Chemical Sensors for High Temperature Hydrothermal Fluids

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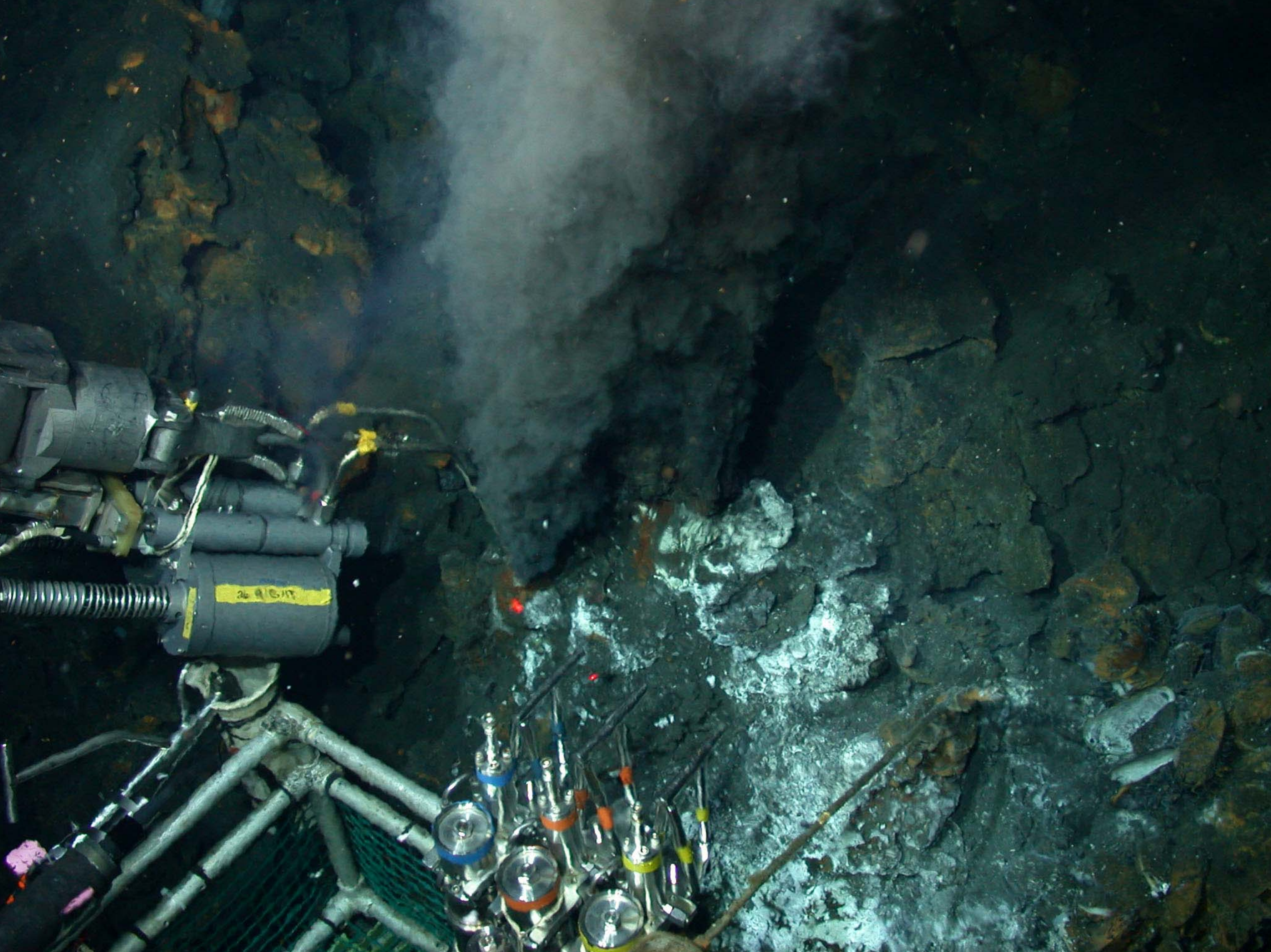
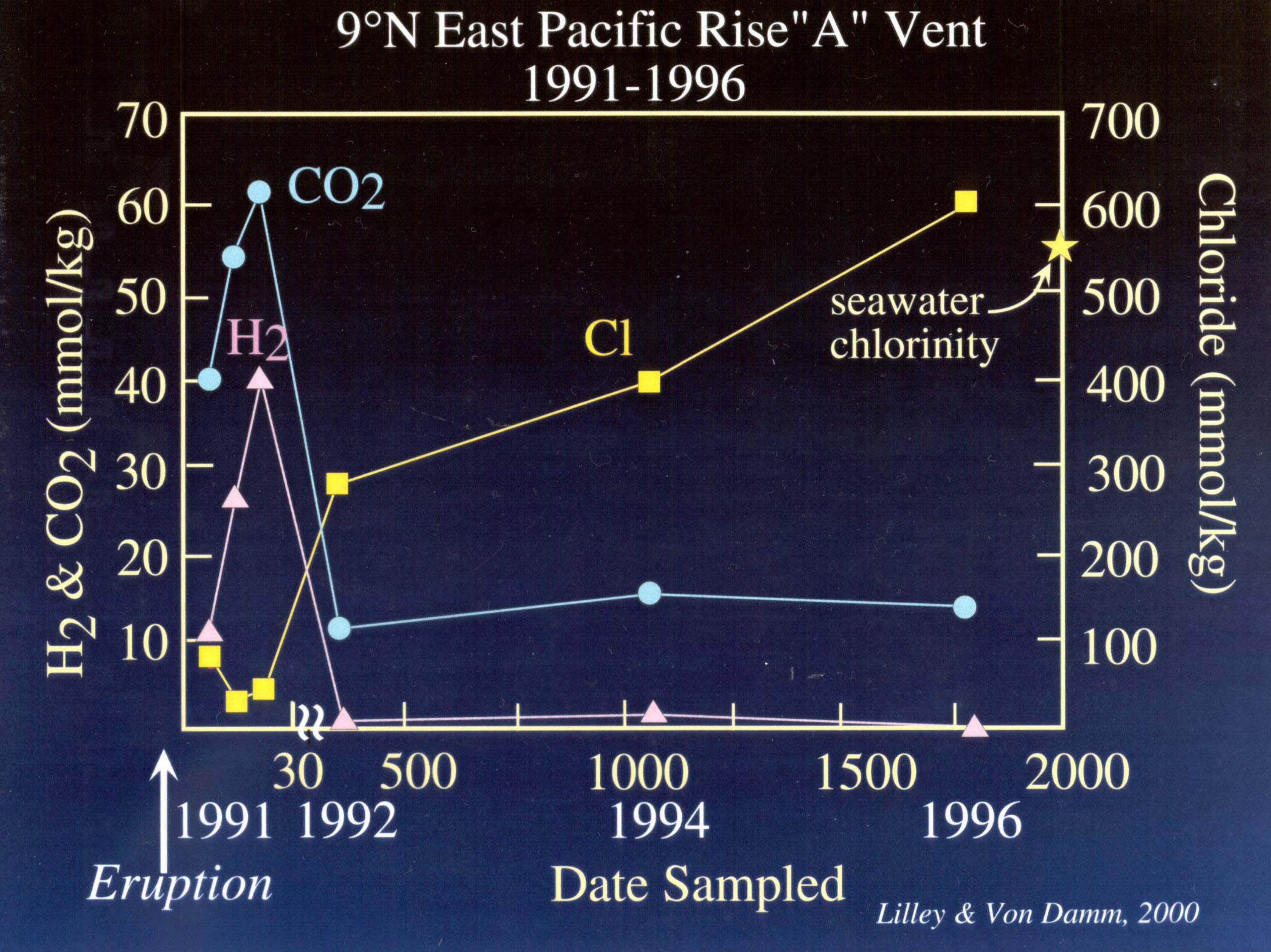
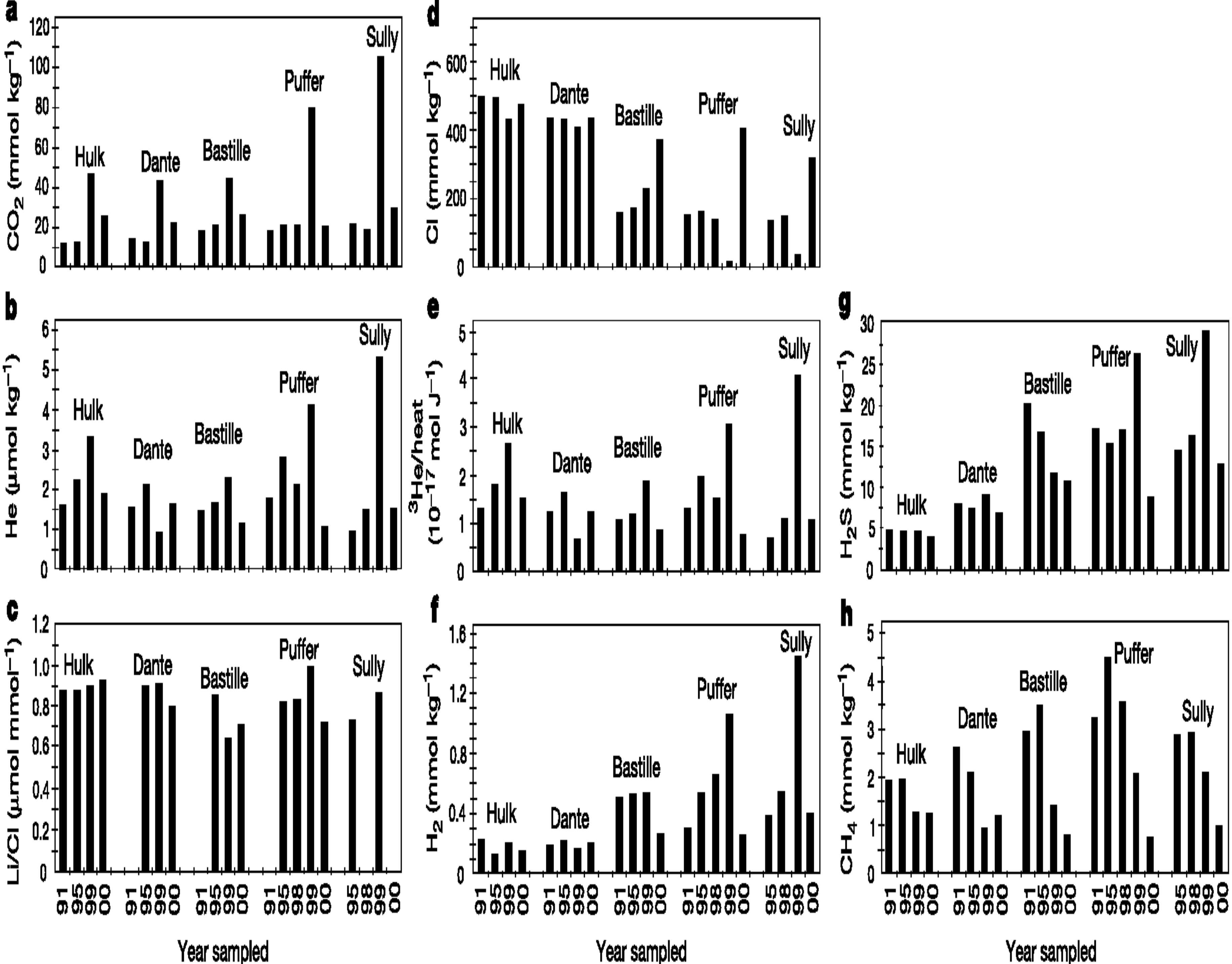



9°N East Pacific Rise"A" Vent
1991-1996
70
60
50
40
30
20
10
H_2 & CO_2 (mmol/kg)
CO_2
H_2
Cl
seawater
chlorinity
700
600
500
400
300
200
100
Chloride (mmol/kg)
30
500
1000
1500
2000
1991
1992
1994
1996
Eruption
Date Sampled
Lilley & Von Damm, 2000



a
CO_2 (mmol kg^{-1})
Hulk
Dante
Bastille
Puffer
Sully
b
He (μmol kg^{-1})
c
Li/Cl (μmol mmol^{-1})
d
Cl (mmol kg^{-1})
e
^{3}He/heat (10^{-17} mol J^{-1})
f
H_2 (mmol kg^{-1})
g
H_2S (mmol kg^{-1})
h
CH_4 (mmol kg^{-1})
Year sampled

Focus of Interest in my Lab

• Chloride	Phase Separation
• Hydrogen	Water/Rock Reactions
• Carbon Dioxide	Magmatic

Materials

Good	Maybe	Bad
Titanium	Inconel	Stainless
Gold	Hastelloy C	Nickel
Diamond	Sapphire	Ruby
Graphite		C. Zirconia

Conductance is a Proxy for Salt Content

The solution acts as a resistor: Ohm's law for a solution

$$V = IR \quad \Rightarrow \quad R = \frac{V}{I}$$

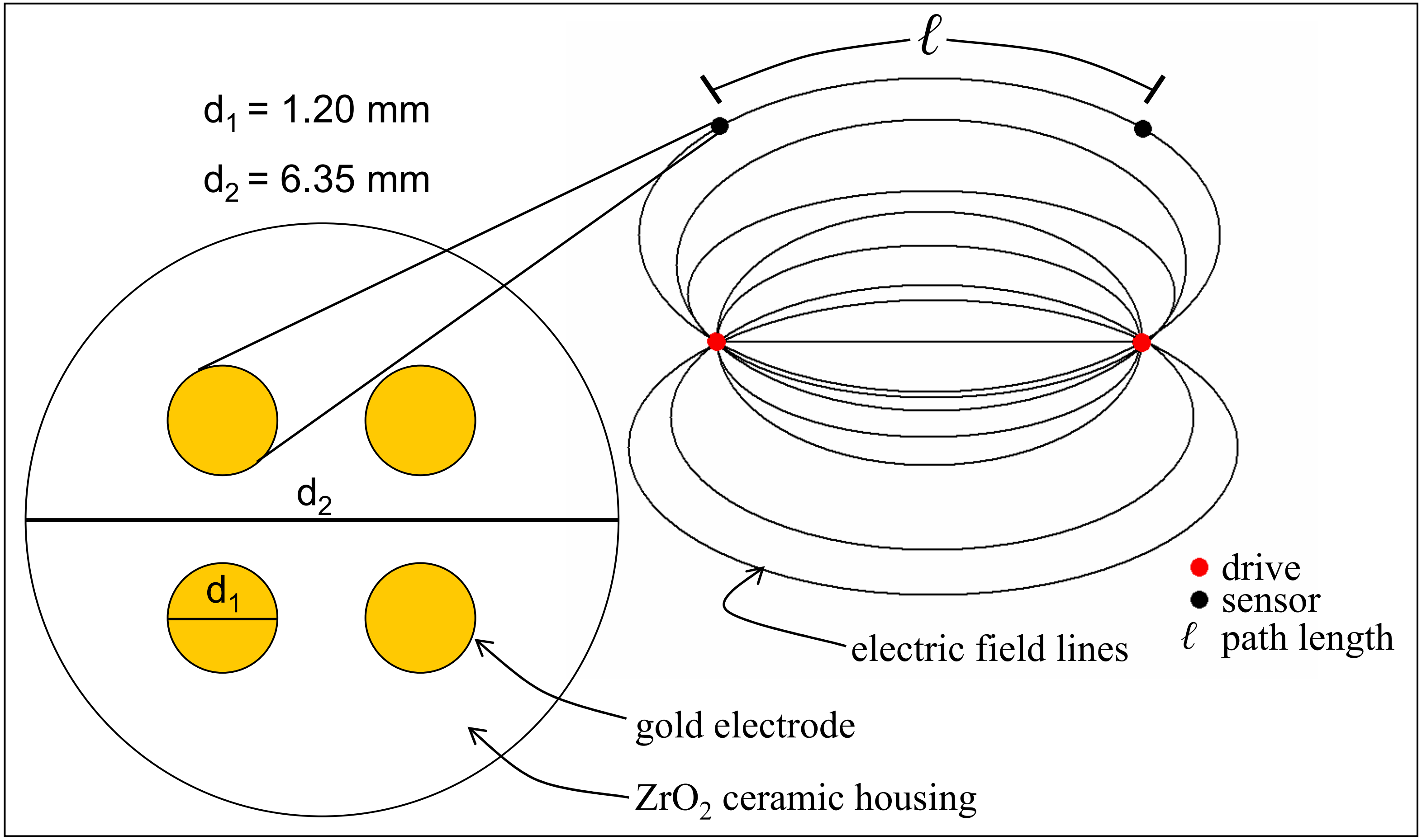
Reciprocal, R of resistance gives conductance, L

$$\frac{1}{R} = L = \frac{I}{V}$$

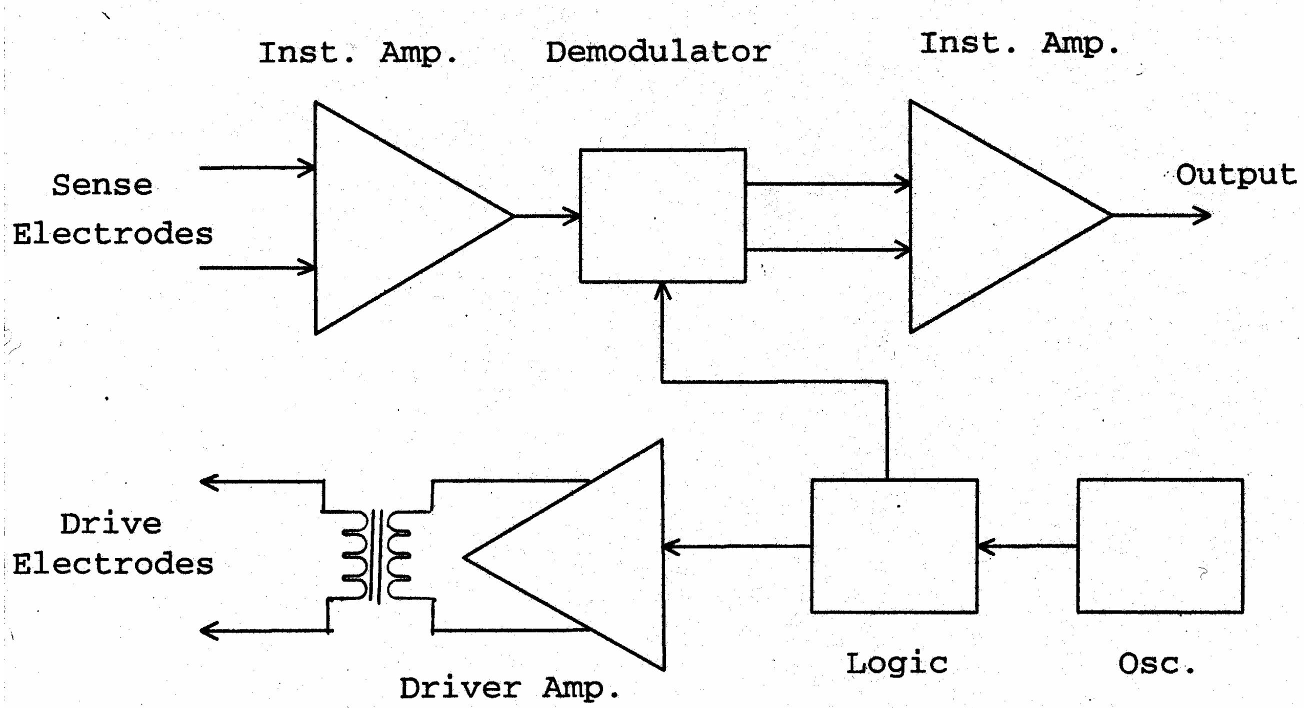
$$L \,\alpha\, \text{current}, I \quad \Rightarrow \quad I \,\alpha\, \text{density of charge carriers}$$

In solution, the charge carriers are ions, so condutcance is porportional to the concentration of ions, i.e. salt content

Schematic of probe tip and physics of the measurement



Block Diagram of Resistivity Electronics



Details

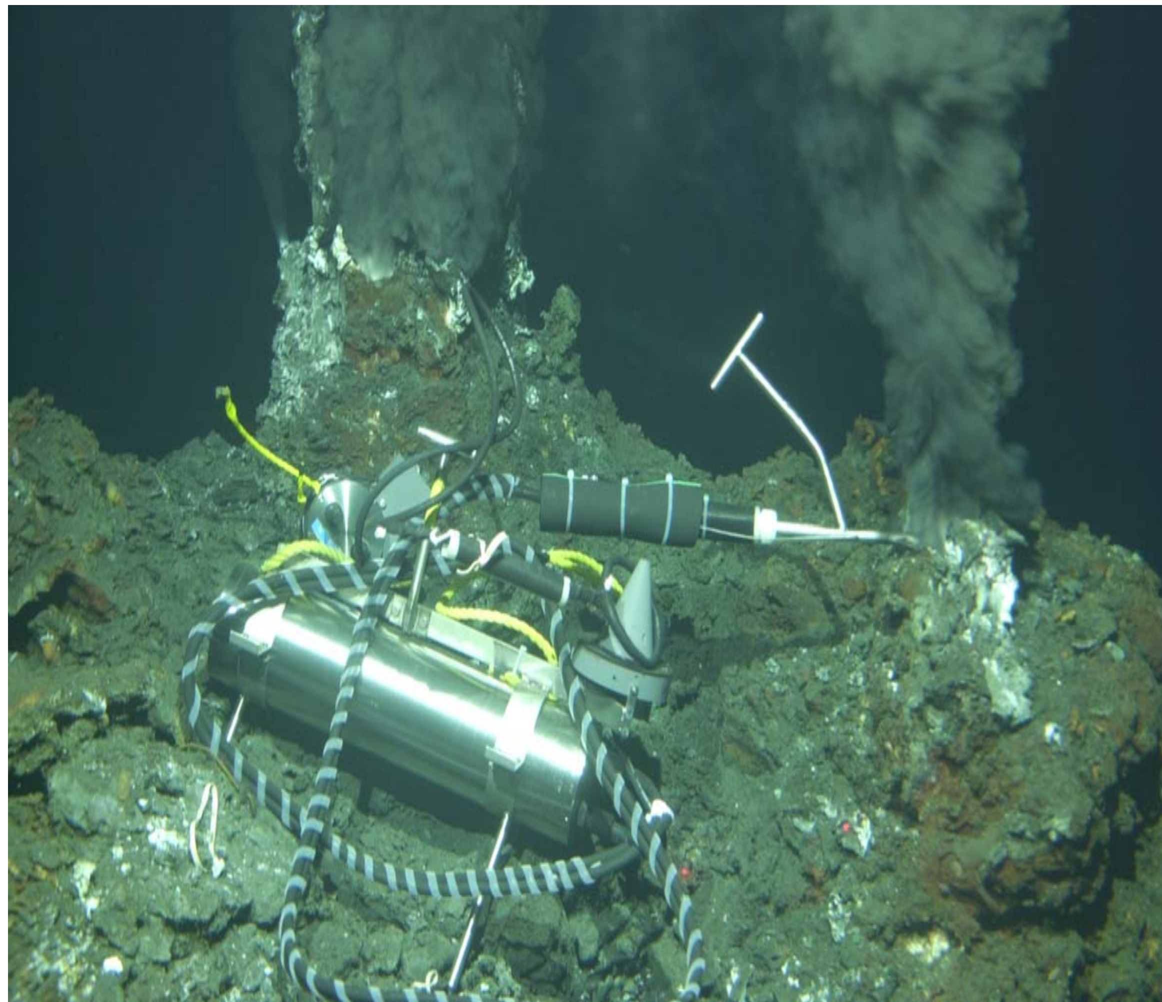
- Processor is an Onset TT8V2 (TxBasic)
- 8 Channels of 12 bit A/D
- 2 GB Flash Memory
- With 3 DD Li batteries and a 15 min duty cycle, the operational life is 660 days

Pictures of Instrument Components

Sensor Housing

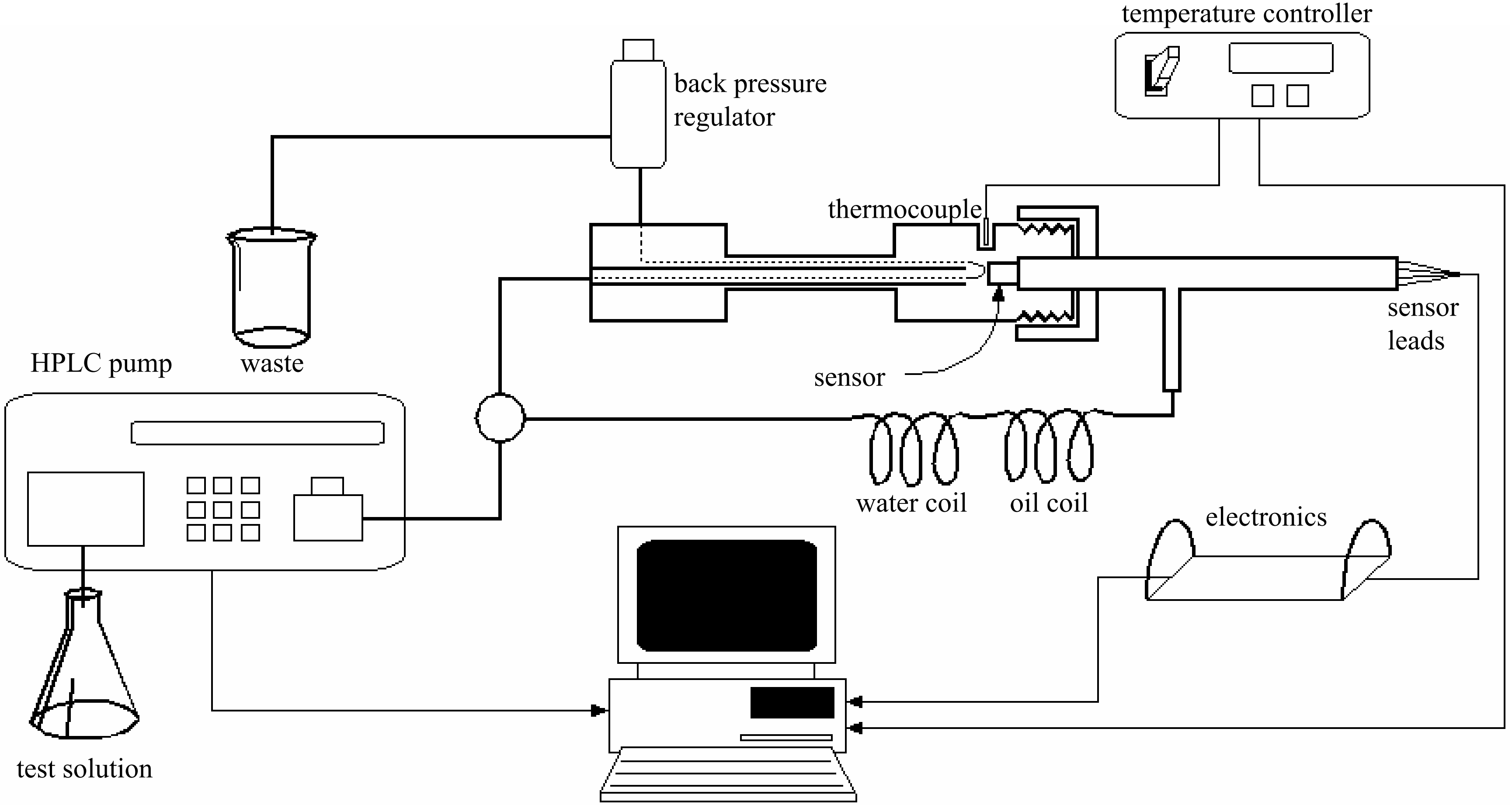
Sensor Face

Resistivity-temperature probe Deployment at Sully

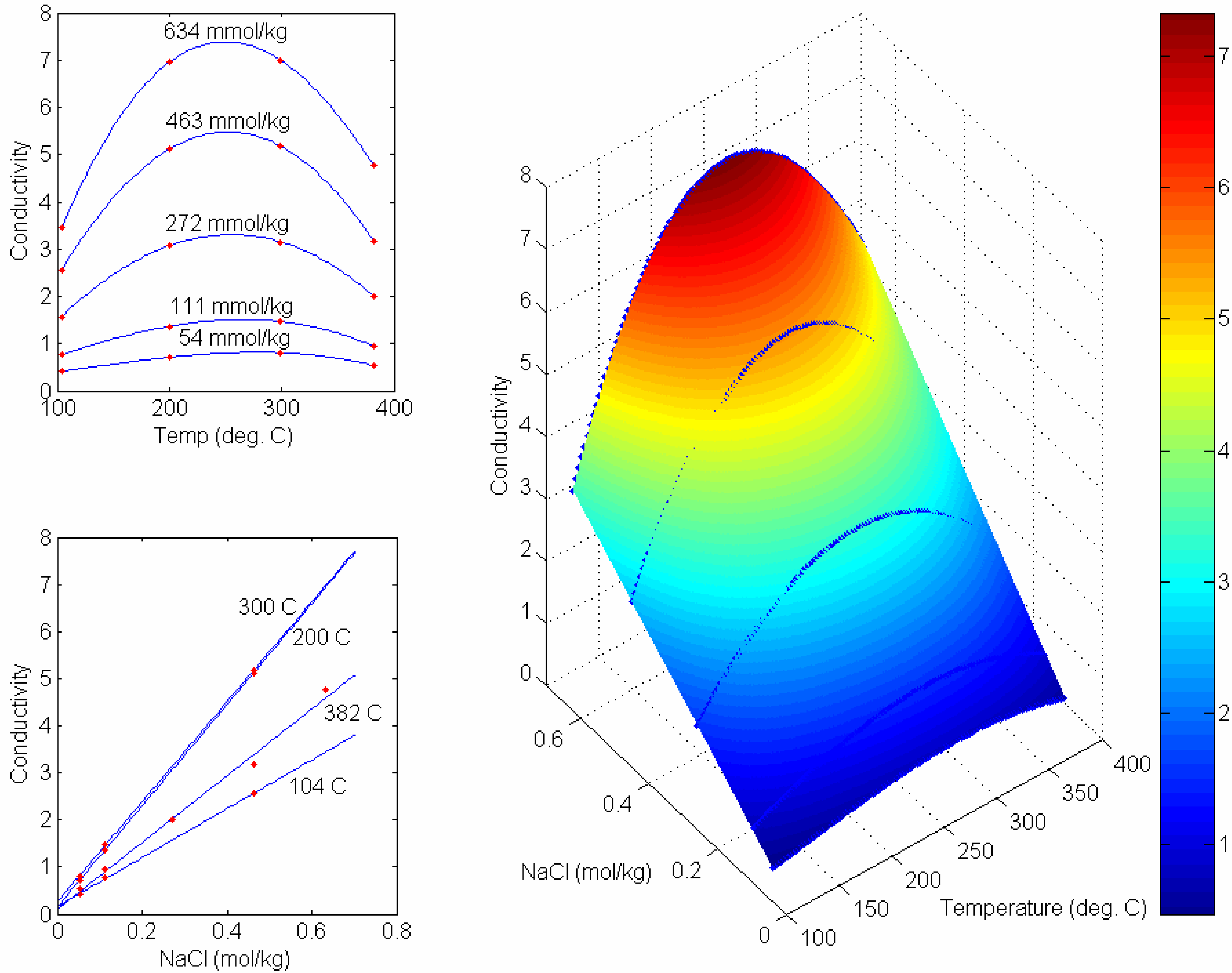



L1
Length : 136.0 um

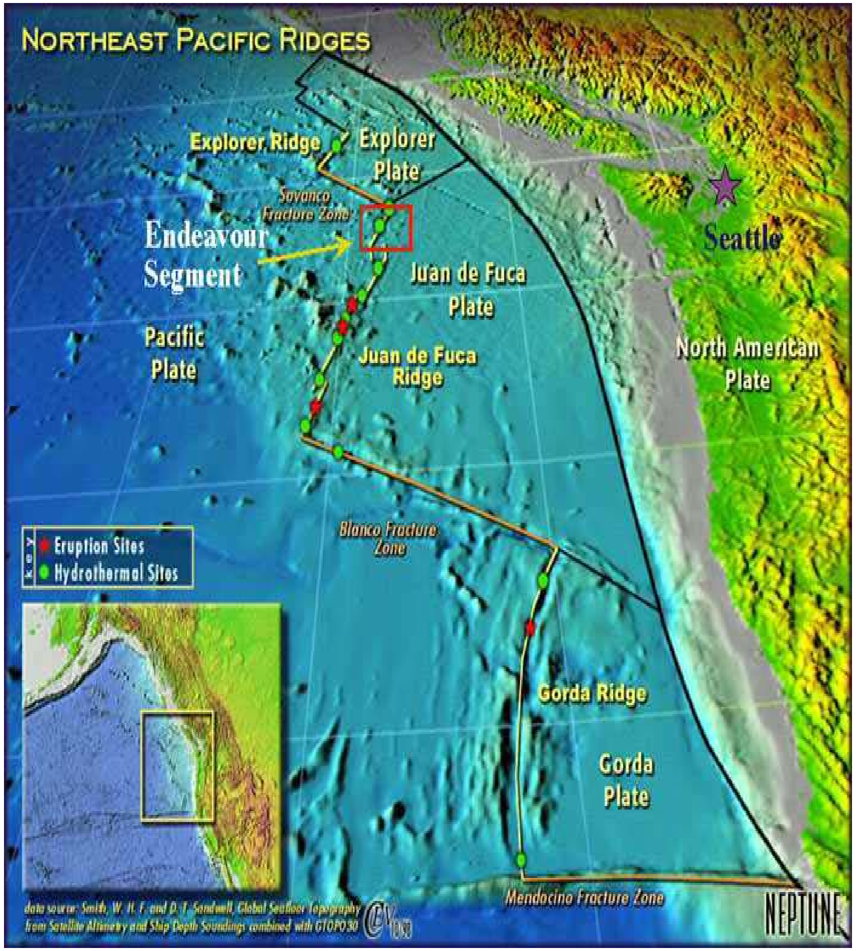
Experimental Apparatus



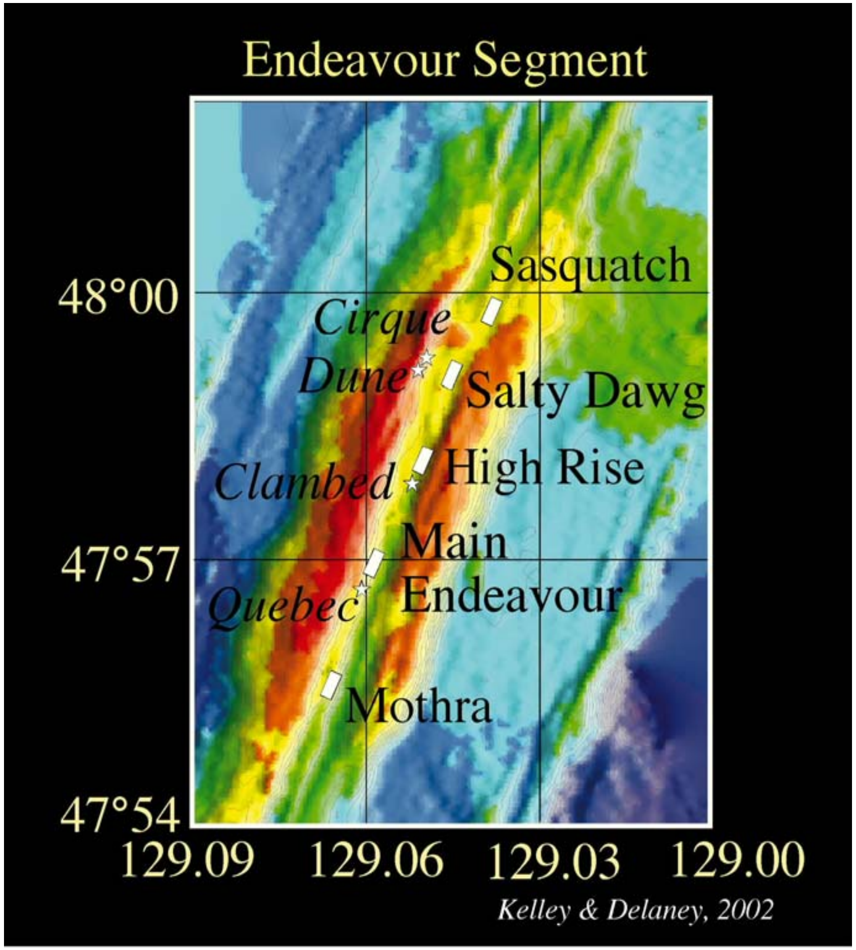
Sensor Calibration



Experimental Site: Main Endeavour Field

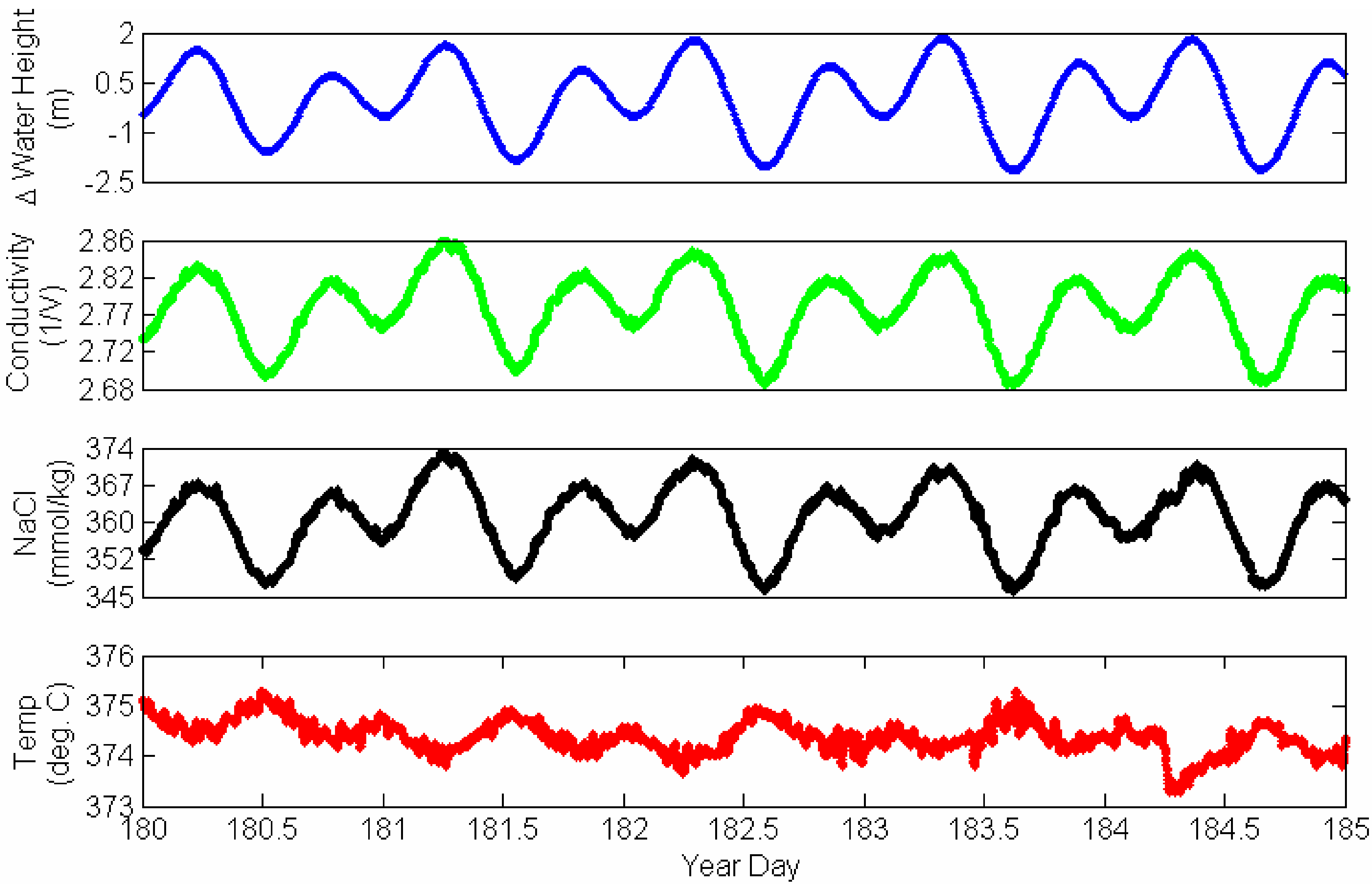


Courtesy of Neptune Website

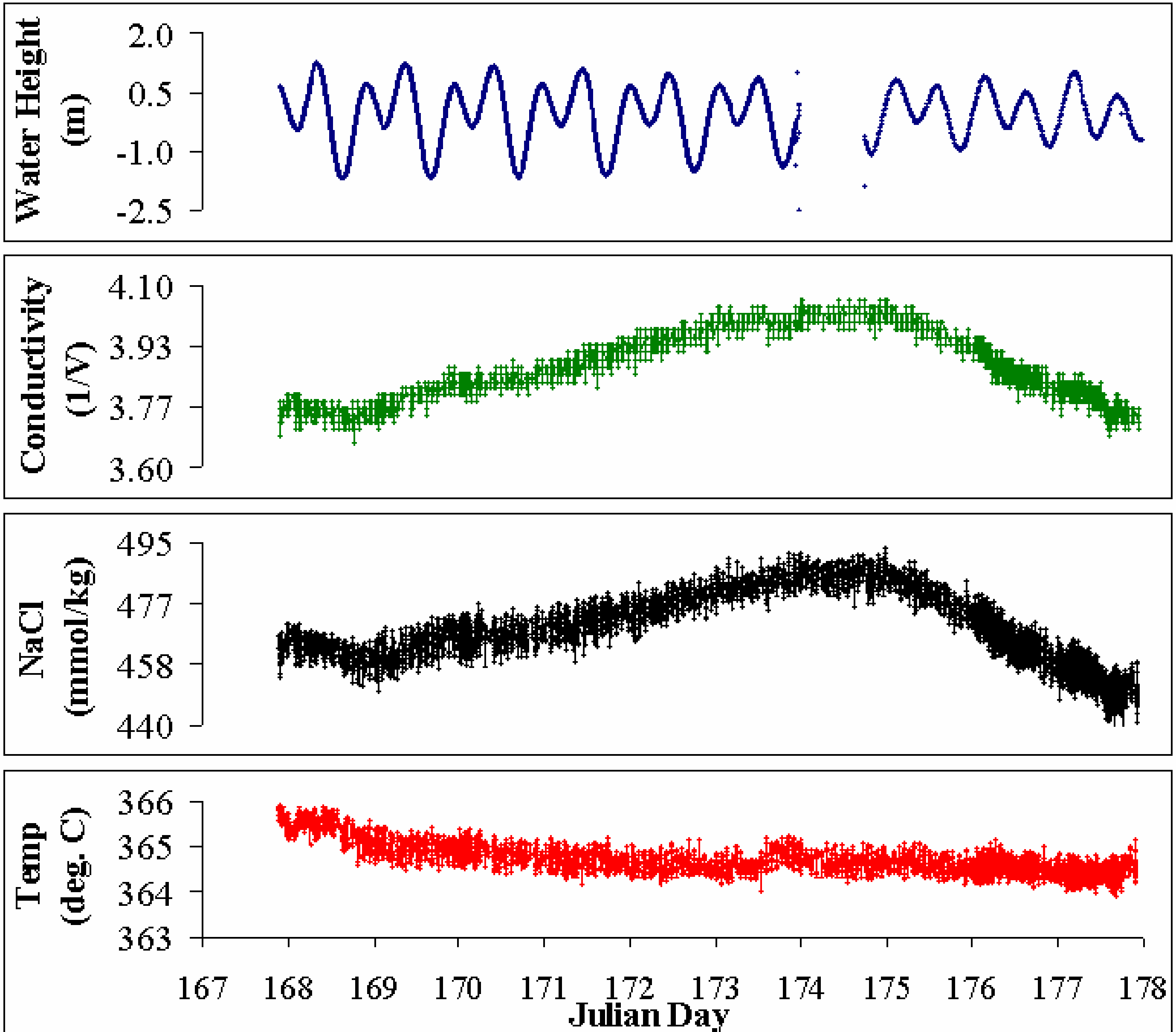


Kelley & Delaney, 2002

Milli-Q, Deployment #1, 5 Day Snapshot



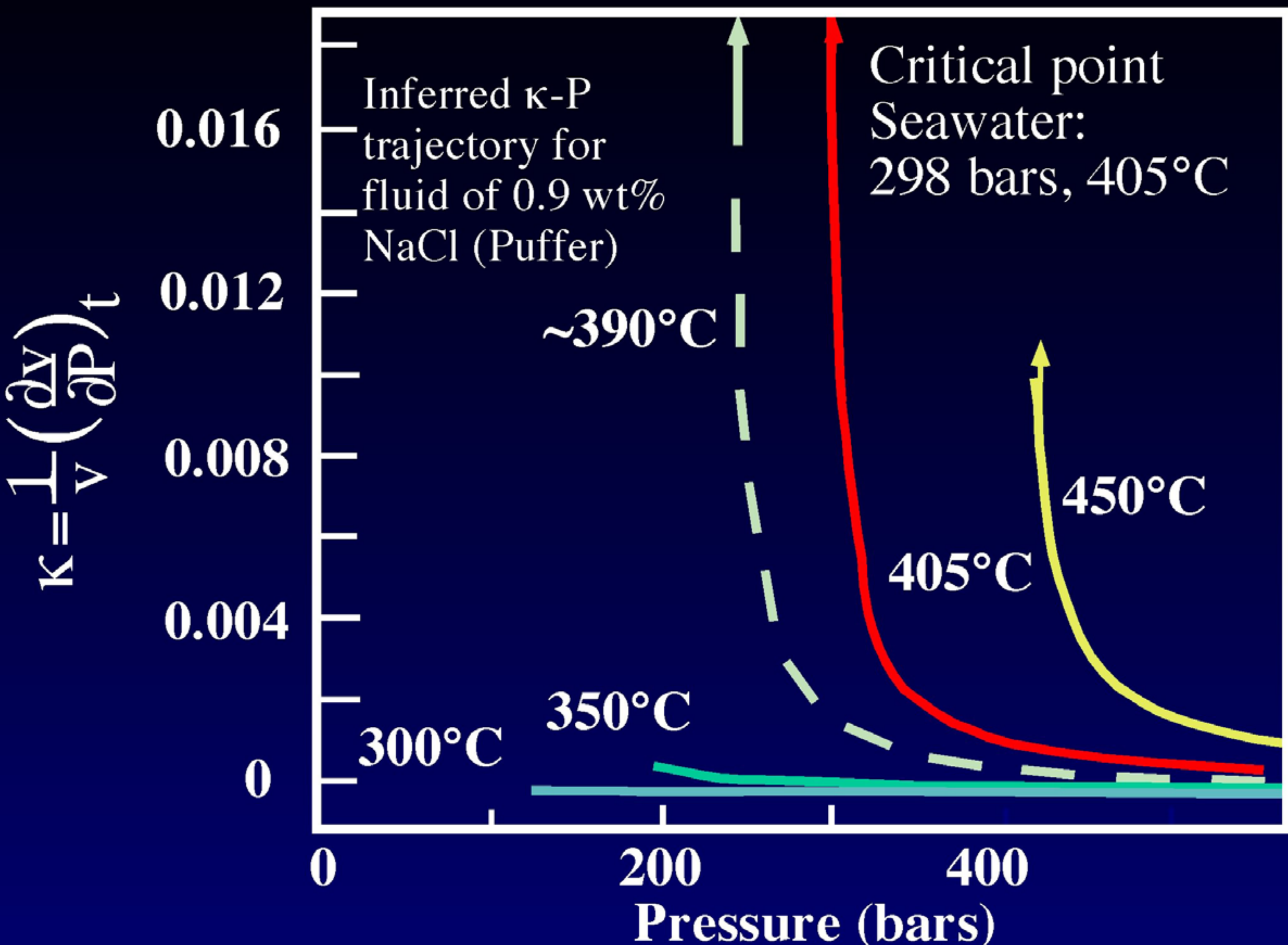
Grotto, Deployment #1



Possible reasons for oscillatory fluid properties

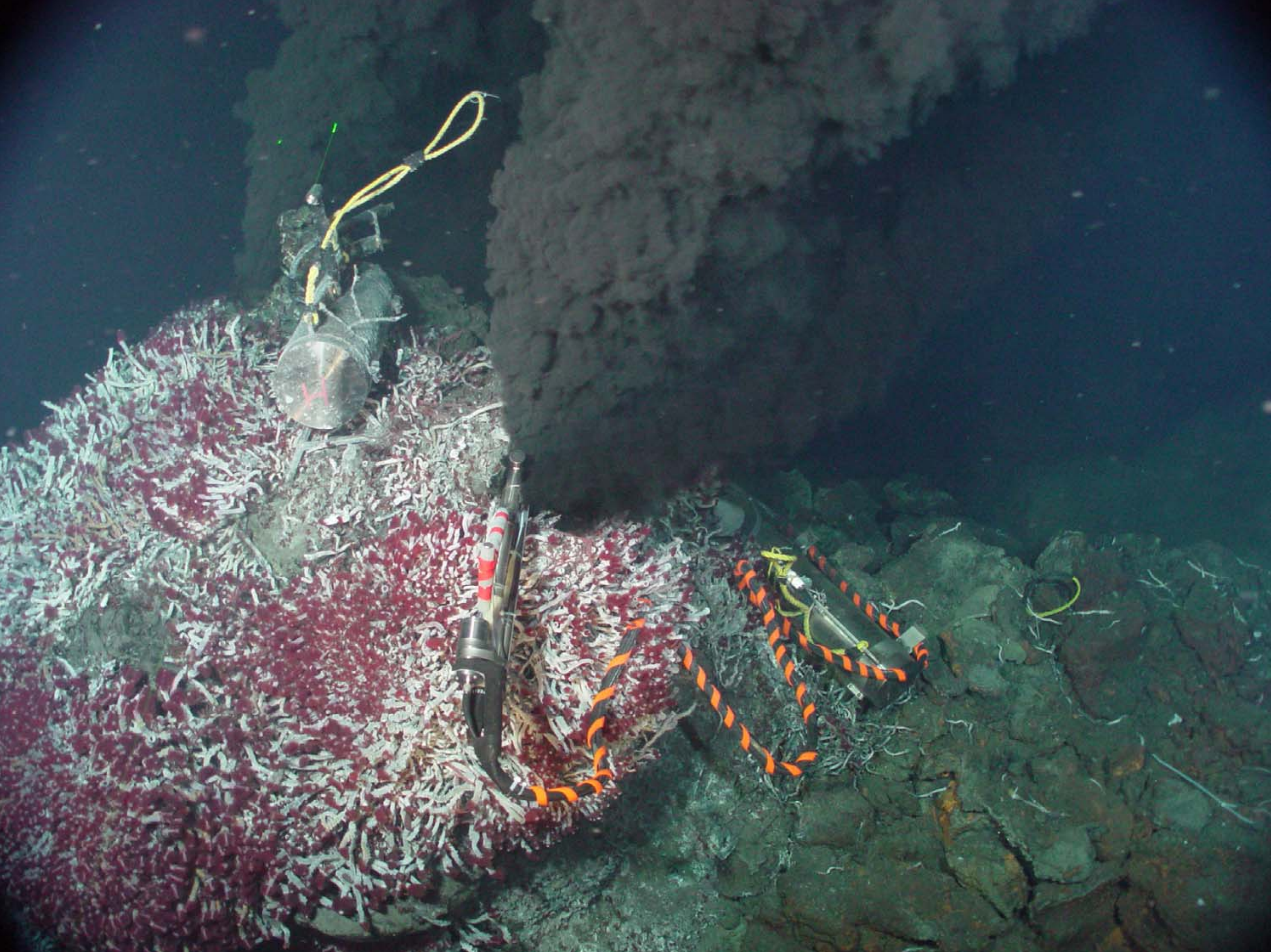
- Tidally modulated seawater entrainment (data do not support)
- Changing conditions of phase separation (no phase lag)
- Variable subsurface mixing of phase separated fluids (fits data best)

Isothermal compressibility (κ)



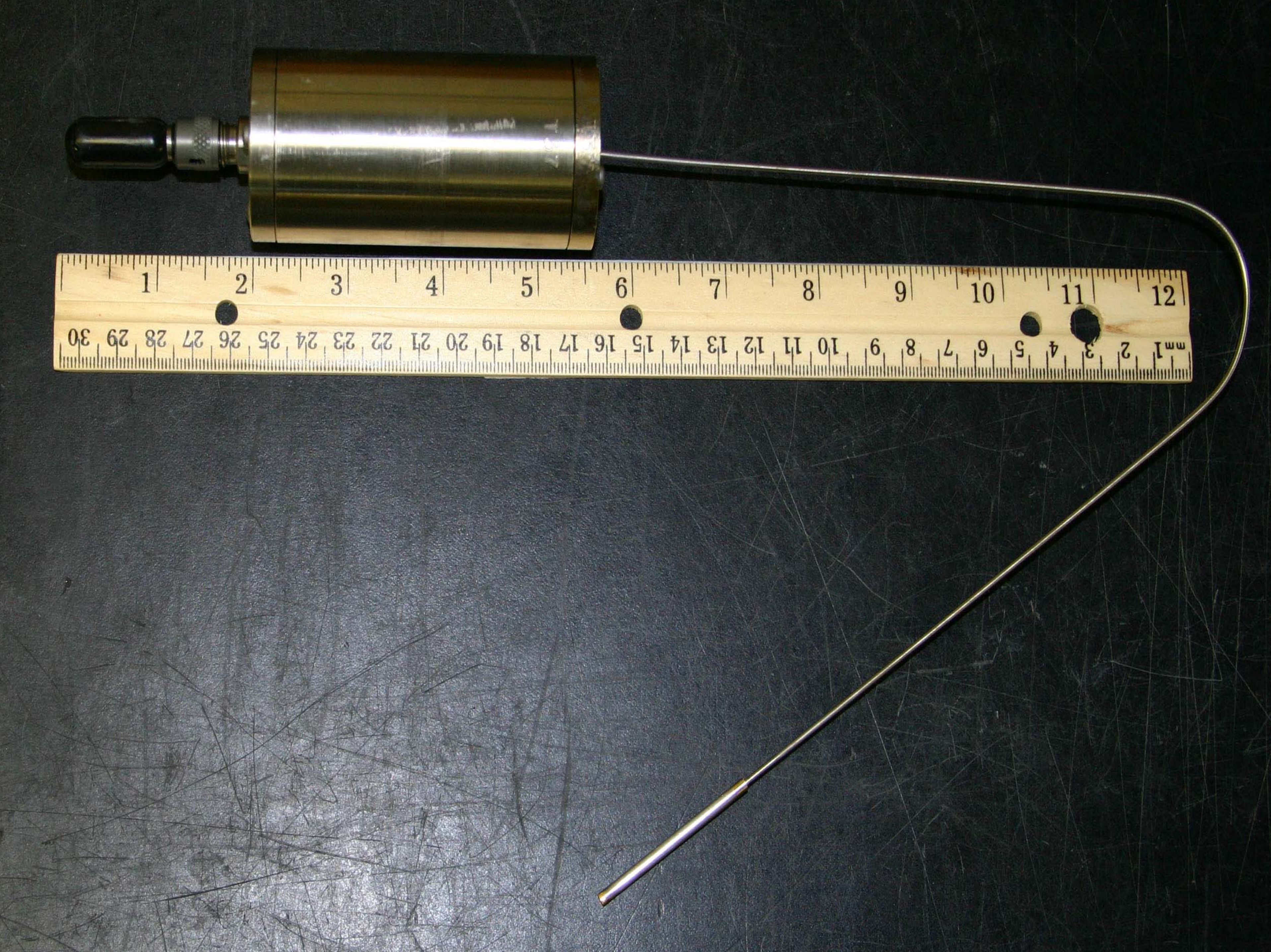
The Juan de Fuca Keck Experiment

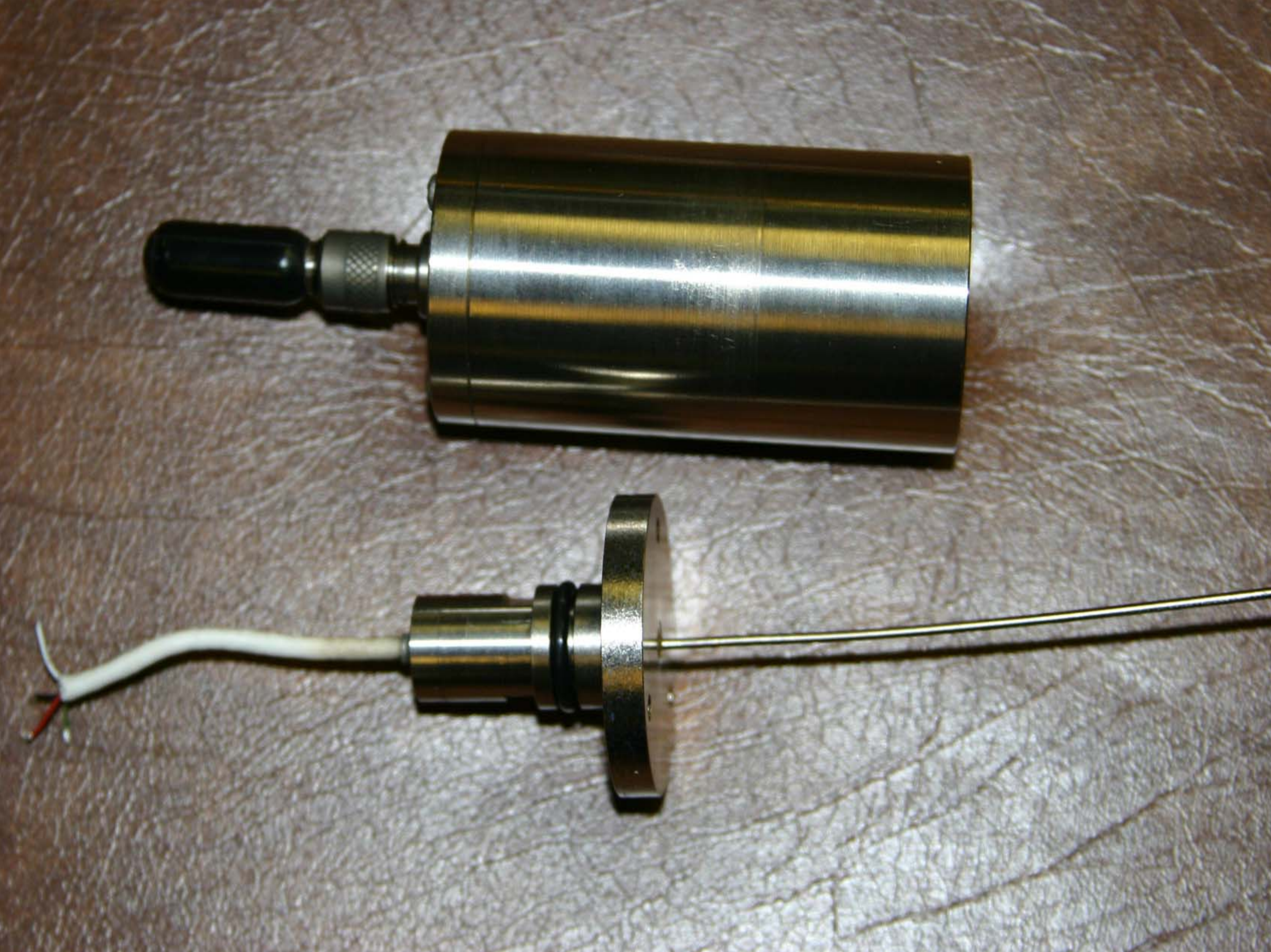
- Nested Seismic Network
- Time-Series Water Samplers
- Resistivity/Temperature Sensors
- Sulfide Chimney Microbial Incubators
- “Real-Time” Instruments at Nootka

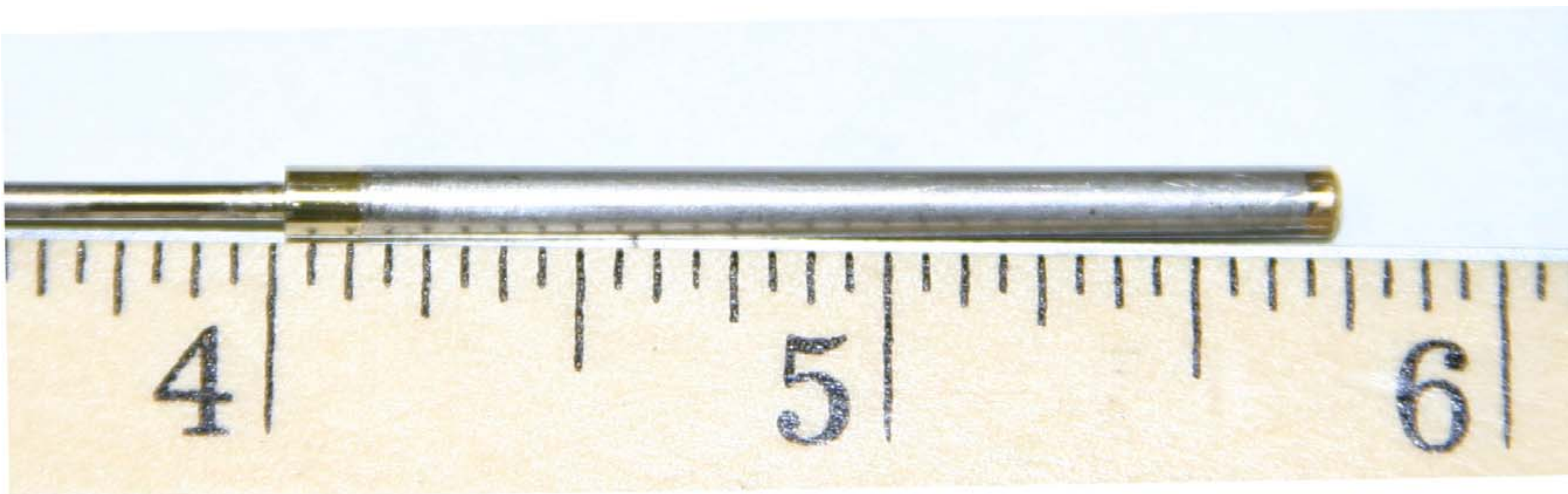


H_2 Sensor Components

- Tubular Au/Pd (50/50) Membrane
- Porous Ceramic Support
- Ti Capillary Tube
- Entran Pressure Sensor (drift - 0.4%/yr)



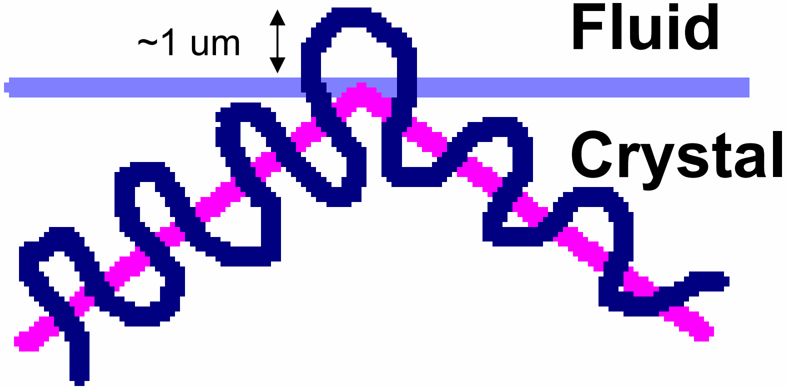



4
5
6

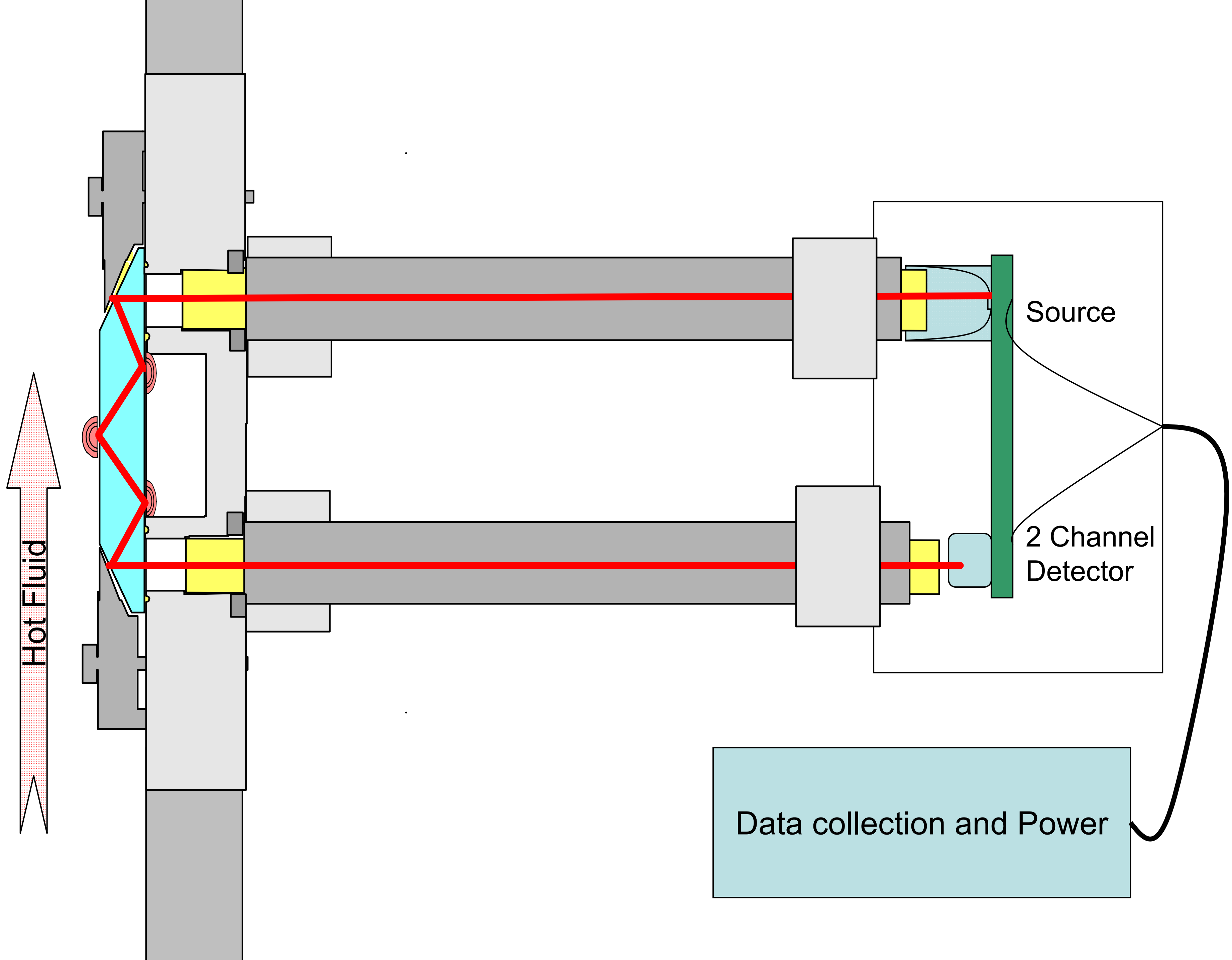
Instruments for CO_2 Measurement

- ATR – Infrared Spectroscopy
- MEMS Gas Chromatography

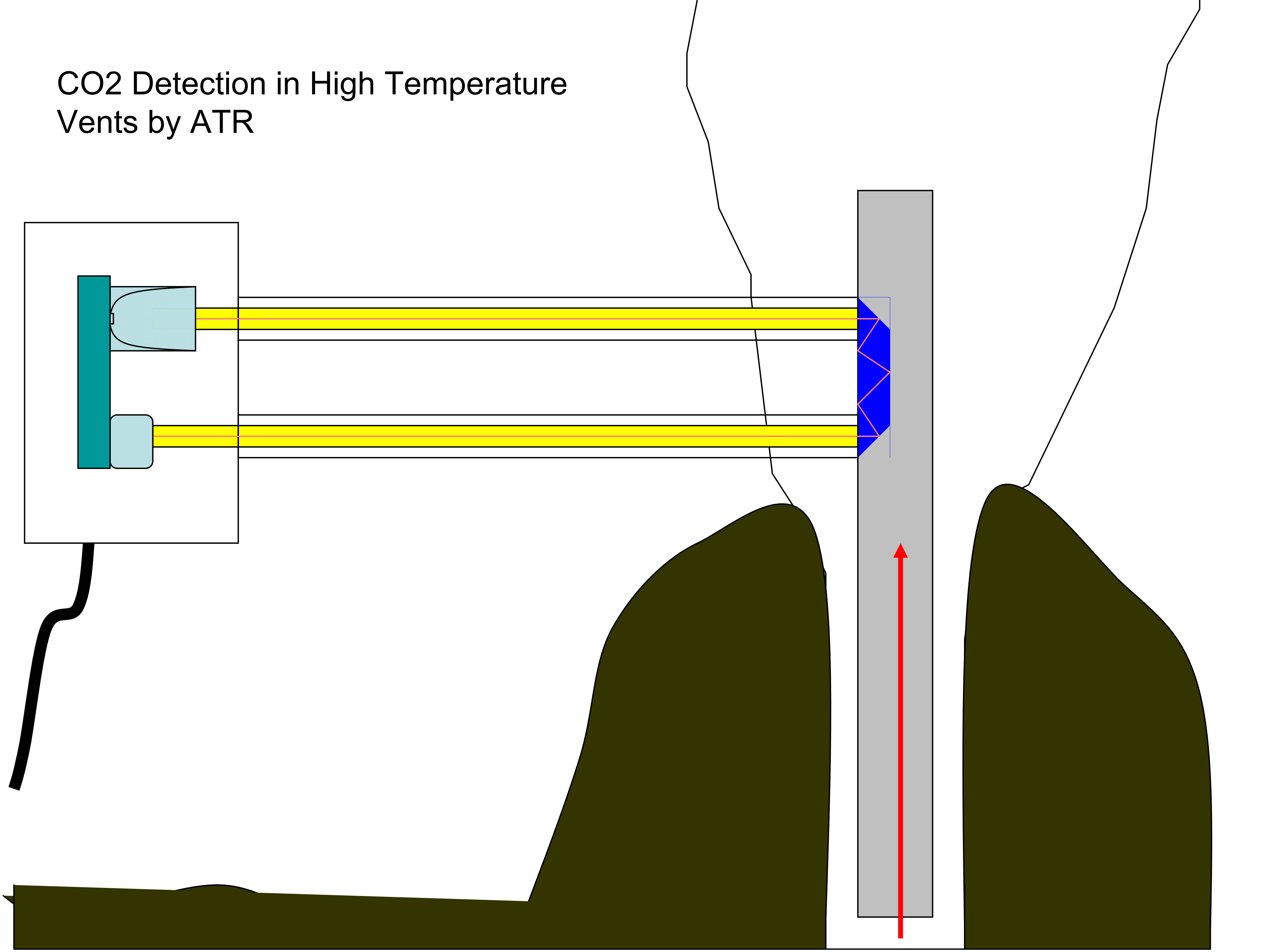
Attenuated Total Reflection (ATR)



- Penetration depth is dependant on wavelength, angle of incidence and refractive index difference
- Attenuation at any wavelength is proportional to concentration of absorbing substance (CO_2) in the fluid
- Physical effects can be compensated using a reference wavelength


Source
2 Channel
Detector
Hot Fluid
Data collection and Power

CO2 Detection in High Temperature Vents by ATR



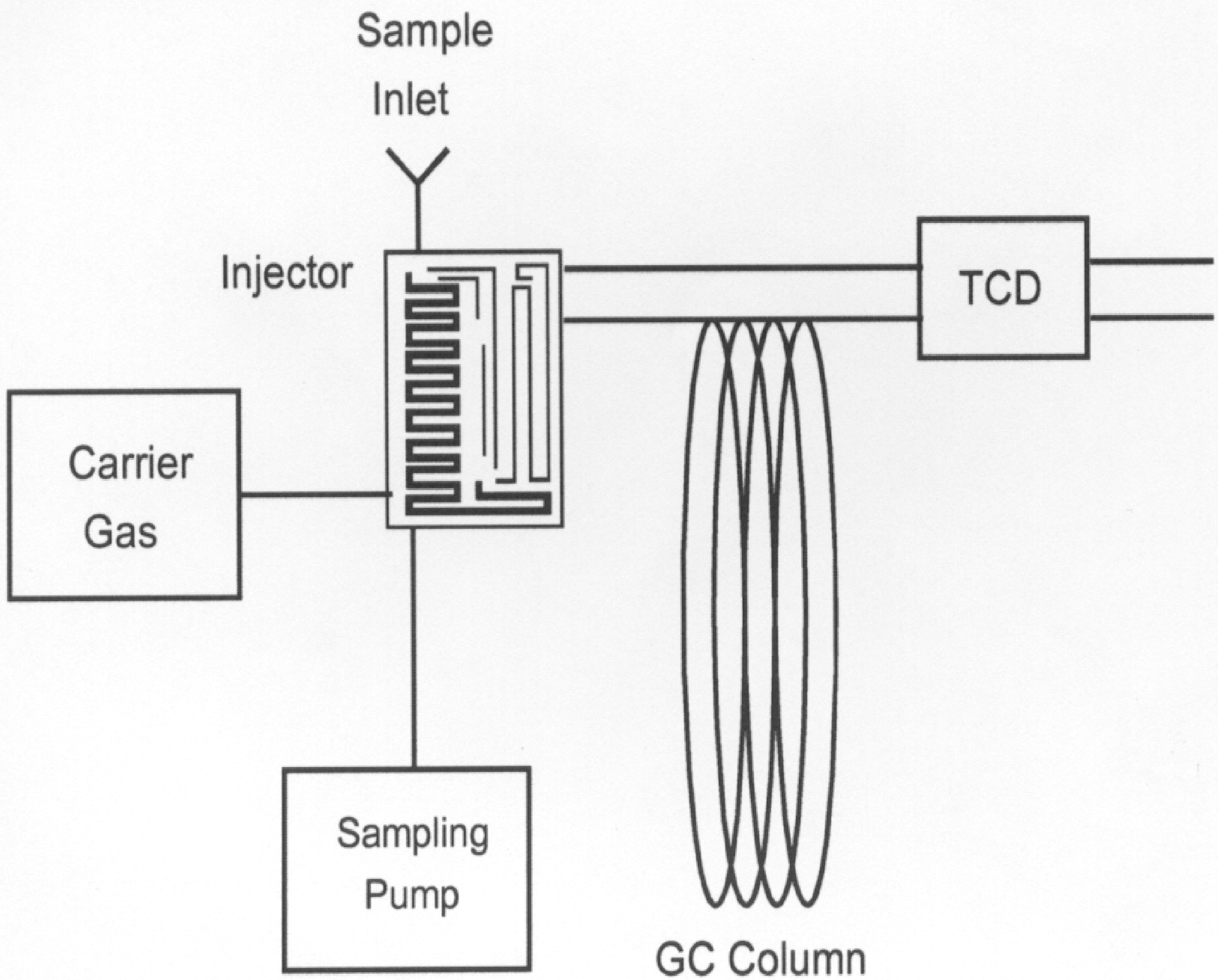
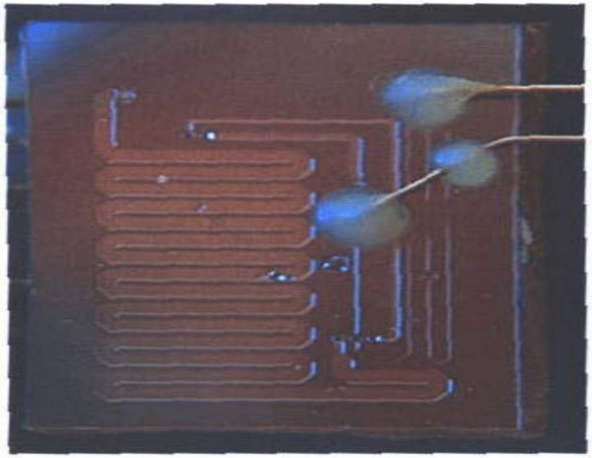


Figure 1. Overview of MEMS-based micro-gas chromatograph (see text).



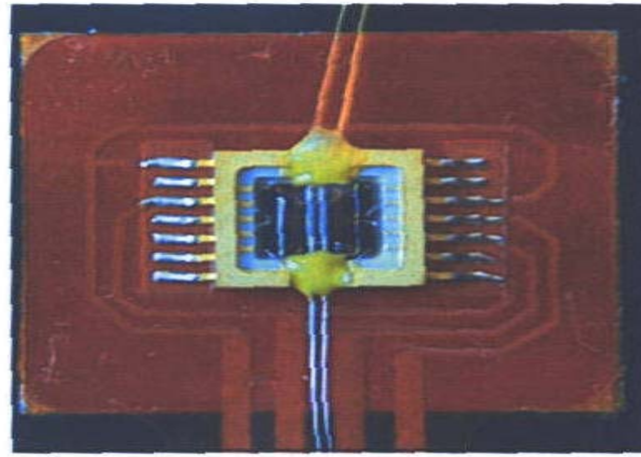


Figure 2. (a) Silicon micro-machined GC injection valve and (b) thermal conductivity detector.

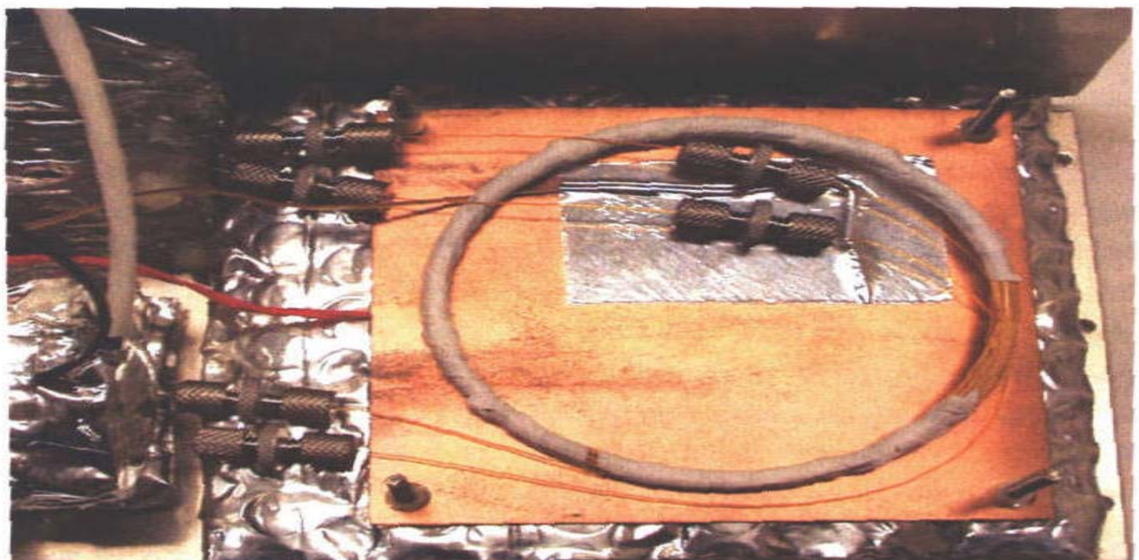
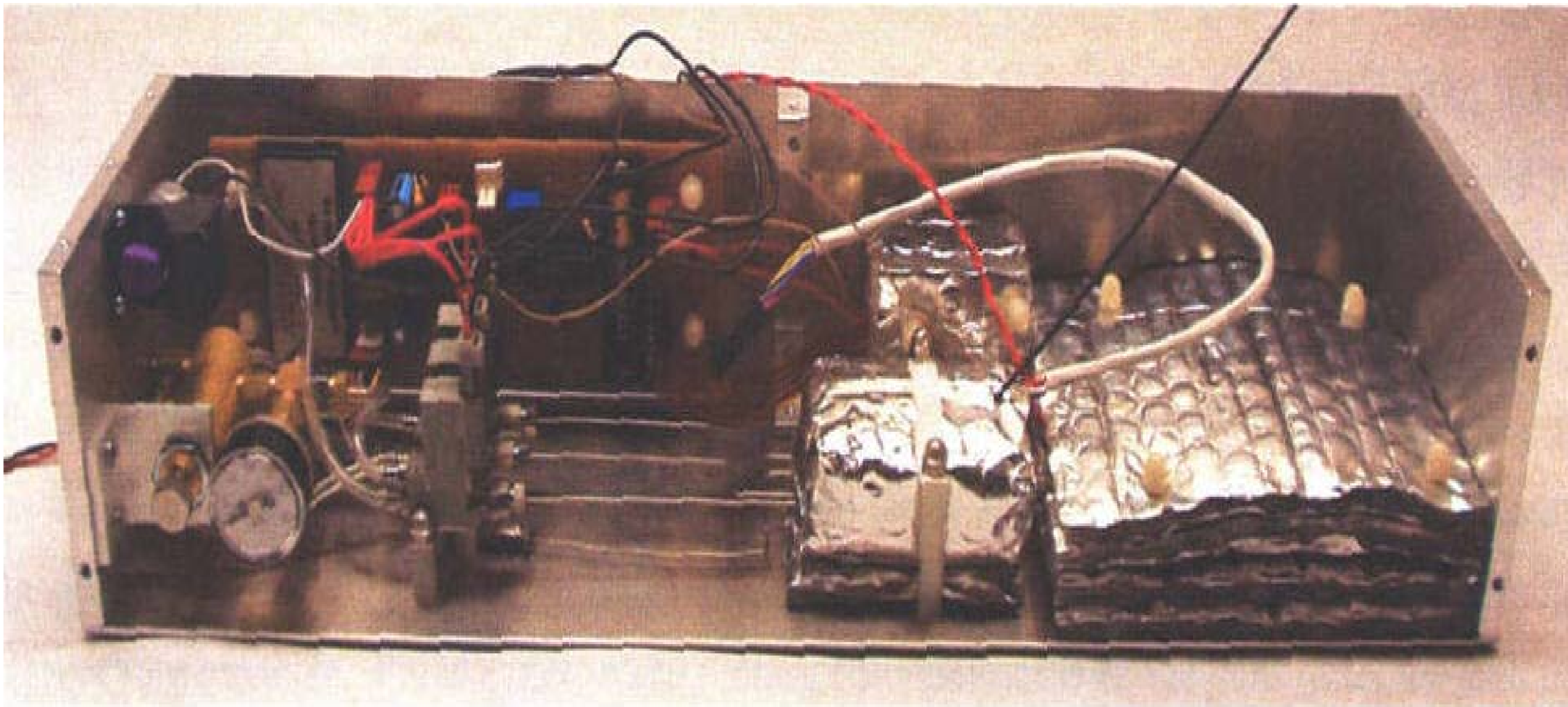


Figure 3. GC column assembly (see text).



Conclusions

- We have an instrument to measure chloride which has been calibrated and successfully utilized in high temperature fluids
- Data collected by these instruments exhibits strong correlations with tidal changes in seafloor pressure at some vents
- Analysis of this data suggests a subsurface mixing regime involving critical or near critical fluids depleted in chloride with respect to seawater and cooled brines enriched in chloride
- Further work must be done to constrain the parameters of the proposed mixing
- We await a major seismic event
- Much work remains to be done on both H_2 and CO_2 sensors