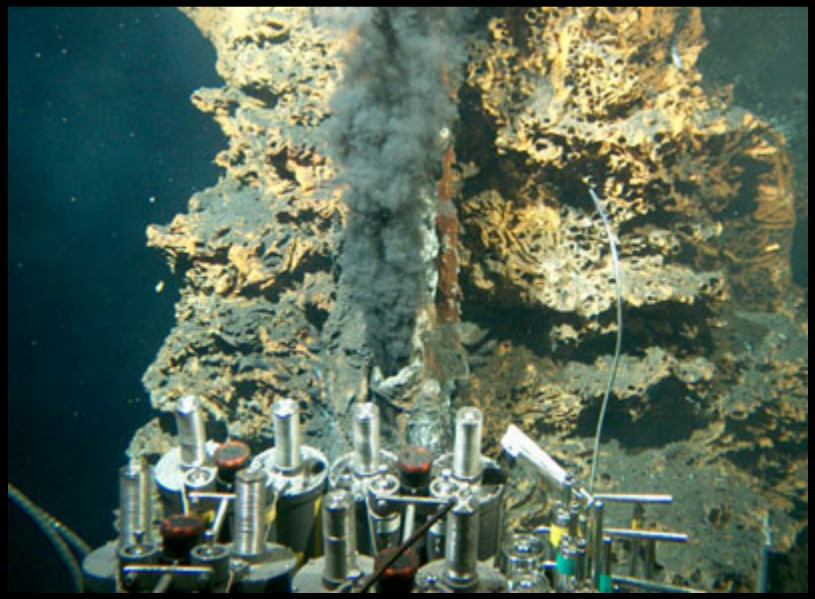
In-situ chemistry of seafloor hydrothermal vent fluids

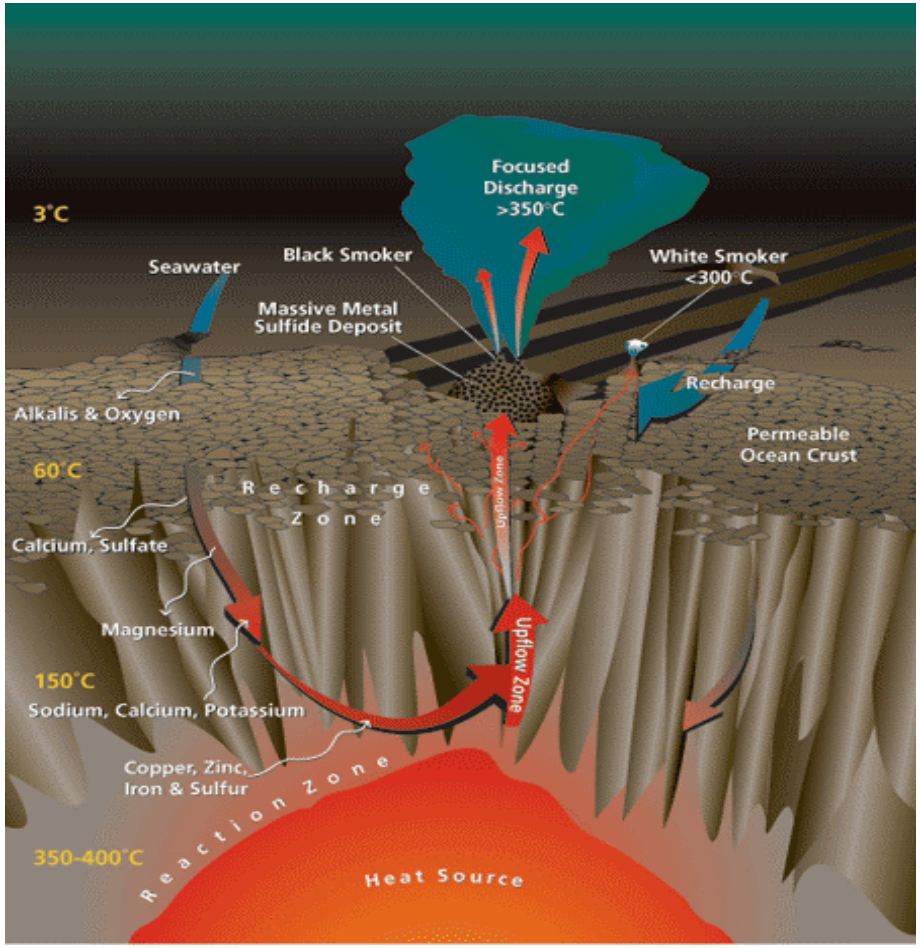
W.E. Seyfried, Jr., Kang Ding and Zhong Zhang
Department of Geology and Geophysics
University of Minnesota

Hydrothermal Processes at MOR's



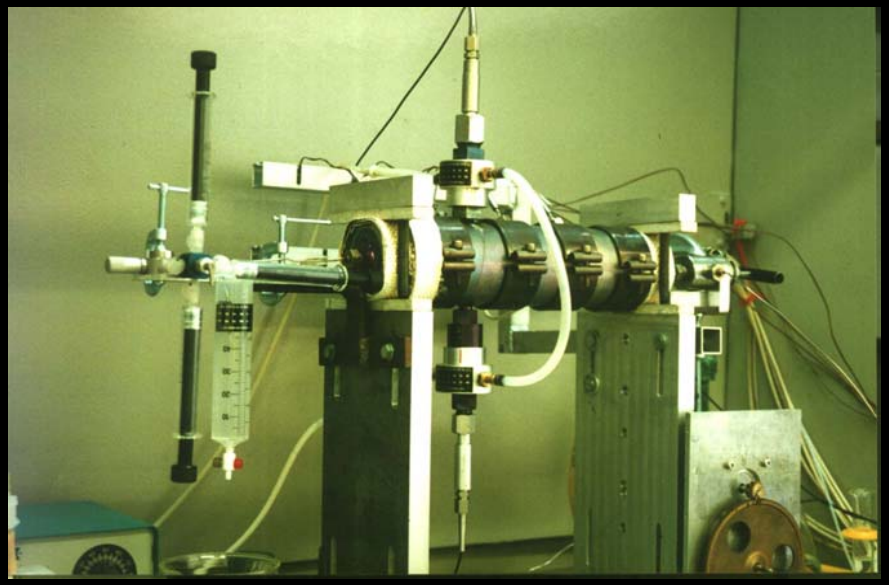
- ~25% of Earth heat loss
- Temperatures in excess of 388°C at vent
- Generally acidic measured pH
  - Non-conservative
- Moderately reducing
  - Non-conservative
- Critical need for *in-situ* measurements for pH and redox

Subseafloor Hydrothermal System



S. E. Humphris (WHOI)

Ti flow-through vessel for sensor development at high temperature and pressure condition



pH Sensor

Ag | AgCl | Cl^-, H^+, H_2O | $ZrO_2(9\%Y_2O_3)$ | HgO | Hg

$$pH_{T,P} = \frac{F}{2.303RT}\left\{\Delta E^{\circ}_{cell} - \Delta E_{meas.}\right\} - \log\left(\frac{aCl^-}{aH_2O^{1/2}}\right)$$

Dissolved H_2 Sensor

Pt or Au | H_2, H^+, H_2O | $ZrO_2(Y_2O_3)$ | HgO | Hg

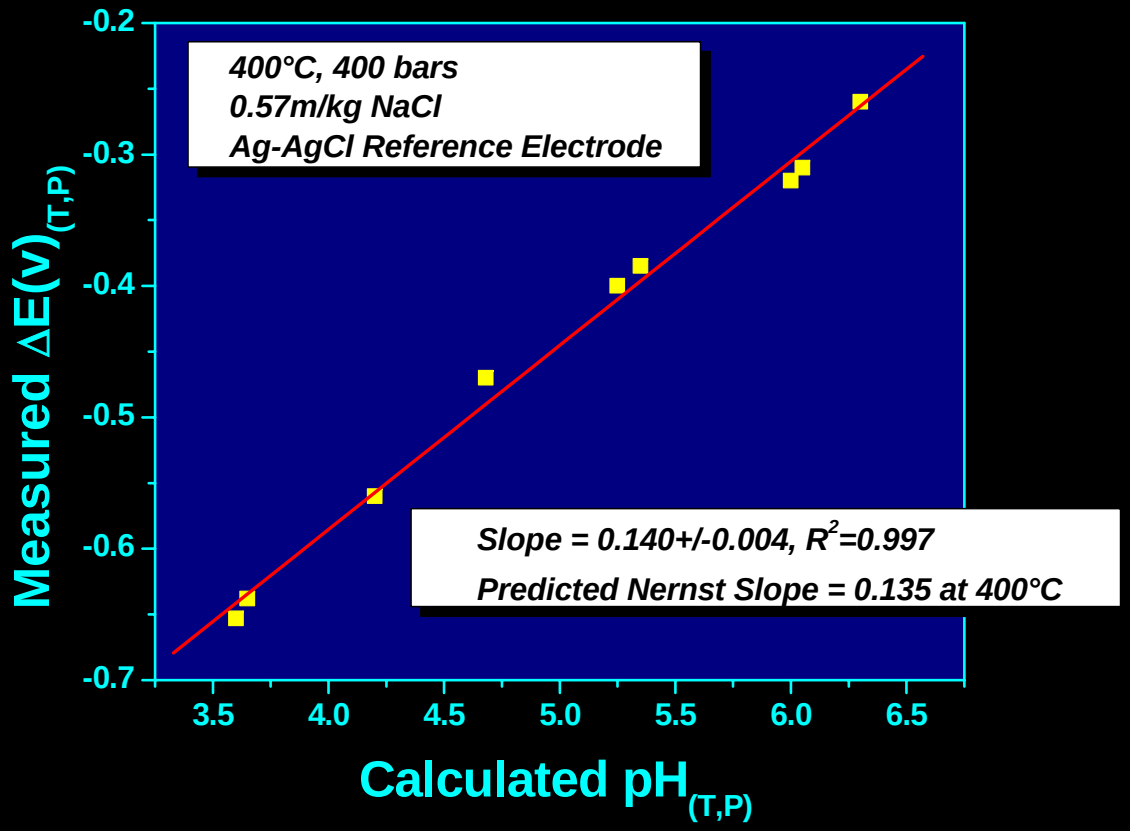
$$\log aH_2 = \frac{2F}{2.303RT}\left\{\Delta E_{meas.} - E^{\circ}_{cell}\right\} - \log\left(\frac{K_{H2}}{aH_2O}\right)$$

Dissolved H_2S Sensor

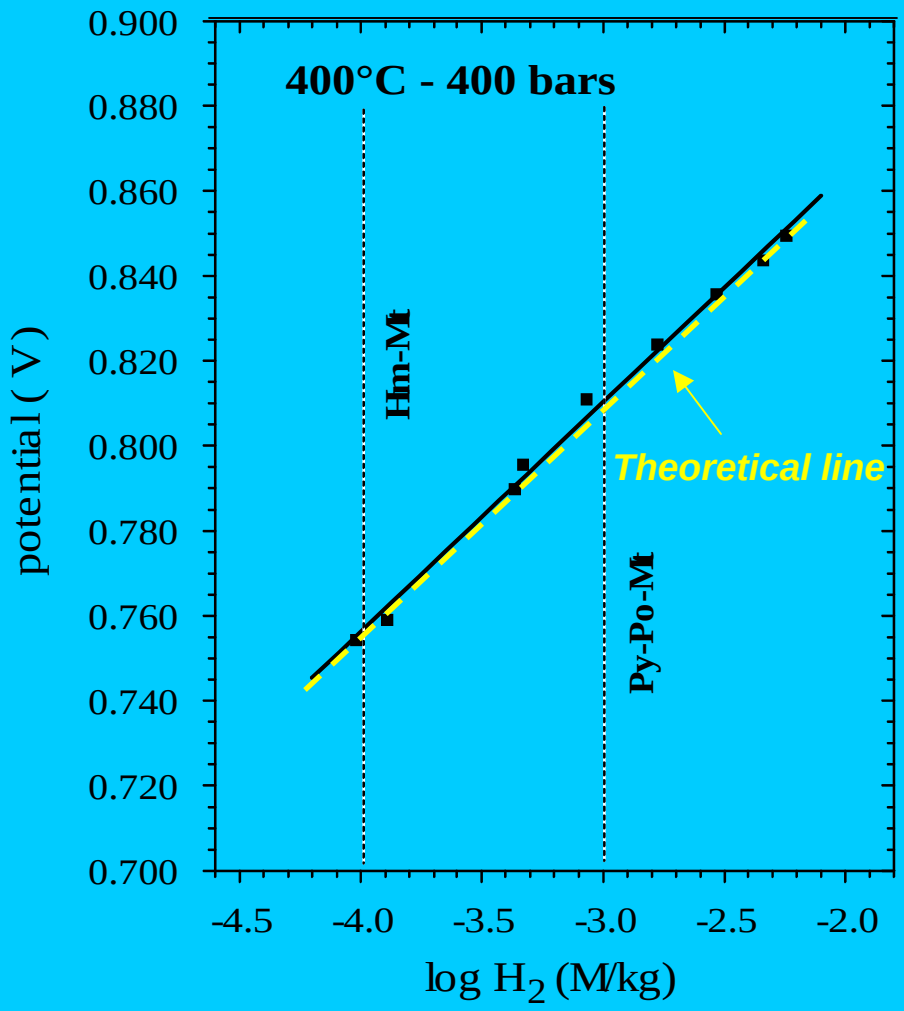
M | M_xS | H_2S, H^+, H_2O | $ZrO_2(Y_2O_3)$ | NiO | Ni

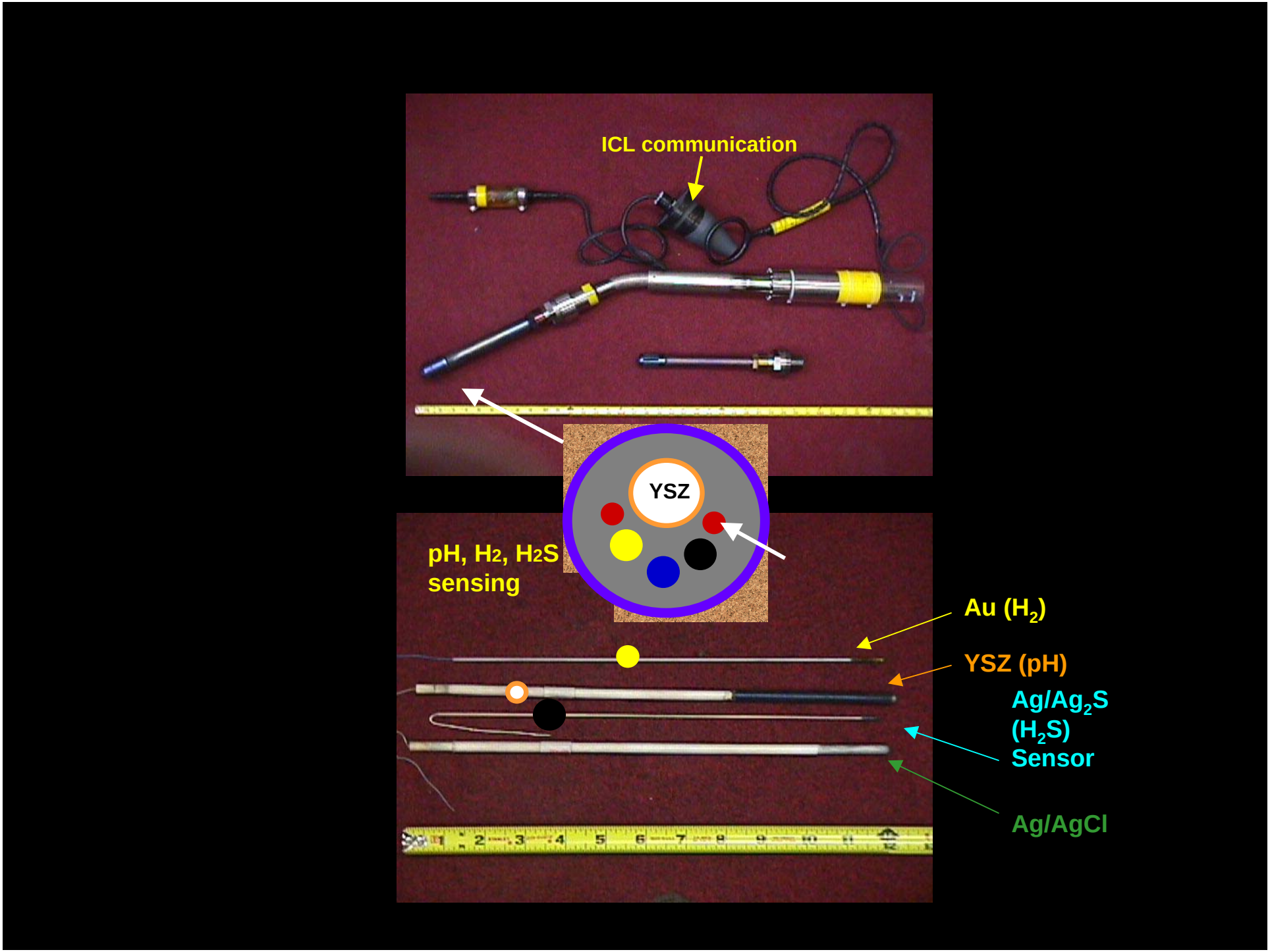
$$\log aH_2S = \frac{2F}{2.303RT}\left\{\Delta E_{meas.} - E^{\circ}_{cell}\right\} - \log\left(\frac{K_{H2S}}{aH_2O}\right)$$

Lab Measured Potential (YSZ) against Theoretically Predicted (HKF) pH(in-situ)

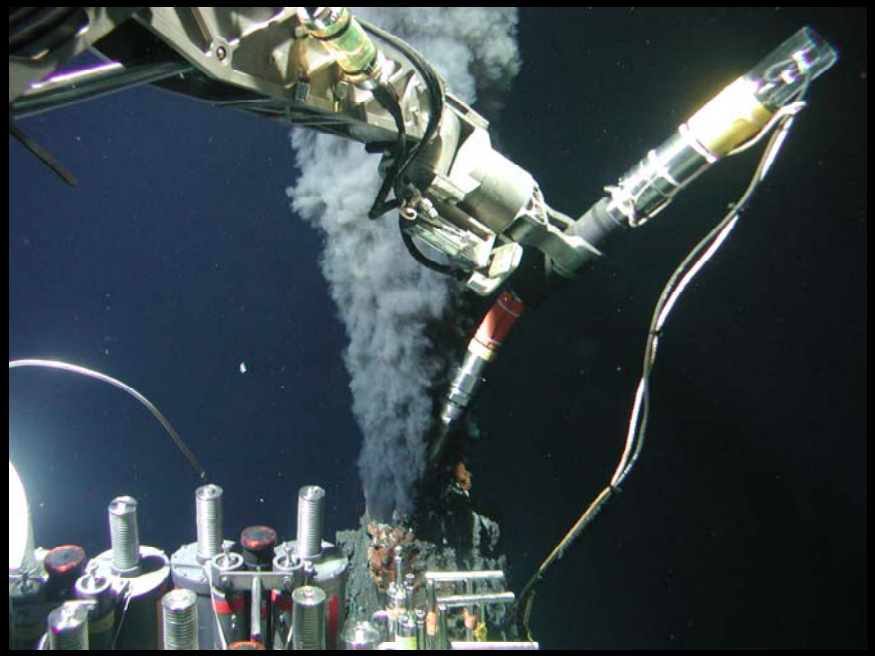


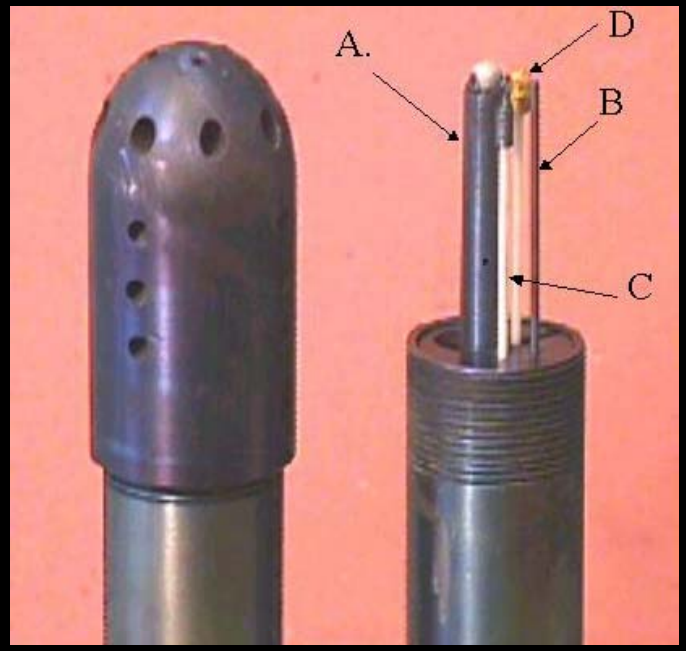
Experimental Calibration of YSZ-Au Sensor for H_2 Determination




ICL communication
YSZ
pH, H2, H2S sensing
Au (H2)
YSZ (pH)
Ag/Ag2S (H2S) Sensor
Ag/AgCl

Seafloor Deployment: Real Time

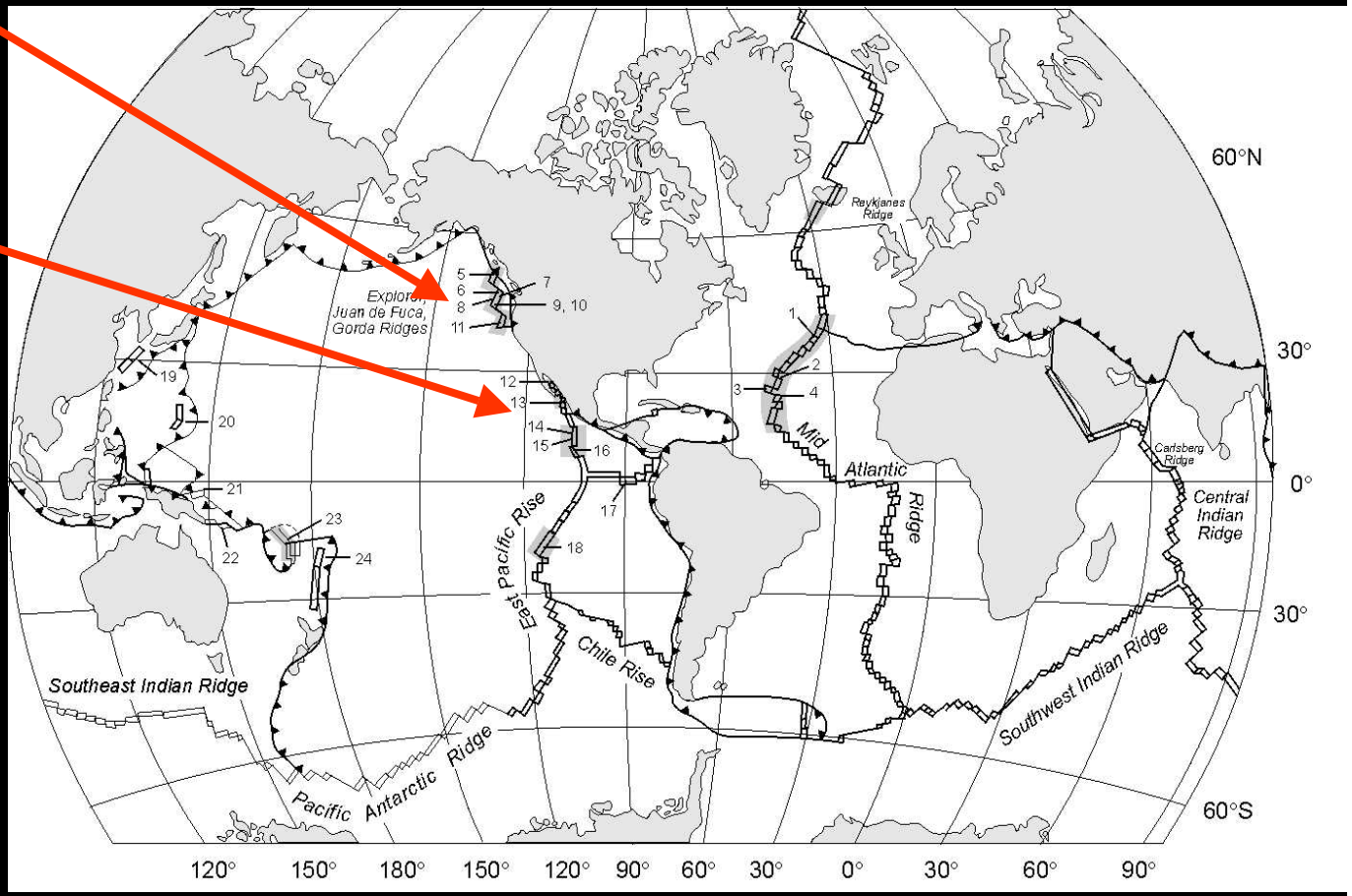




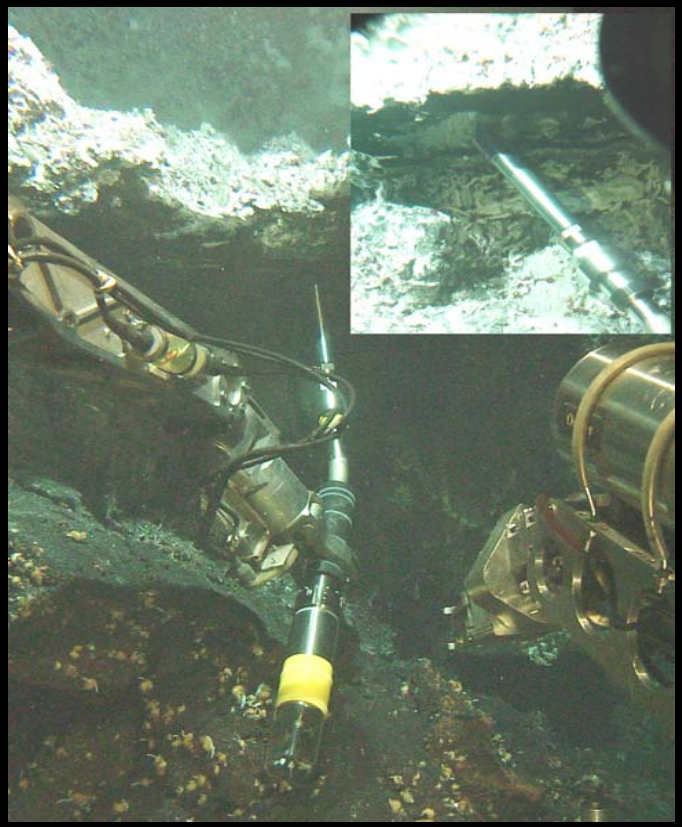
Chemical Sensor Studies of Hydrothermal Vents at Mid-Ocean Ridges

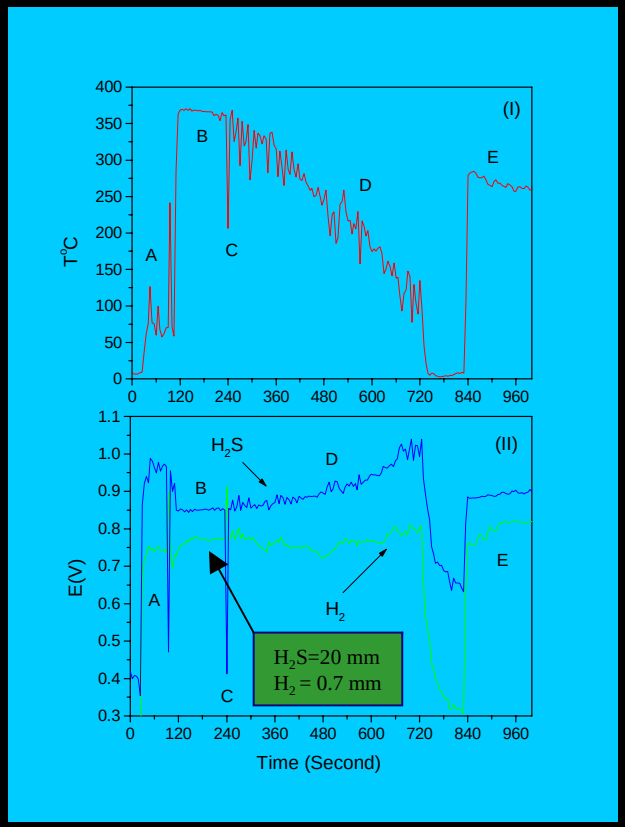
Main Endeavour Field, JDF

EPR, 9-10°N



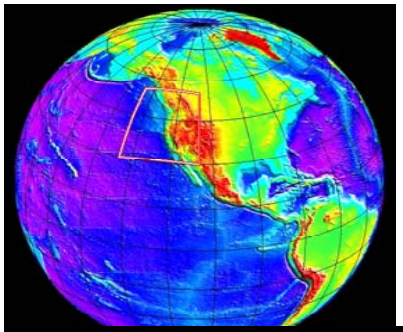
In-situ Measurements of H2 and H2S at MEF, JDF





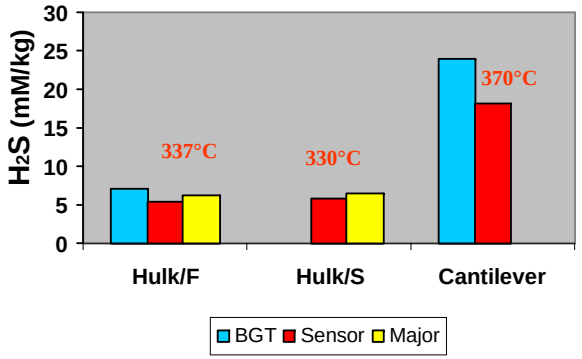
Ding et al. 2001

In-Situ Dissolved Gases at MEF- Comparisons with Conventional Measurement Techniques

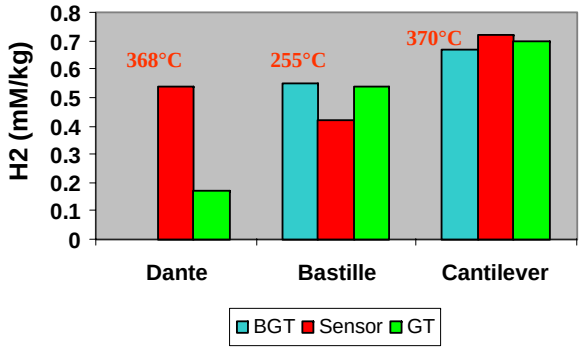


Endeavour vent field
Juan de Fuca Ridge

Comparison of dissolved H2S concentrations measured by using different methods

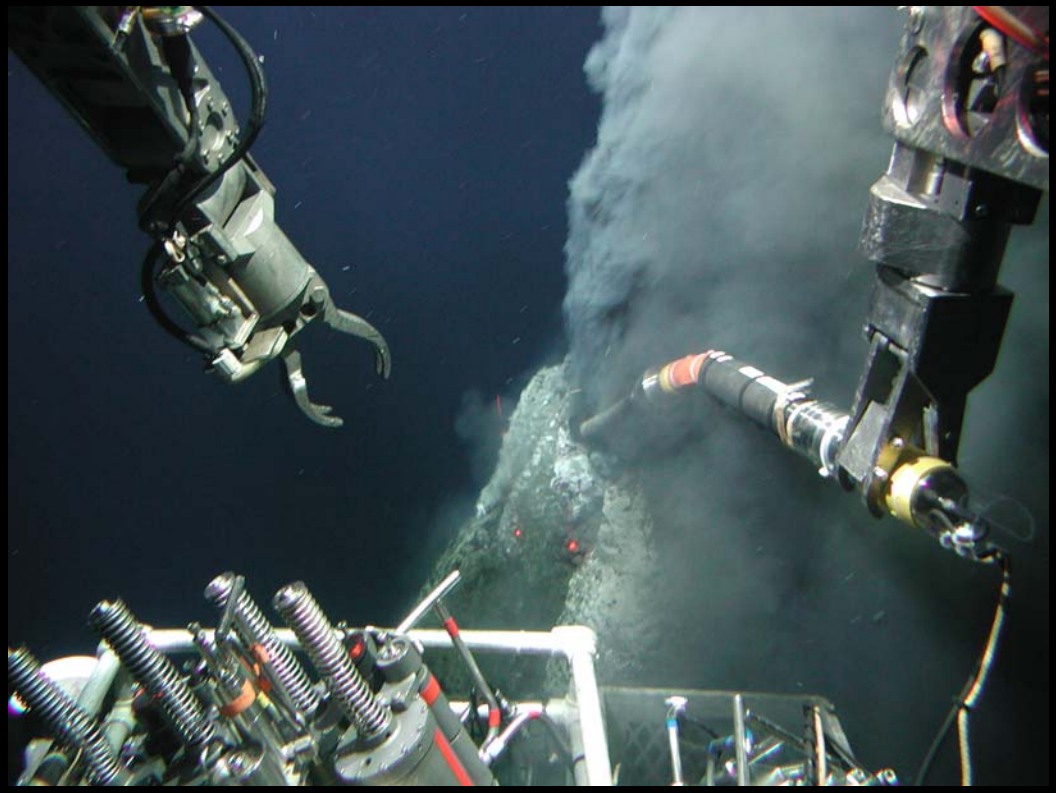


Comparison of dissolved H2 concentrations measured by using different methods

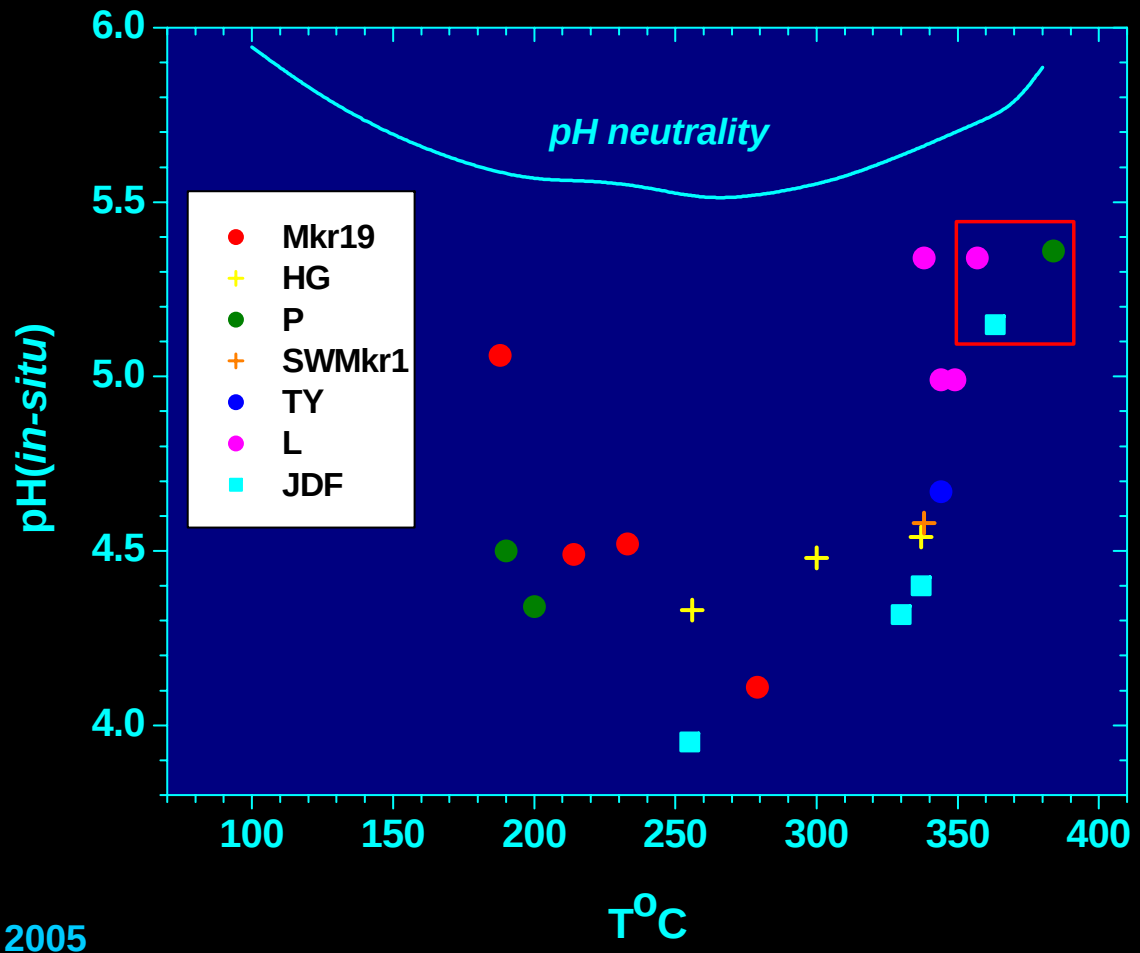


Ding et al., EPSL, 2001

In-situ Controls on Vent Fluid-Seawater Mixing

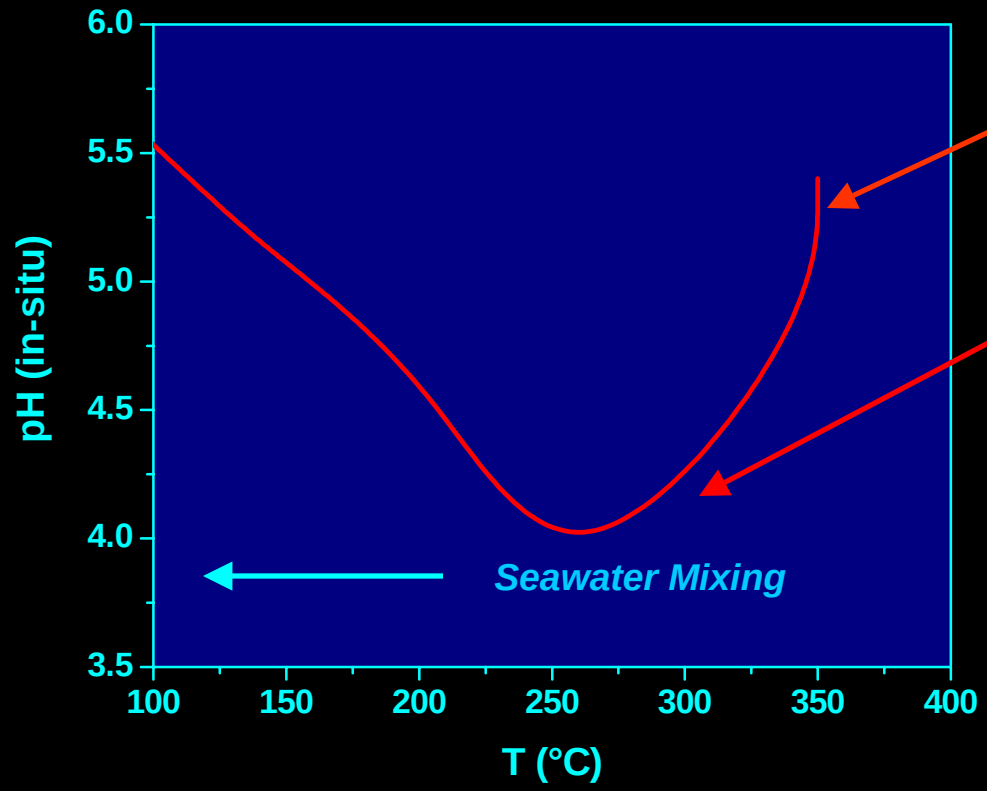


In-Situ pH versus Vent Temperature



Ding et al. 2005

Theoretical Model of pH Change during Seawater-Vent fluid mixing

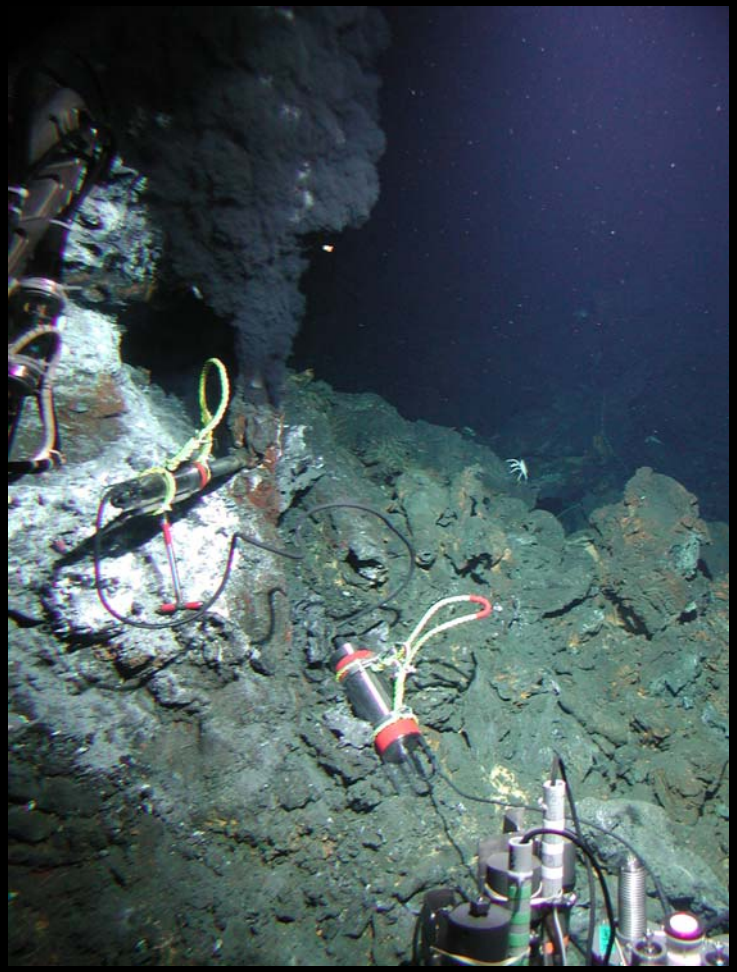


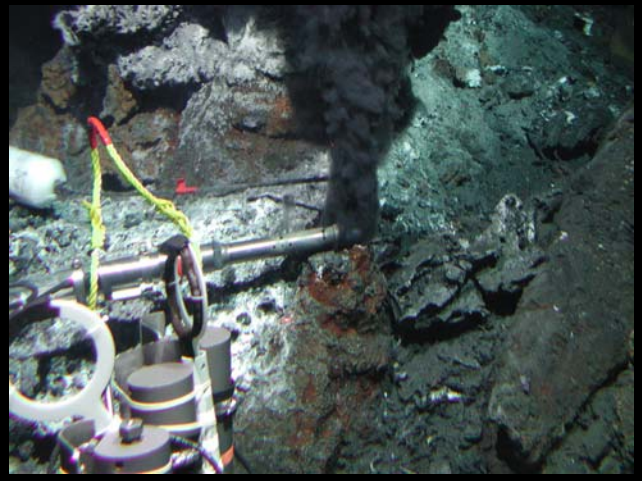
P Vent, EPR 9.50°N

Fe and H2S-rich

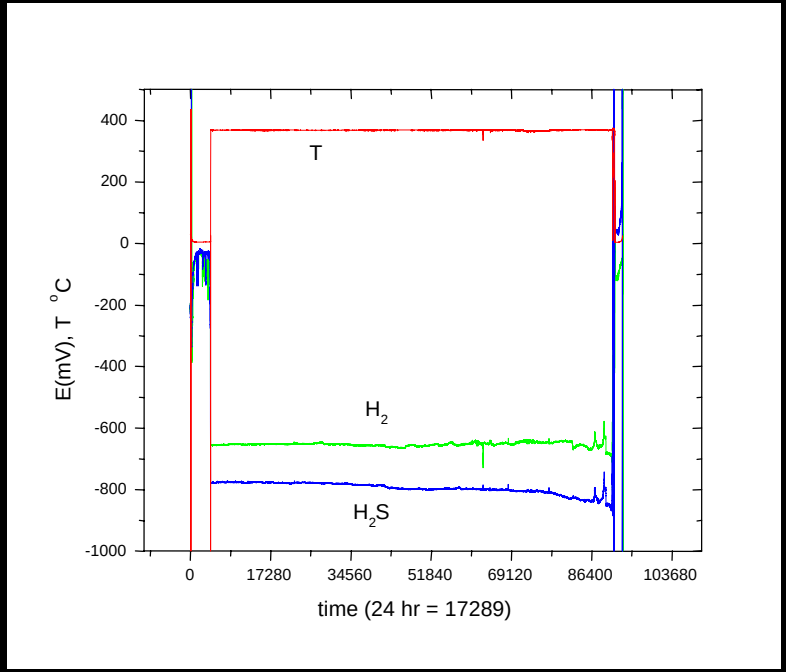
Pyrite Precipitation Region

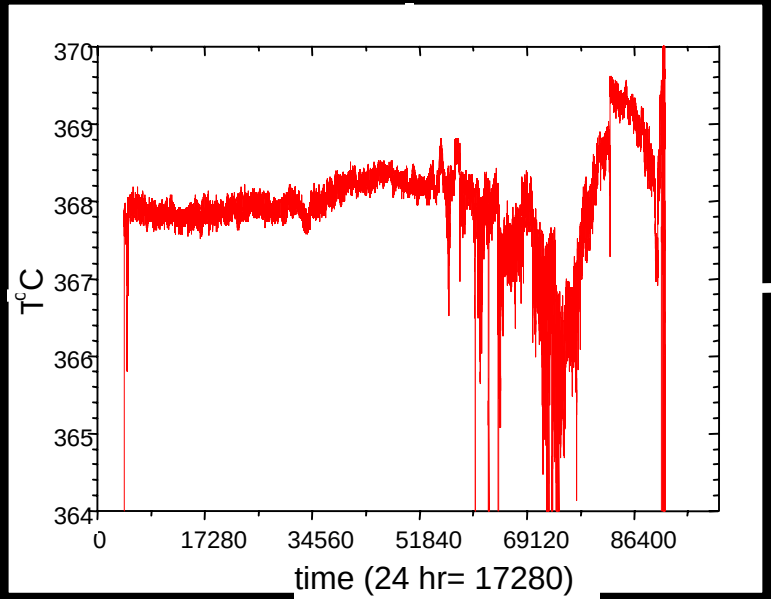
Sensor Deployment at P-Vent, EPR 9°50’N



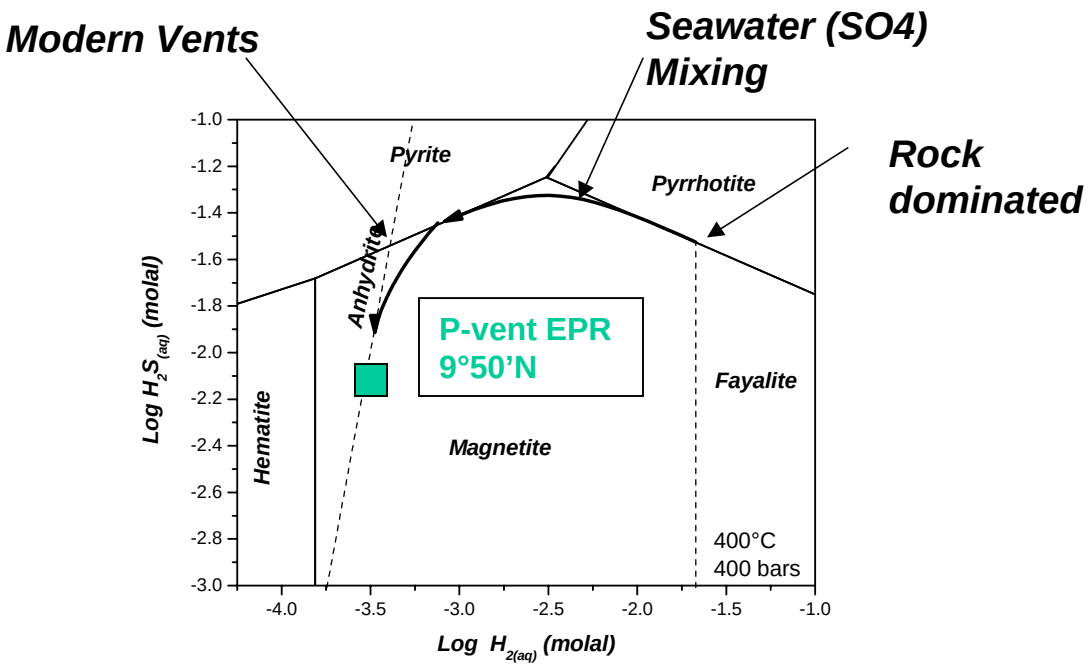


Sensor Deployment at P-Vent, EPR 9°50'N: Temperature, H2 and H2S Record





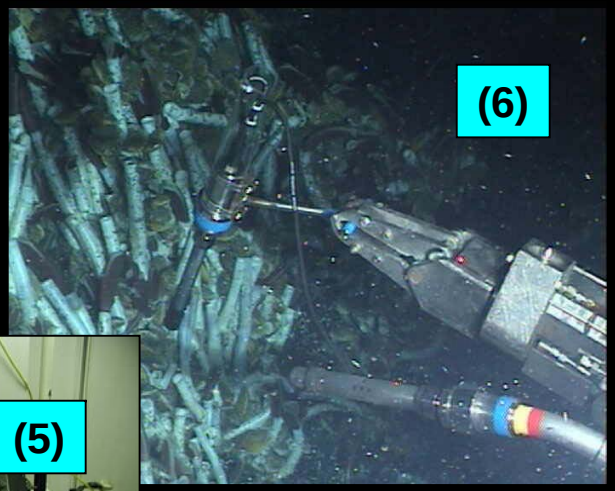
Redox Relations/Evolution at Hydrothermal vents

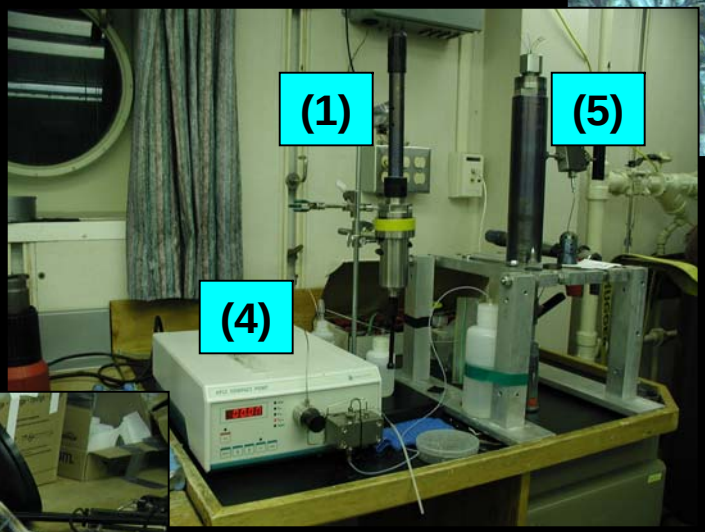


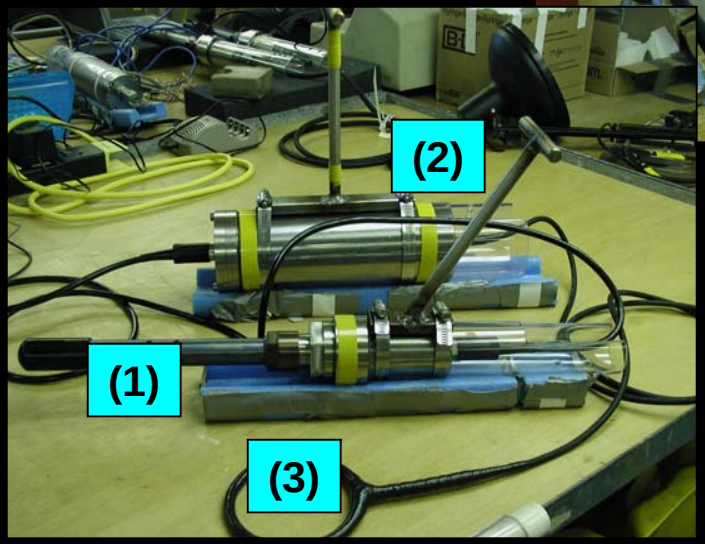
Tica Vent 9°50’N EPR

- Chemical and biological feedback
- Black smoker at ~ 330°
- Riftia community 8-26°C

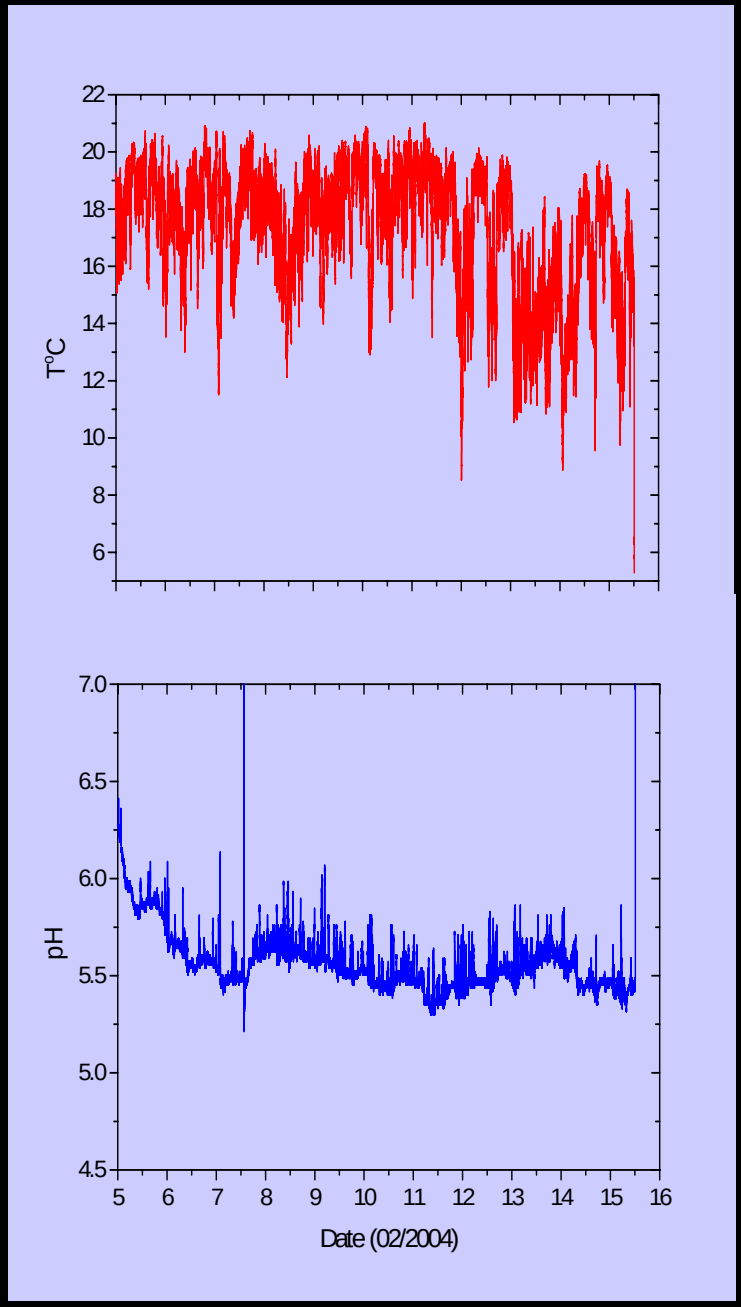
The sensor unit was tested under the operational condition on ship board before and after deployment.

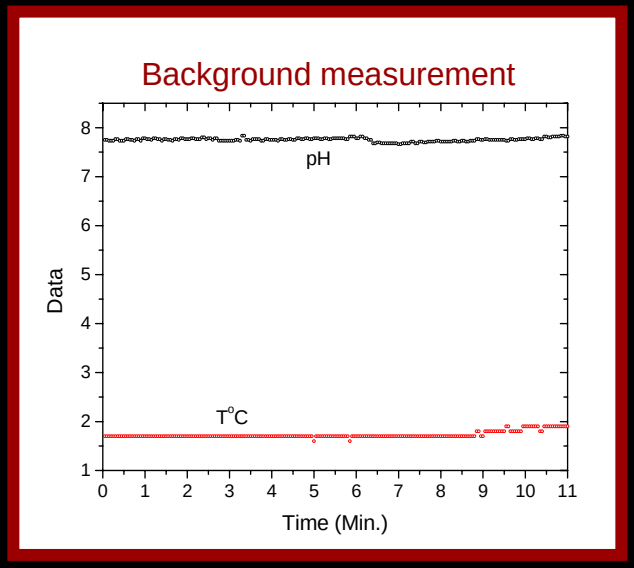






(1) Sensor
(2) Data logger
(3) ICL communication line
(4) HPLC pump
(5) High Pressure testing vessel
(6) Field deployment

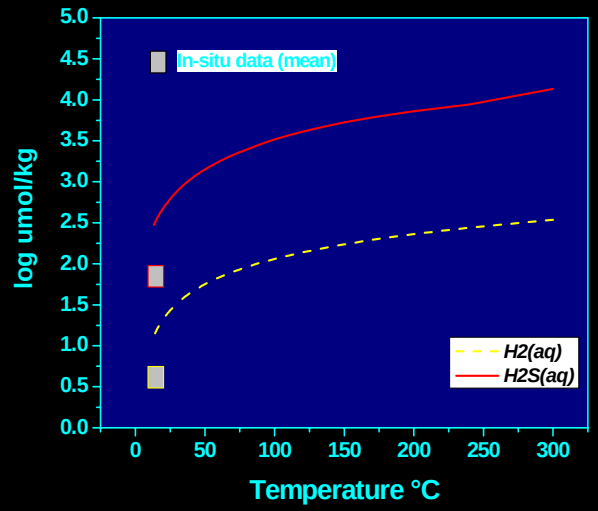




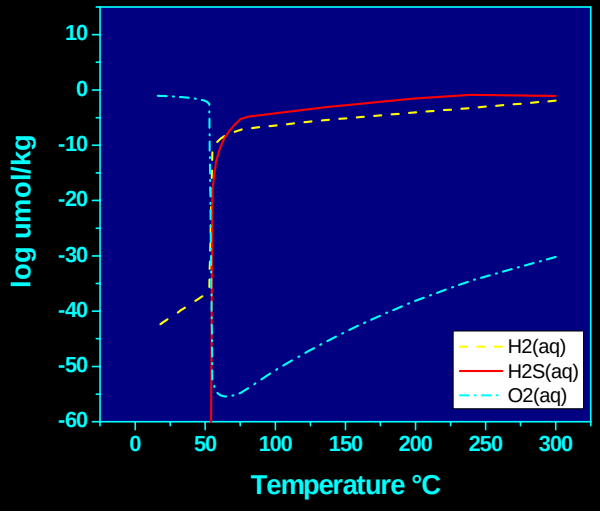
Temperature and pH(in-situ) at the base of tubeworm colony at Tica.

- ***Temperature variability---~12-22°C***
- ***pH variability—6.5 to 5.5 with time-substantially lower than background seawater values.***

In-situ H_2S and H_2 data in comparison with theoretical prediction



1. ***H_2 Redox decoupled during cooling***



2. ***H_2 Redox coupled during cooling***

Conclusions

- In-situ measurement and monitoring pH and Redox (H_2, H_2S) of hydrothermal vent fluids has been demonstrated at a range of conditions and vent sites
  - High temperature vent fluids (EPR 9°N,P-vent)
    - Slightly acidic, only moderately reducing
      - » Compositional and temperature stability on the order of days
    - In-situ data confirm seawater mixing and pH lowering
  - Diffuse flow fluids at Tica reveal complex time series patterns involving temperature, pH, H_2 and H_2S
    - Seawater mixing and biogeochemical processes
    - Linkage between diffuse flow and high temperature venting?