} + S^o + 2\ H_2O$ abiotic process

We now have evidence for soluble Mn(III)-complexes in the Black Sea

Hydrothermal Vents at 9º 50’ N East Pacific Rise





Fe, S chemistry
Origin of Life, of organic compounds and a source of H_2 at HYDROTHERMAL VENTS

$FeS + H_2S \longrightarrow FeS_2 + H_2$ (Wachterhauser's hypothesis)

Voltammetry can measure FeS_{aq} (molecular clusters) and H_2S

Apply *in situ* solid state electrodes to look for (micro)organisms that can benefit from this reaction or the products of this reaction

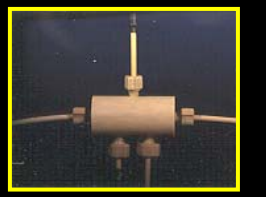
Apply *in situ* solid state electrodes to understand the chemical reason why organisms live in different ecological niches

General Block Diagram of IN SITU submersible Electrochemical Instrument

Electrode Wand

Working Electrodes (Au/Hg)

Flow cell



Counter Electrode (Pt)

Reference Electrode (Ag / AgCl)

Alvin hull

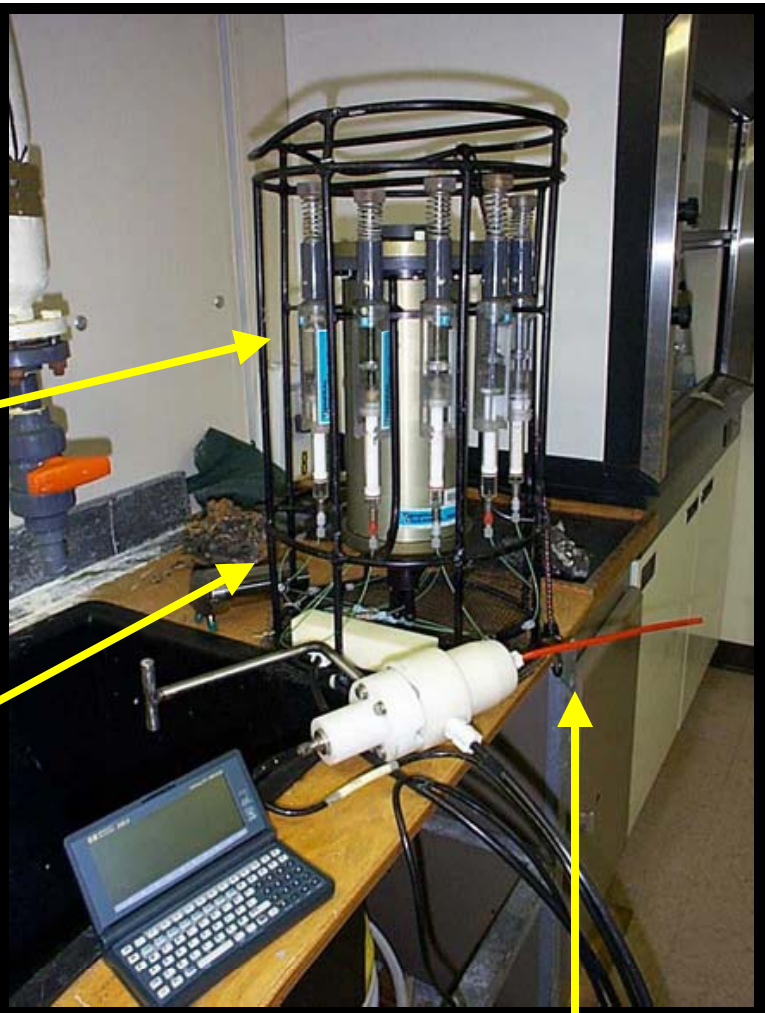
AIS, DLK-SUB-1 Electrochemical Analyzer

Laptop Computer In Alvin

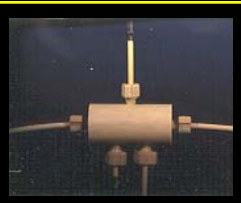
"SIPPER"

Discrete micro-water sampler

- 12 channel syringe samplers
- 10 ml max volume



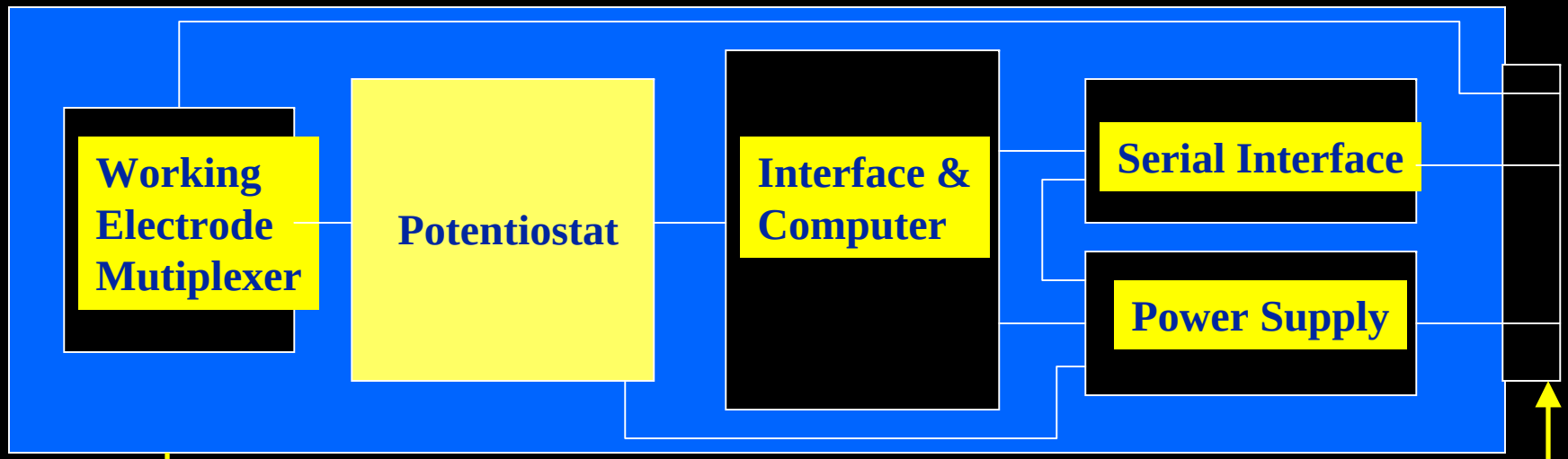
- electrochemical flow cell can be mounted

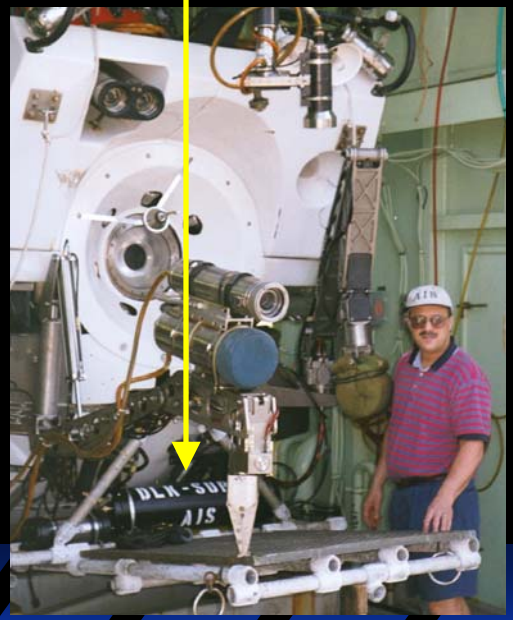


- Seabird pump provides flow through capability

PEEK tubing, *in situ* electrodes and thermocouple

Block Diagram of AIS, DLK-SUB-1





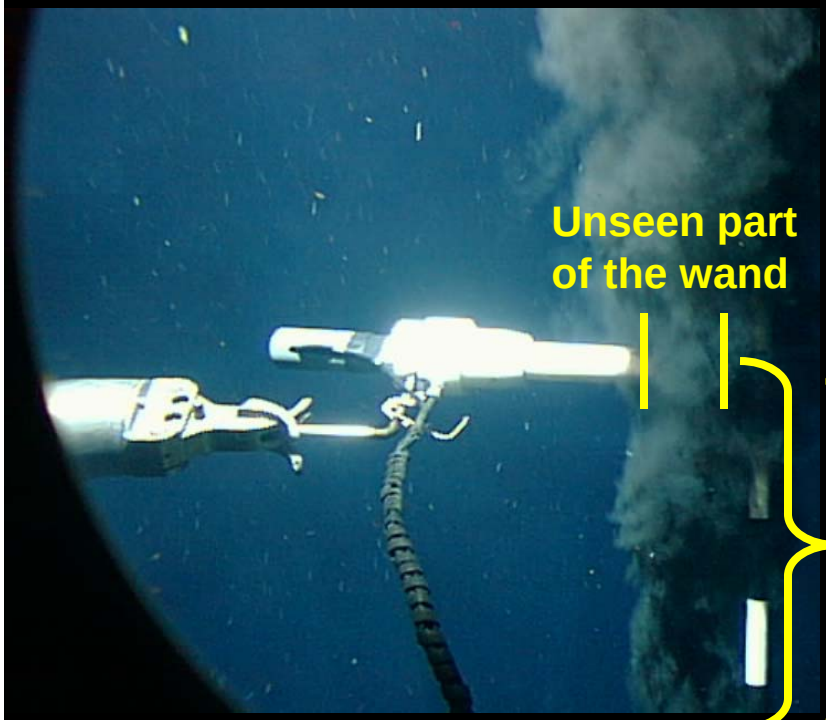
Bulkhead Connectors

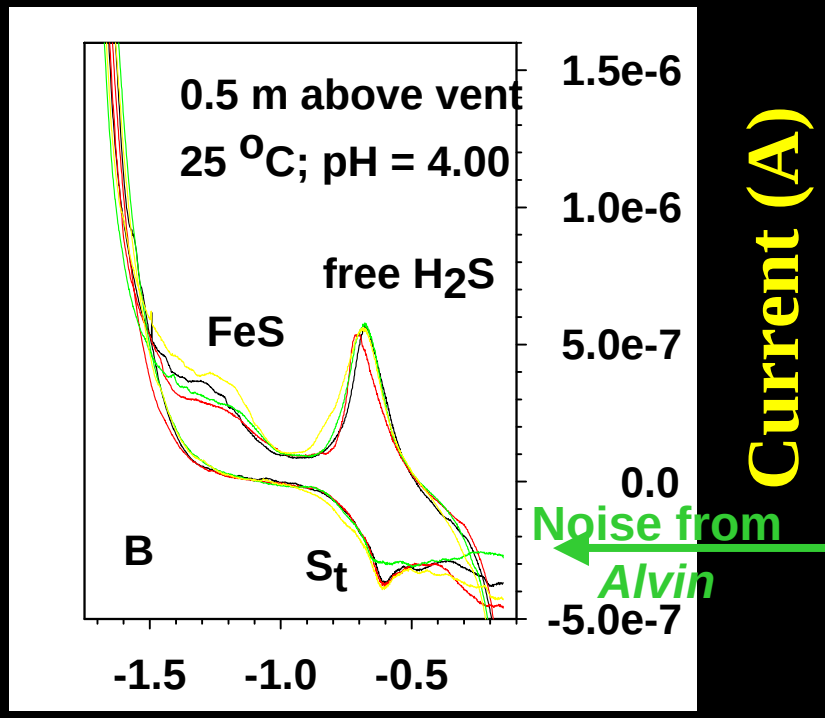
Pressure Housing

Analytical Instrument Systems, Inc.

By: Donald B. Nuzzio, Patent Pending

Black Smoker Voltammetry Speciation Data- 0.5 m above vent chimney

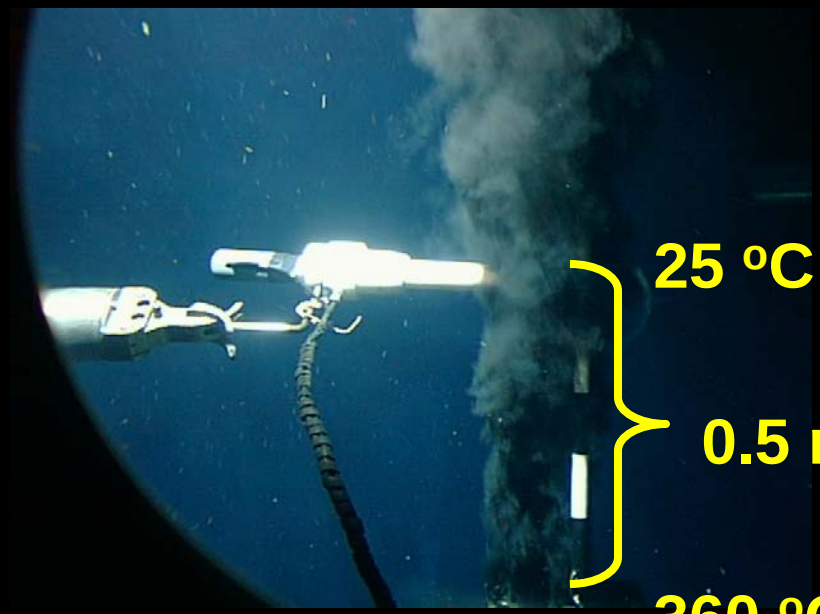


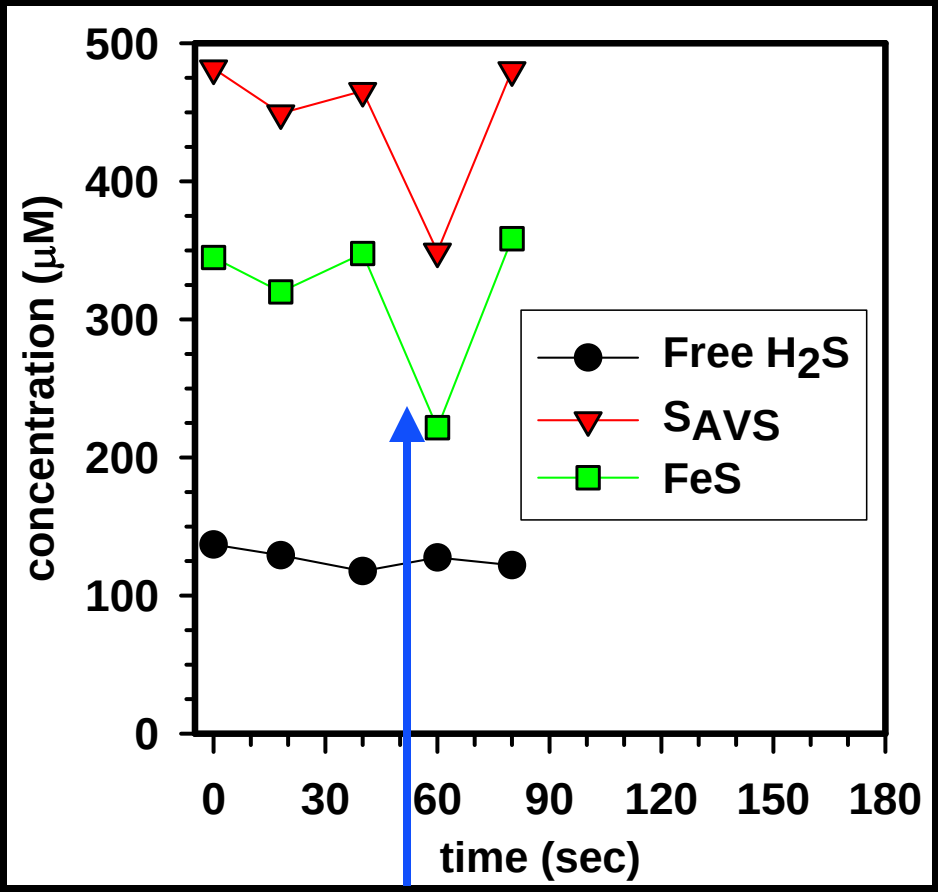


- Major signals for Free H_2S and FeS_{aq}
- O_2 not detected

$$S_t = S_{AVS} = FeS_{aq} + H_2S$$

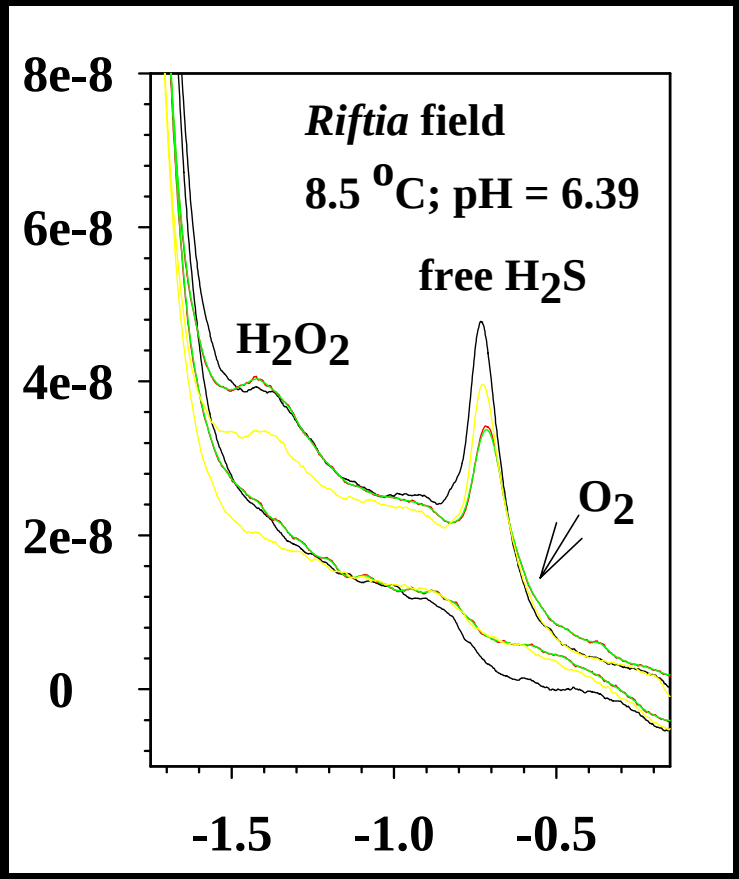
Sulfur chemistry 0.5 m above a Black Smoker





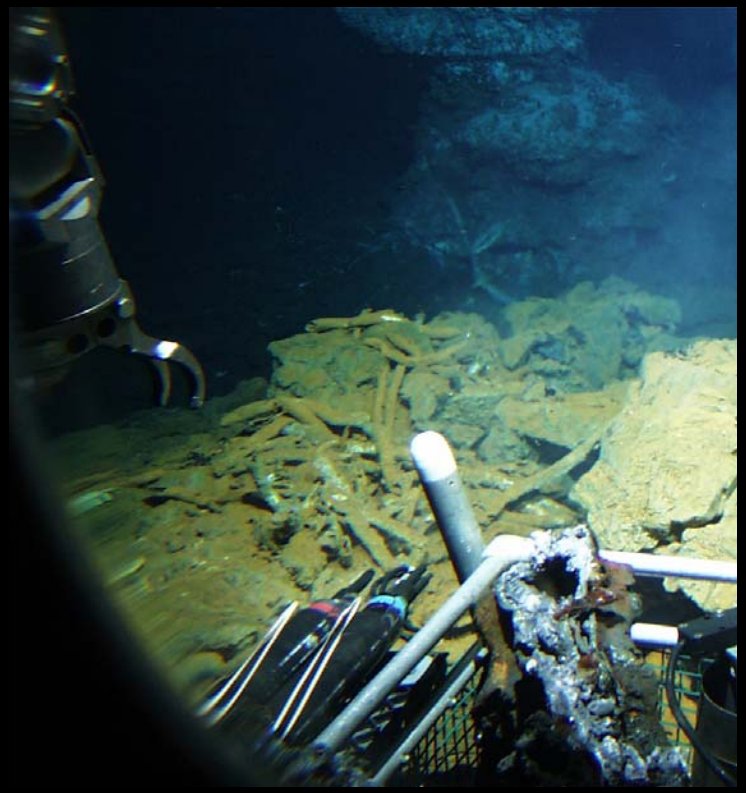
Electrical noise from *Alvin*

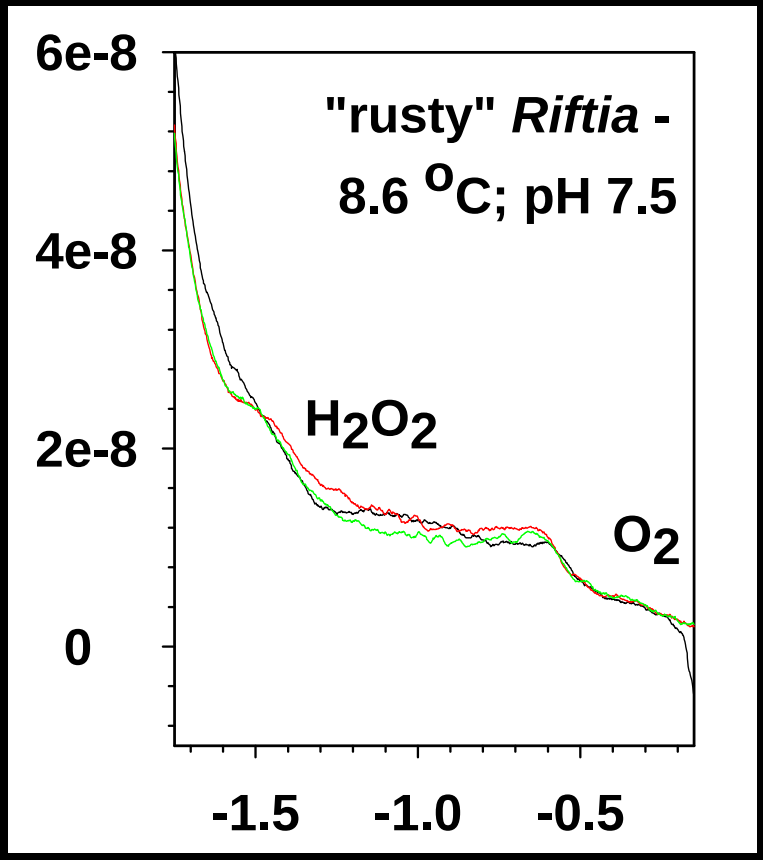
Near Plume of *Riftia*



- H_2S/HS^- and O_2 only
- No FeS_{aq}
- polysulfides can be present
- chemoautotrophs require H_2S

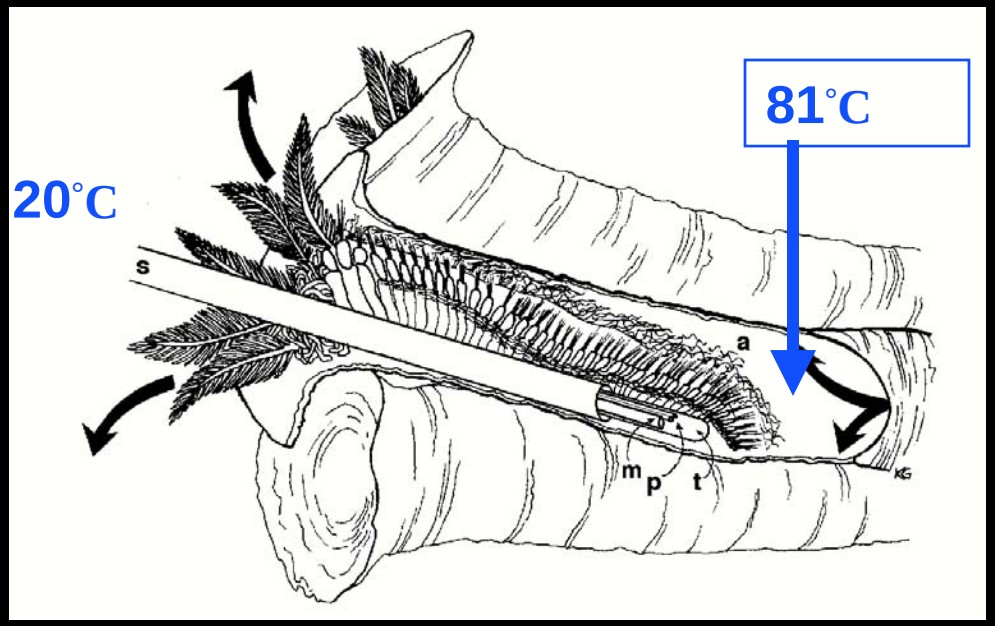
“Rusty” Riftia

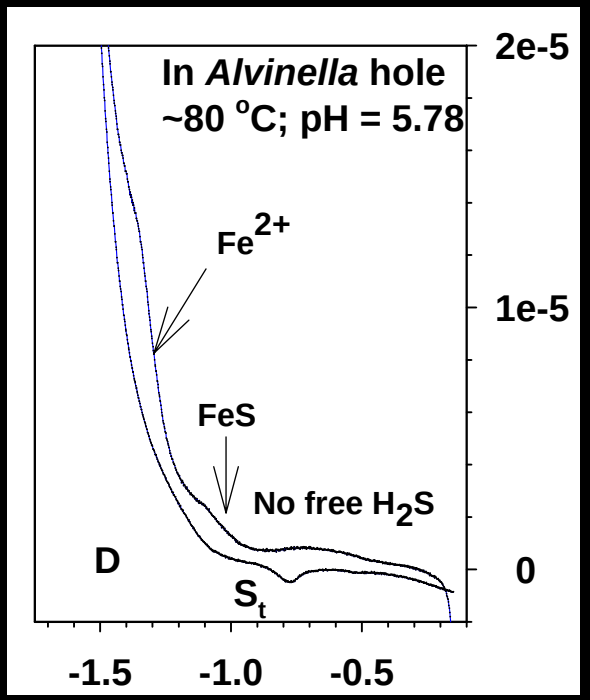




- Near ambient conditions
- O_2 only dominant signal
- Tubes encrusted with Fe (III)
- NO LIVING TUBEWORMS

Pompeii Worm Habitat Characterization

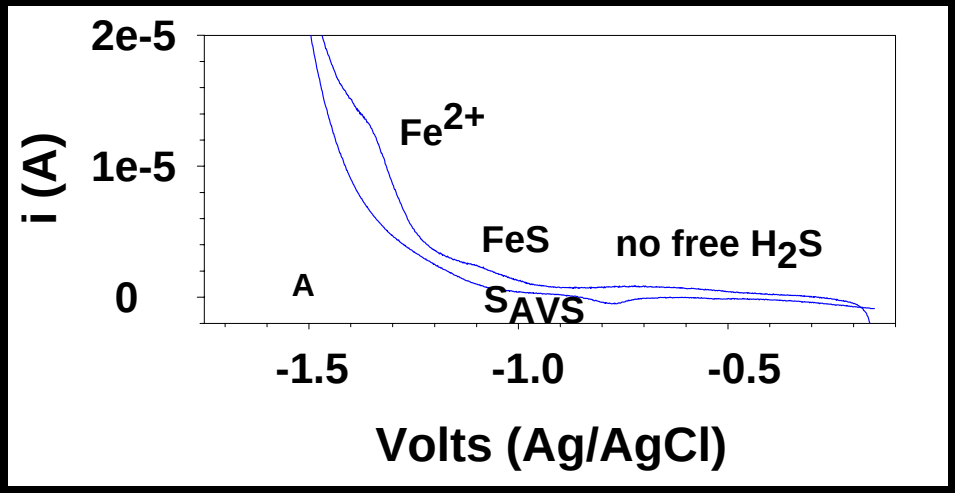


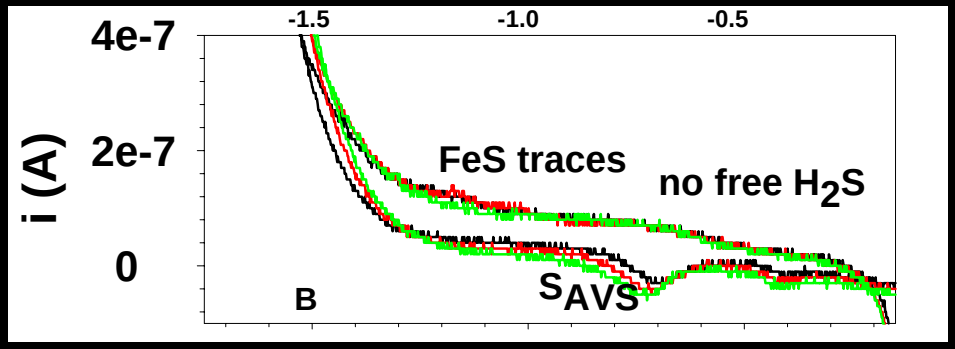


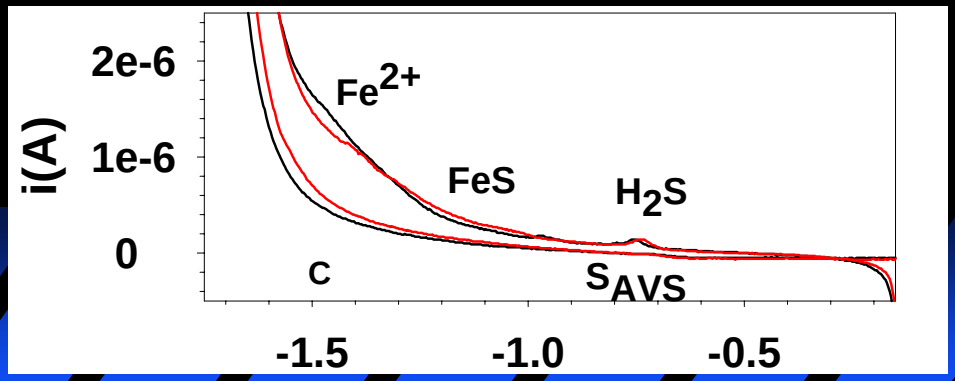
- Major signals due to FeS_{aq} + Fe^{2+}
- Free H_2S/HS^- was not detected
- O_2 not detected
- Epibionts not chemoautotrophic

Electrode helps understand ecological niches; Luther et al 2001

Change in chemical speciation at hydrothermal vents







$H_2S + Fe^{2+} \leftrightarrow FeS_{aq} + 2H^+$

In *Alvinella* tube, 80 ± 20 °C - 250 atm

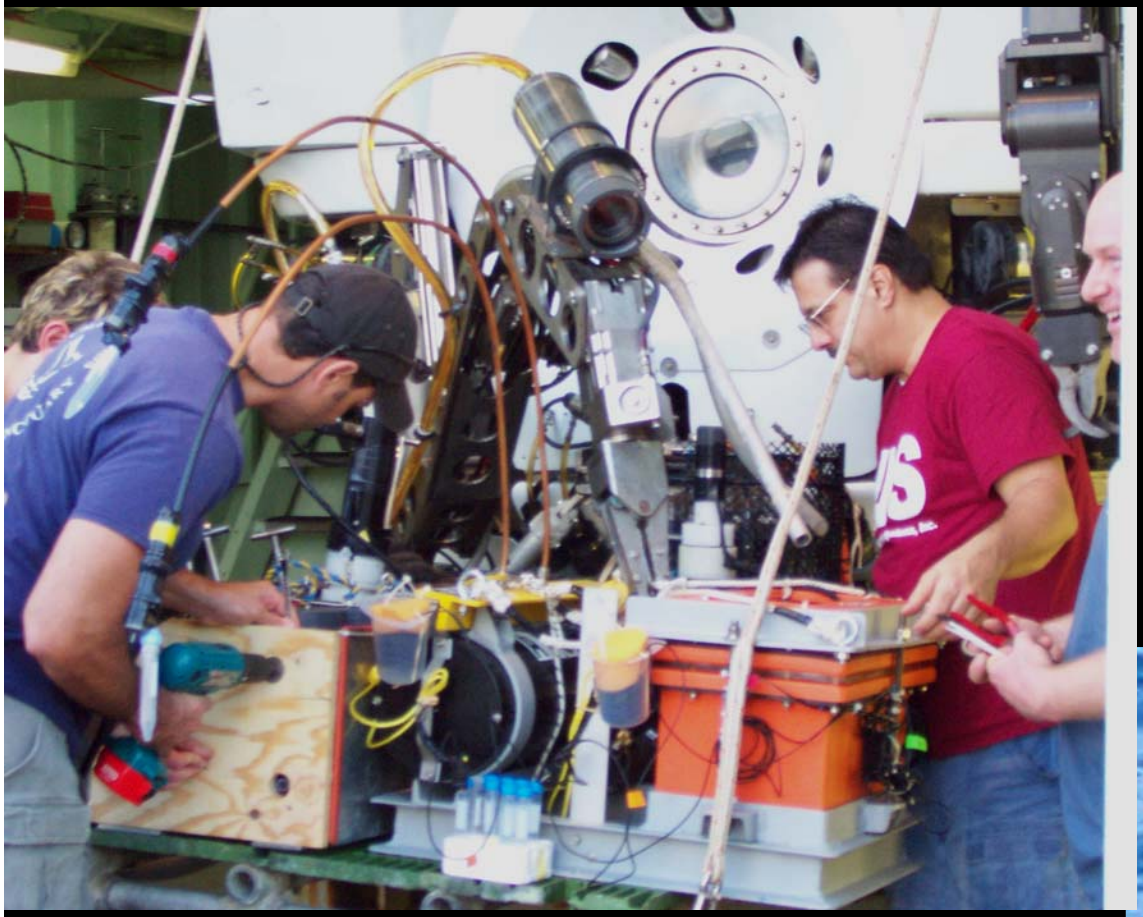
In flow cell; 2 °C 250 atm

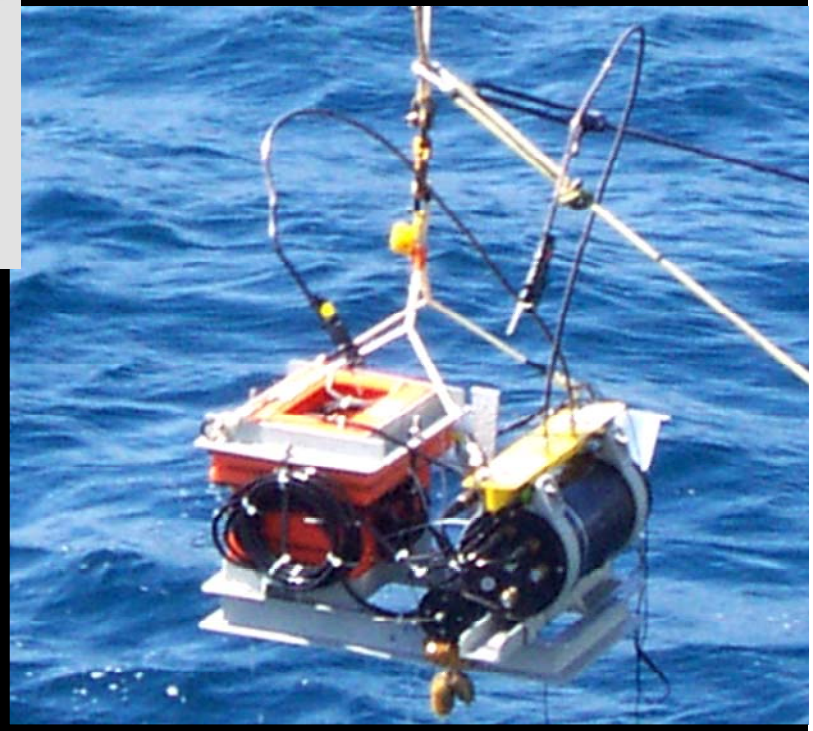
Aboard ship lab 22 °C; 1 atm

$FeS_{aq} + 2H^+ \leftrightarrow H_2S + Fe^{2+}$

Shift in equilibrium; LeChatelier

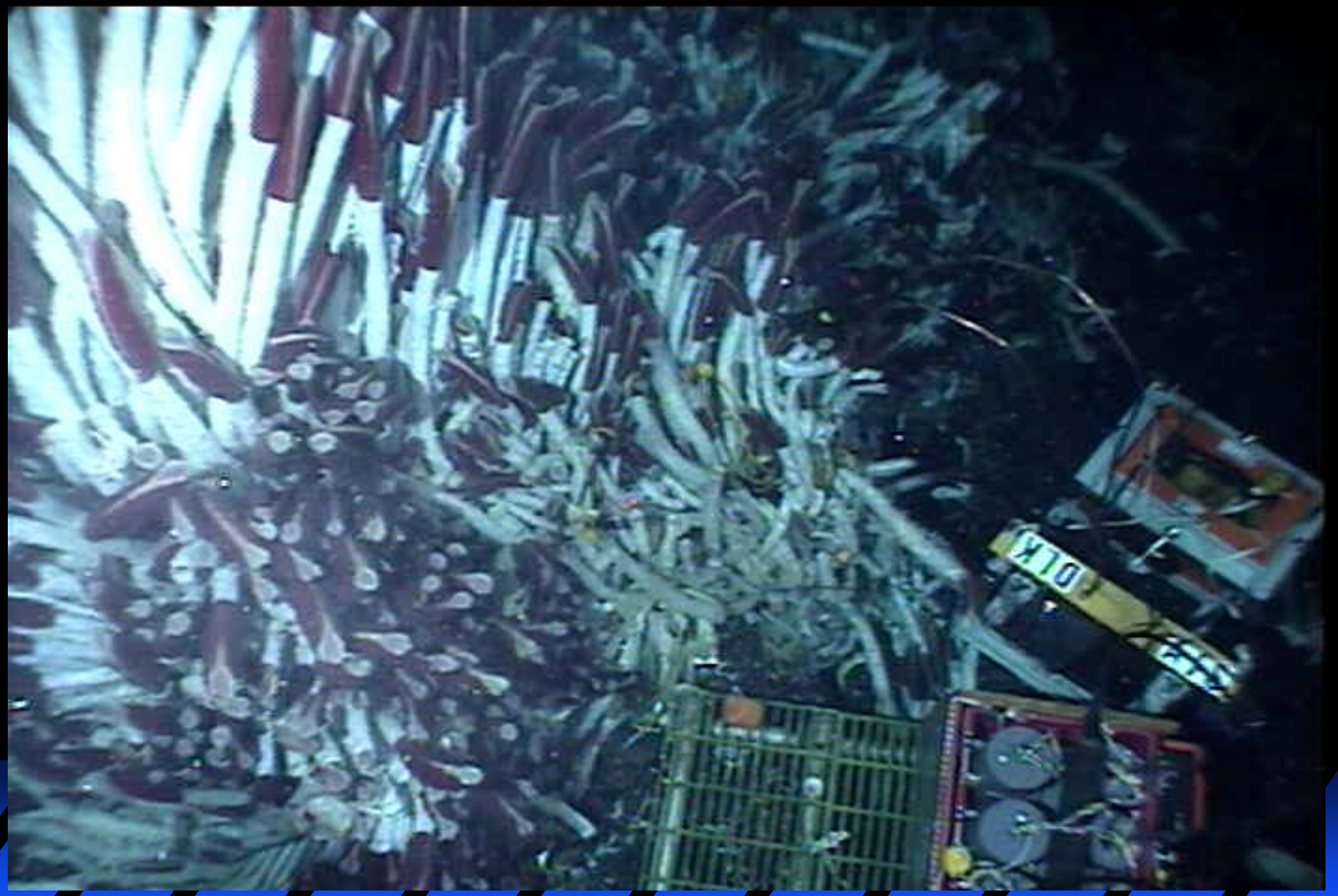
ISEA





December ’03 TICA site

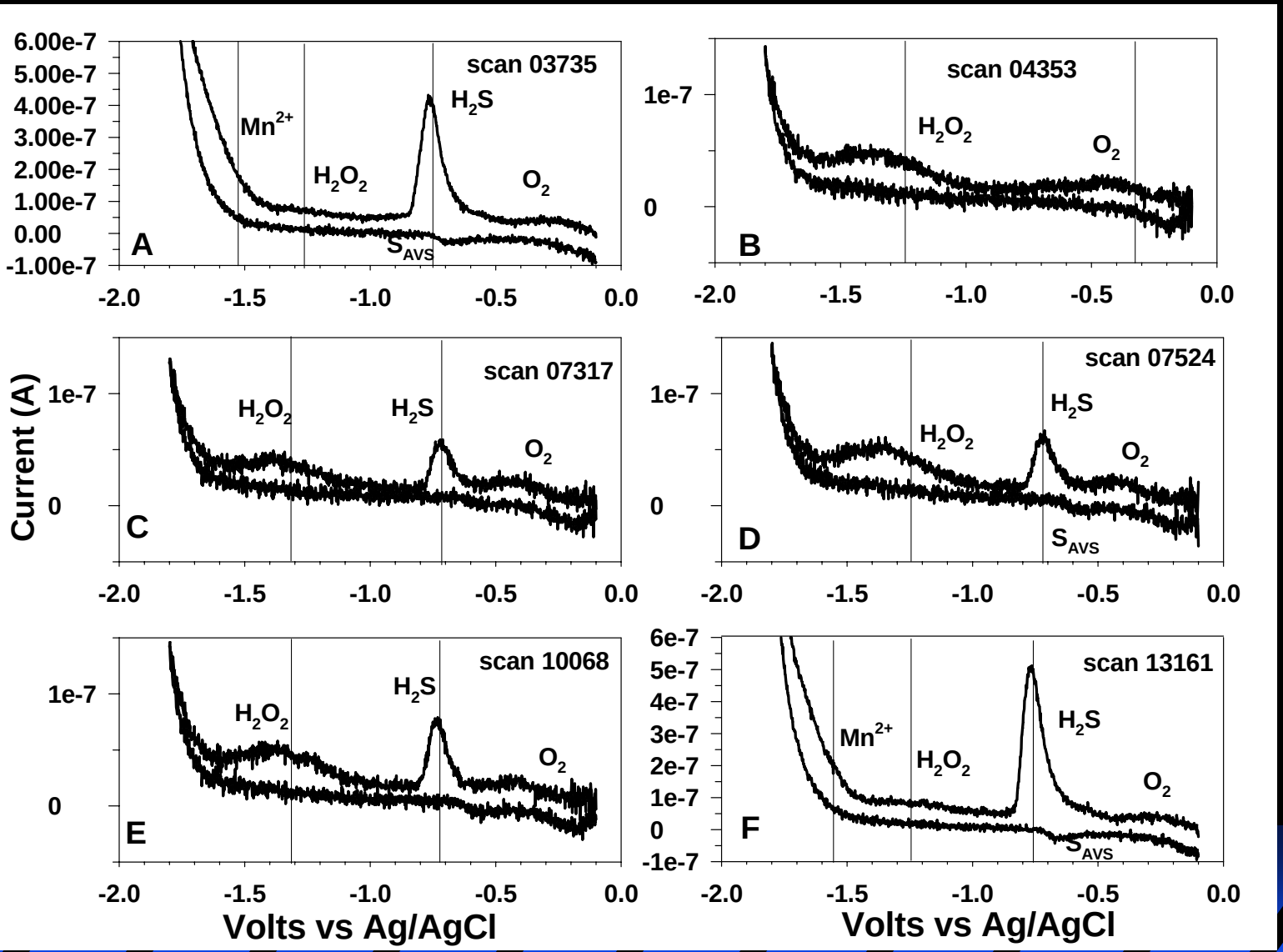
Riftia pachyptila



December ’03 TICA site

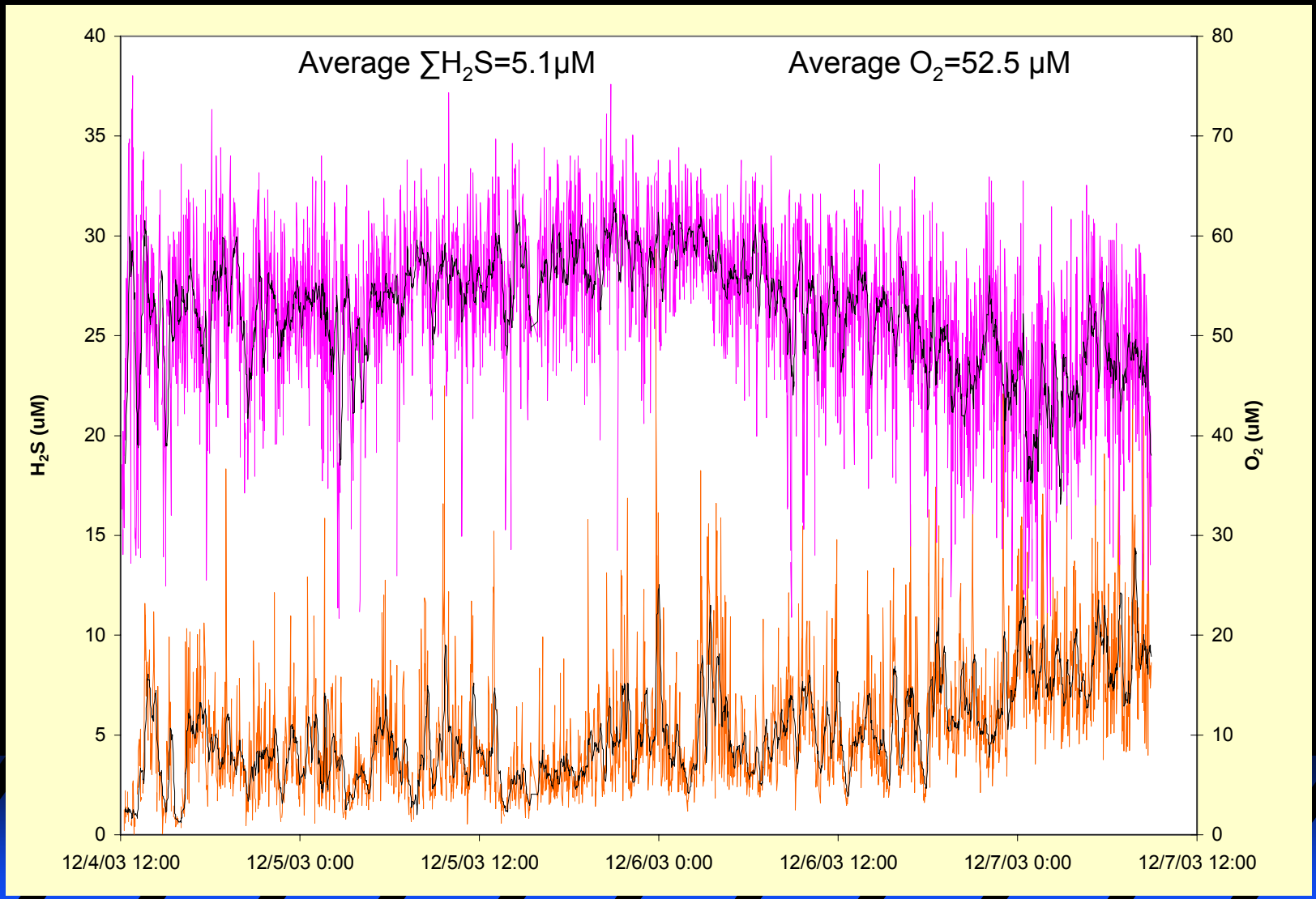
Riftia pachyptila

Representative Voltammetry Scans



TICA-Electrode 1

(Yellow Vemco Probe)



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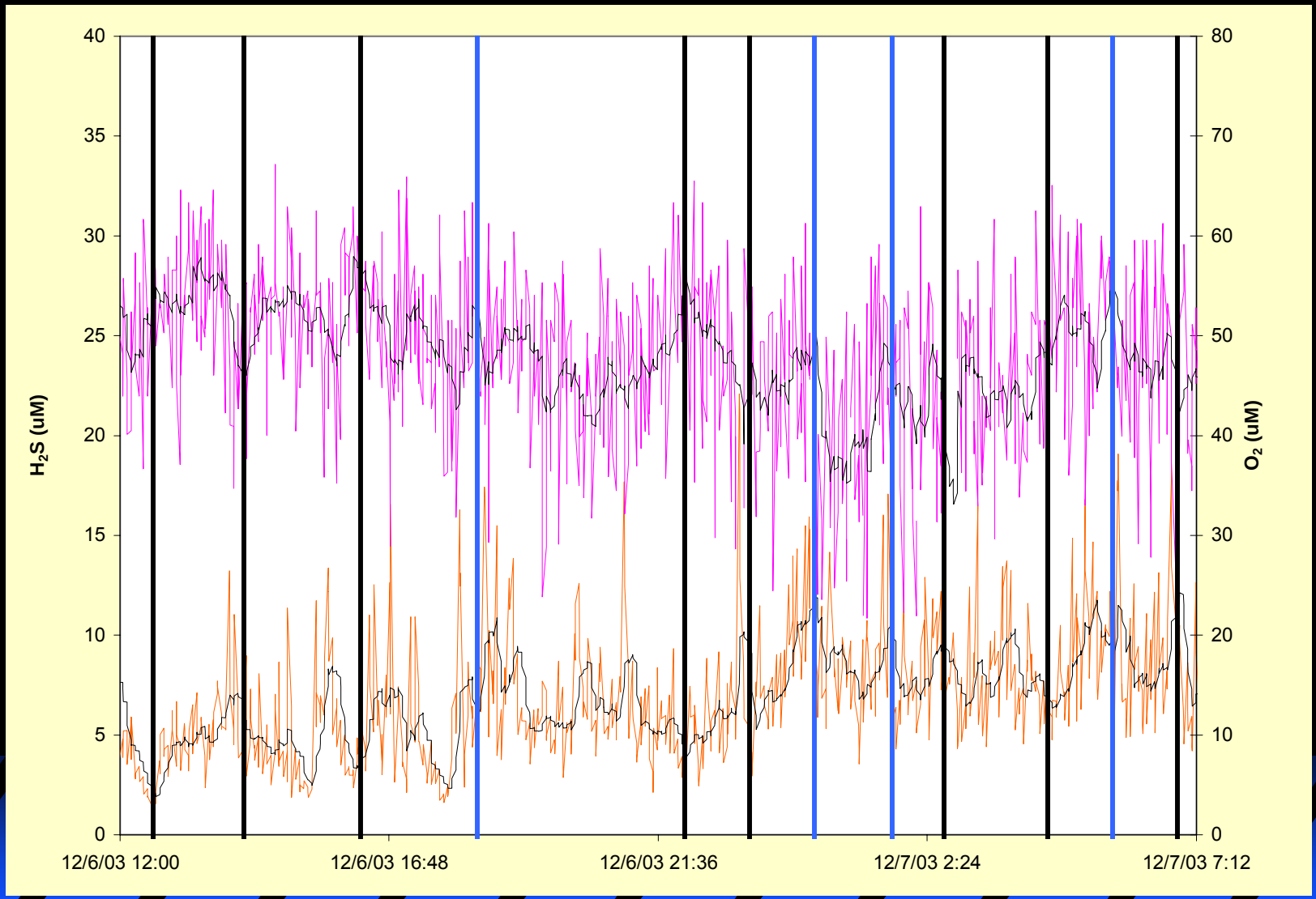

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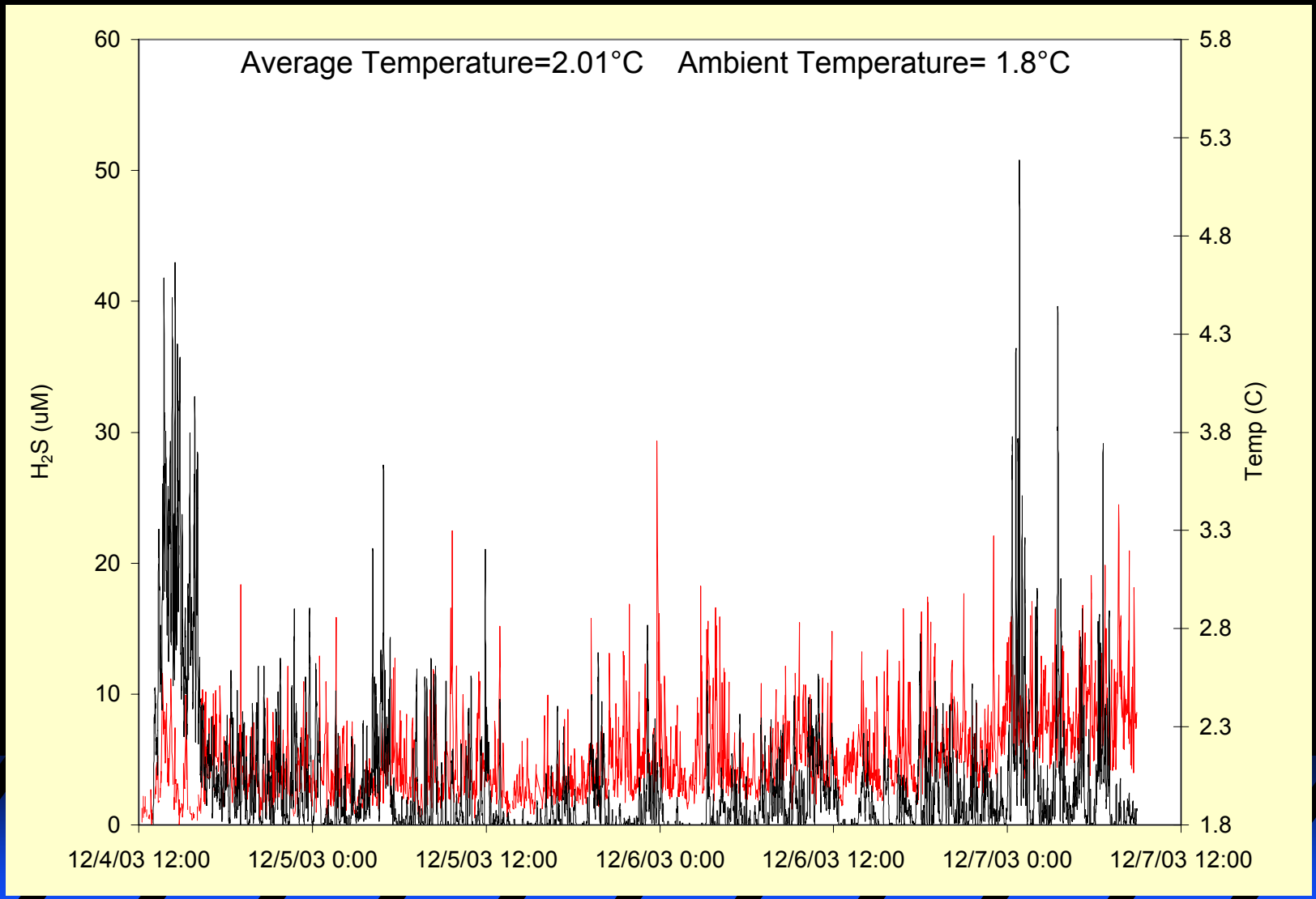

Conclusions

- In areas of diffuse flow, H_2S concentrations can vary by 3 orders of magnitude in a short time period (minutes).
- O_2 and H_2S generally anti-correlate but sometimes correlate above *Riftia*.
- Variability in H_2S is different near different *Riftia* tubeworms over short spatial scales (30cm) and appears related to electrode positioning above an organism versus in between organisms.
- The degree of changes in H_2S and temperature at the denuded mussel bed are smaller than those observed near *Riftia*.
- Temperature may not be a conservative tracer of vent chemistry in areas of diffuse flow due to *physical mixing* when measurements are taken above the organisms maximum height.