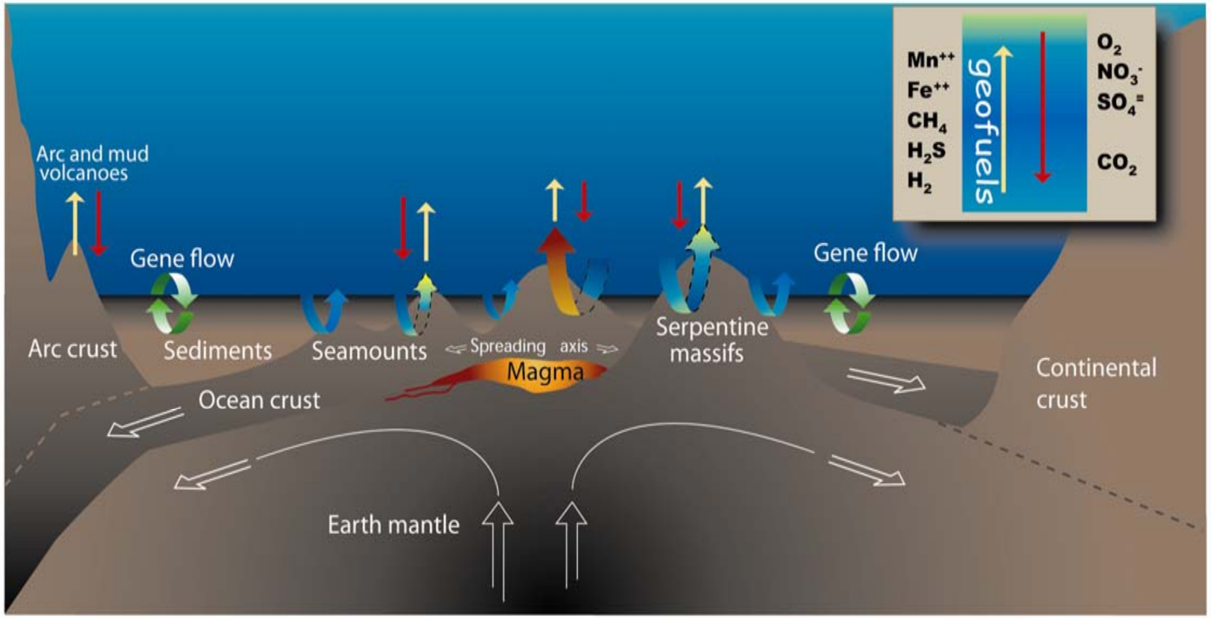
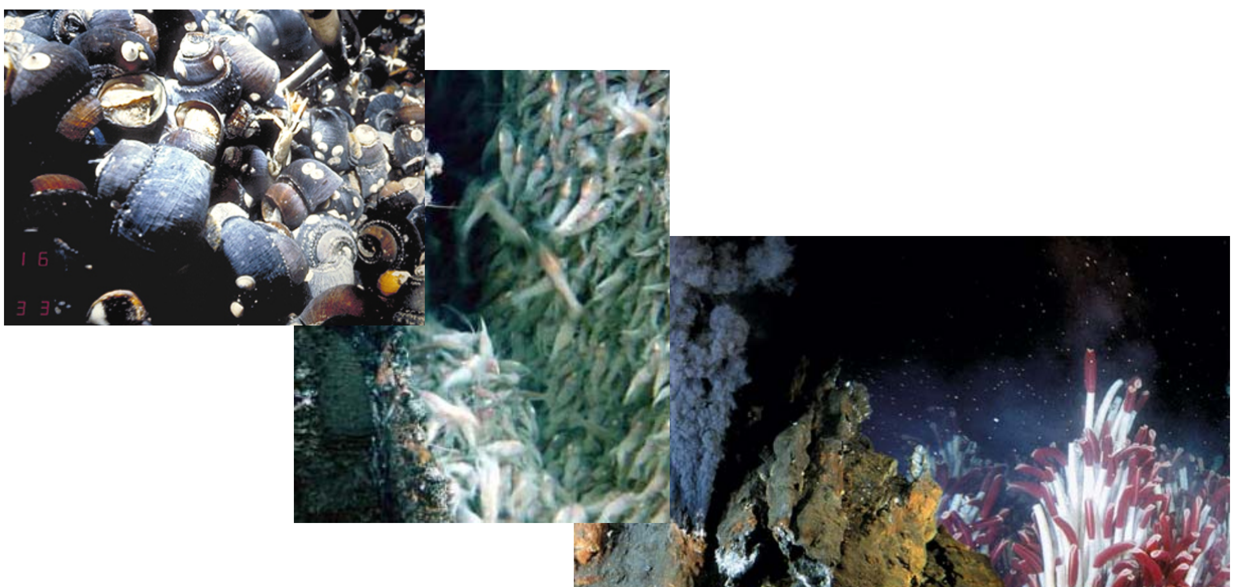
Geochemical diversity of hydrothermal systems: Thermodynamic constraints on biology

Wolfgang Bach
University of Bremen, Germany

Lithosphere-Biosphere Interactions in Hydrothermal Vents





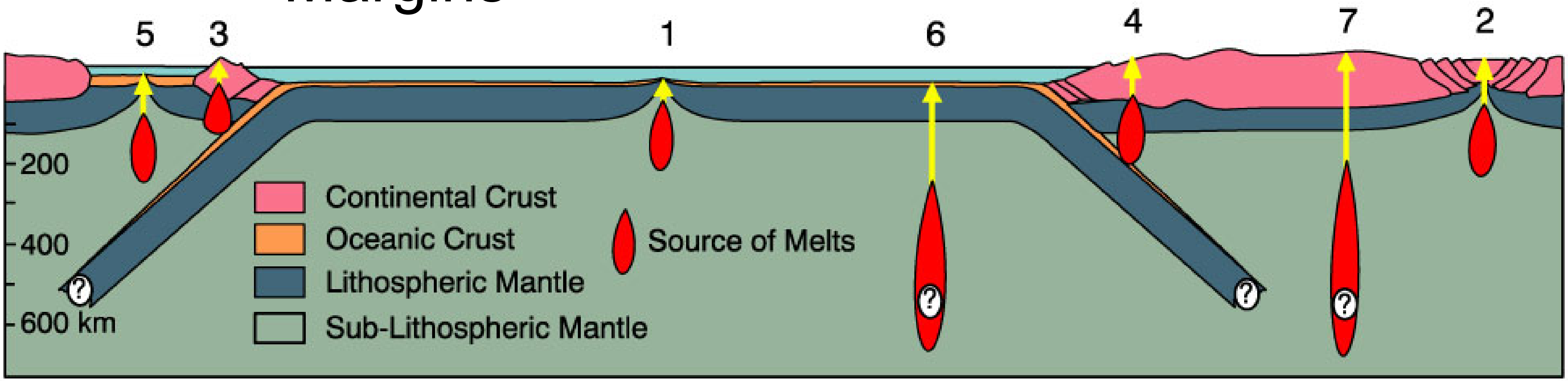
Driven by geochemical energy – **powered by *geofuels***

Highly diverse: chemically and biologically

Dynamically linked with plate tectonics

Plate Tectonic - Igneous Genesis

1. Mid-ocean Ridges
2. Intracontinental Rifts
3. Island Arcs
4. Active Continental Margins
5. Back-arc Basins
6. Ocean Island Basalts
7. Miscellaneous Intra-Continental Activity



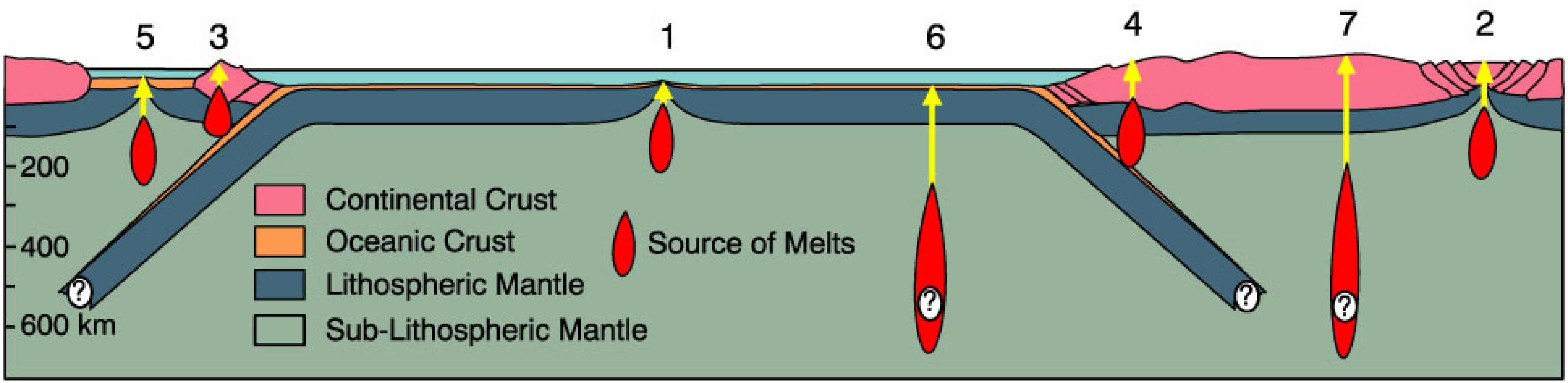
Winter (2003)

Plate Tectonic - Igneous Genesis

3,5) Subduction zones
Recycling of volatiles (and solutes) in →
Re-gassing the mantle (C,S,H) →
Wet melting →
High fO_2

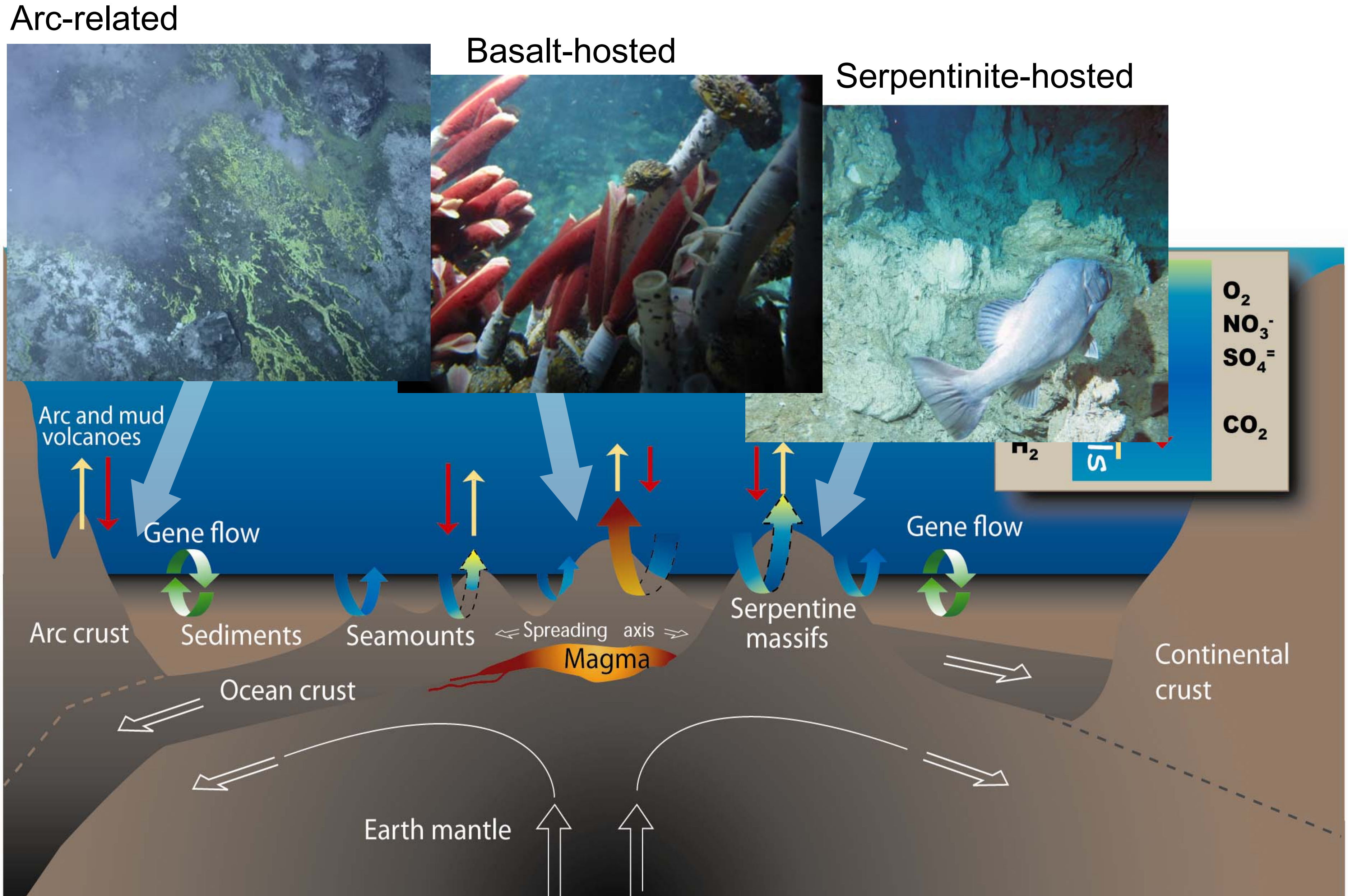
1) Mid-ocean ridges
Melting of depleted and degassed upper mantle
→Magmas have low gas contents →
Dry melting →
Low fO_2

6) Ocean island volcanoes
Melting of deeper, less degassed mantle
→Magmas have moderate gas contents (C,H) →
Low fO_2



Winter (2003)

Geofuel diversity in submarine geotectonic settings

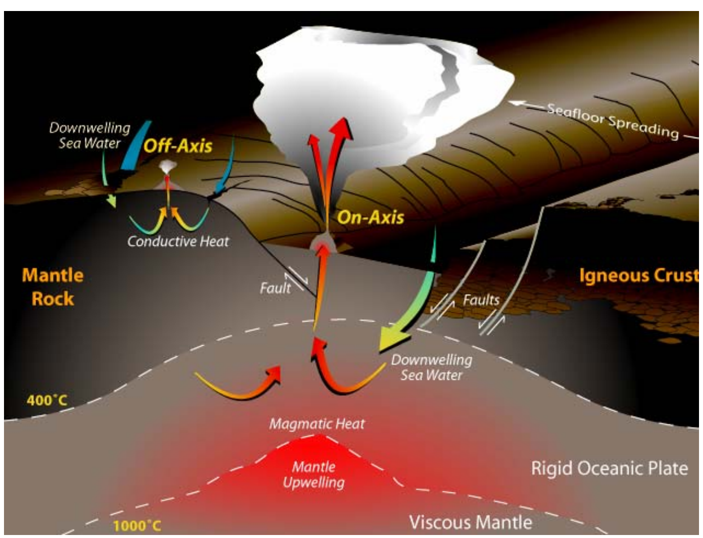


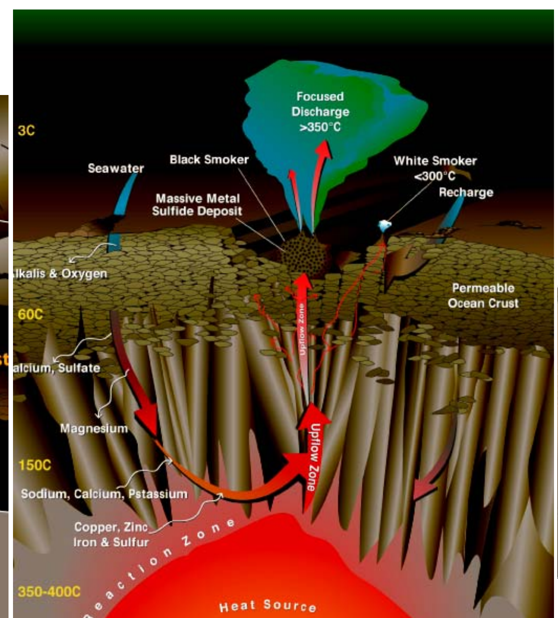
Diversity of systems: physical/chemical differences

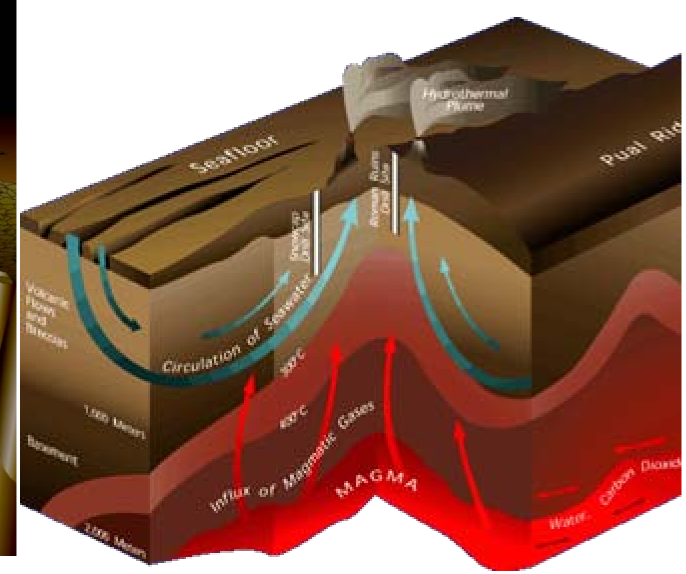
MOR, Subduction
<u>*Peridotite-hosted*</u>
- pH 3 to 12
- Reducing conditions
- Negligible magma volatile flux?
- Abiotic organics?
- Early Earth analogs

MOR, Ocean Islands
<u>*Basalt-hosted*</u>
- pH 3 to 5
- Relatively oxidizing conditions
- Variable H_2-CO_2 volatile flux
- Global relevance

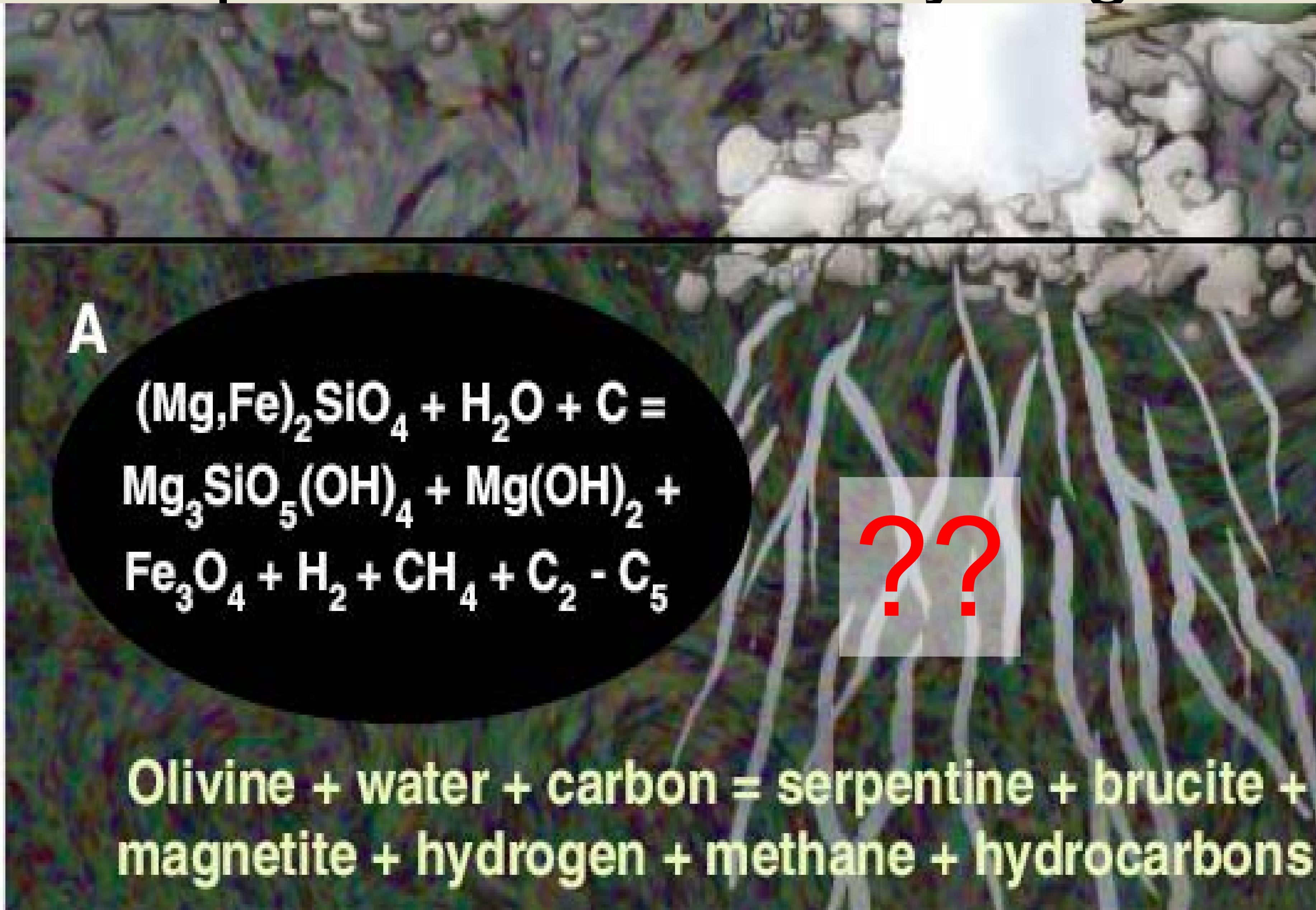
MOR, Subduction
<u>*Felsic rock-hosted*</u>
- pH <1-3
- Very oxidizing conditions
- Variable H_2O-CO_2-SO_2-HCl volatile flux
- Variable water (variable boiling temperatures)



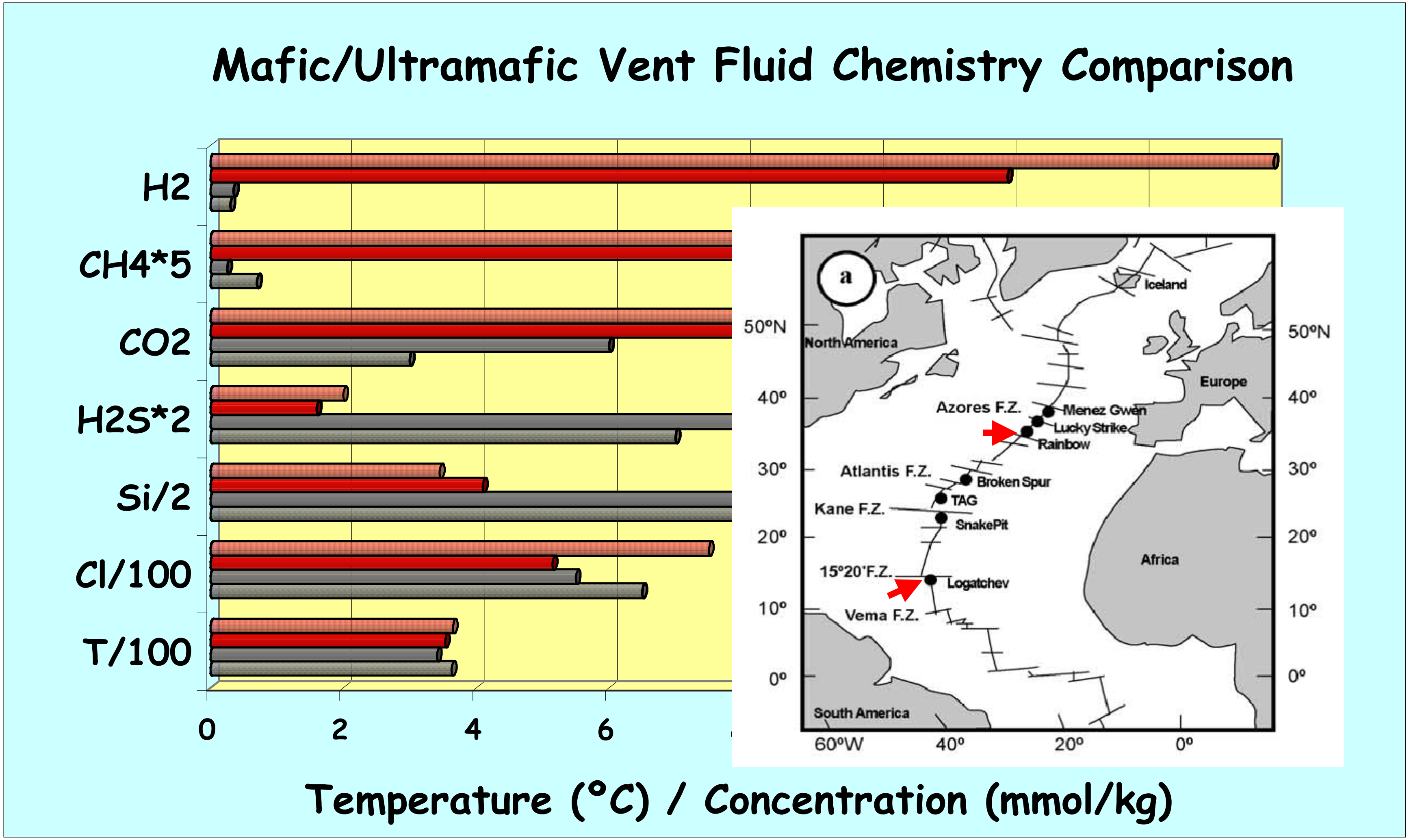




Serpentinization and hydrogen



Peridotite-Hosted Hydrothermal Systems

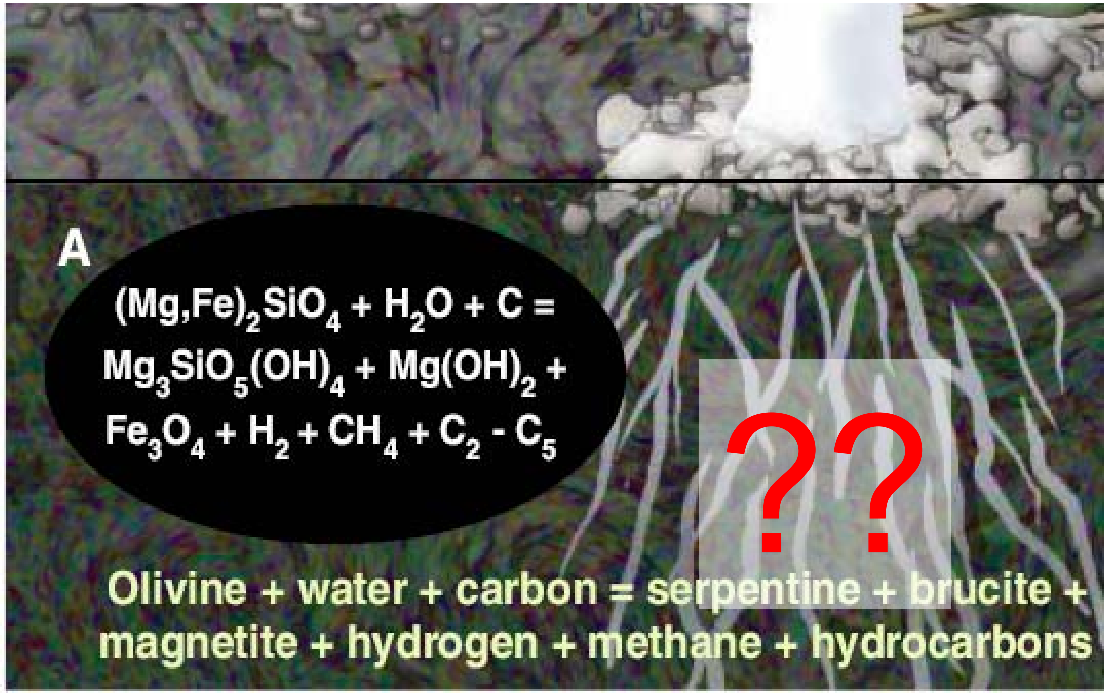


Data: Charlou et al. (2002)

Peridotite-Hosted Hydrothermal Systems

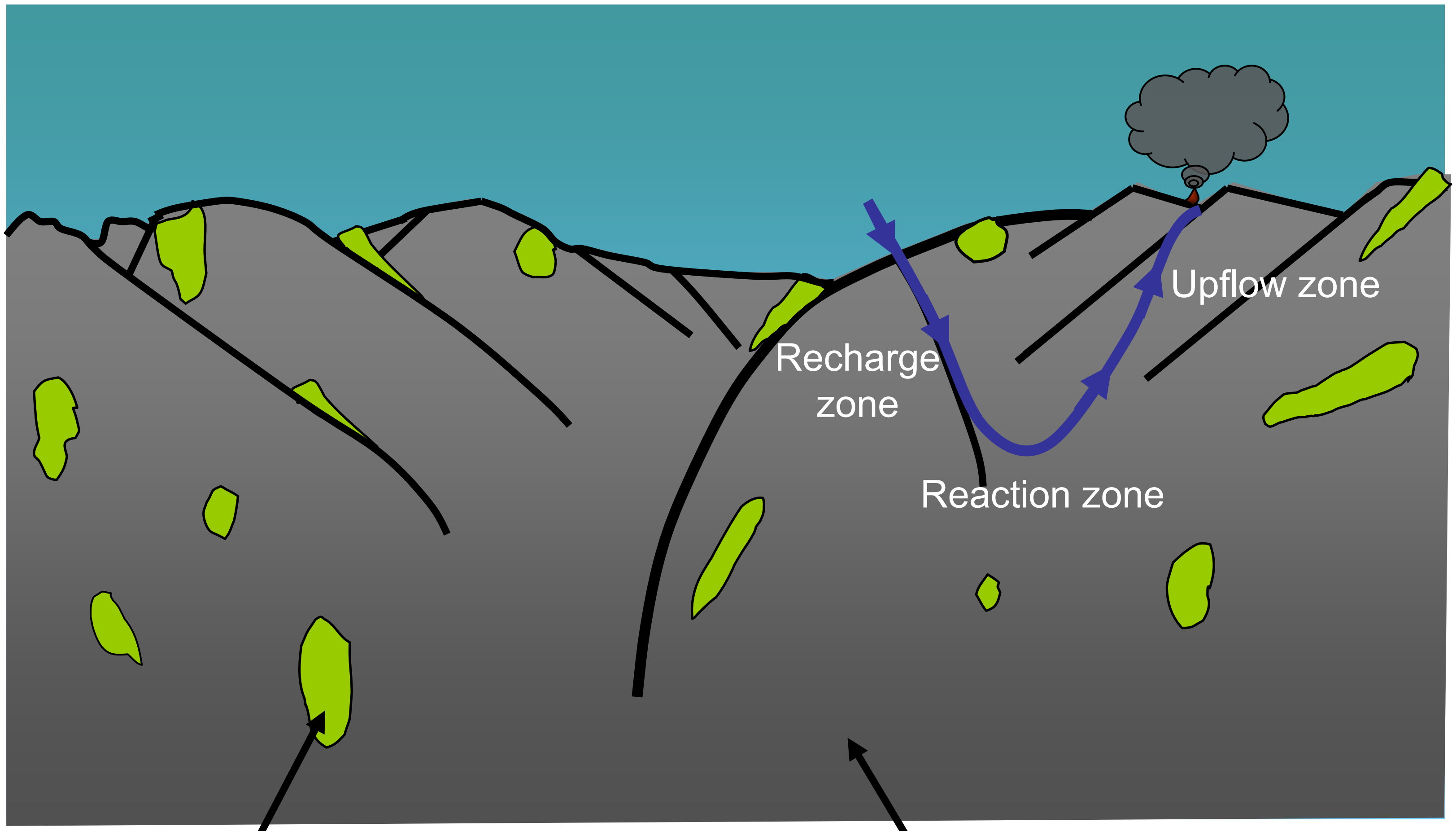
$$2FeO + H_2O \rightarrow Fe_2O_3 + H_2$$

$$4H_2 + CO_2 \rightarrow CH_4 + 2H_2O$$



Serpentinization: Geochemical Modeling

Geochemical reaction path model (EQ3NR/6)

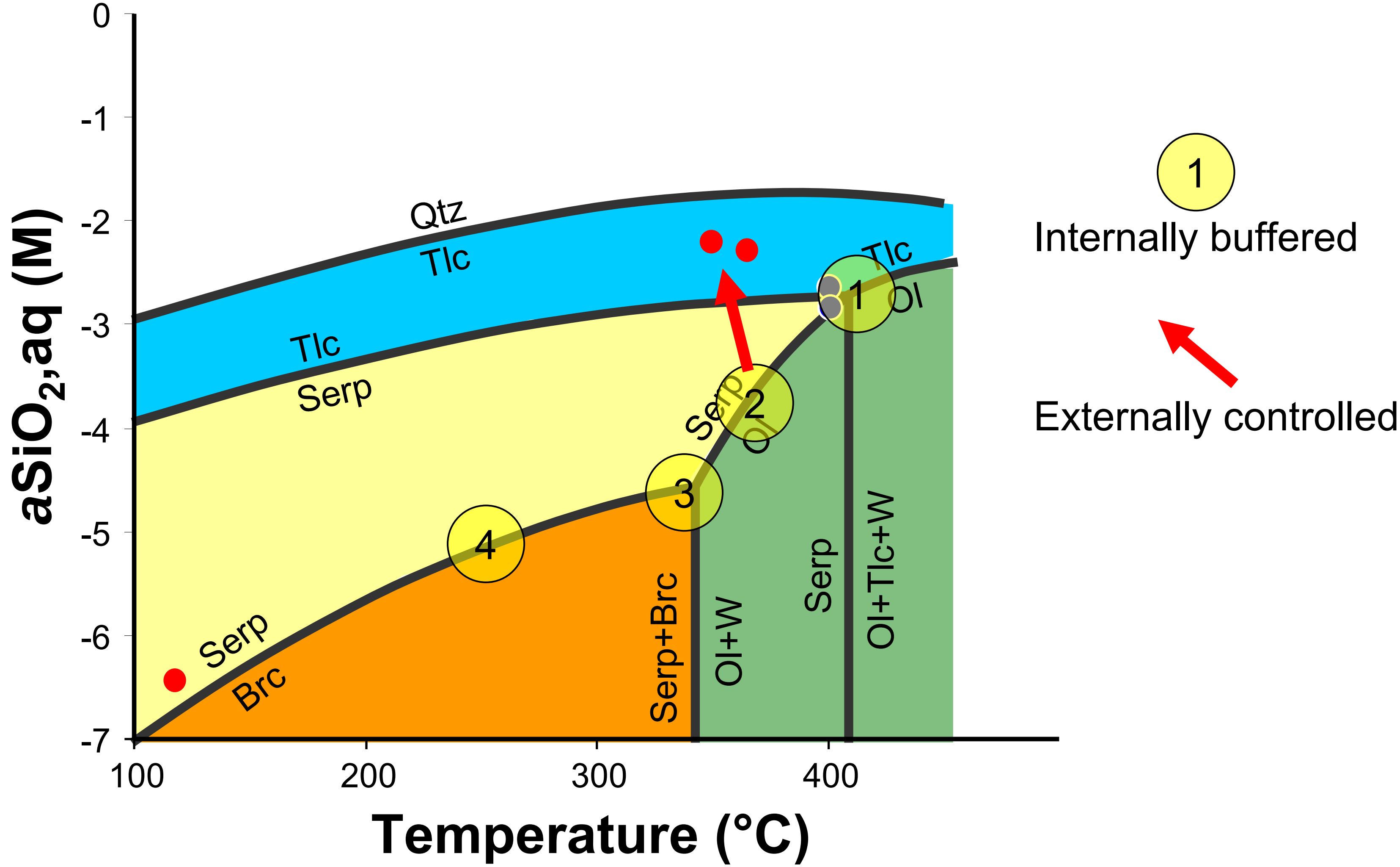


Gabbro intrusion

Peridotite (± altered)

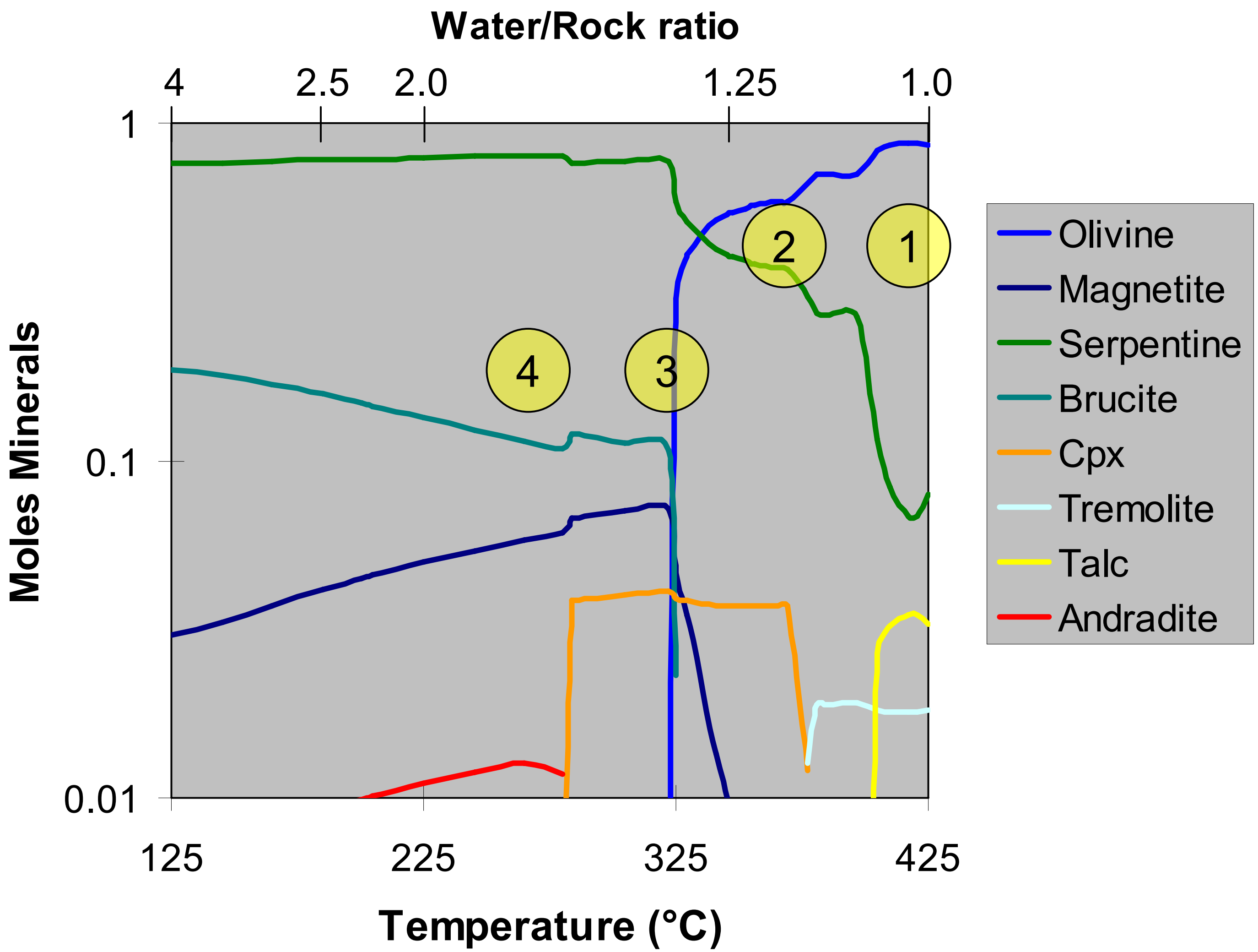
Serpentinization of the oceanic lithosphere

$MgO-SiO_2-H_2O$ phase relations at 500 bar



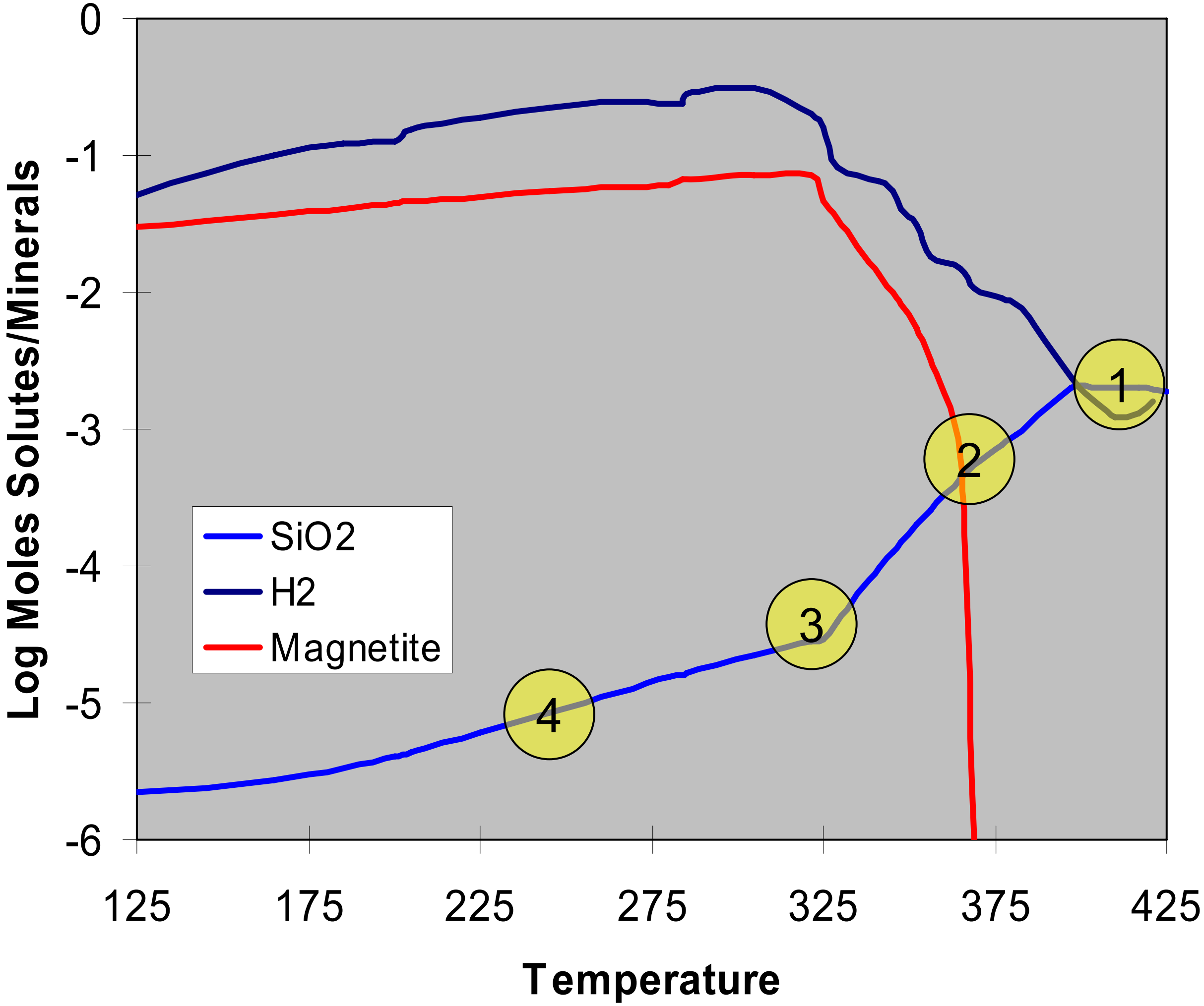
Serpentinization: Geochemical Modeling

Phase relations



Serpentinization: Geochemical Modeling

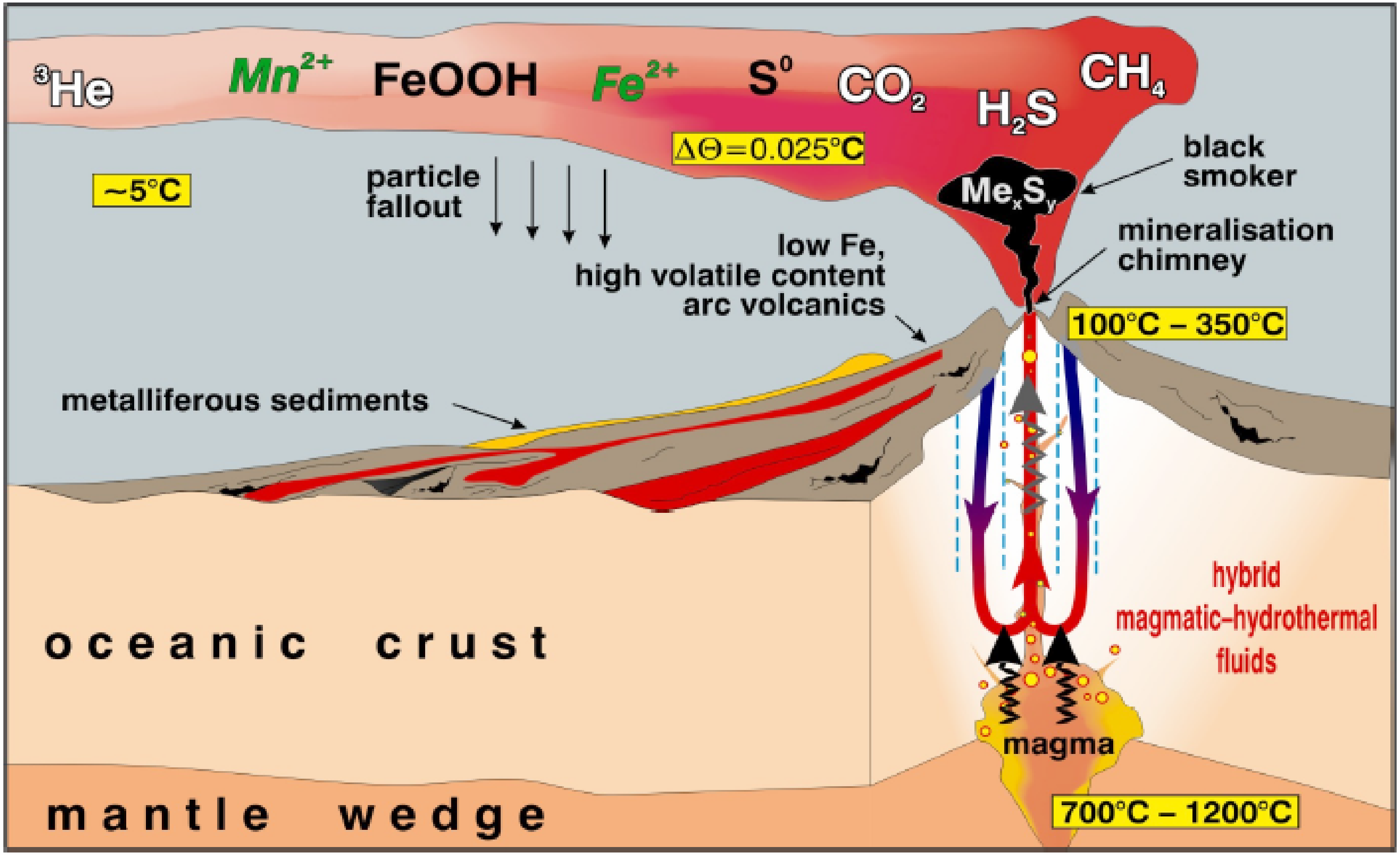
Fluid compositions



Hydrogen yields in serpentinization are high, because phase assemblages are low silica activity

$1.5Fe_2SiO_4 + H_2O \rightarrow Fe_3O_4 + 1.5SiO_2(aq) + H_2(aq)$

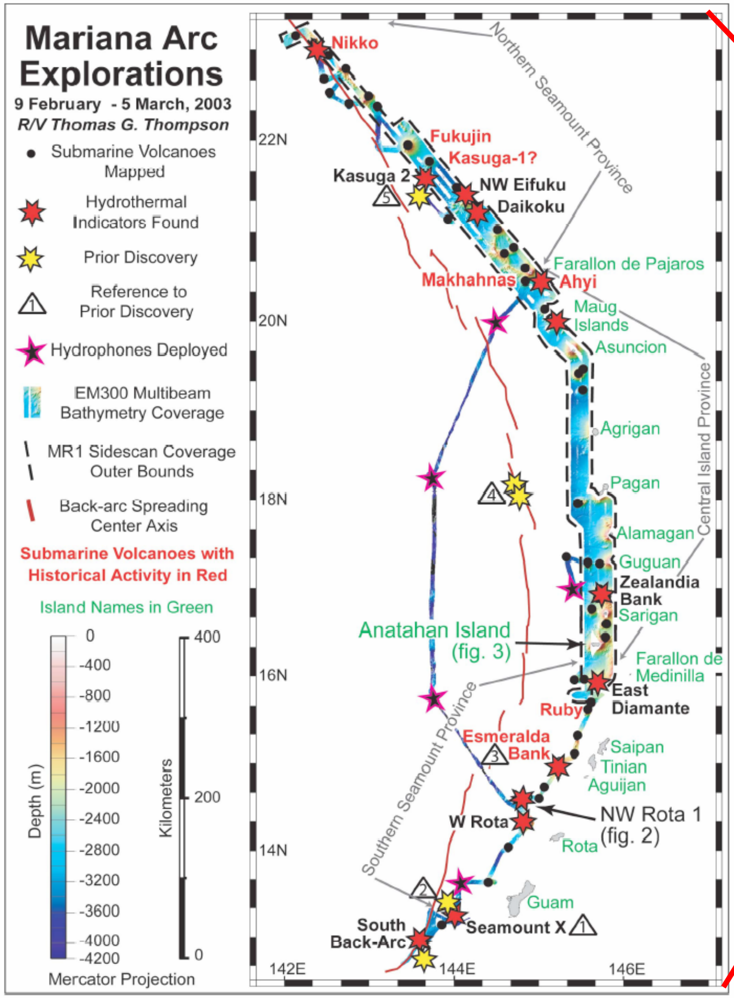
Arc volcano hydrothermal system

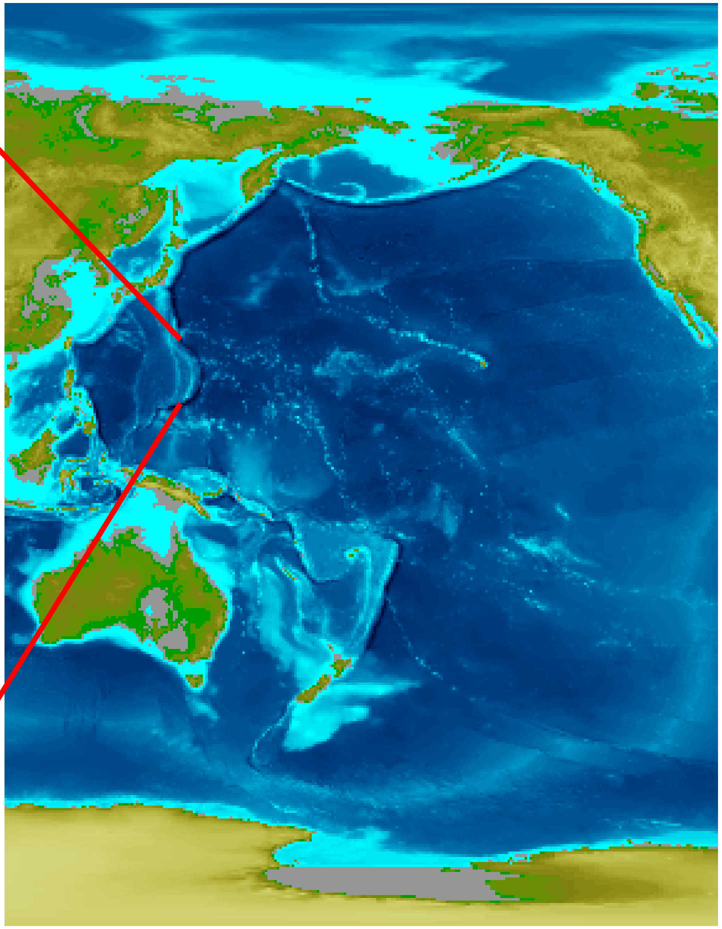


Gary Massoth et al.

Mariana and other arc systems

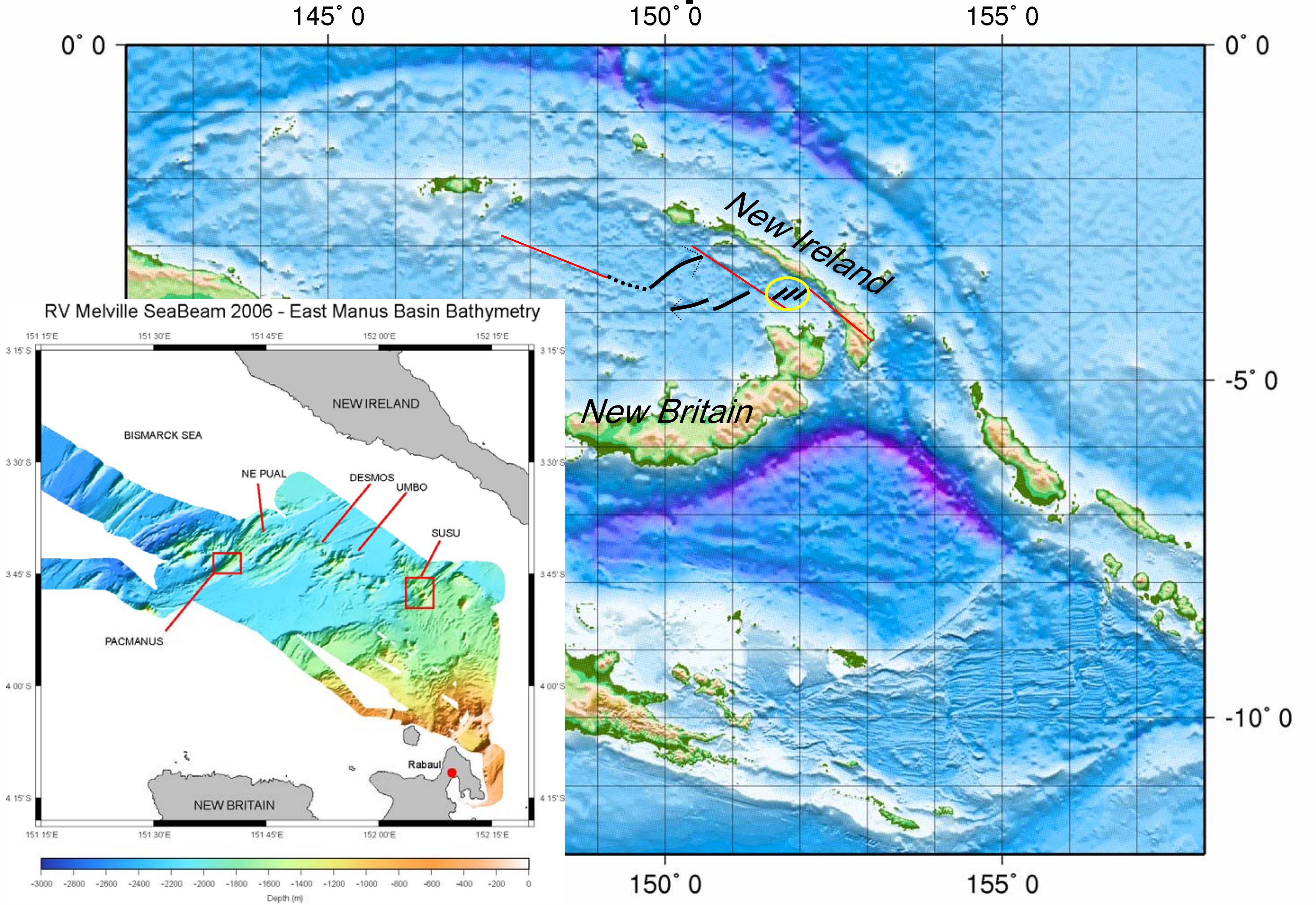
sulfuric and carbonic acid springs



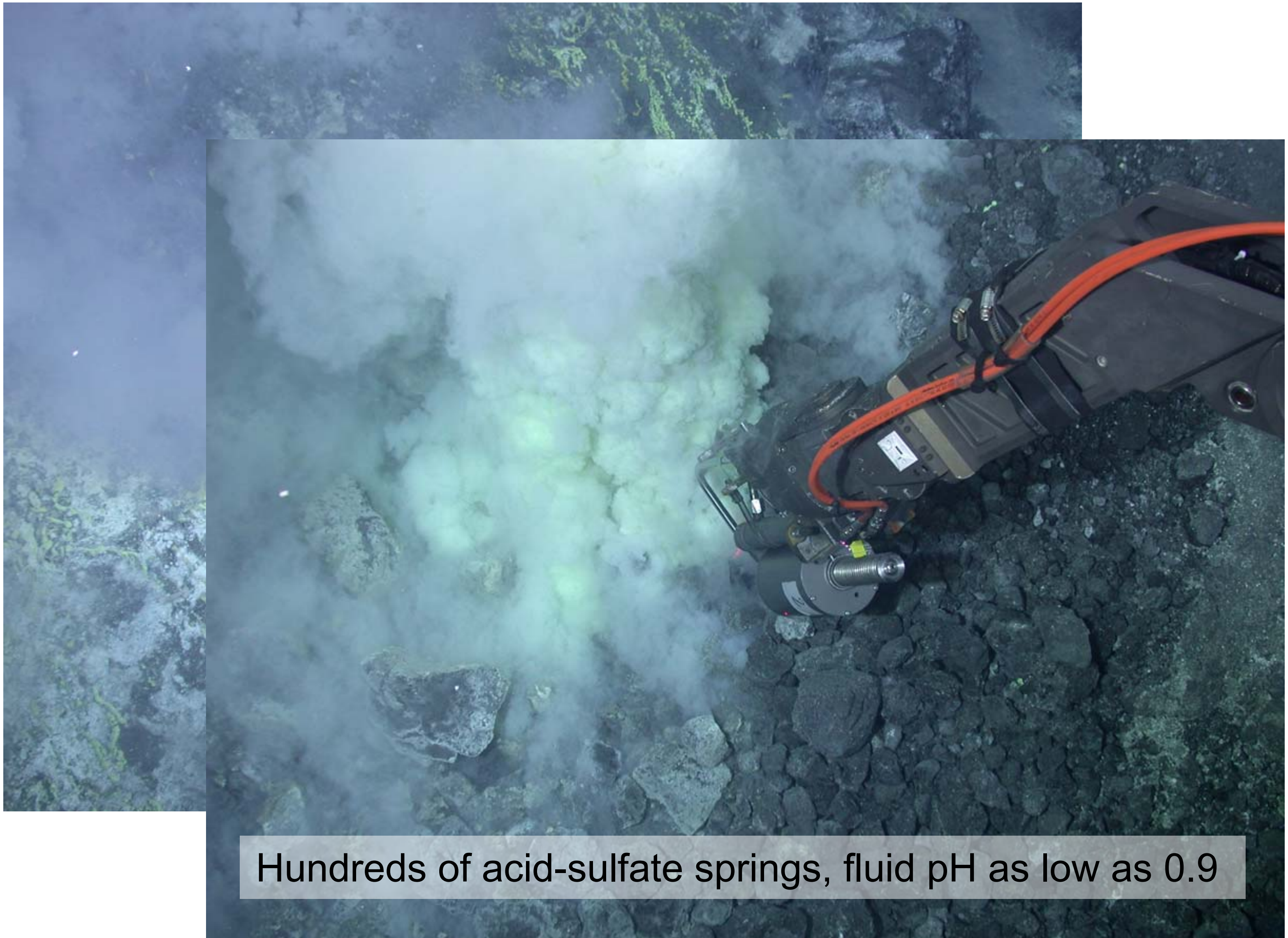


Embley et al. (2004)

Manus Basin, Papua New Guinea

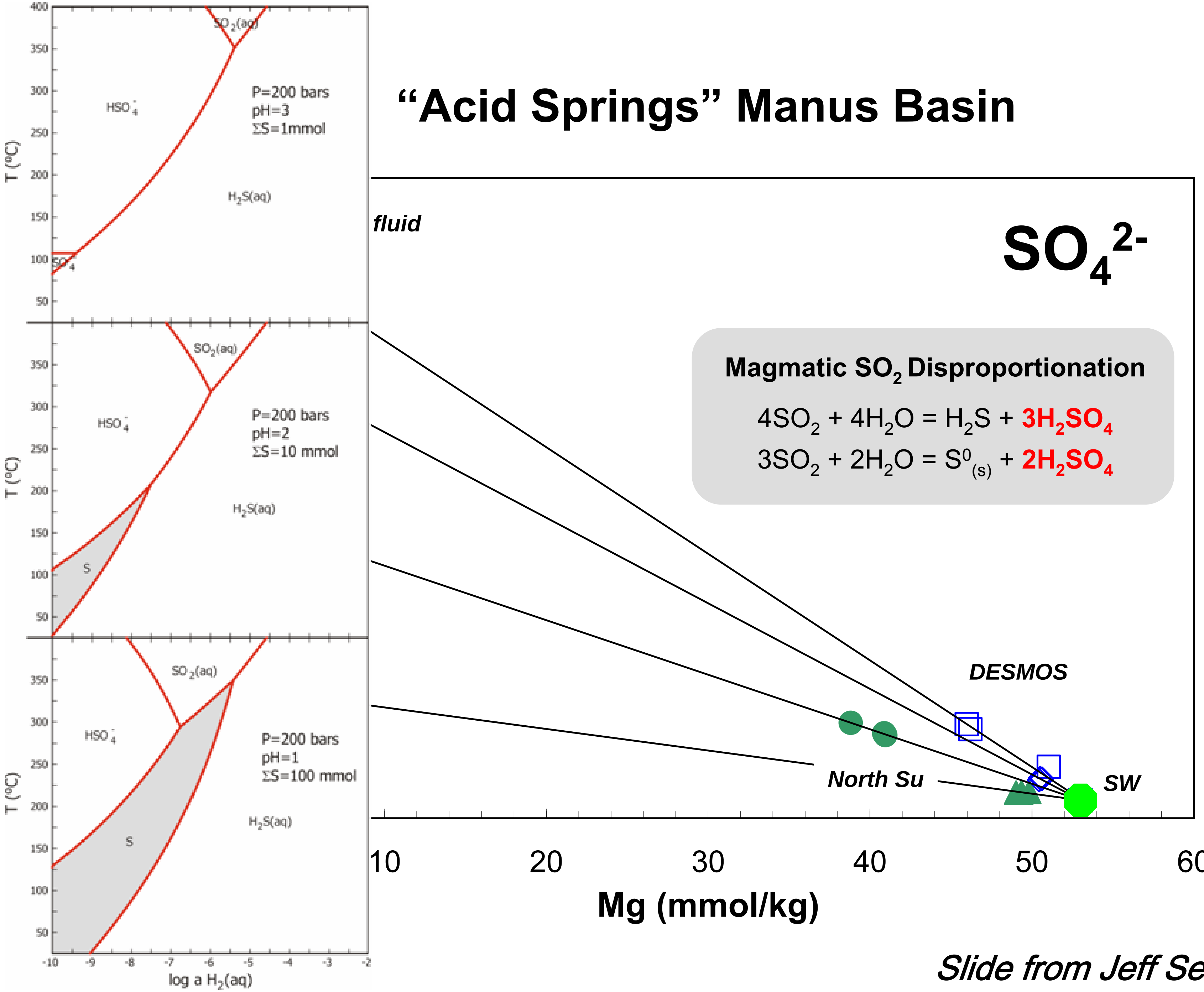


North Su



Hundreds of acid-sulfate springs, fluid pH as low as 0.9

"Acid Springs" Manus Basin



Magmatic SO_2 Disproportionation

$4SO_2 + 4H_2O = H_2S + \mathbf{3H_2SO_4}$

$3SO_2 + 2H_2O = S^0_{(s)} + \mathbf{2H_2SO_4}$

Slide from Jeff Seewald

Geochemistry – Biology relations: Gibbs Free Energy

$$H_2(aq) + S^0 \rightarrow H_2S(aq)$$

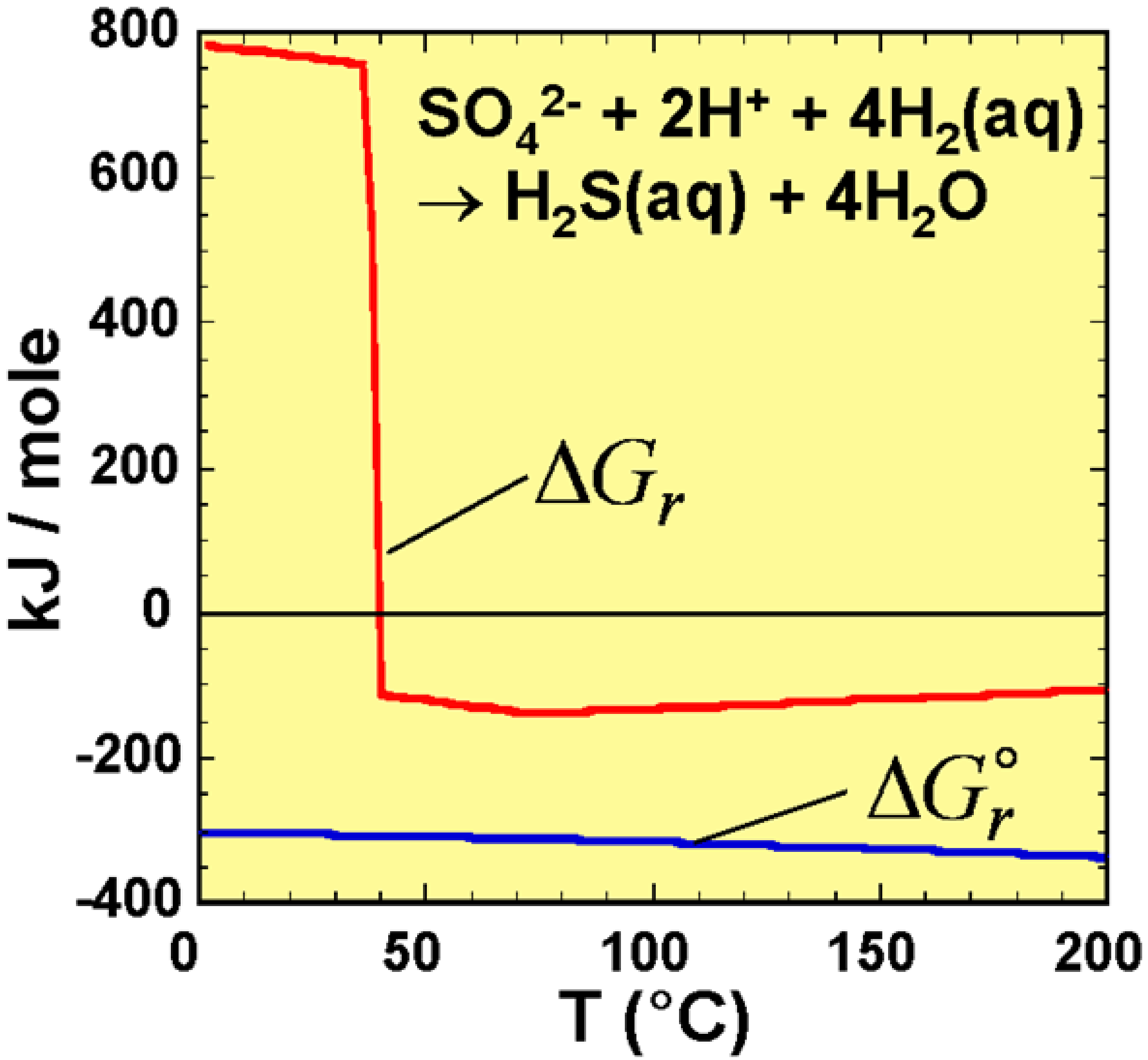
$$\Delta G_r^\circ = \Delta G^\circ_{H_2S(aq)} - \Delta G^\circ_{H_2(aq)} - \Delta G^\circ_{S^0}$$

$$\Delta G^\circ_{P,T} = \Delta G^\circ_f - S^\circ_{298}\left(T - 298\right) + \int_{298}^{T} C^\circ_P dT - T\int_{298}^{T} C^\circ_P d\ln T + \int_{1}^{P} V^\circ dP$$

$$\Delta G_r = \Delta G_r^\circ + RT\ln Q_r$$

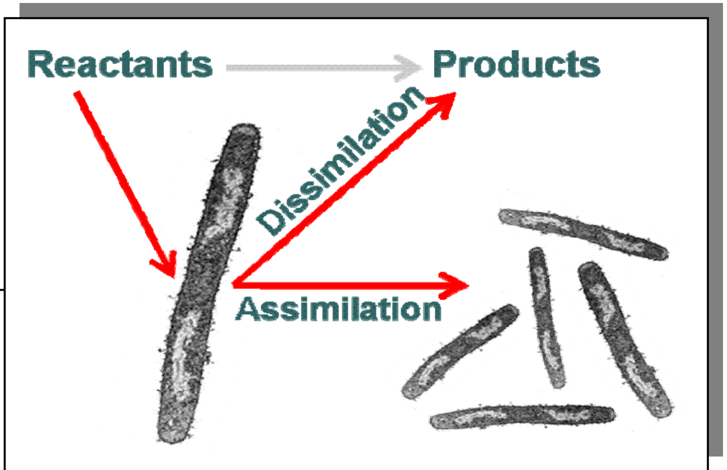
$$Q_r = \frac{a_{H_2S(aq)}}{a_{H_2(aq)}\, a_{S^0}} = \frac{m_{H_2S(aq)}\gamma_{H_2S(aq)}}{m_{H_2(aq)}\gamma_{H_2(aq)}}$$

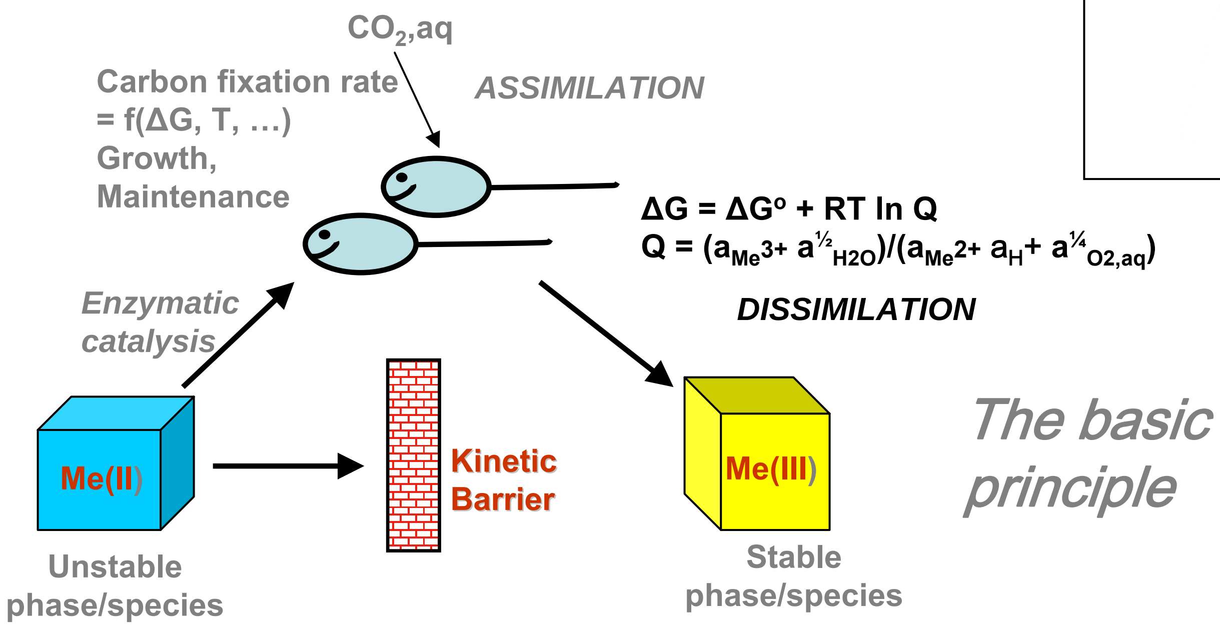
Energetics from mixing hydrothermal fluids with seawater



Slide from Jan Amend, redrawn from McCollom & Shock (1997)

Thermodynamics → Tracing the energy across the interface between geology and biology





$\Delta G = \Delta G^{o} + RT \ln Q$

$Q = (a_{Me^{3+}}\, a^{1/2}_{H2O})/(a_{Me^{2+}}\, a_{H} + a^{1/4}_{O2,aq})$

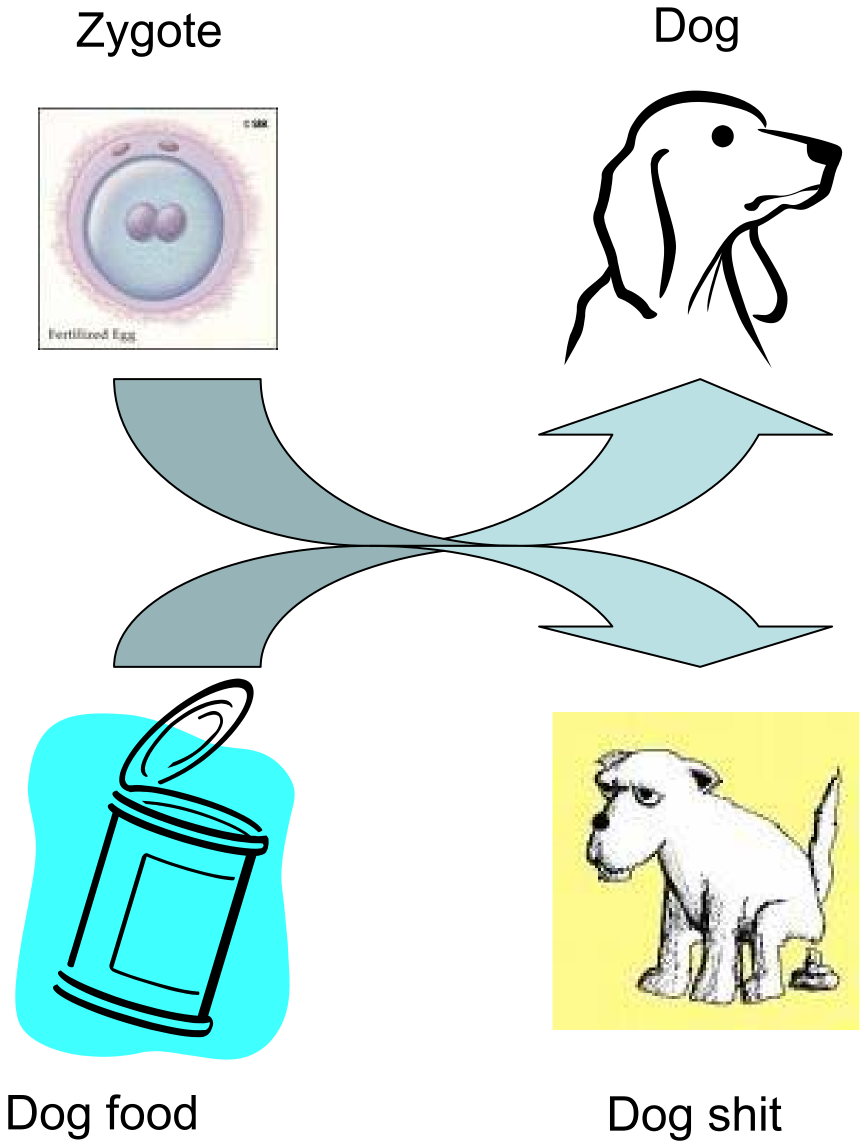
$Me^{2+} + ¼\, O_2,aq + H^+ \quad = \quad Me^{3+} + ½\, H_2O$ (Step of overall reaction that can be mined for energy)

Thermodynamics in Biology

- What is life in terms of thermodynamics?
  - Sustaining disequilibria … and
  - increasing entropy … by
  - **using energy!**

- What is the source of the energy?
  – Light (photosynthesis)
  – Chemical bonds in organics (heterotrophy)
  – Electron transfers (chemosynthesis)

$\Delta G = \Delta H - T\Delta S$

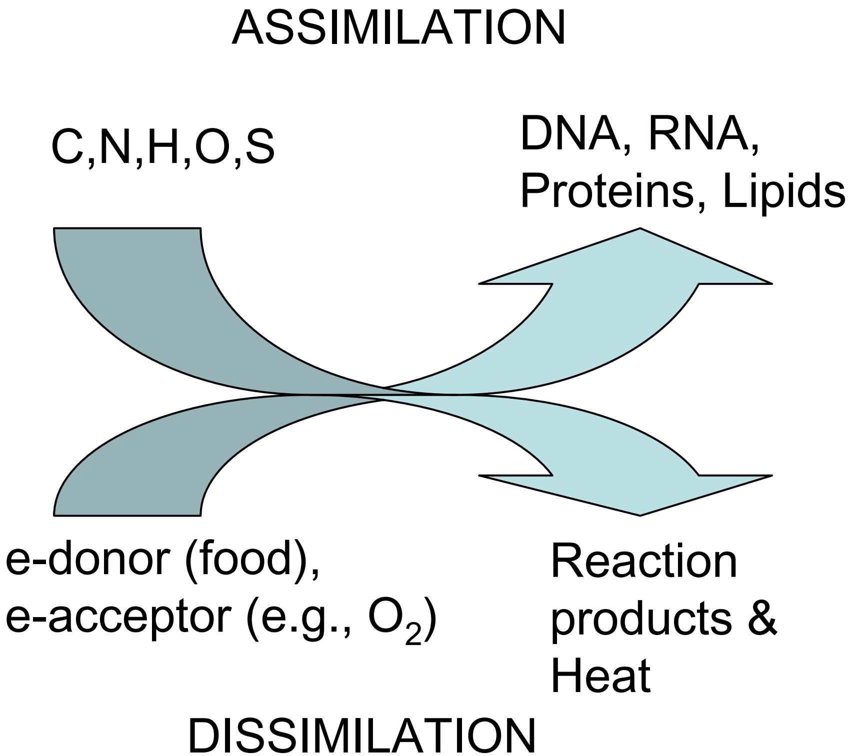


$$\Delta G > 0$$
$$\Delta S < 0$$

$$\Delta G < 0$$
$$\Delta S > 0$$

$$\Delta G_{total} < 0$$
$$\Delta S_{total} > 0$$

$\Delta G = \Delta H - T\Delta S$



$\Delta G > 0$
$\Delta S < 0$

$\Delta G < 0$
$\Delta S > 0$

Only a fraction of the energy can be used to make biomass → $\Delta G_{total} < 0$, $\Delta S_{total} > 0$

Bioenergetics

Energetic costs of building biomass
(from McCollom & Amend, 2005)

<u>In theory</u> (McCollom & Amend, 2005)
1.4 kJ / g cellular biomass (anaerobes)
18.4 kJ / g cellular biomass (aerobes)
Anabolic advantage of living anaerobically

<u>In reality</u> (Heijnen & van Dijken, 1992)
30-40 kJ / g cellular biomass (anaerobes using H_2 as e-donor)
80-170 kJ / g cellular biomass (others)

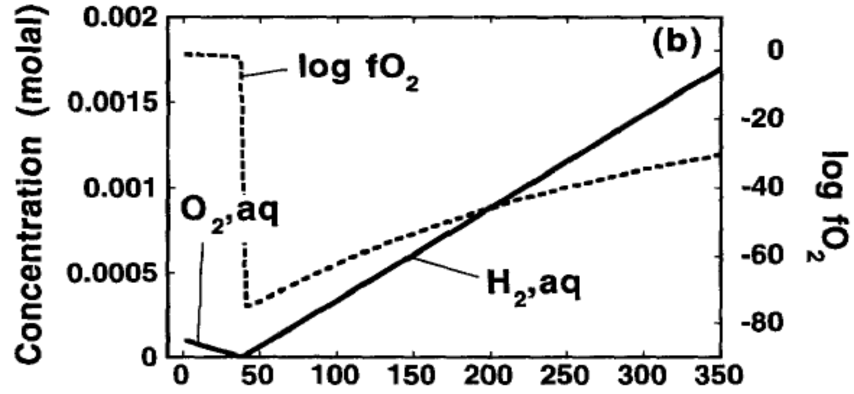
→ Only about 10% efficiency
→ 90% get lost in form of heat and waste products
→ This is increasing entropy in the surrounding

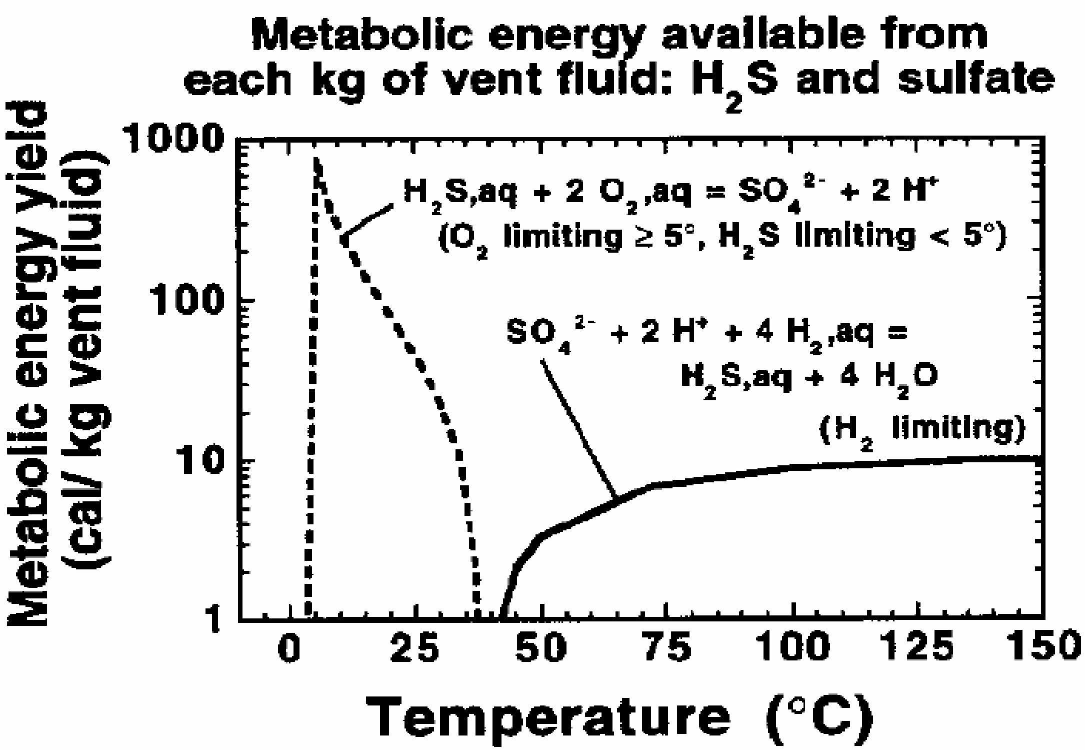
Chemolithoautotrophic biomass production estimates

- Axial hydrothermal vents: ~10^{13} g C/ yr (McCollom and Shock, 1997)
- Hydrothermal plumes: ~10^{12} g C/ yr (McCollom 2000)
- Ridge flanks/weathering: ~10^{12} g C/ yr (Bach and Edwards, 2003)

- Photosynthetic: ~10^{17} g C/ yr (Whitman et al., 1997)
- Sulfate reduction in marine sediments: ~2 x 10^{12} g C/ yr (Bach and Edwards, 2003 based on sulfate flux rates from D'Hondt et al., 2002)

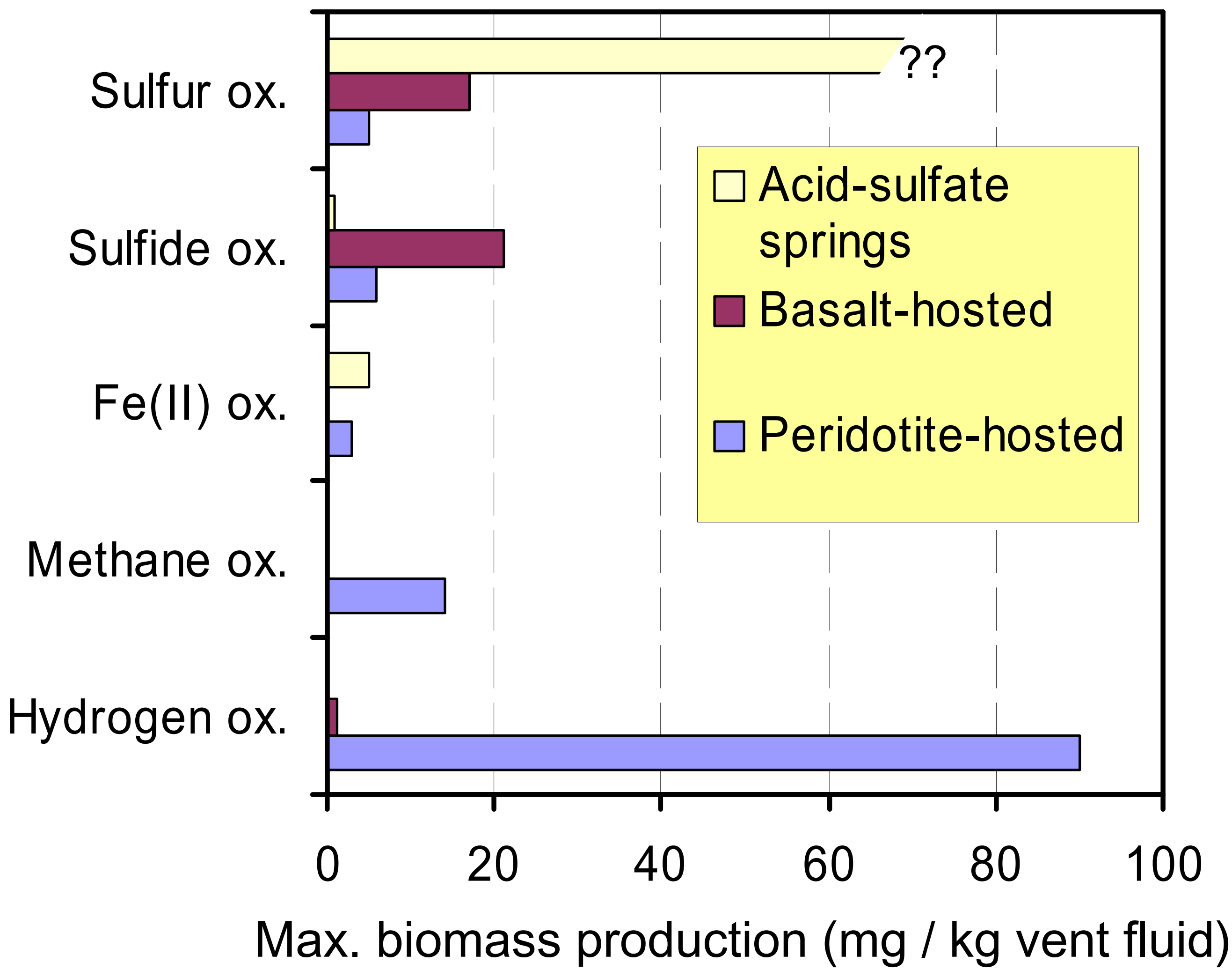
What reactions are exergonic?





McCollom & Shock (1997)

What reactions support how much biomass?



Sources of dihydrogen

Hydrogen can be generated abiotically by:

(1) Reactions between C-O-H(-S) species in melts and vapors

(2) Decomposition of methane at T>600°C

(3) Radiolysis of water by radioaktive decay of U, Th, and 40-K

(4) Catalysis of silicates under stress in the presence of water

(5) Hydrolysis by ferrous minerals in mafic and ultramafic rocks

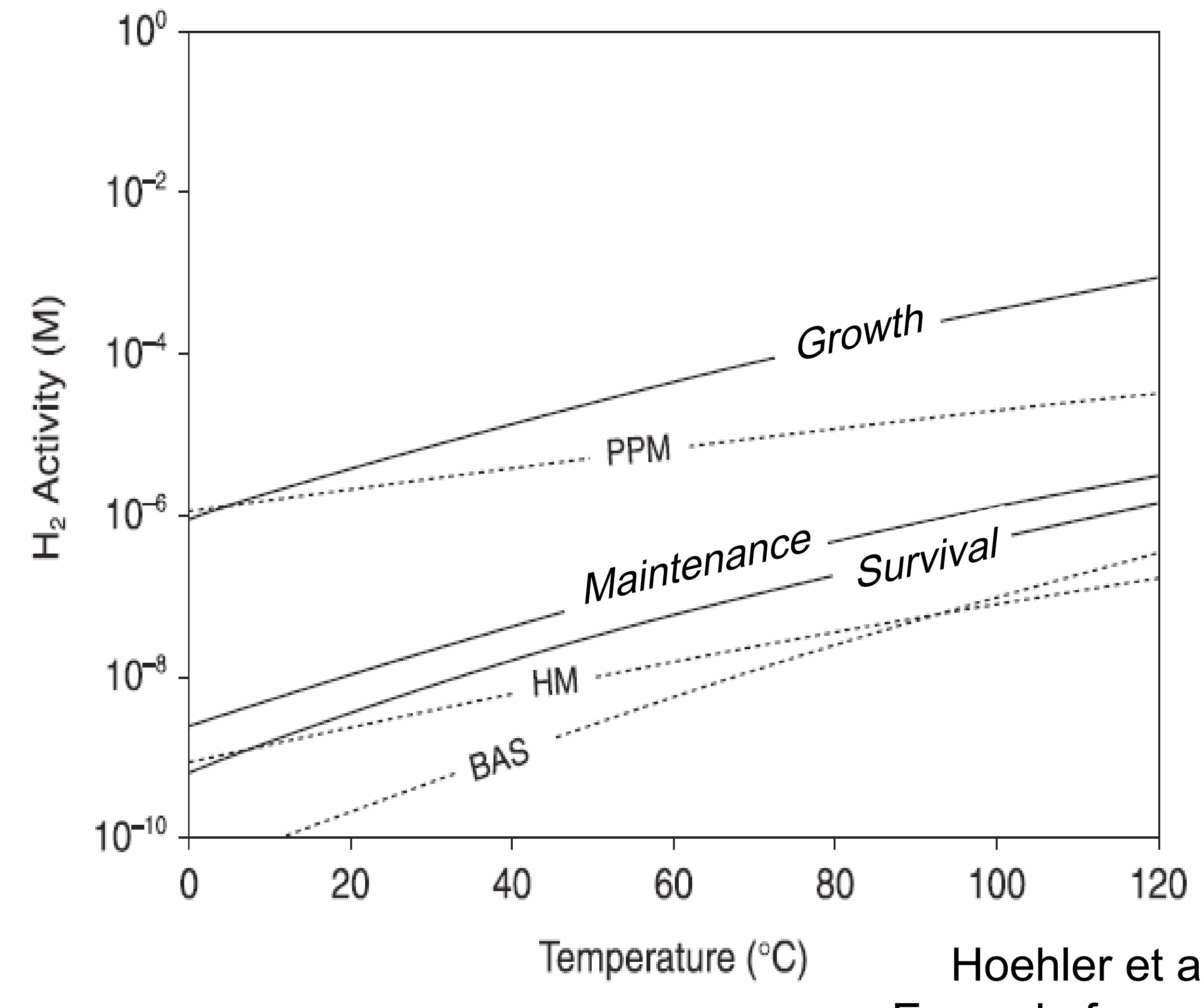
Away from magmatic centers, only pathways 3-5 are viable.

(3) Radiolysis can support on the order of 1,000-10,000 cells per cm^3 in marine sediments (Spivack et al., in press)

(4) Happens, but is likely not a continuous source of hydrogen

(5) Investigated here

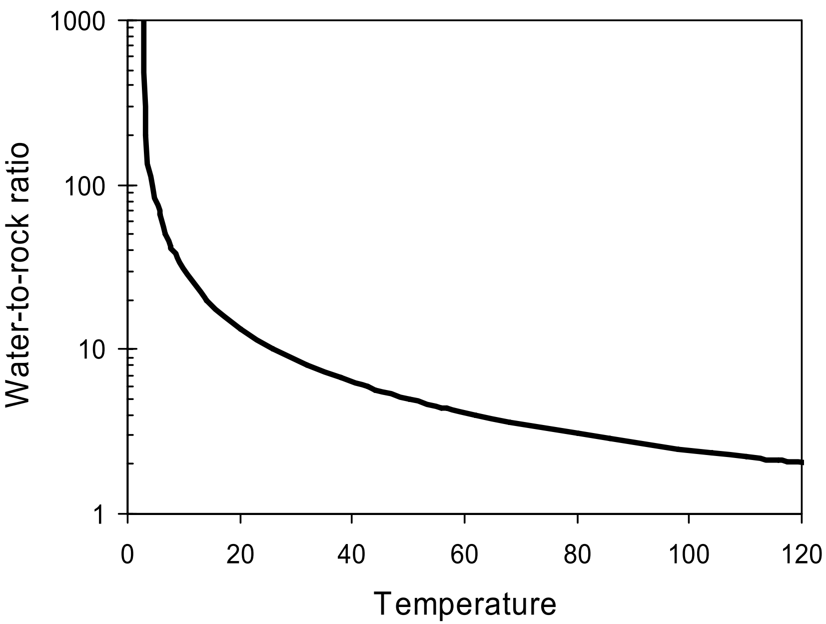
Hydrogen demand and supply



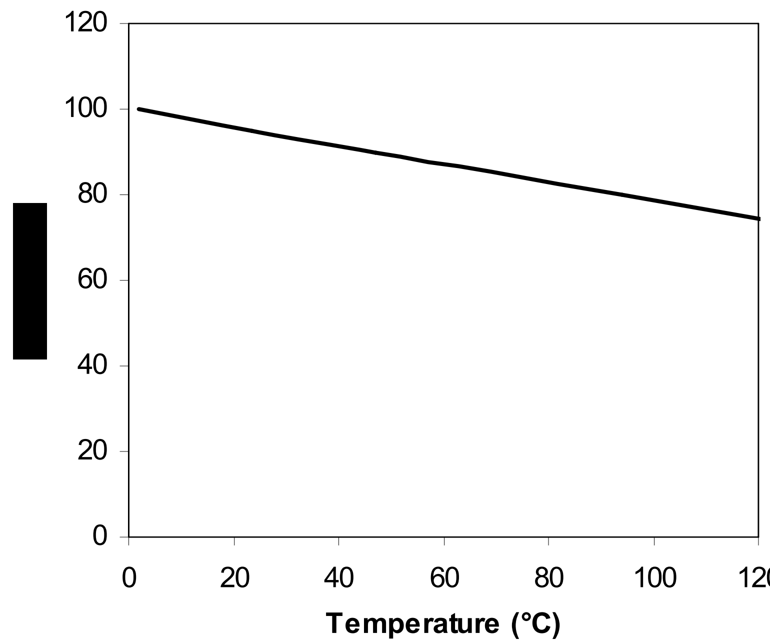
Hoehler et al. (2004)
Example for methanogens

Hydrogen demand and supply

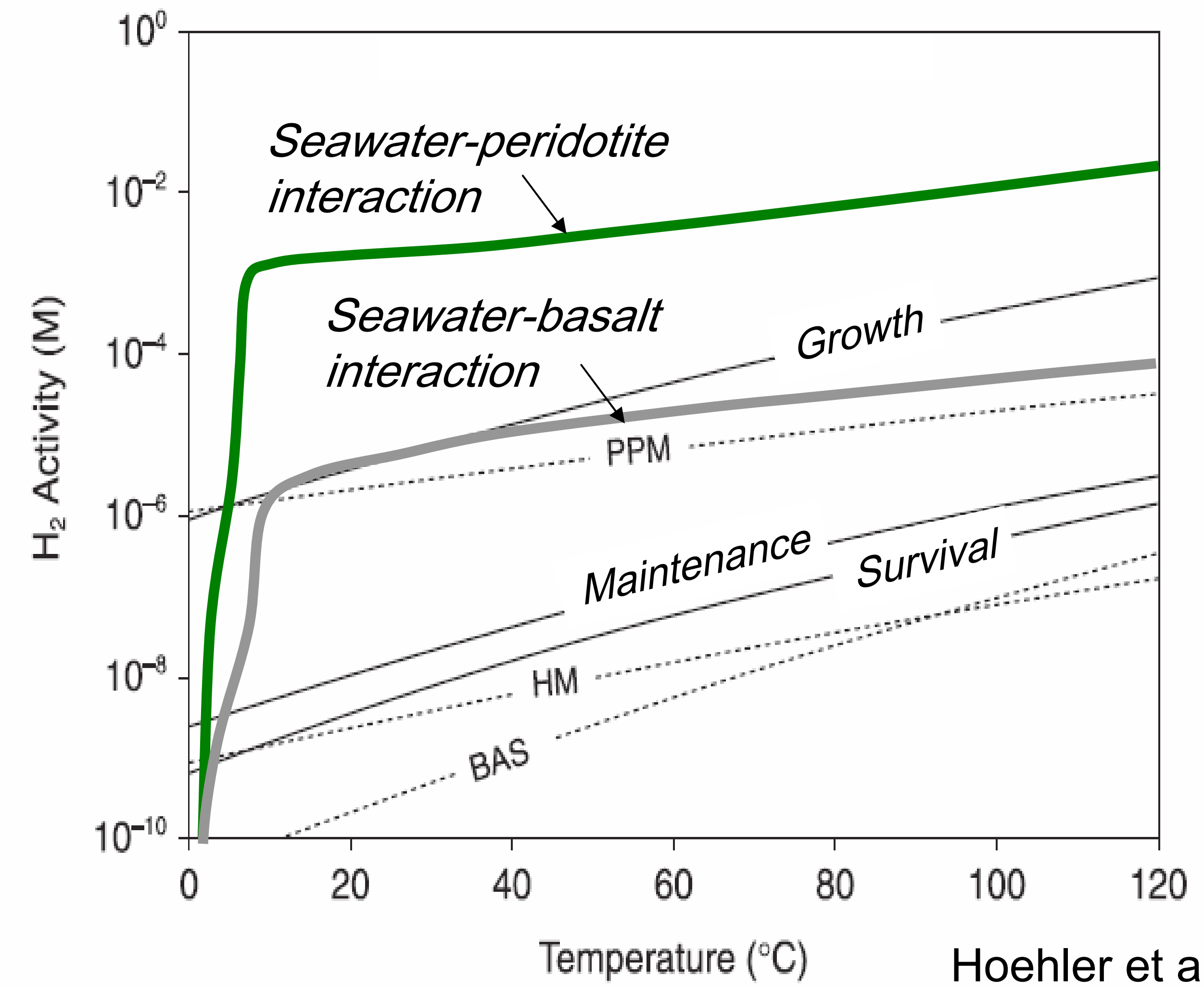
- Source: Water-rock Interaction
@ T=2-120°C



- Source: Water-rock interaction @>350-400°C, followed by mixing with cold seawater

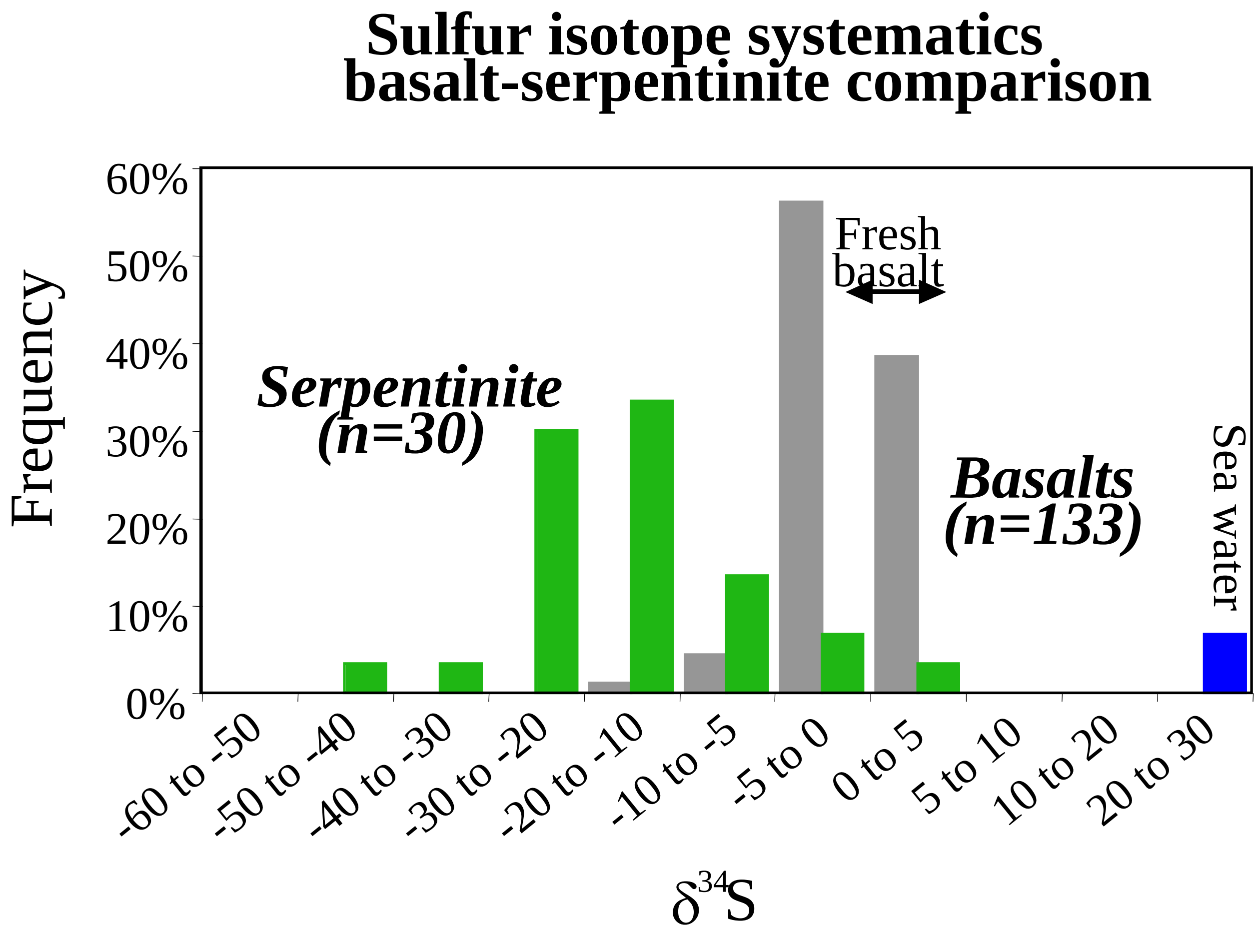


Hydrogen demand and supply



Hoehler et al. (2004)
Example for methanogens

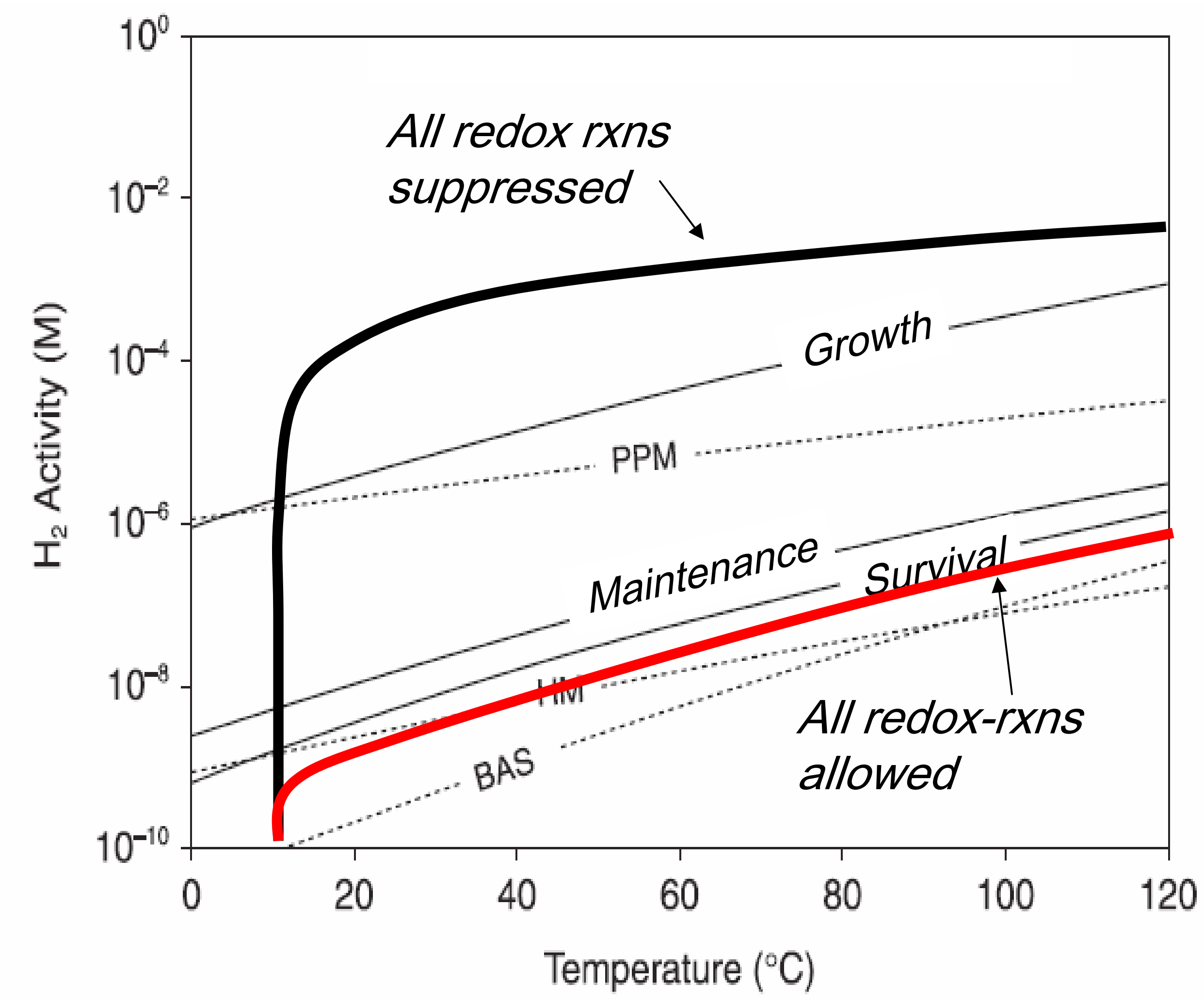
Isotopic record of sulfate reduction in basalt and serpentinite



Data: Jeff Alt

Hydrogen demand and supply

Seawater – vent fluid mixing

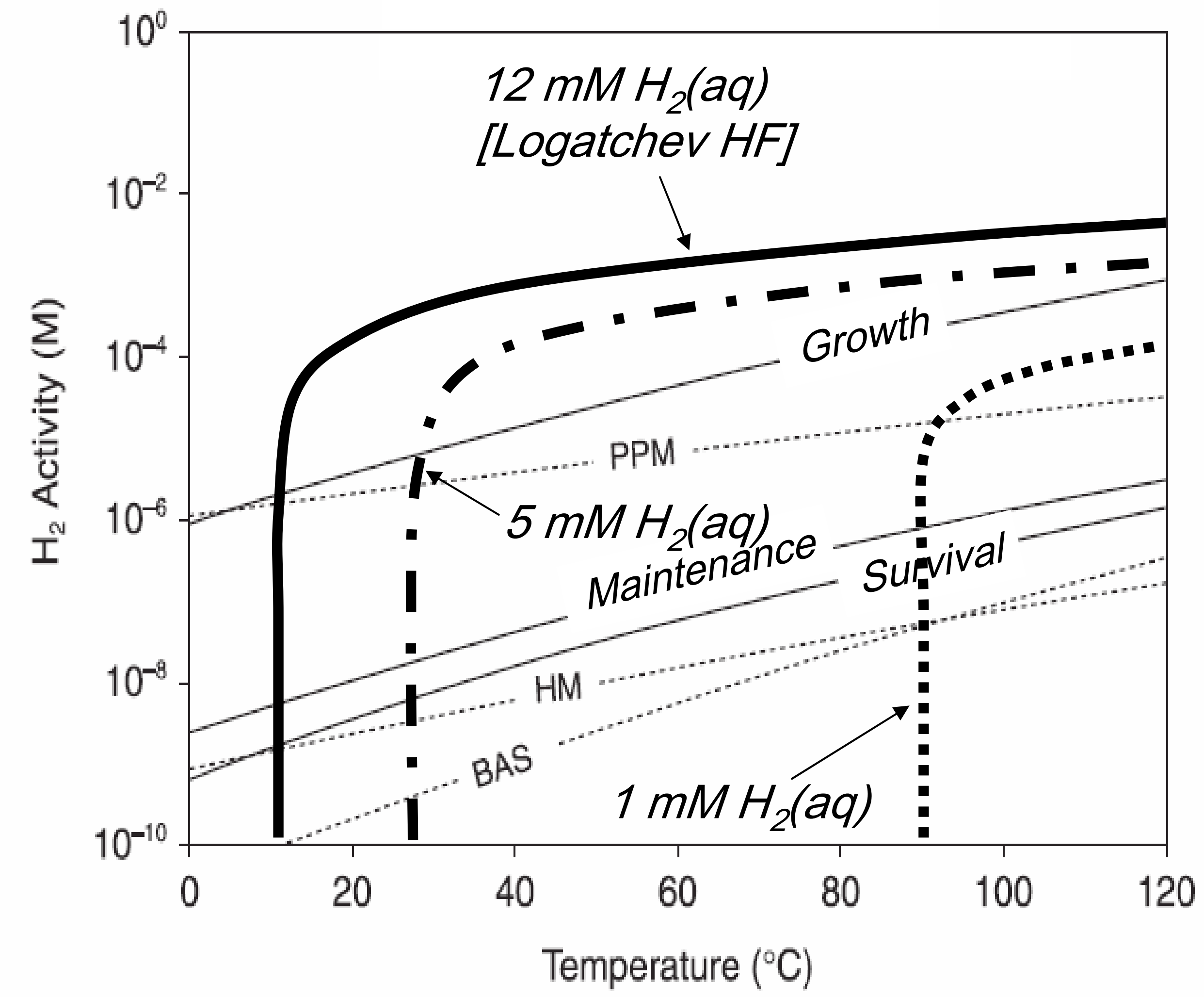


Logatchev fluid mixed with sea water

H_2-O_2 is allowed to equilibrate

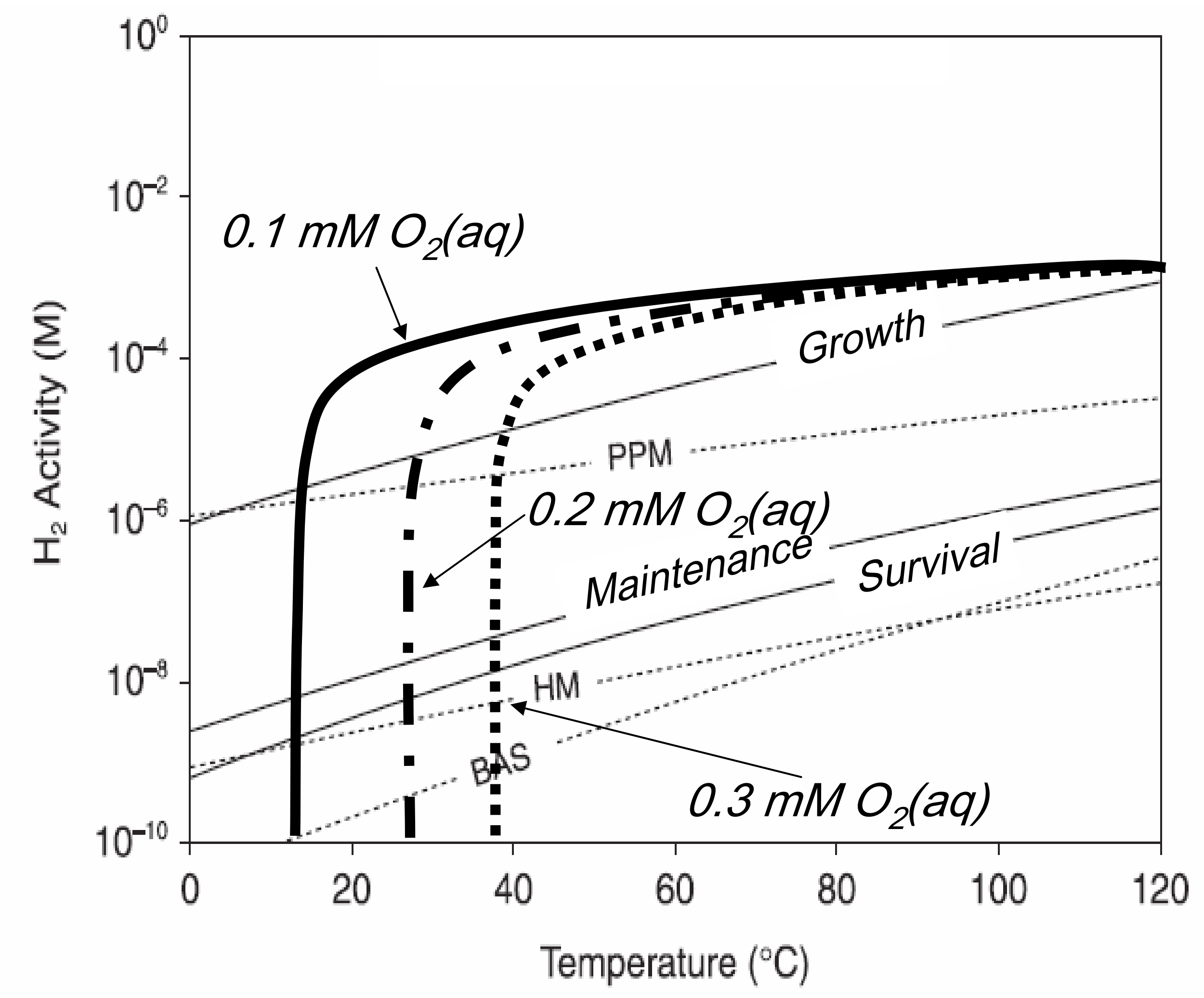
Hydrogen demand and supply

Seawater – vent fluid mixing



Hydrogen demand and supply

Seawater – vent fluid mixing



Summary

- Vent fluid compositions differ fundamentally in different plate tectonic settings.
- Phase equilibria in the deepest and hottest part of hydrothermal systems set the fluid chemistry that is further modified by mixing with cold seawater, creating disequilibria
- Another way of creating habitable conditions for microbial life is in water-rock reaction systems running at temperatures too low for the system to reach equilibrium
- Life is ineffcient in harvesting the geochemical energy, but relations between the amount of energy and the production of biomass can be expected
- The primary fuel for microbial biomass production is: H_2S in basalt-hosted, H_2 and CH_4 in serpentinization, and S and Fe in felsic rock hosted systems
- In mixing environments, the transition between anoxic and oxic conditions depends on the compositions of the mixing fluids and the kinetics of the H_2-consuming redox reactions

Acknowledgments

For discussions and materials:

- Tom McCollom, Dionysis Foustoukos, Jan Amend, Art Spivack (Thermodynamics and bioenergetics)
- Katrina Edwards (Deep biosphere)
- Jeff Seewald, Paul Craddock, Eoghan Reeves (Manus Basin fluid chemistry)
- Frieder Klein, Michael Hentscher (Geochemical modeling)
- Ron Frost (Petrology)
- Nicole Dubilier (Geofueled vent biology)

For funding:

- NSF and DFG

- InterRidge folks for invitation

Silica-metasomatism in the oceanic lithosphere

MgO-SiO_2-H_2O phase relations at 500 bar