

Geochemical modeling of vent fluid-seawater interactions



Image from NOAA-PMEL.



photo by Pat Hickey.

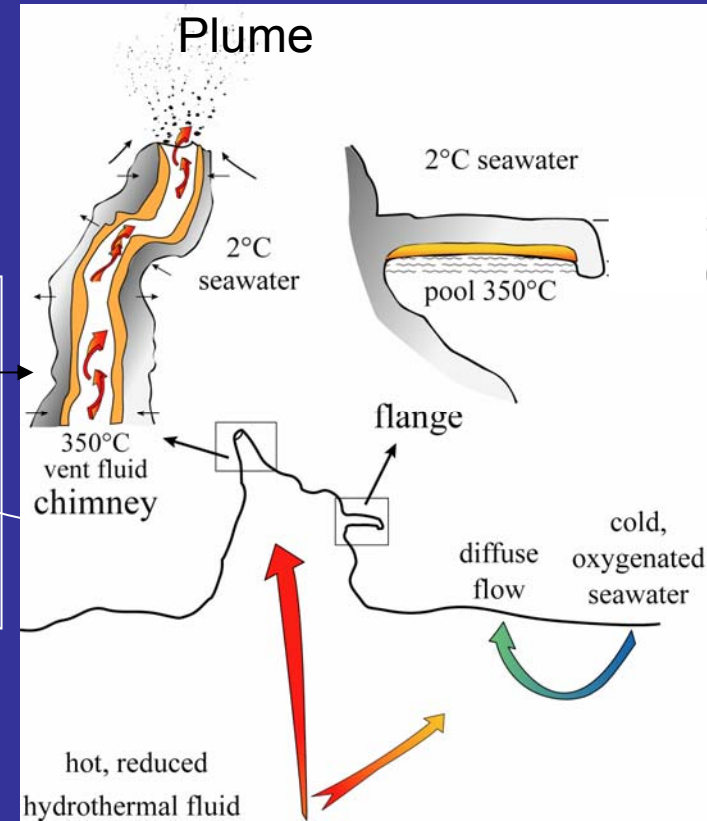
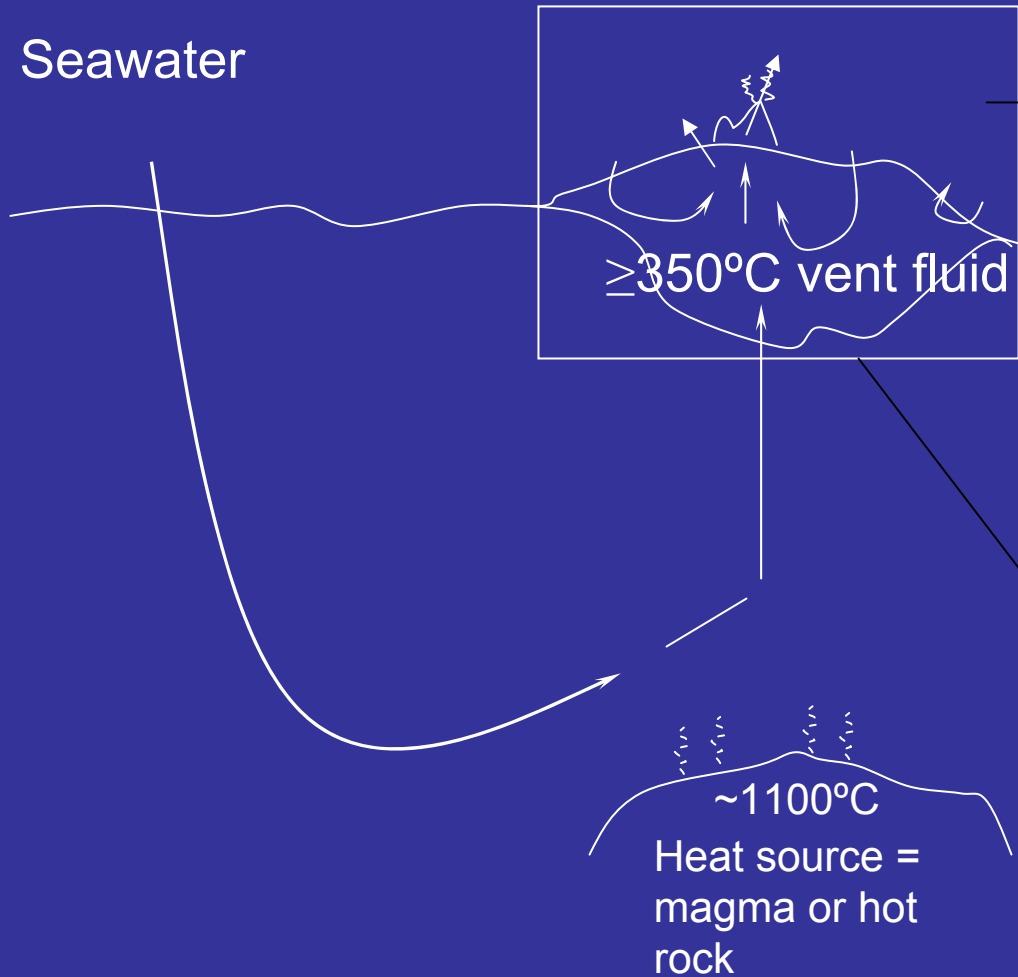
Meg Tivey, Associate Scientist
Dept of Marine Chemistry and Geochemistry
Woods Hole Oceanographic Institution
Woods Hole, MA 02543

Research funded by



Styles of vent fluid-seawater mixing

Seawater

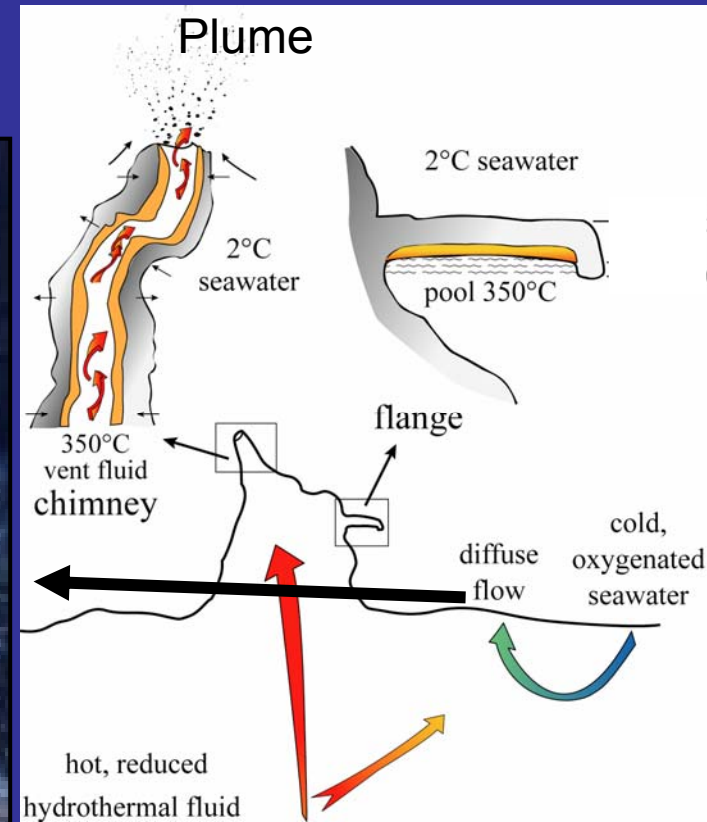


This presentation will focus on styles of mixing at and beneath active vent fields

Styles of vent fluid-seawater mixing



Image from NOAA-PMEL.

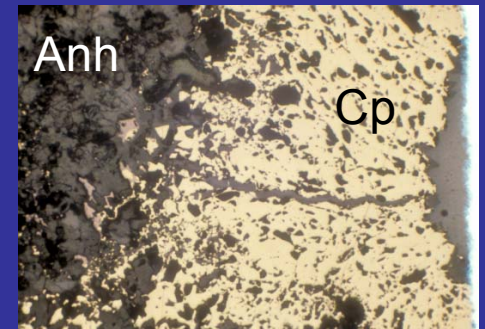
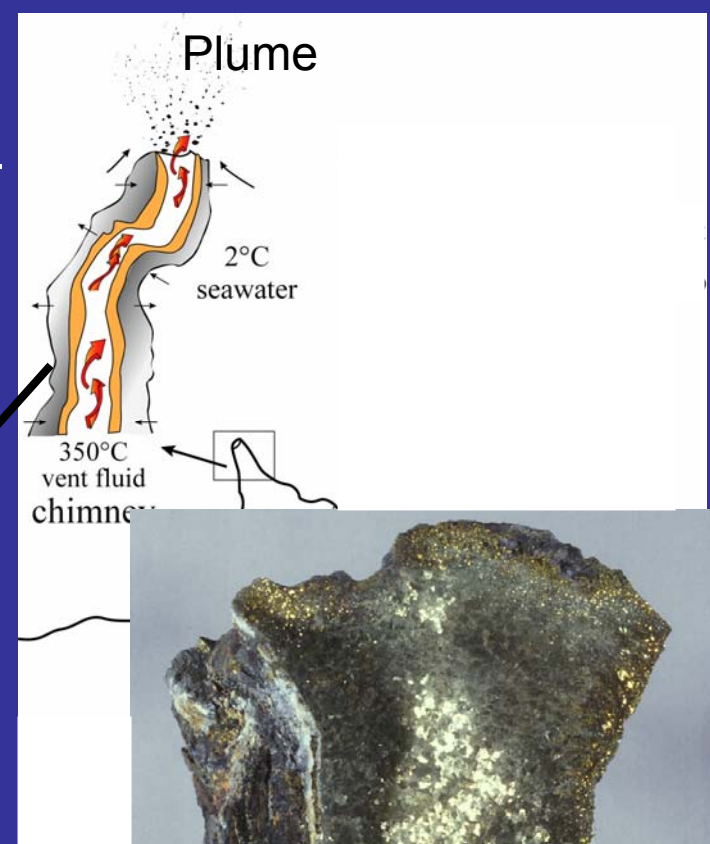


Mixing of vent fluid and seawater in the subsurface

Styles of vent fluid-seawater mixing

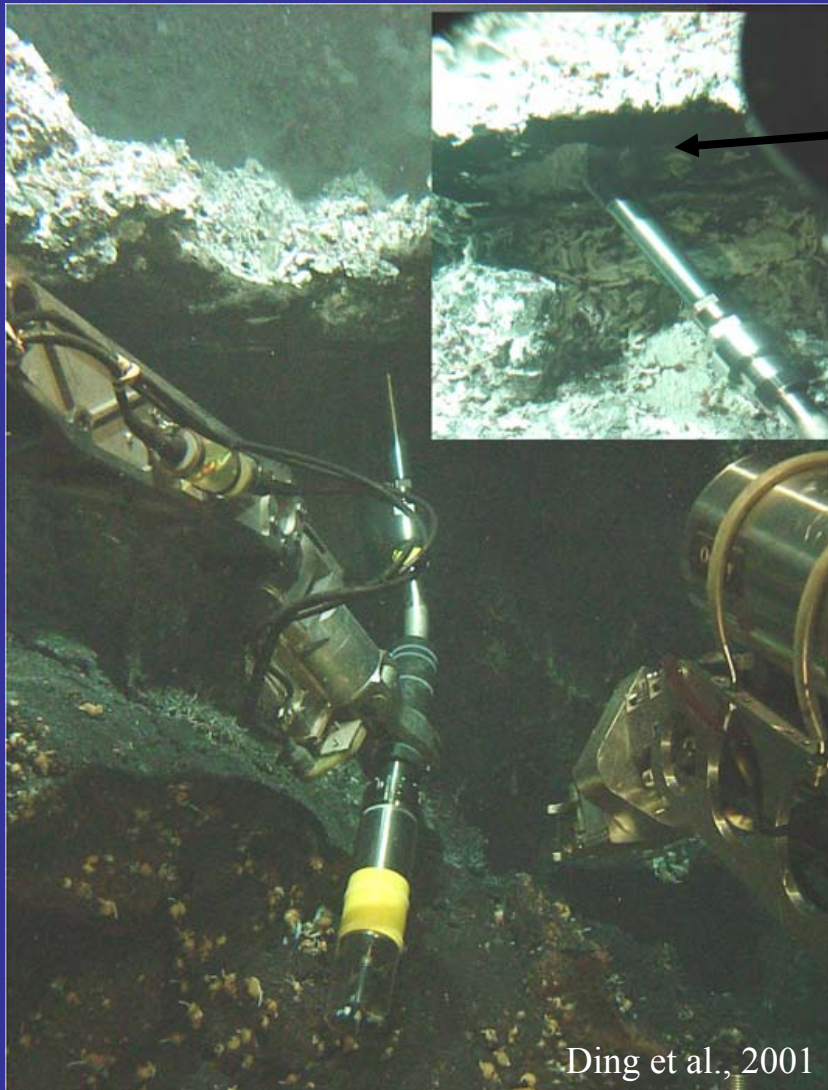


photo by Pat Hickey.

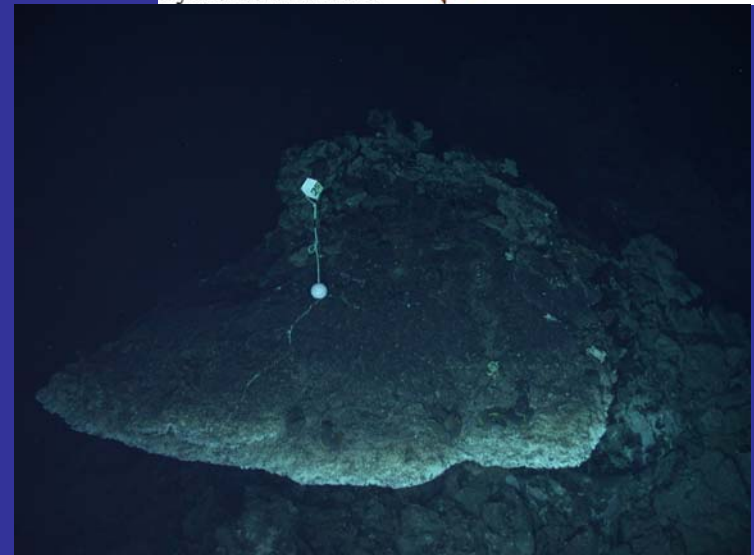
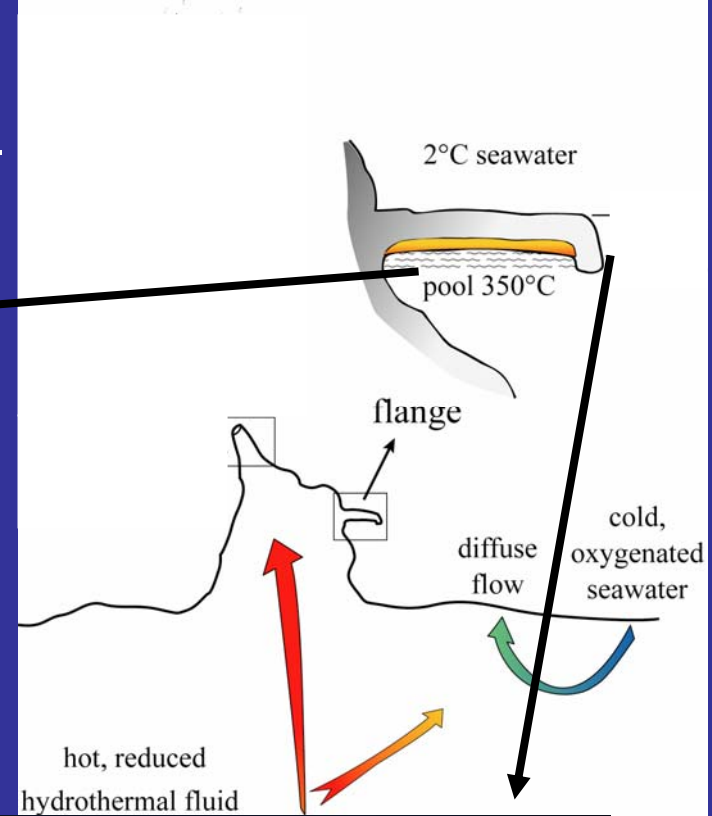


Mixing of vent fluid and seawater in chimney walls

Styles of vent fluid-seawater mixing



Ding et al., 2001



Mixing of vent fluid and seawater in flanges

Styles of vent fluid-seawater mixing

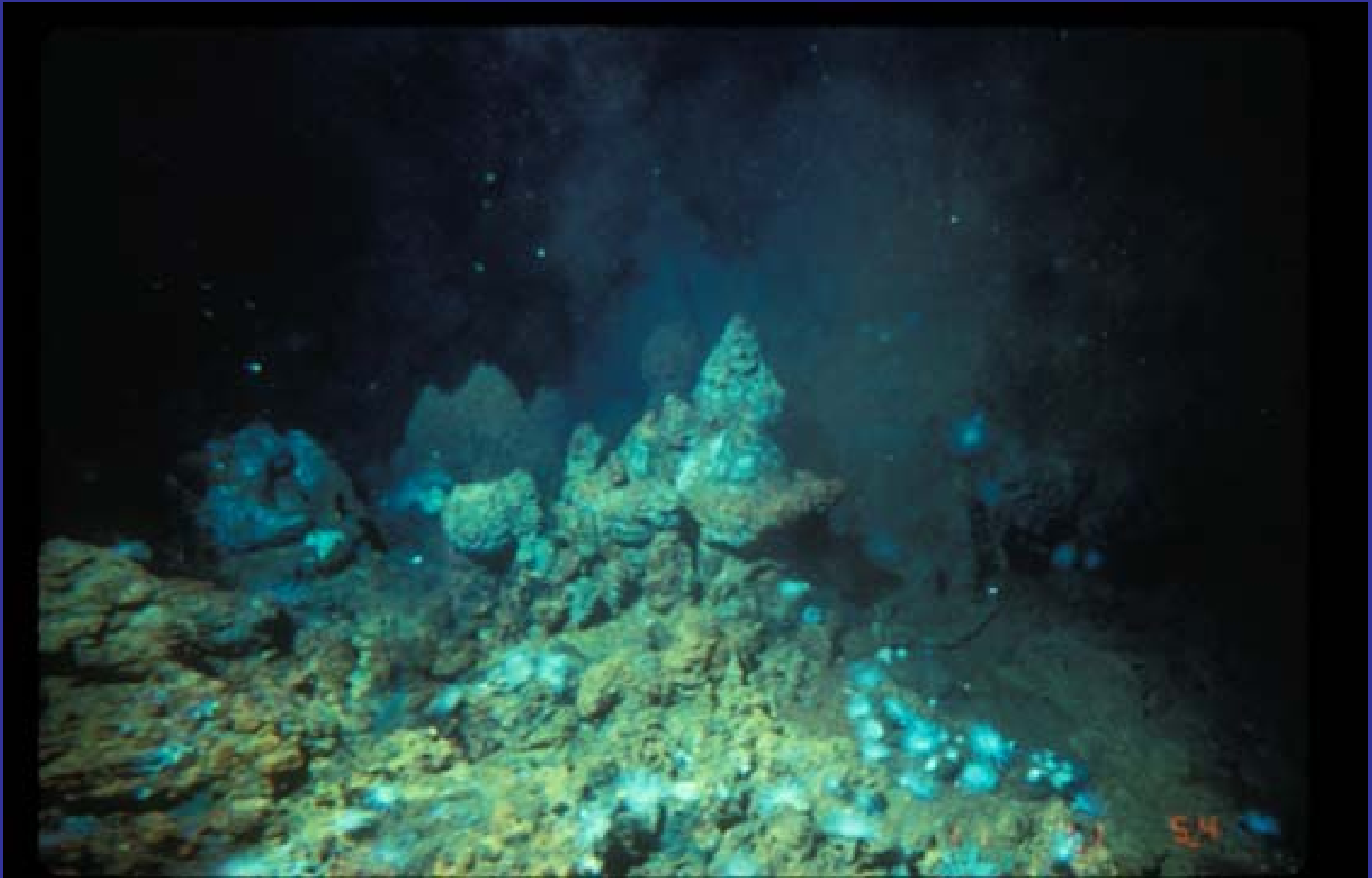
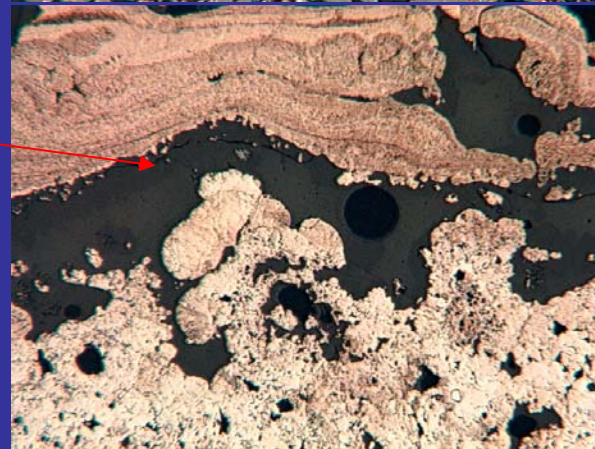
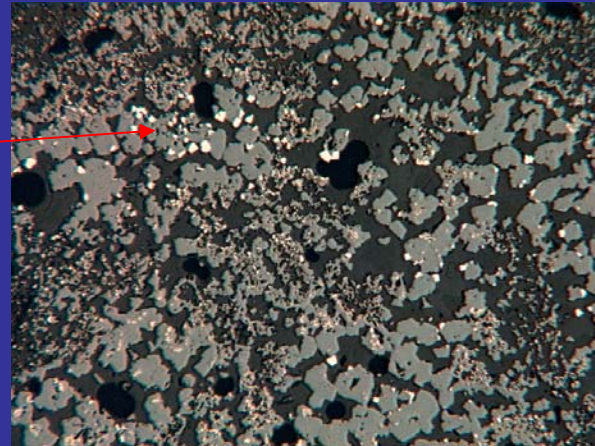
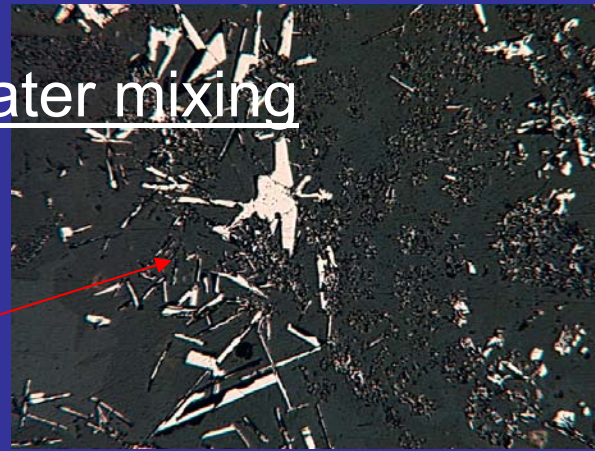
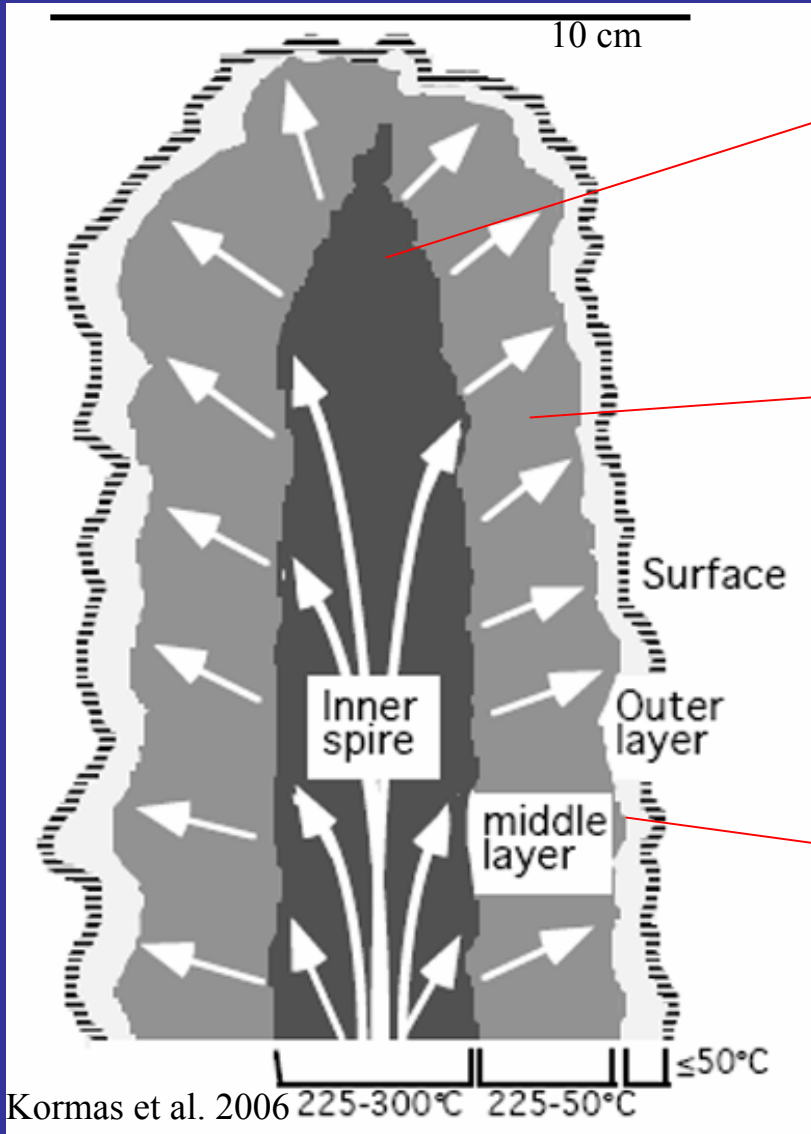


Photo taken by submersible *Alvin* of white smokers at TAG active hydrothermal mound, G.Thompson/P.Rona Chief Scientists, 1990. Mixing of vent fluid and seawater in diffusers

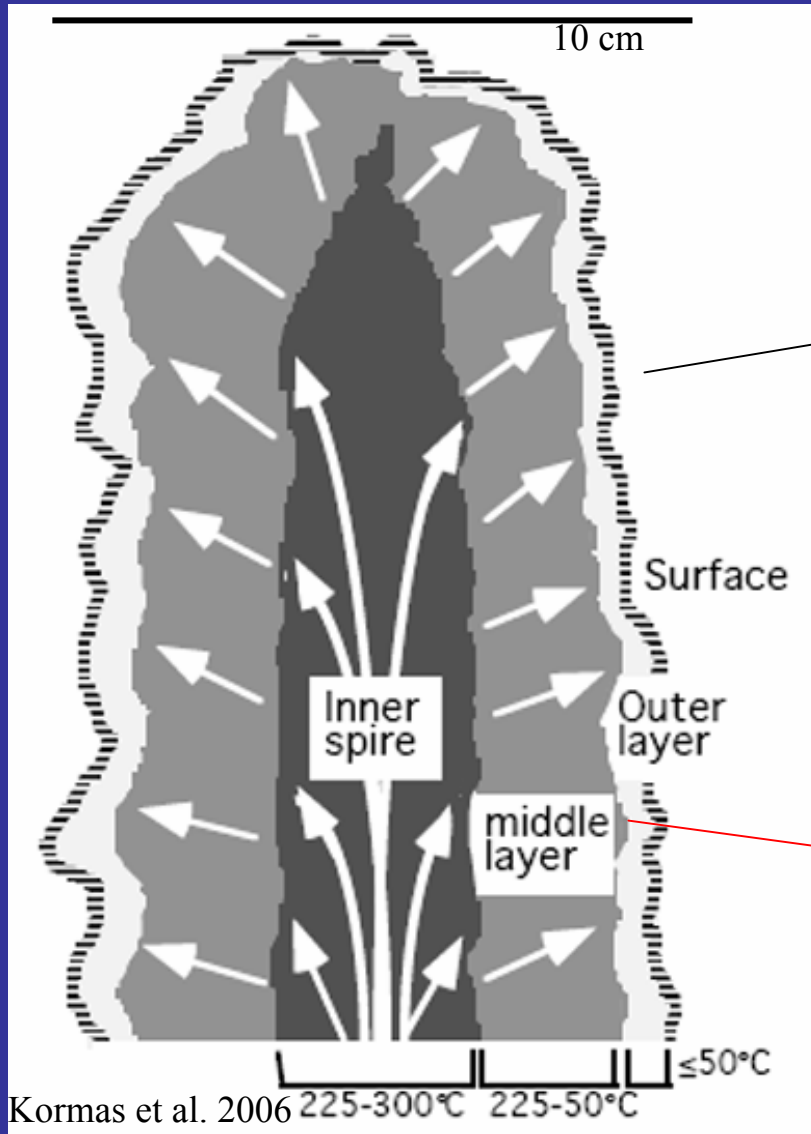
Styles of vent fluid-seawater mixing



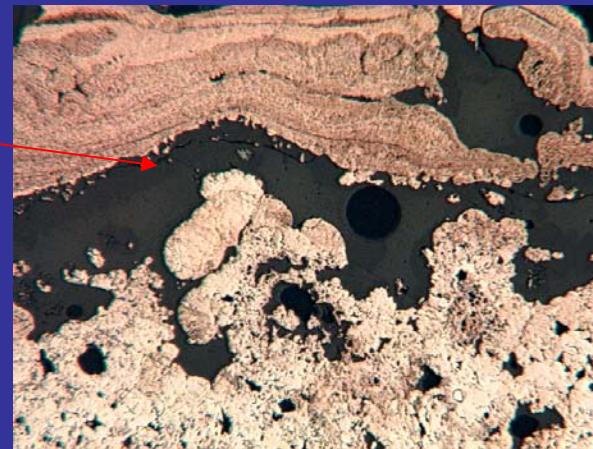
In diffusers, relatively high rates of vent fluid flow through very porous (48% to 87% pore space) zones.

2 mm

Styles of vent fluid-seawater mixing



Le Bris et al.,
2005

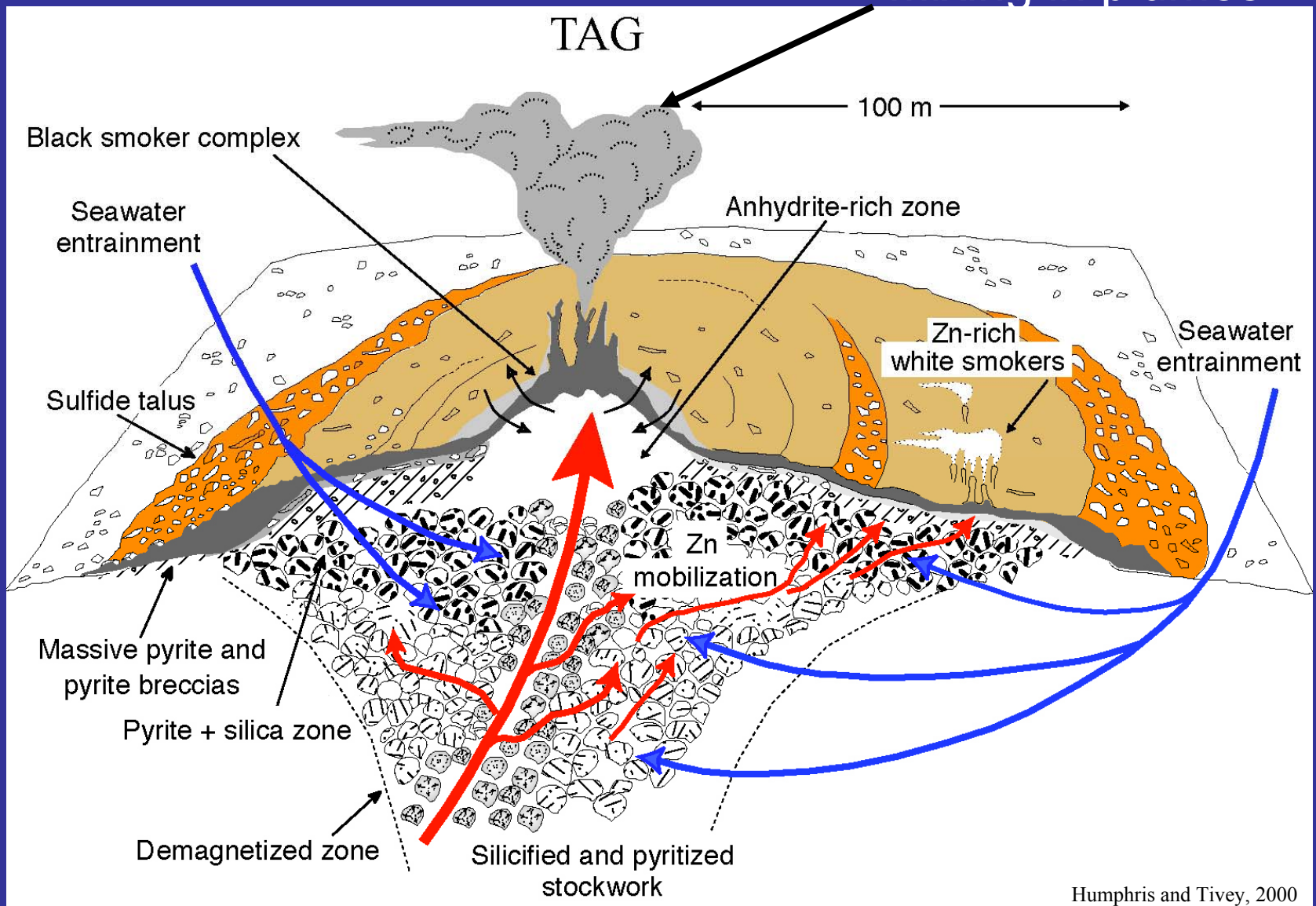


2 mm

In diffusers, outer surfaces are often colonized, with fluid flowing outward across communities.

Styles of vent fluid-seawater mixing

Mixing in plumes



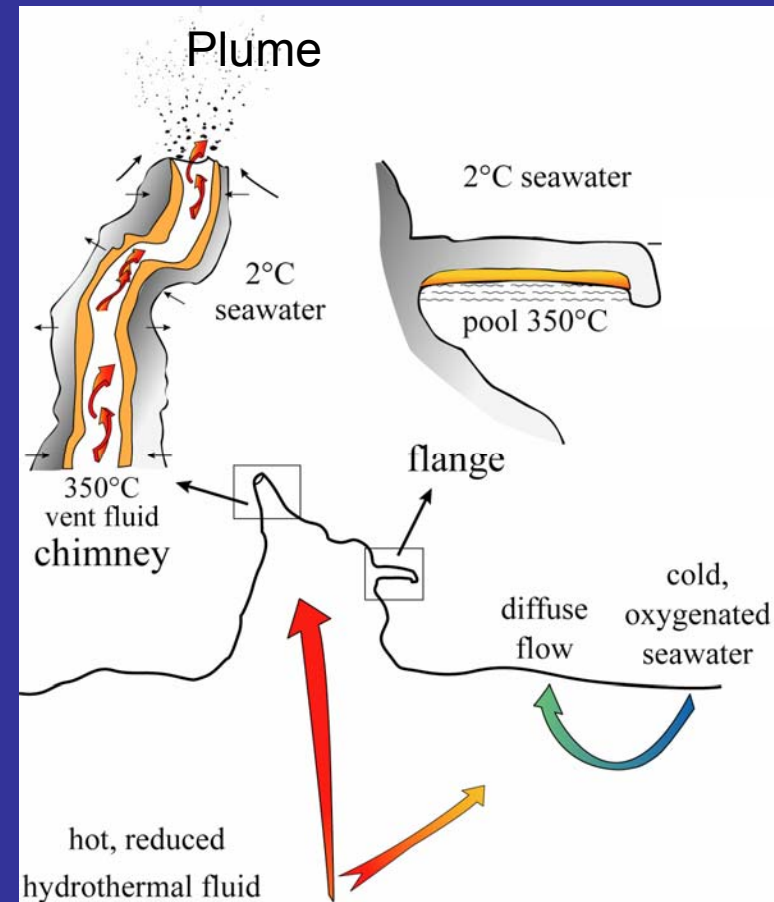
I. Styles and models of mixing between two fluids

In crust

In deposits at seafloor

In plumes

Have just reviewed many of the different styles



I. Styles and models of mixing between two fluids

In crust

In deposits at seafloor

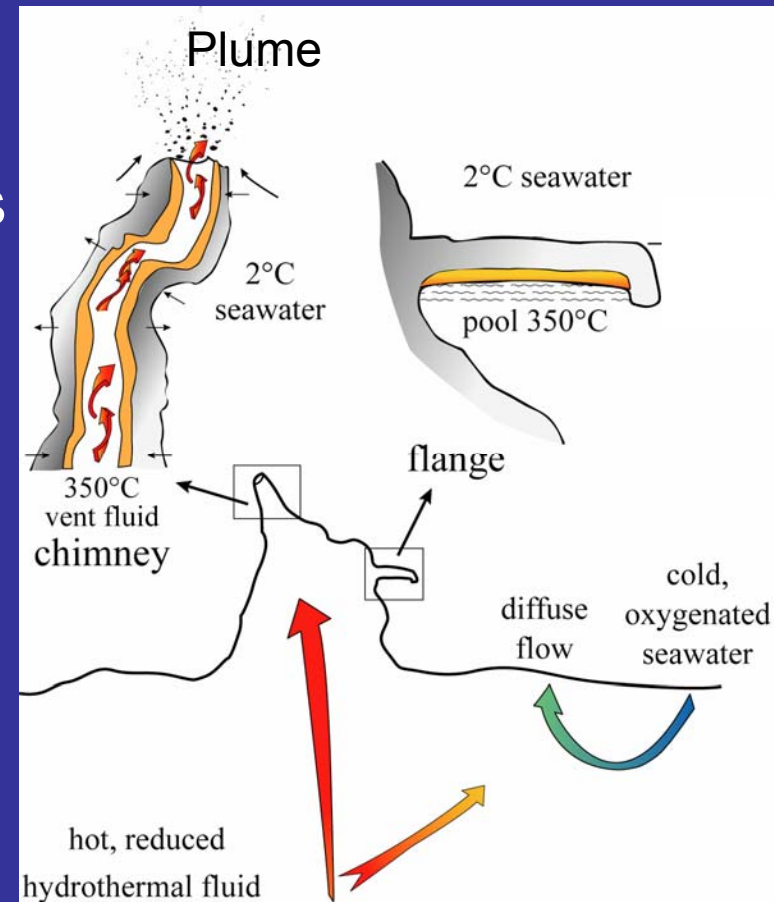
In plumes

II. Reasons to quantify mixing styles

Estimate environmental conditions in inaccessible locations

Calculate available metabolic energy

Why quantify mixing styles?



I. Styles and models of mixing between two fluids

In crust

In deposits at seafloor

In plumes

II. Reasons to quantify mixing styles

Estimate environmental conditions in inaccessible locations

Calculate available metabolic energy

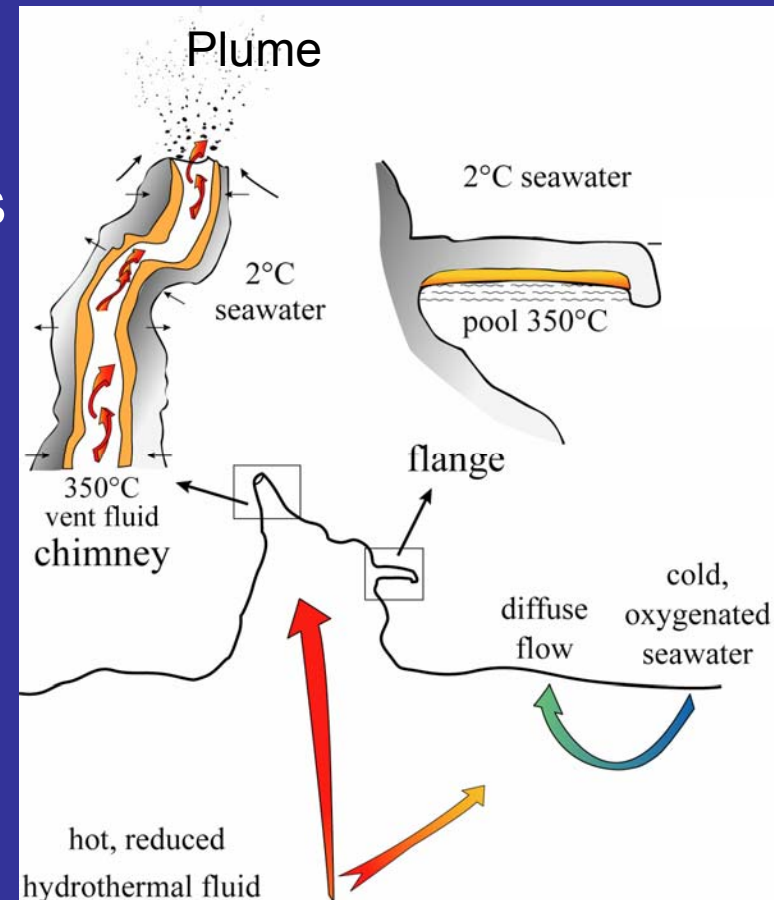
III. Tools available

Computer codes

Thermodynamic data

Information on kinetics

Will first review the available tools



I. Styles and models of mixing between two fluids

In crust

In deposits at seafloor

In plumes

II. Reasons to quantify mixing styles

Estimate environmental conditions in inaccessible locations

Calculate available metabolic energy

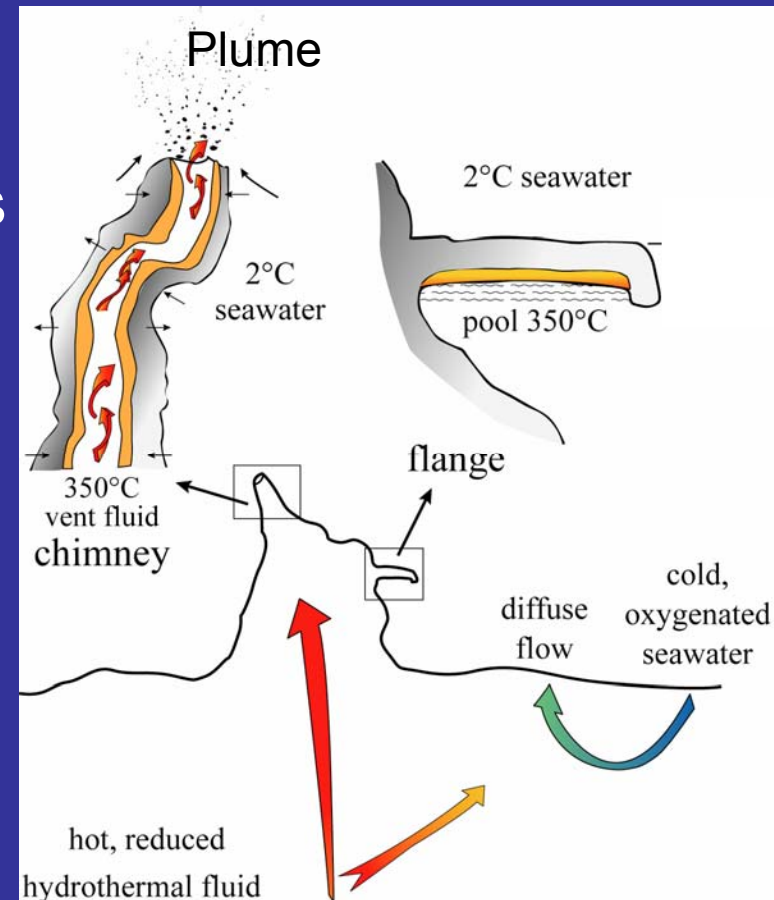
III. Tools available

Computer codes

Thermodynamic data

Information on kinetics

IV. Best tools for specific environments



I. Styles and models of mixing between two fluids

In crust

In deposits at seafloor

In plumes

II. Reasons to quantify mixing styles

Estimate environmental conditions in inaccessible locations

Calculate available metabolic energy

III. Tools available

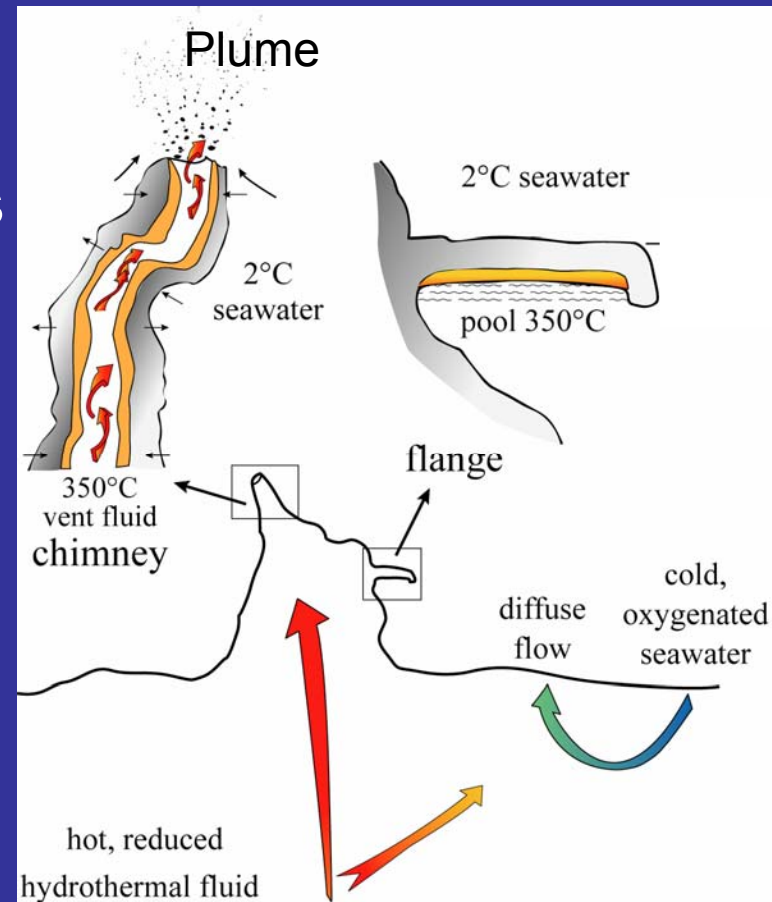
Computer codes

Thermodynamic data

Information on kinetics

IV. Best tools for specific environments

V. Sensitivity of results to assumptions made



I. Styles and models of mixing between two fluids

In crust

In deposits at seafloor

In plumes

II. Reasons to quantify mixing styles

Estimate environmental conditions in inaccessible locations

Calculate available metabolic energy

III. Tools available

Computer codes

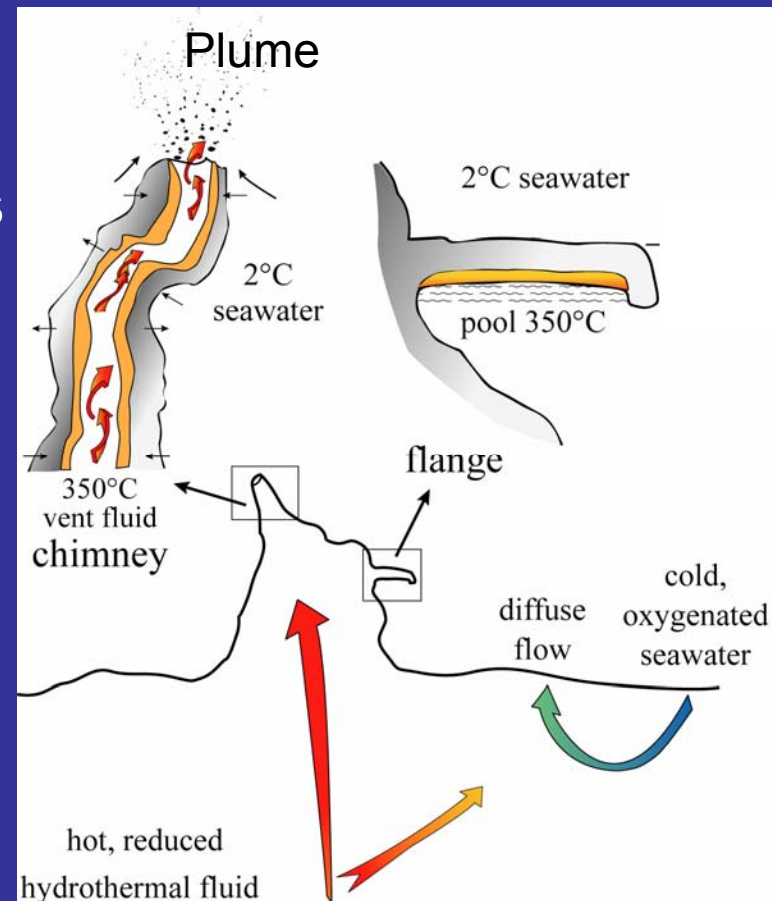
Thermodynamic data

Information on kinetics

IV. Best tools for specific environments

V. Sensitivity of results to assumptions made

VI. Limitations in current ability to quantify processes



Tools available

▶ I. Distribution of species as fn of T (MINEQL, EQ3, REACT)

Sensitivity to input

- A. thermodynamic data
- B. fluid composition data
- C. temperature data

II. Path reaction

- A. assumptions about kinetics
- B. assumptions about whether T is conservative

III. Transport-reaction

- A. small scale across steep gradients
- B. large scale at low transport rates
- C. assumptions – kinetics, boundary conditions, steady-state

Distribution of species as function of T, P

Fluid composition	
	OBS
	mmol/kg
Ca ²⁺	15.6
Mg ²⁺	0
K ⁺	23.2
Na ⁺	428.5
Fe ²⁺	1.664
Mn ²⁺	0.960
Ba ²⁺	0.008
Zn ²⁺	0.106
Pb ²⁺	0.000308
Cu ⁺	0.035
CO ₂	6
CH ₄	0.07
SO ₄ ²⁻	0
NH ₄ ⁺	--
Cl ⁻	489
HS ⁻	7.3
SiO ₂	17.6
H ₂	1.673
pH, 25°C	3.4
T (°C)	350

Distribution of species as function of T, P

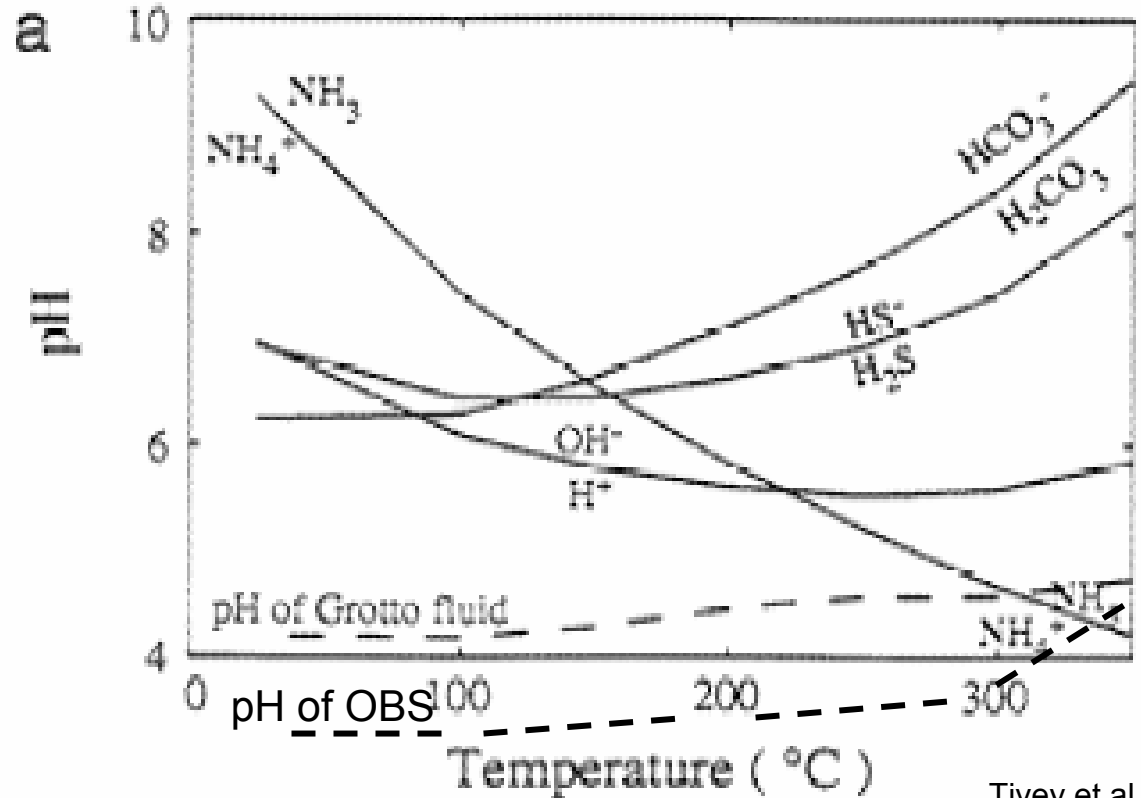
Thermodynamic data:
SUPCRT92
(Johnson et al., 1992;
additional internally
consistent data)

Fluid composition		
	OBS	
	mmol/kg	
Ca ²⁺	15.6	
Mg ²⁺	0	
K ⁺	23.2	
Na ⁺	428.5	
Fe ²⁺	1.664	
Mn ²⁺	0.960	
Ba ²⁺	0.008	
Zn ²⁺	0.106	
Pb ²⁺	0.000308	
Cu ⁺	0.035	
CO ₂	6	
CH ₄	0.07	
SO ₄ ²⁻	0	
NH ₄ ⁺	--	
Cl ⁻	489	
HS ⁻	7.3	
SiO ₂	17.6	
H ₂	1.673	
log fO ₂	-30.4	←
pH, 25°C	3.4	
pH, in situ	4.3	←
T (°C)	350	←

Distribution of species as function of T, P

Table 4. Fluid composition

OBS
mmol/kg



Tivey et al., 1999

Thermodynamic data:
SUPCRT92
(Johnson et al., 1992;
additional internally
consistent)

SiO ₂	17.6
H ₂	1.673
log fO ₂	-30.4
pH, 25°C	3.4
pH, in situ	4.3
T (°C)	350



Von Damm et al., 1985

Tools available

I. Distribution of species as fn of T (MINEQL, EQ3, REACT)

Sensitivity to input

A. thermodynamic data

B. fluid composition data

C. temperature data

▶ II. Path reaction (EQ6, REACT)

A. assumptions about kinetics

B. assumptions about whether T is conservative

III. Transport-reaction

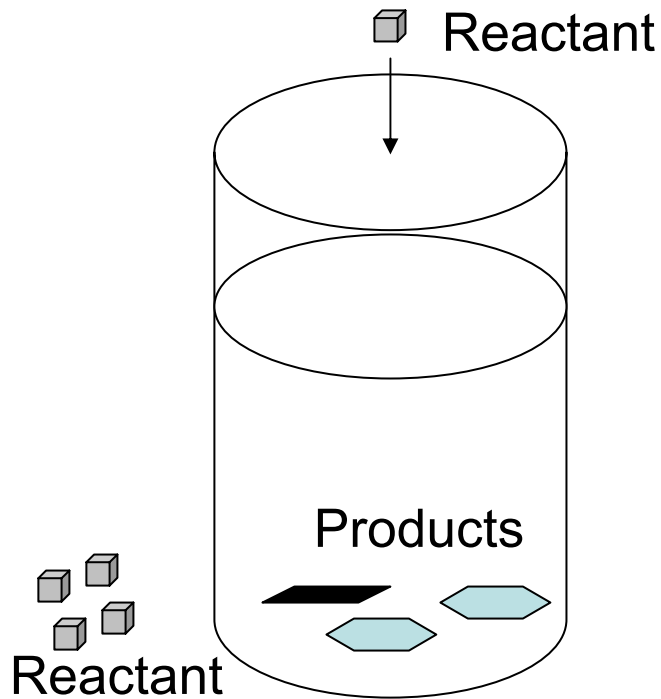
A. small scale across steep gradients

B. large scale at low transport rates

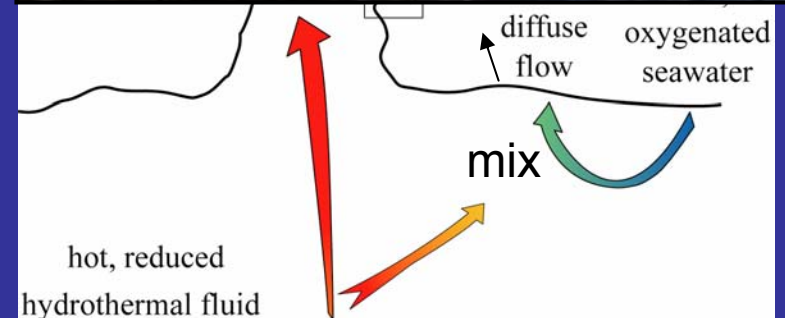
C. assumptions – kinetics, boundary conditions, steady-state

Path reaction (EQ6, REACT)
assumptions about kinetics
assumptions about whether T
is conservative

Titration process

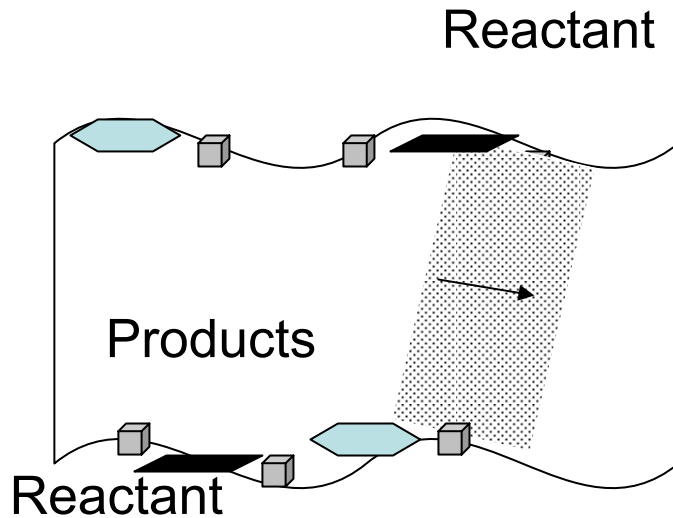


after Wolery and Daveler, 1992

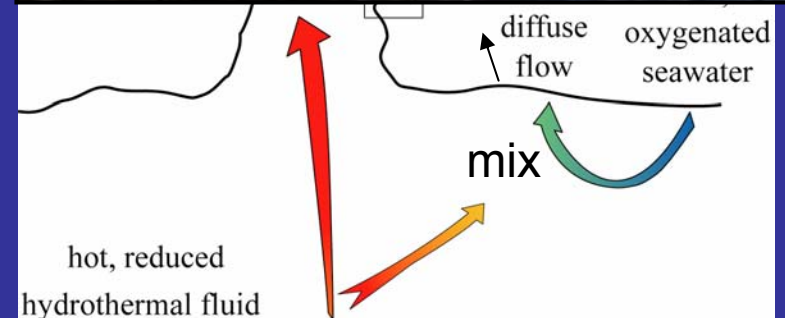


Path reaction (EQ6, REACT)
assumptions about kinetics
assumptions about whether T
is conservative

Flow through open system

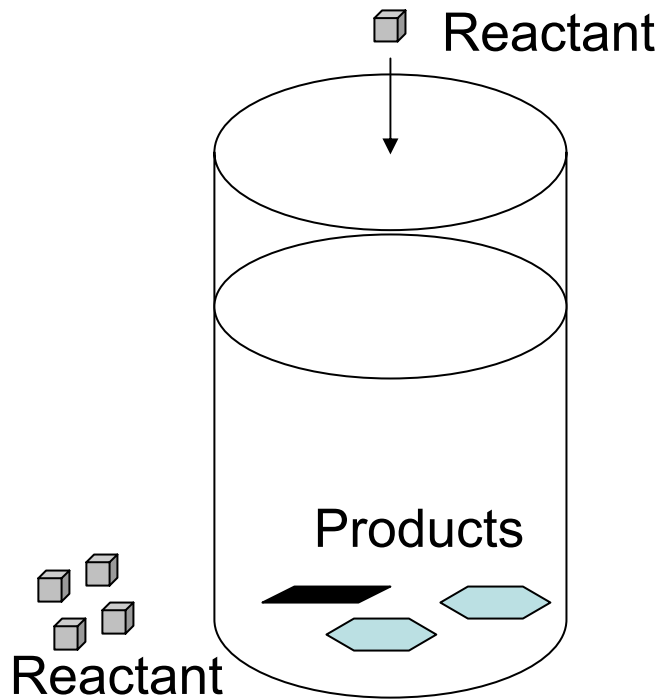


after Wolery and Daveler, 1992

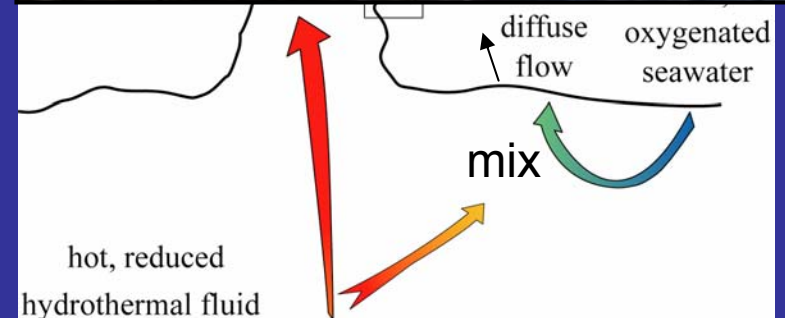


Path reaction (EQ6, REACT)
assumptions about kinetics
assumptions about whether T
is conservative

Titration process

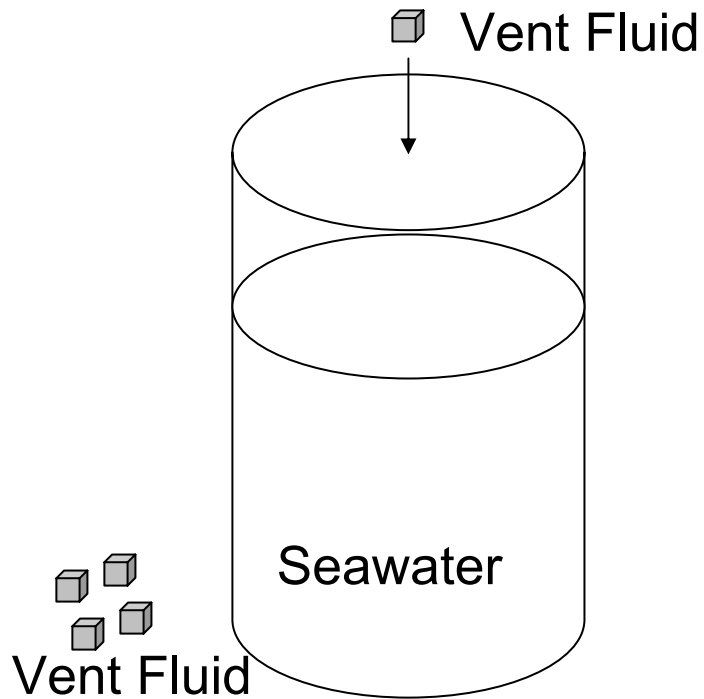


after Wolery and Daveler, 1992

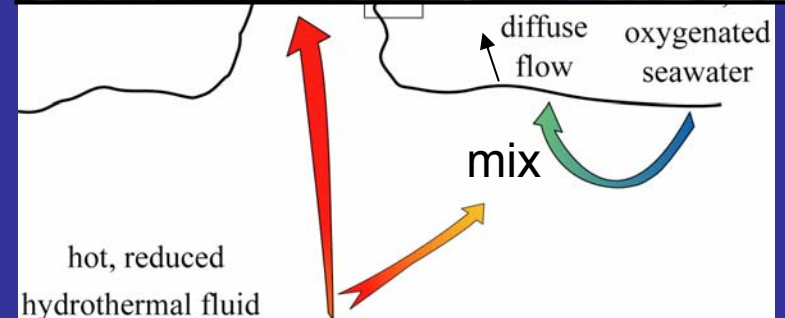


Path reaction (EQ6, REACT)
assumptions about kinetics
assumptions about whether T
is conservative

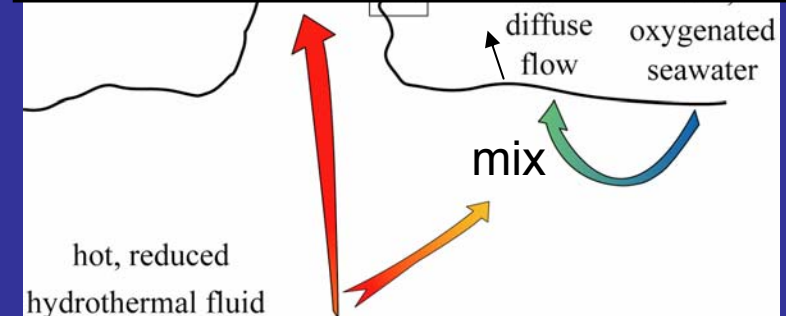
Titration process

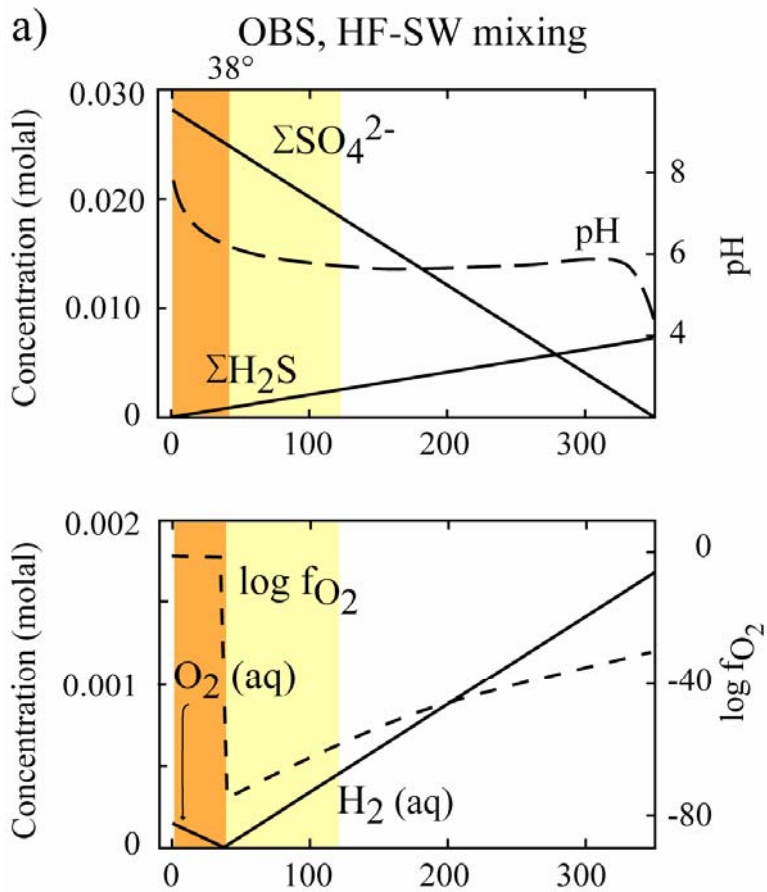


after Wolery and Daveler, 1992



Path reaction (EQ6, REACT)
 assumptions about kinetics
 assumptions about whether T
 is conservative





From McCollom and Shock, 1997

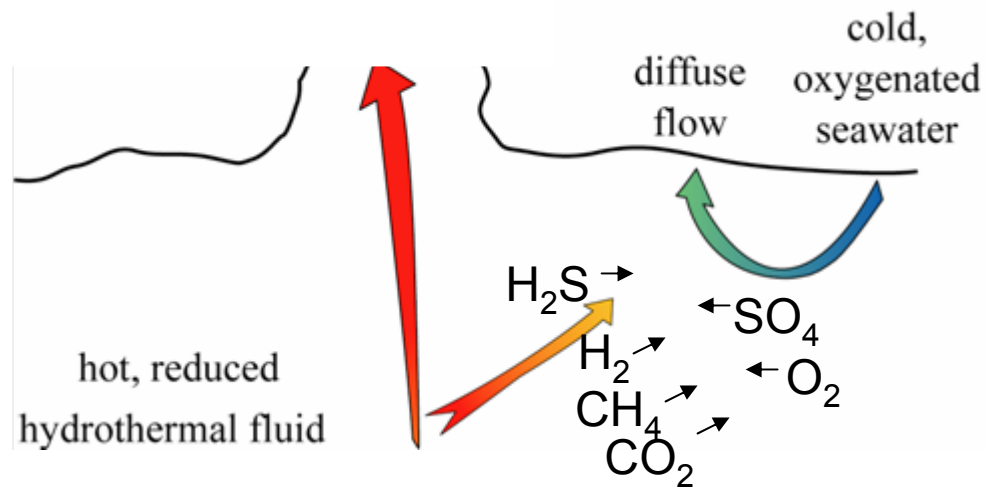
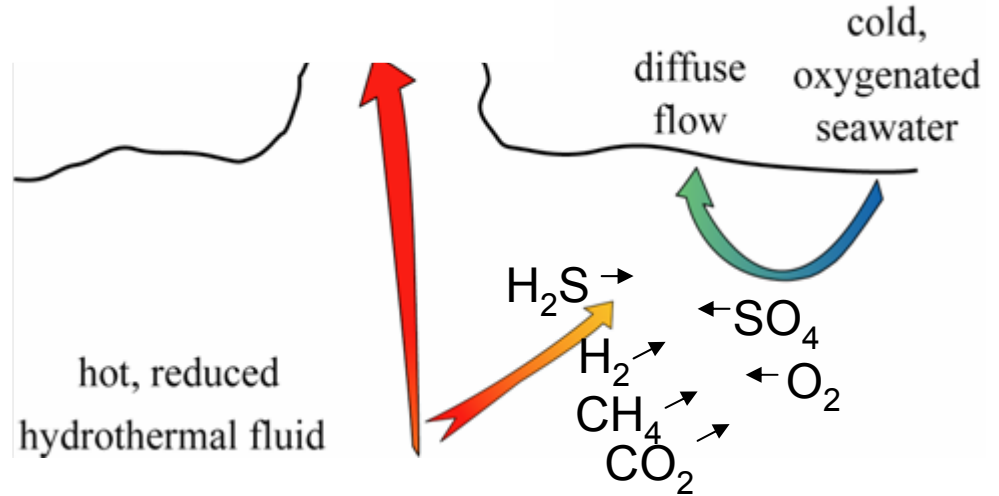
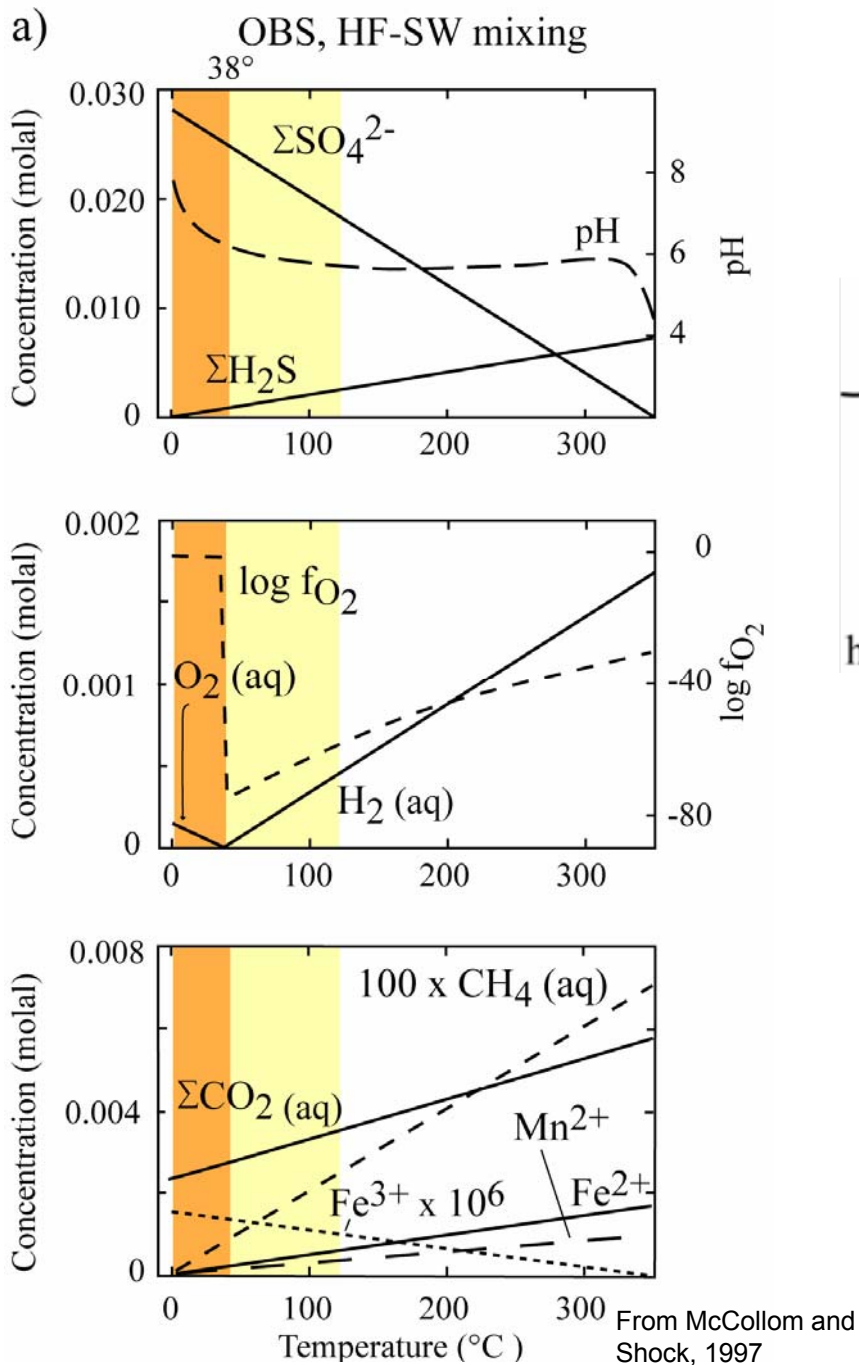


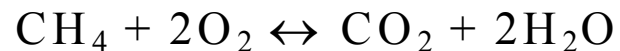
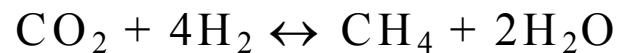
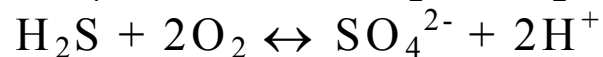
Table 3. Metabolic reactions considered.

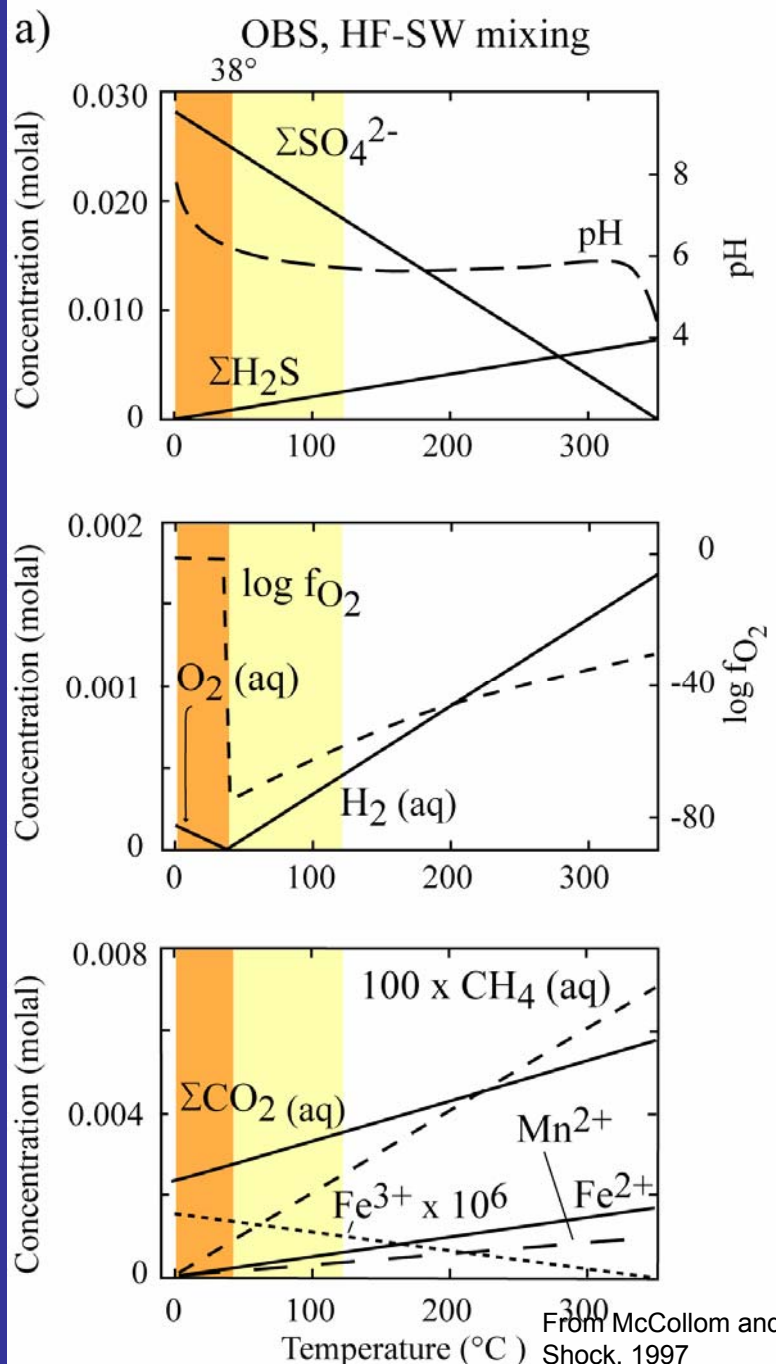
Energy source	Reaction
Sulfate reduction	$\text{SO}_4^{2-} + 2\text{H}^+ + 4\text{H}_2 \leftrightarrow \text{H}_2\text{S} + 4\text{H}_2\text{O}$
Sulfide oxidation	$\text{H}_2\text{S} + 2\text{O}_2 \leftrightarrow \text{SO}_4^{2-} + 2\text{H}^+$
Methanogenesis	$\text{CO}_2 + 4\text{H}_2 \leftrightarrow \text{CH}_4 + 2\text{H}_2\text{O}$
Methanotrophy	$\text{CH}_4 + 2\text{O}_2 \leftrightarrow \text{CO}_2 + 2\text{H}_2\text{O}$



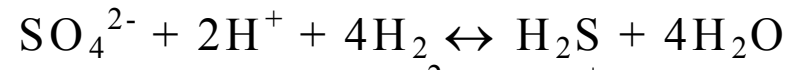
reactions considered.

Reaction





Use to calculate available energy:



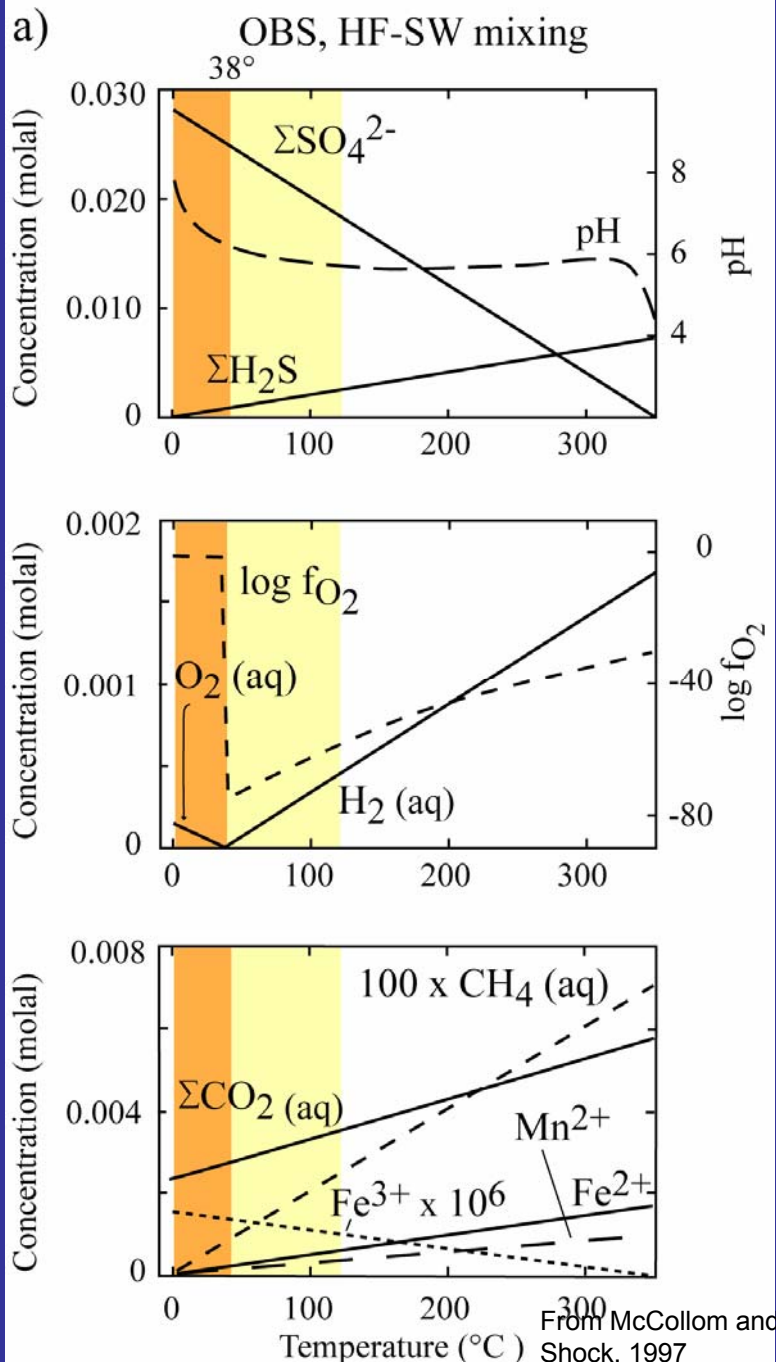
$$\Delta G = \Delta G^\circ + 2.303RT \log Q$$

$$(\Delta G^\circ = -2.303RT \log K_{\text{eq}})$$

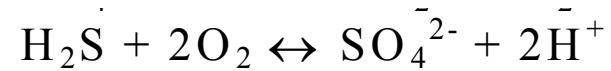
So when $\Delta G = 0$, $K_{\text{eq}} = Q$

$$Q = \frac{a_{\text{H}_2\text{S}}}{[(a_{\text{SO}_4^{2-}})(a_{\text{H}^+})^2(a_{\text{H}_2})^4]}$$

$\Delta G < 0$, energy is available.



Use to calculate available energy:



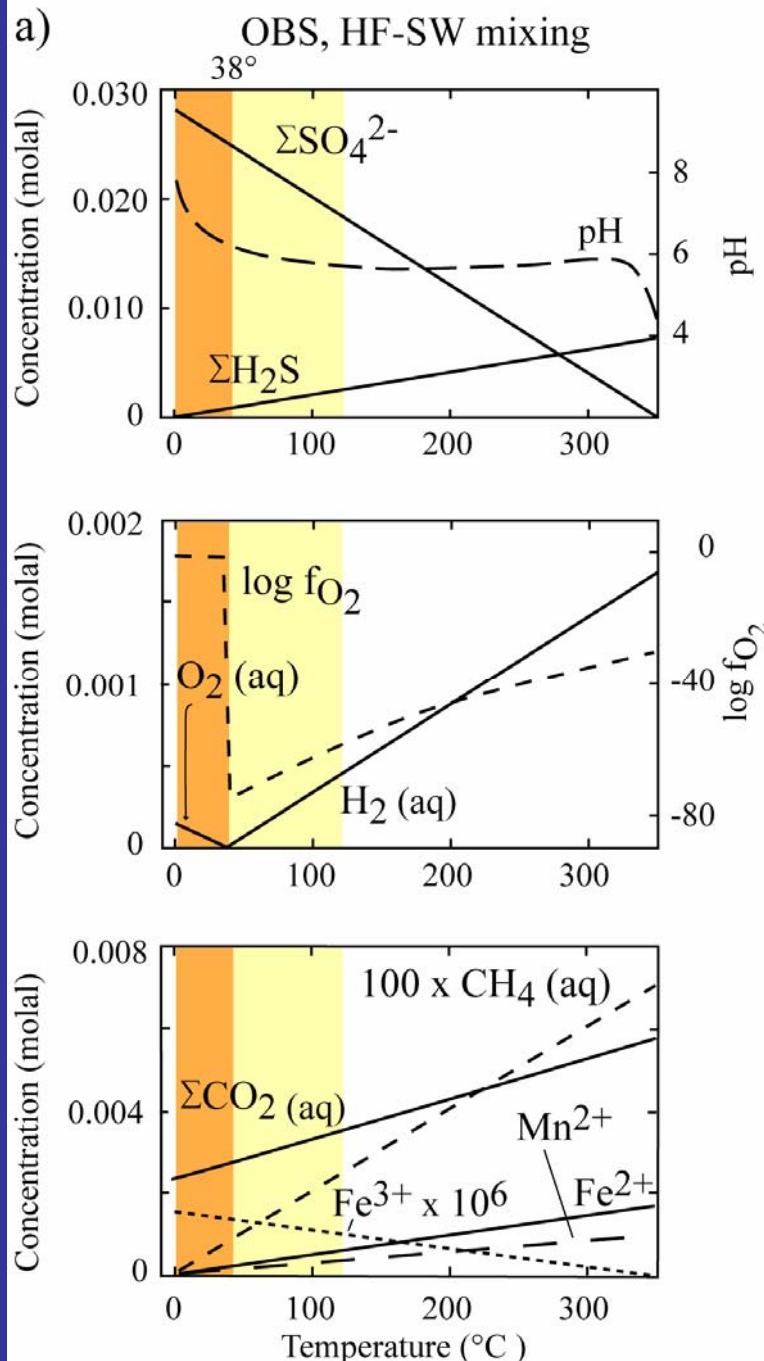
$$\Delta G = \Delta G^{\circ} + 2.303RT \log Q$$

$$(\Delta G^{\circ} = -2.303RT \log K_{\text{eq}})$$

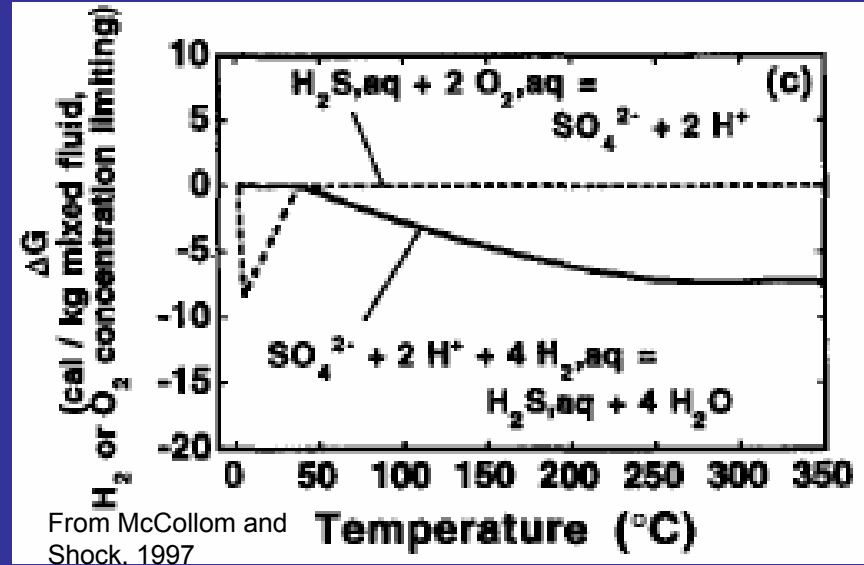
So when $\Delta G = 0$, $K_{\text{eq}} = Q$

$$Q = \frac{(\text{aSO}_4^{2-})(\text{aH}^+)^2}{(\text{aO}_2)^2 (\text{aH}_2\text{S})}$$

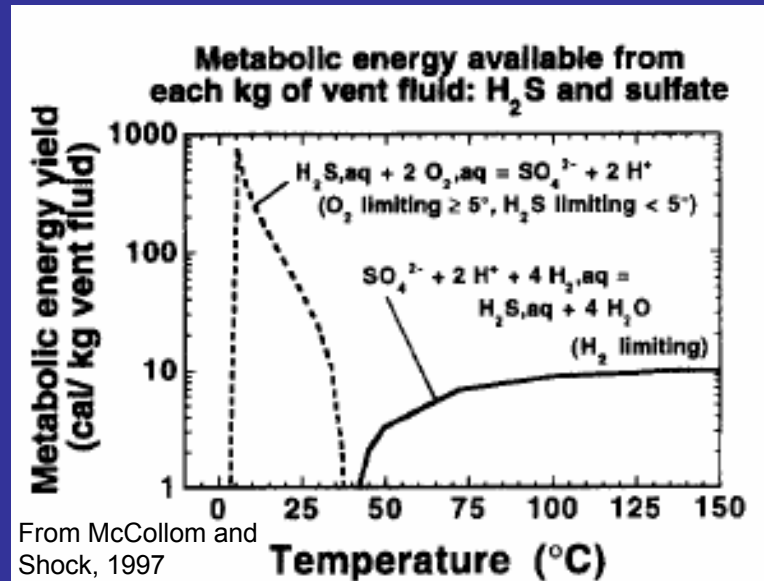
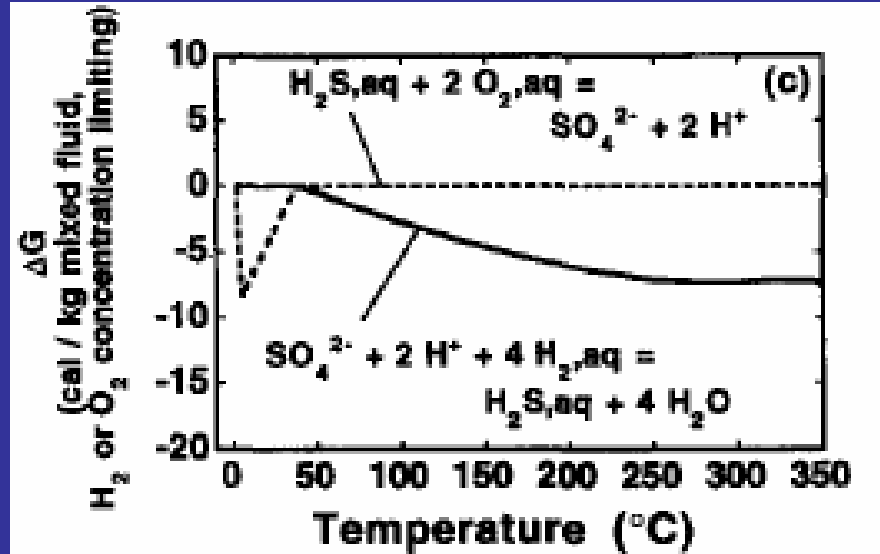
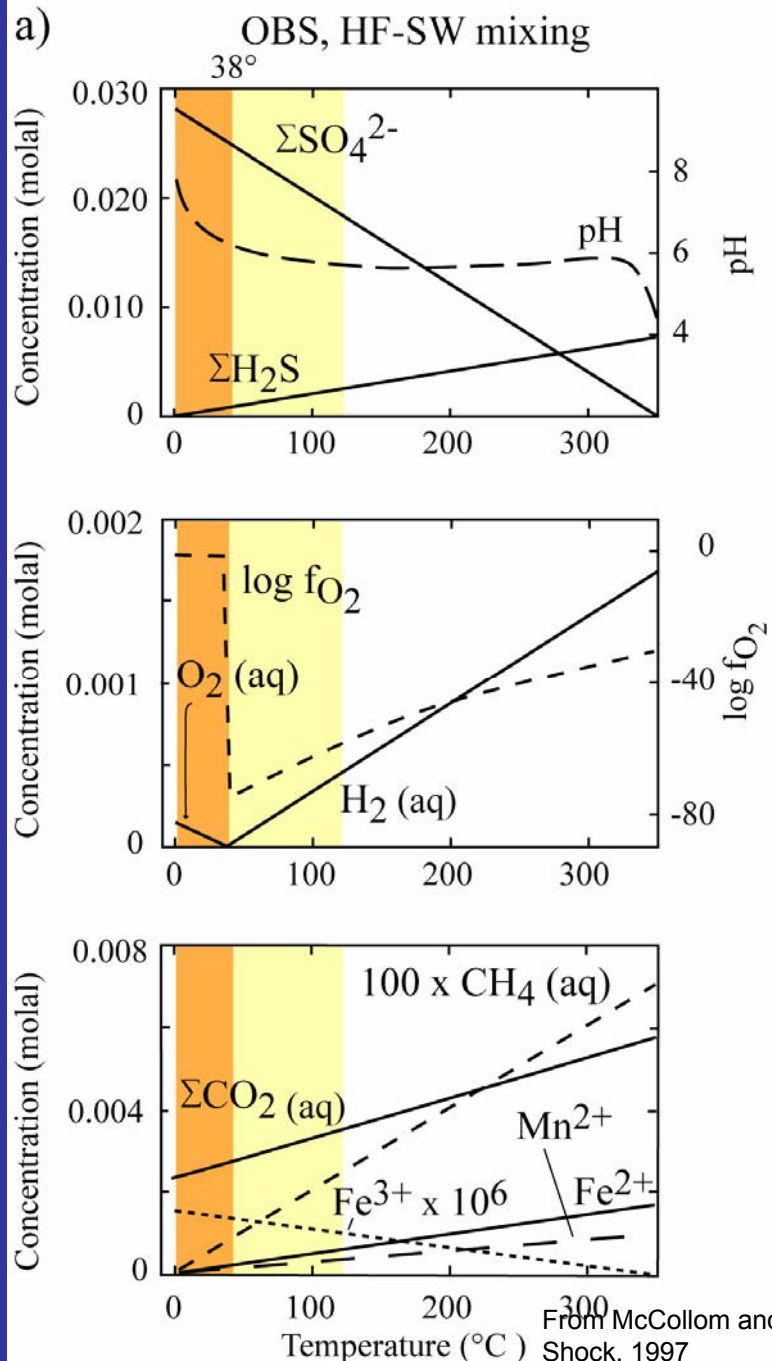
$\Delta G < 0$, energy is available.



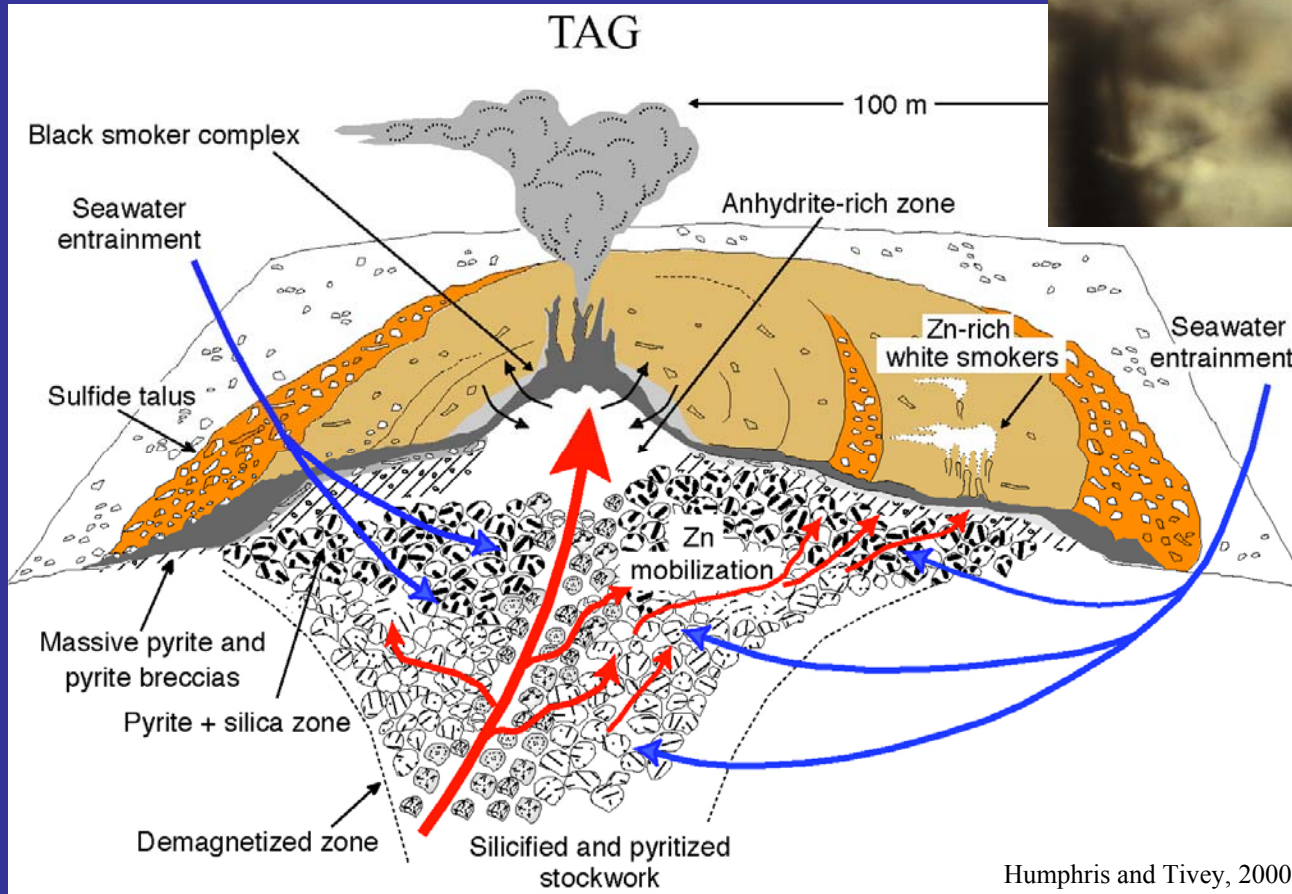
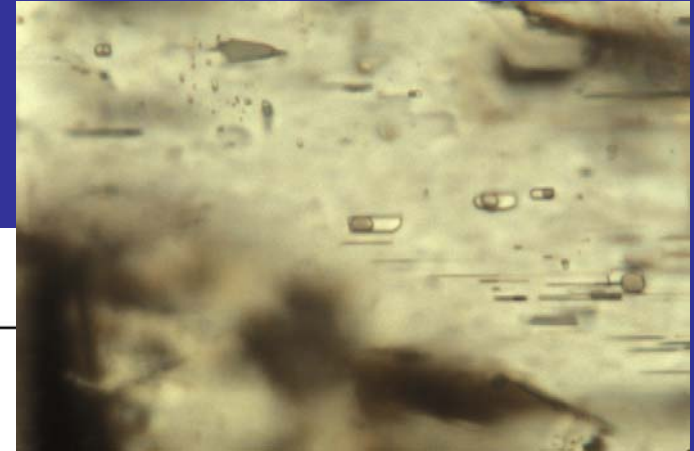
Use to calculate available energy:



Use to calculate available energy:

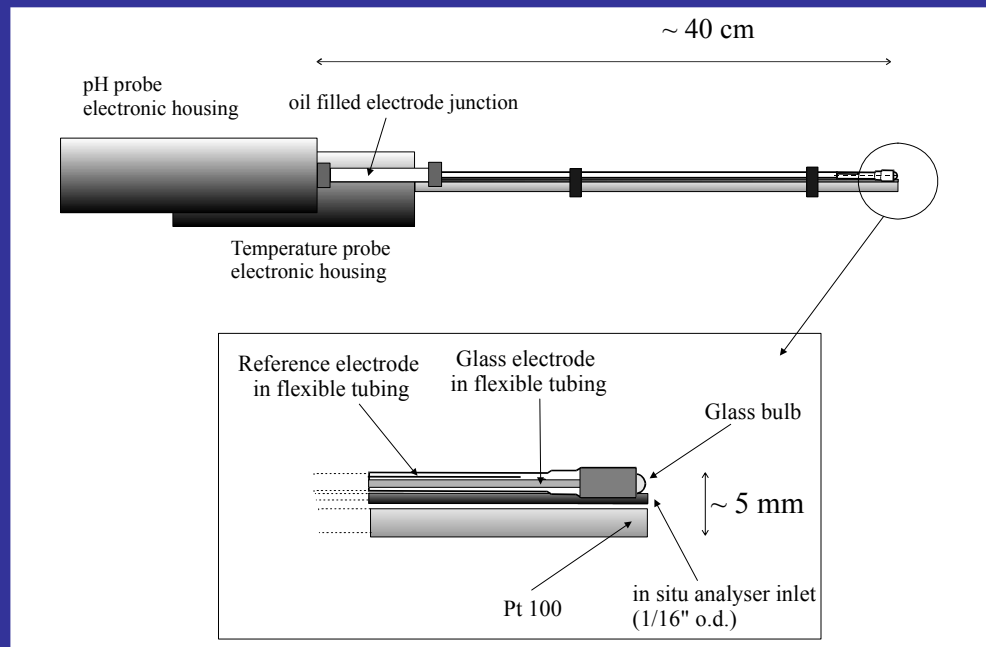


But temperature often NOT conservative.
For example in the TAG active mound,
Sr isotopes indicate mix >50 to 99%
seawater, but fluid inclusion data
indicate temperatures of ~350°C.

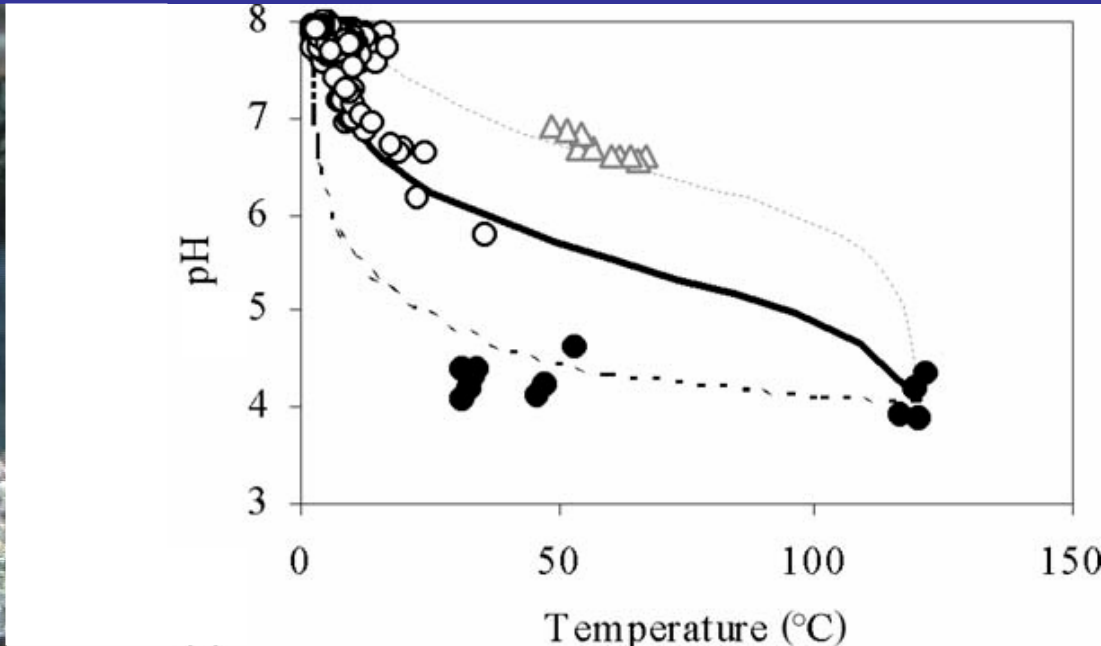


Humphris and Tivey, 2000

Within and around Alvinellid tubes, T – pH best explained by conductive cooling and heating of vent fluid and seawater.



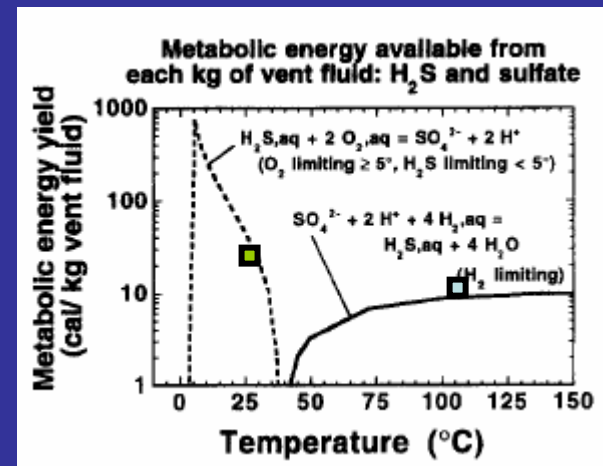
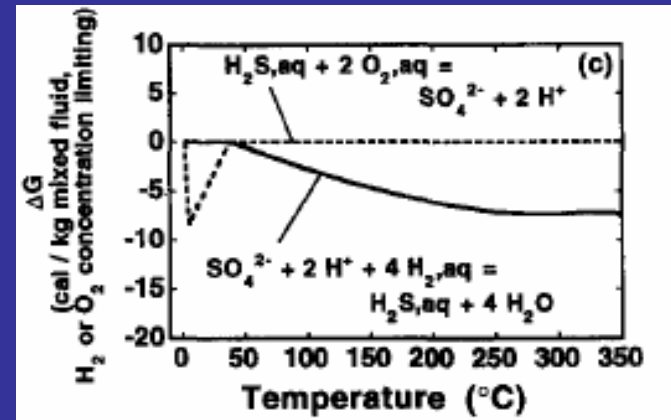
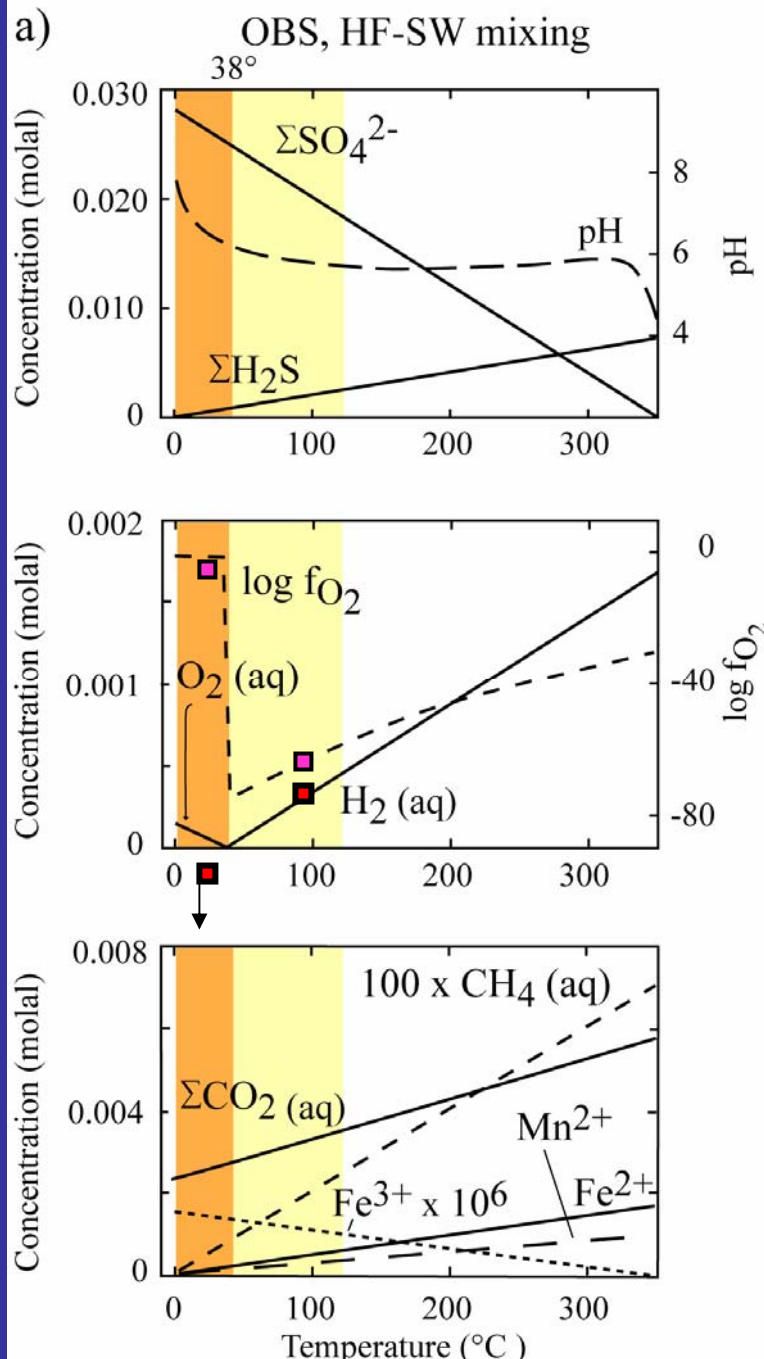
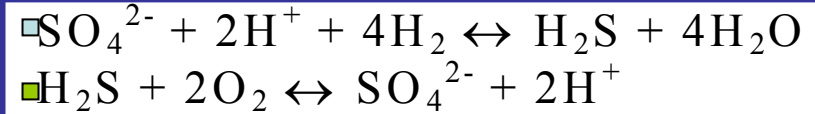
Le Bris et al., 2001



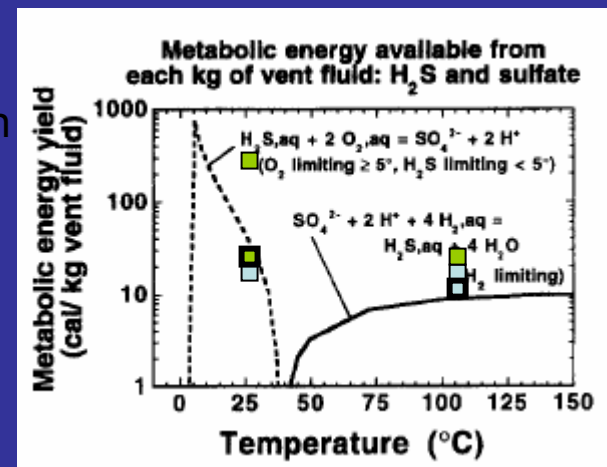
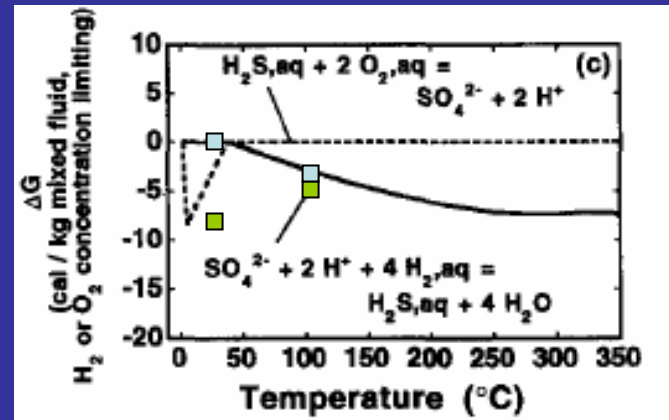
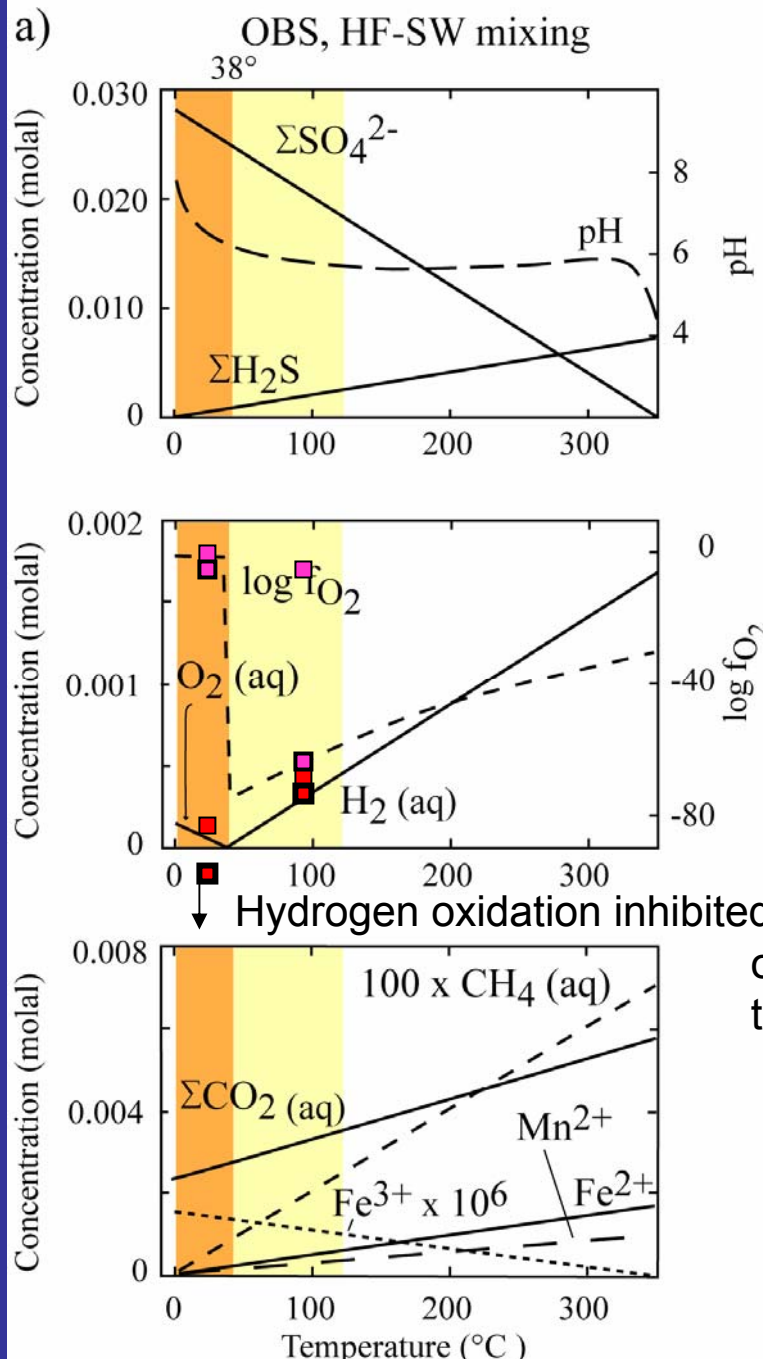
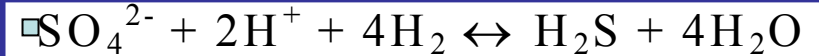
Le Bris et al., 2005

What if inhibit hydrogen oxidation?

$H_2(aq) + 0.5O_2(aq) = H_2O$



What if inhibit hydrogen oxidation?

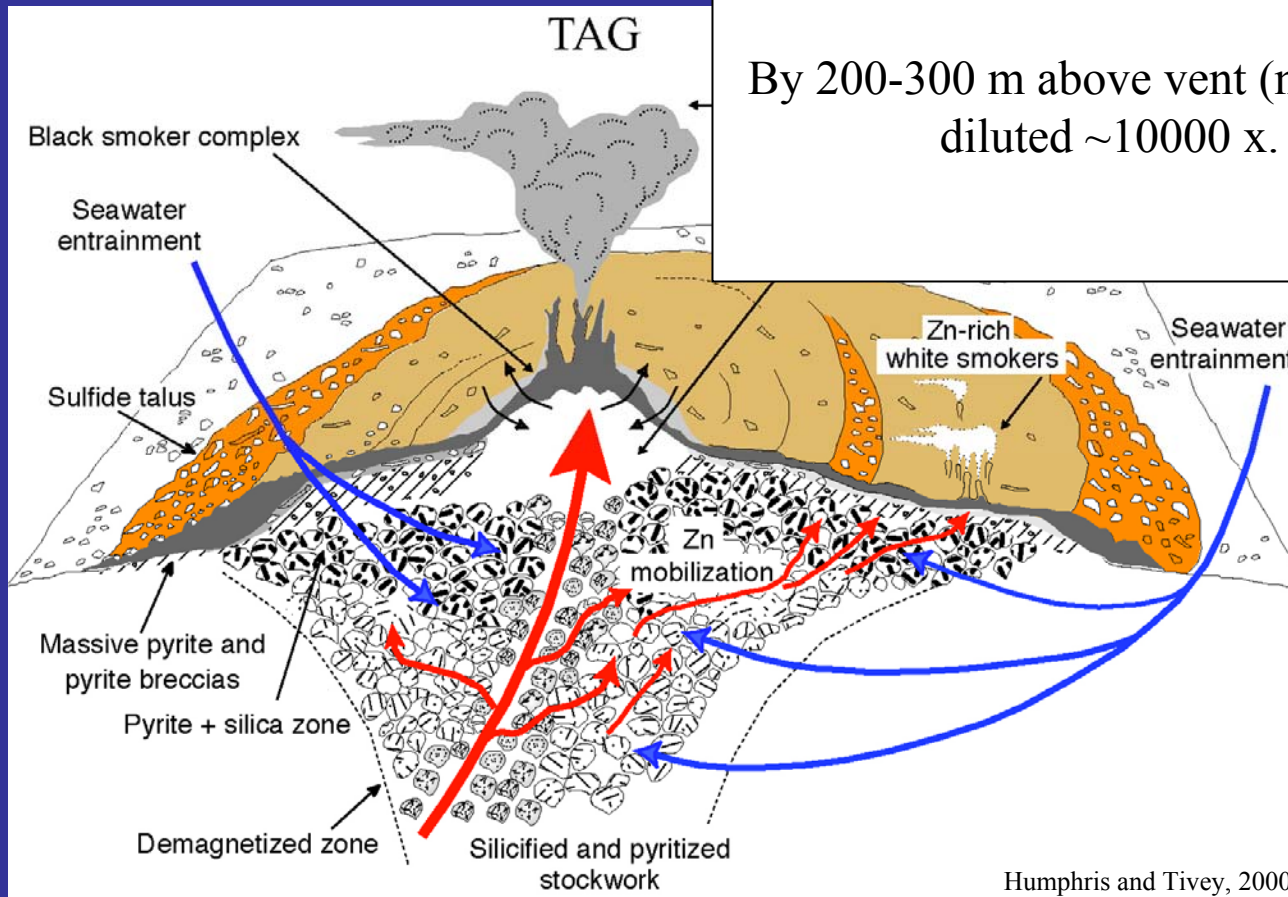


Mixing/reaction in plumes

By 10 m above vent, diluted 100 to 1000x
FeS, (Zn,Fe)S precipitate; H₂(aq) present
in plume (half-life of “oxidative-removal”
~10 h; Kadko et al., 1990)

By 200-300 m above vent (neutrally buoyant)
diluted ~10000 x.

(Feely et al., 1994)



Humphris and Tivey, 2000

Mixing/reaction in plumes

- Mineral precipitation allowed
- Hydrogen oxidation inhibited

Estimated energy available (cal/kg vent fluid):

Oxidation of

Elemental Sulfur ~610

Pyrrhotite ~69

Sphalerite ~18

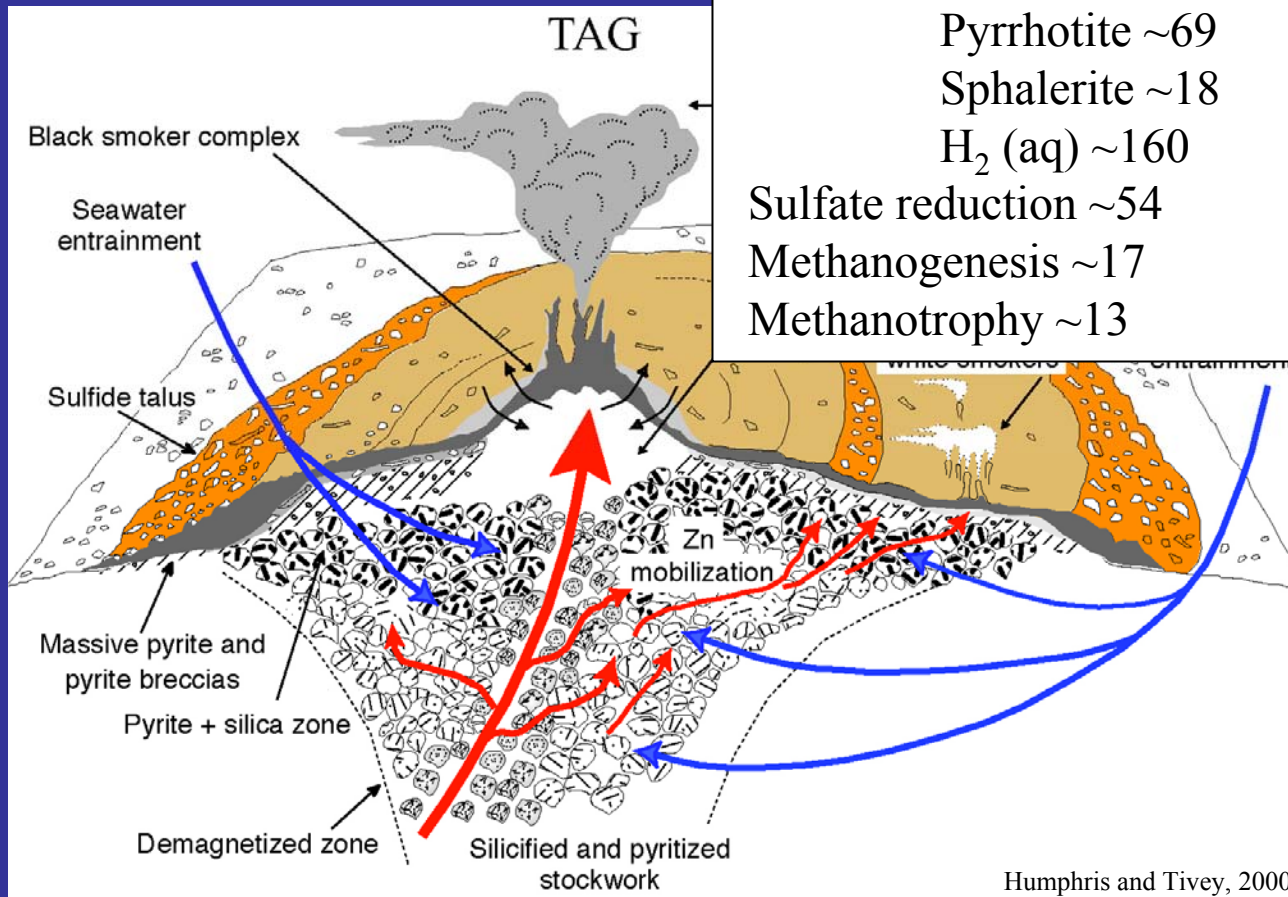
H₂ (aq) ~160

Sulfate reduction ~54

Methanogenesis ~17

Methanotrophy ~13

(McCollom 2000)



Tools available

I. Distribution of species as fn of T (MINEQL, EQ3, REACT)

Sensitivity to input

- A. thermodynamic data
- B. fluid composition data
- C. temperature data

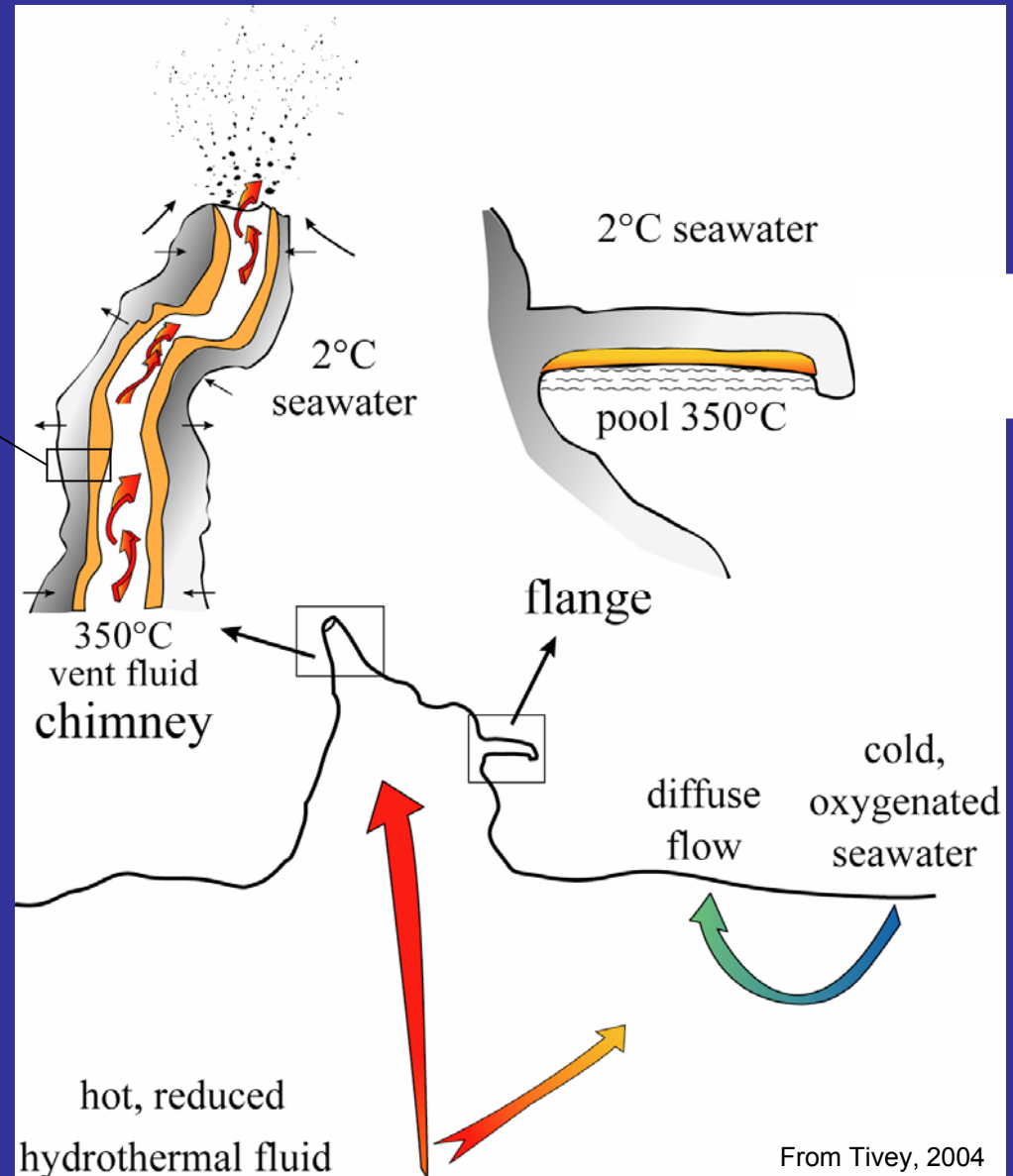
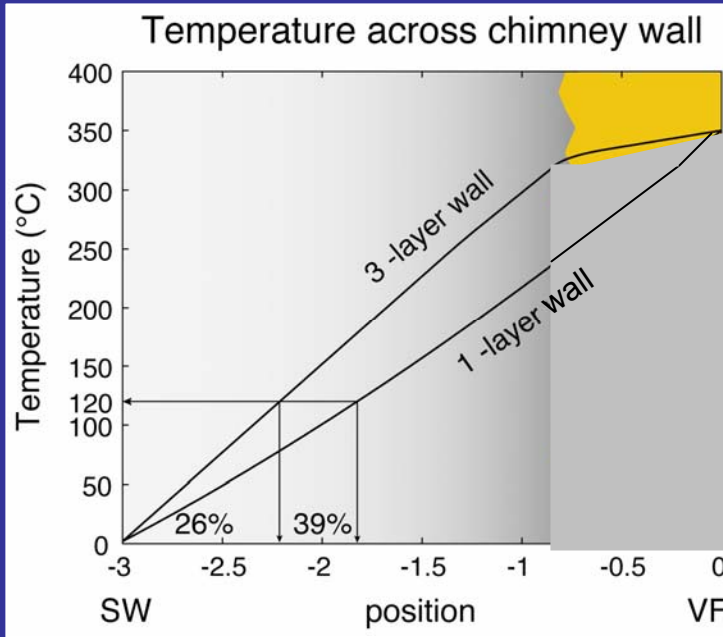
II. Path reaction

- A. assumptions about kinetics
- B. assumptions about whether T is conservative

▶ III. Transport-reaction

- A. small scale across steep gradients
- B. large scale at low transport rates
- C. assumptions – kinetics, boundary conditions, steady-state

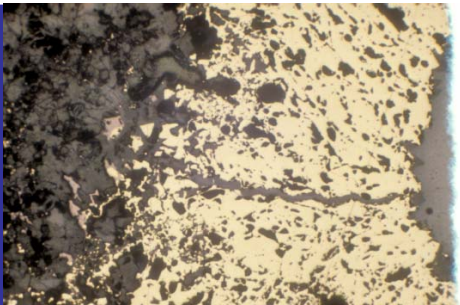
In sulfide-rich vent deposits, must consider transport of heat, which, if by diffusion, is much more rapid than transport of mass:



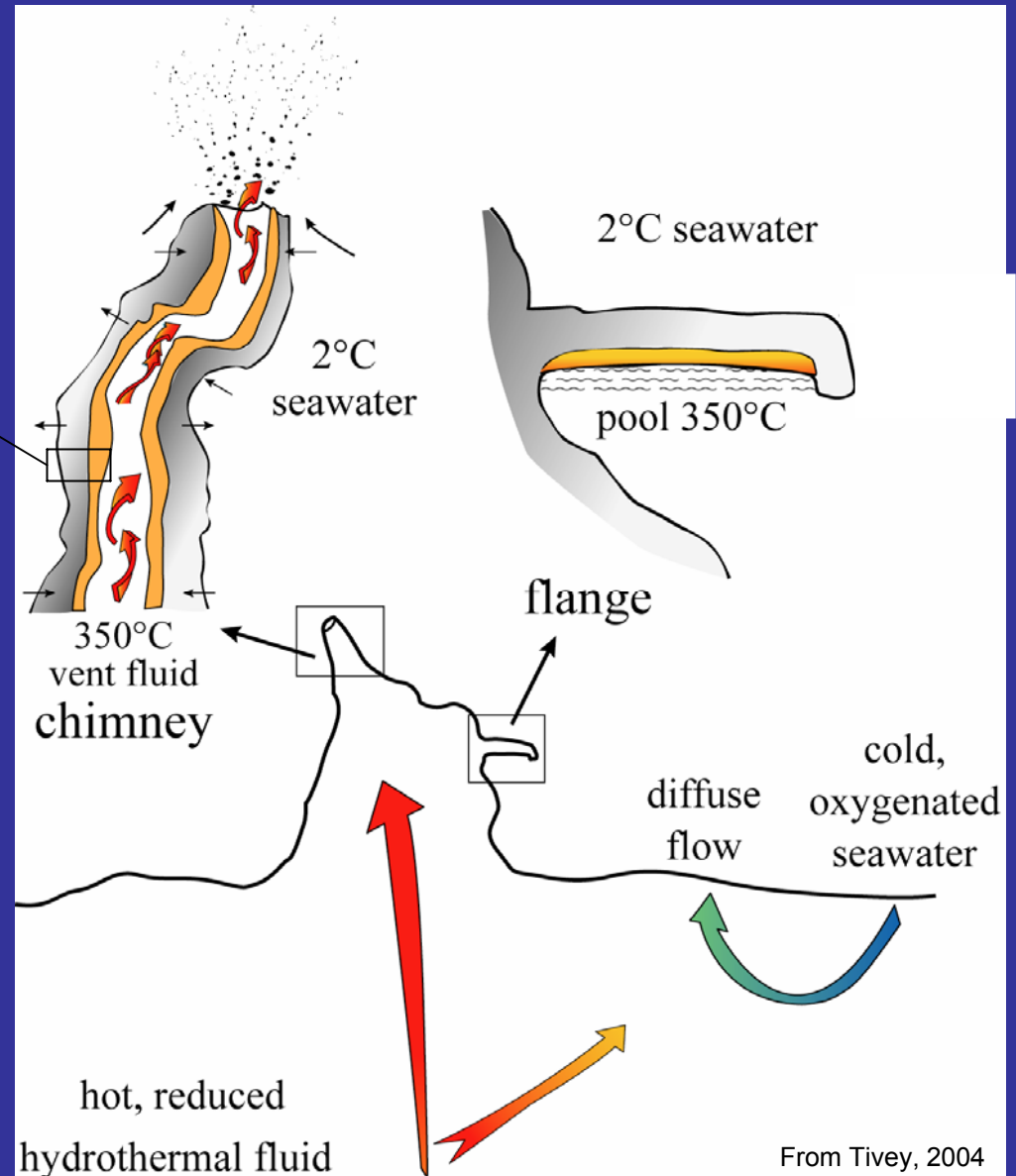
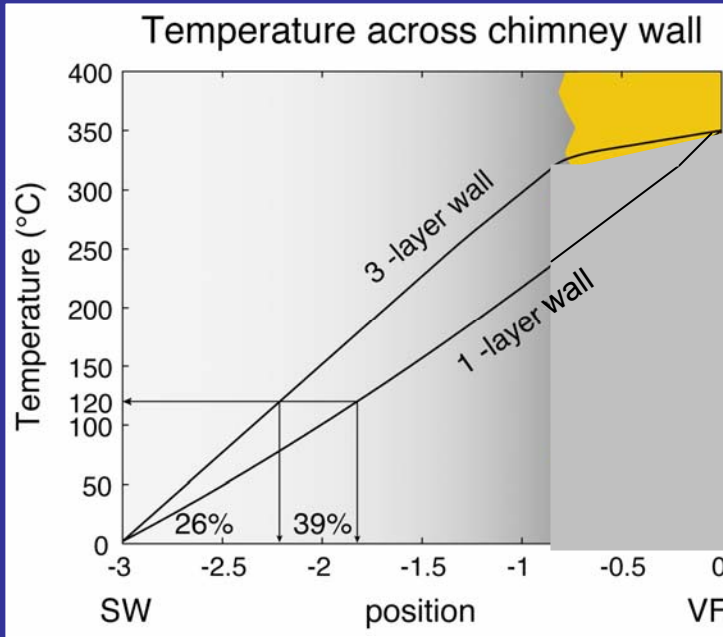
Temperature: conduction advection

$$\frac{\partial}{\partial x} \left(K \frac{\partial T}{\partial x} \right) - \phi u \frac{(\rho C_p) \frac{\partial T}{\partial x}}{(\rho C_p)_m \frac{\partial T}{\partial x}} = \frac{\partial T}{\partial t} = 0$$

0



In sulfide-rich vent deposits, must also consider transport of heat, which, if by diffusion, is much more rapid than transport of mass:



Temperature:

conduction

advection

$$\frac{\partial}{\partial x} \left(K \frac{\partial T}{\partial x} \right) - \phi u \frac{(\rho C_p) / \partial T}{(\rho C_p)_m \partial x} = \frac{\partial T}{\partial t} = 0$$

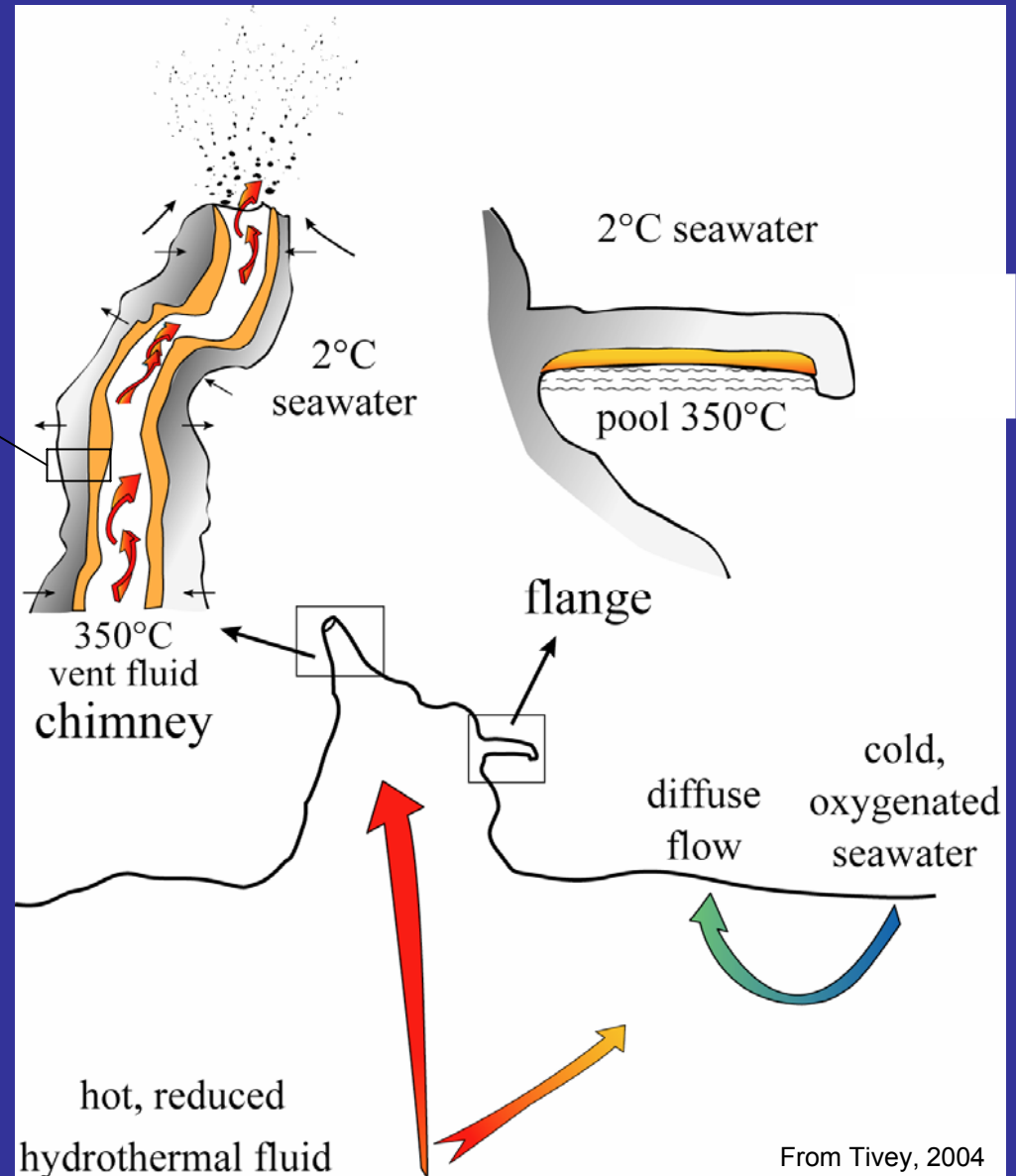
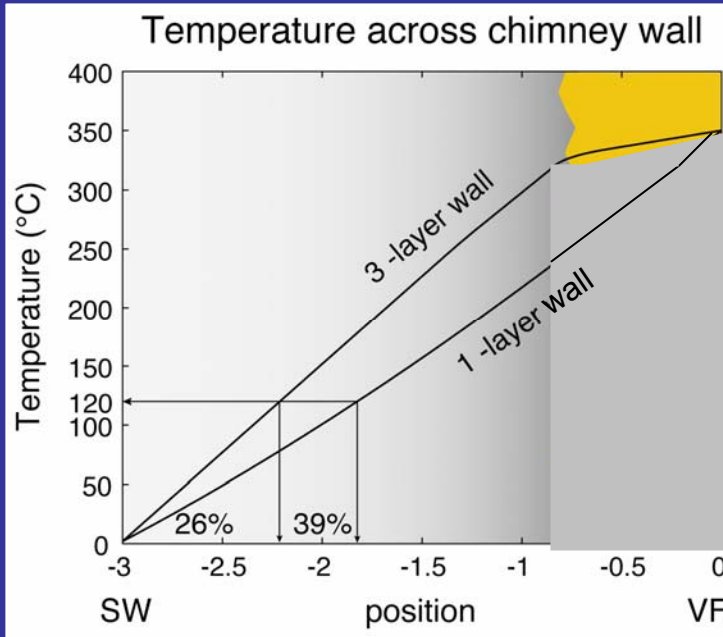
0

$$K \sim 2 \text{ to } 13 \times 10^{-6} \text{ m}^2/\text{s}$$

$$D \sim 1 \text{ to } 30 \times 10^{-9} \text{ m}^2/\text{s}$$

From Tivey, 2004

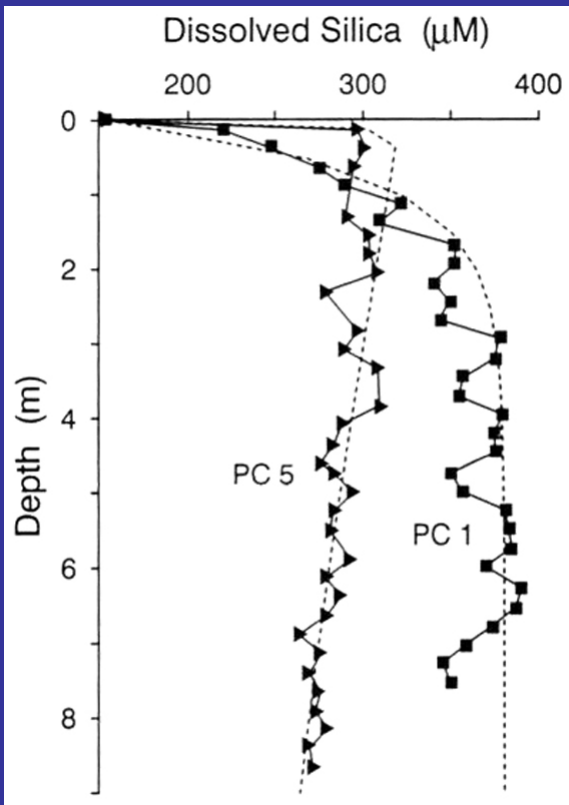
In sulfide-rich vent deposits, must also consider transport of heat, which, if by diffusion, is much more rapid than transport of mass:



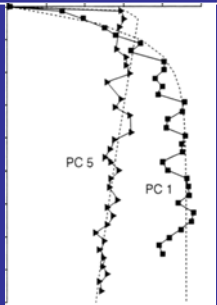
Temperature:
conduction advection

$$\frac{\partial}{\partial x} \left(K \frac{\partial T}{\partial x} \right) - \phi u \frac{(\rho C_p)_l}{(\rho C_p)_m} \frac{\partial T}{\partial x} = \frac{\partial T}{\partial t} = 0$$

At $\phi u > 5 \times 10^{-6} \text{ m/s}$
 T profile affected



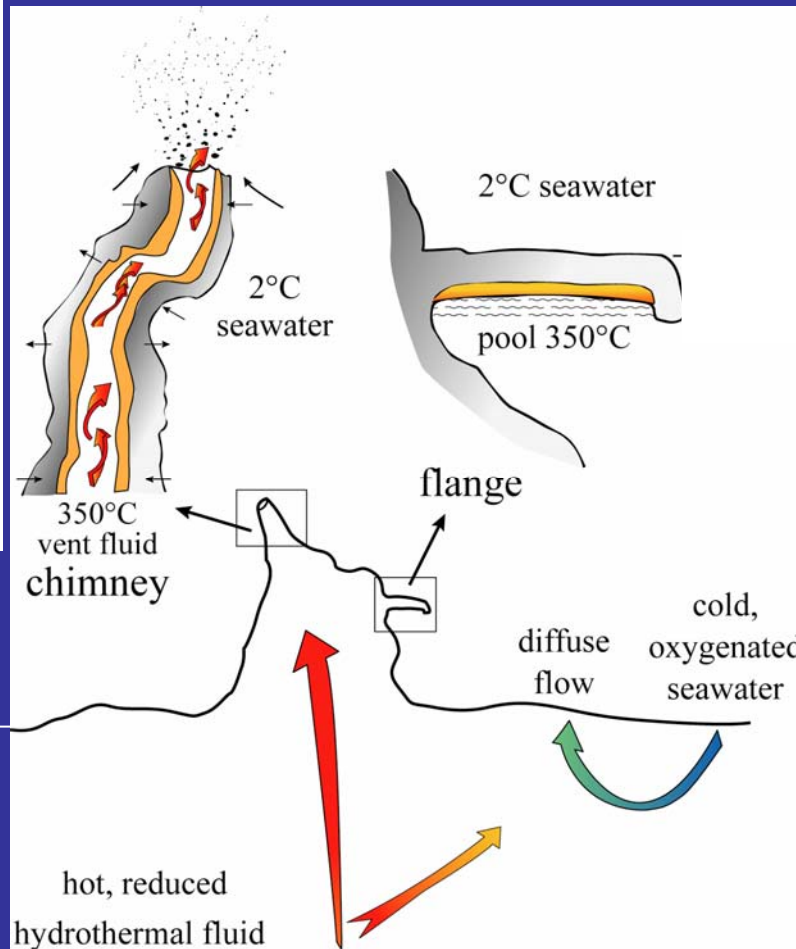
(Wheat and McDuff, 1994)



$$\frac{\partial}{\partial x} \left(D''_i \frac{\partial C_i}{\partial x} \right) \leftarrow \begin{array}{l} \text{diffusion} \\ \text{advection} \\ \text{reaction} \end{array}$$

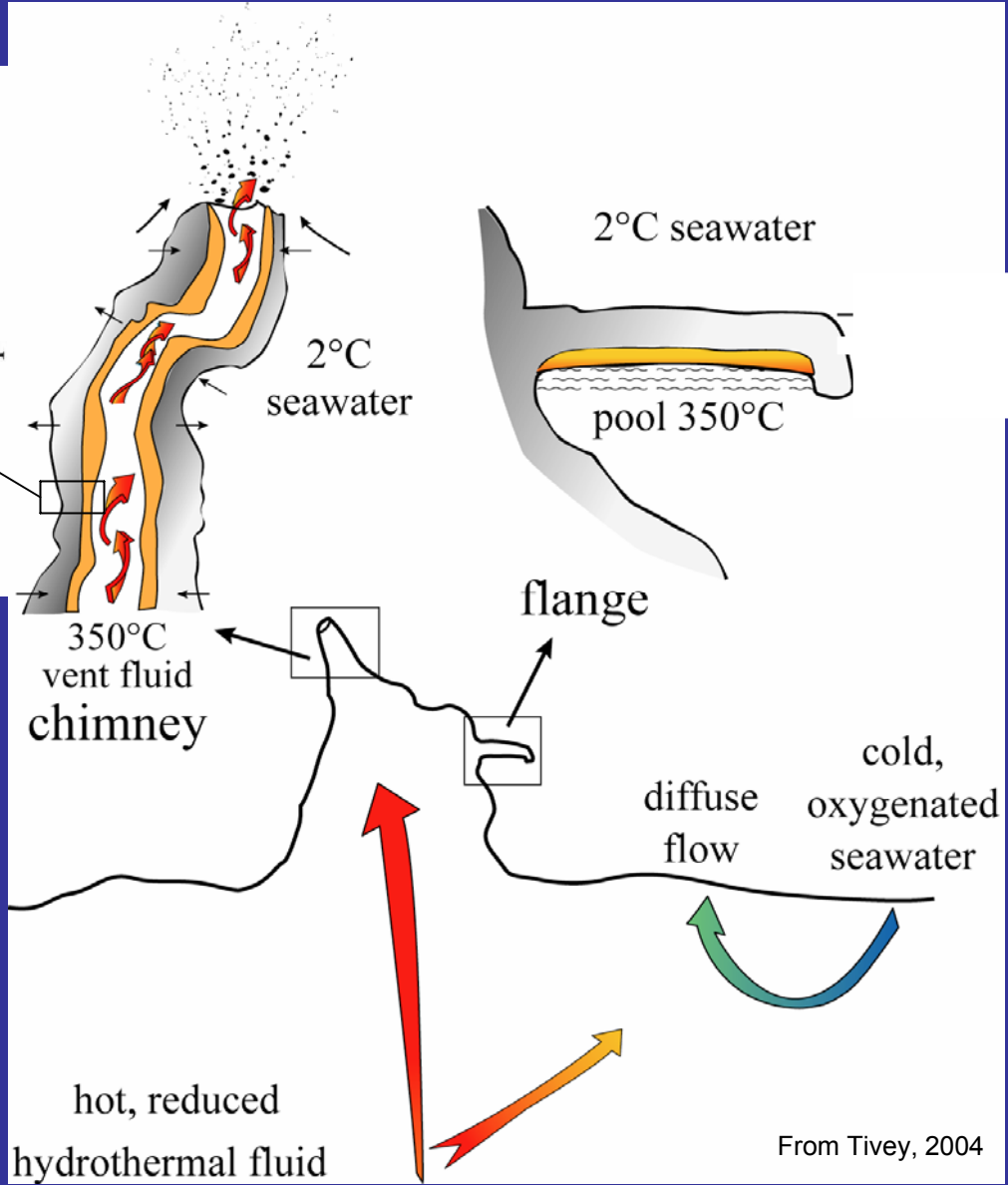
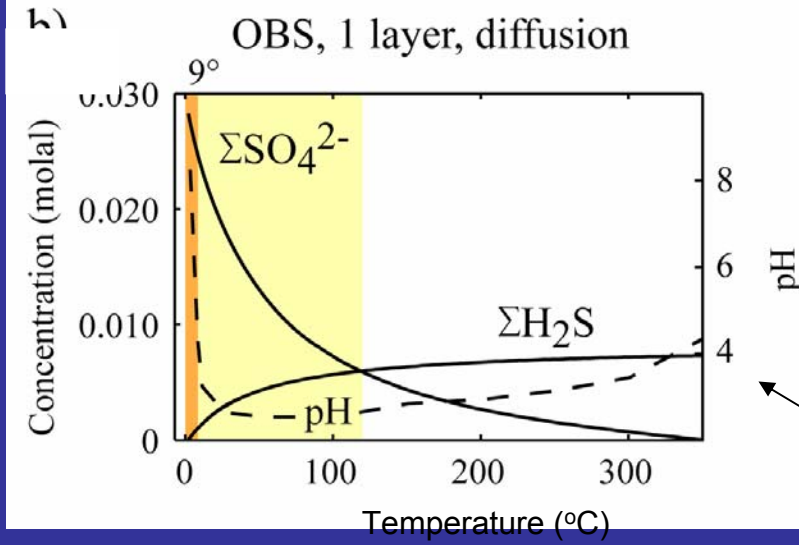
$$-\phi u \frac{\partial C_i}{\partial x} + \phi \sum R_i = \phi \frac{\partial C_i}{\partial t} = 0$$

$$D'' = \phi D_{sed}$$



Transport across chimney walls can be considered in a similar manner as transport in porous sediments, by considering diffusion and advection

From Tivey, 2004



Concentration:

diffusion

$$\frac{\partial}{\partial x} \left(D_i'' \frac{\partial C_i}{\partial x} \right) + \frac{\partial}{\partial x} \left(D_i'' C_i \frac{\partial \ln y_i}{\partial x} \right)$$

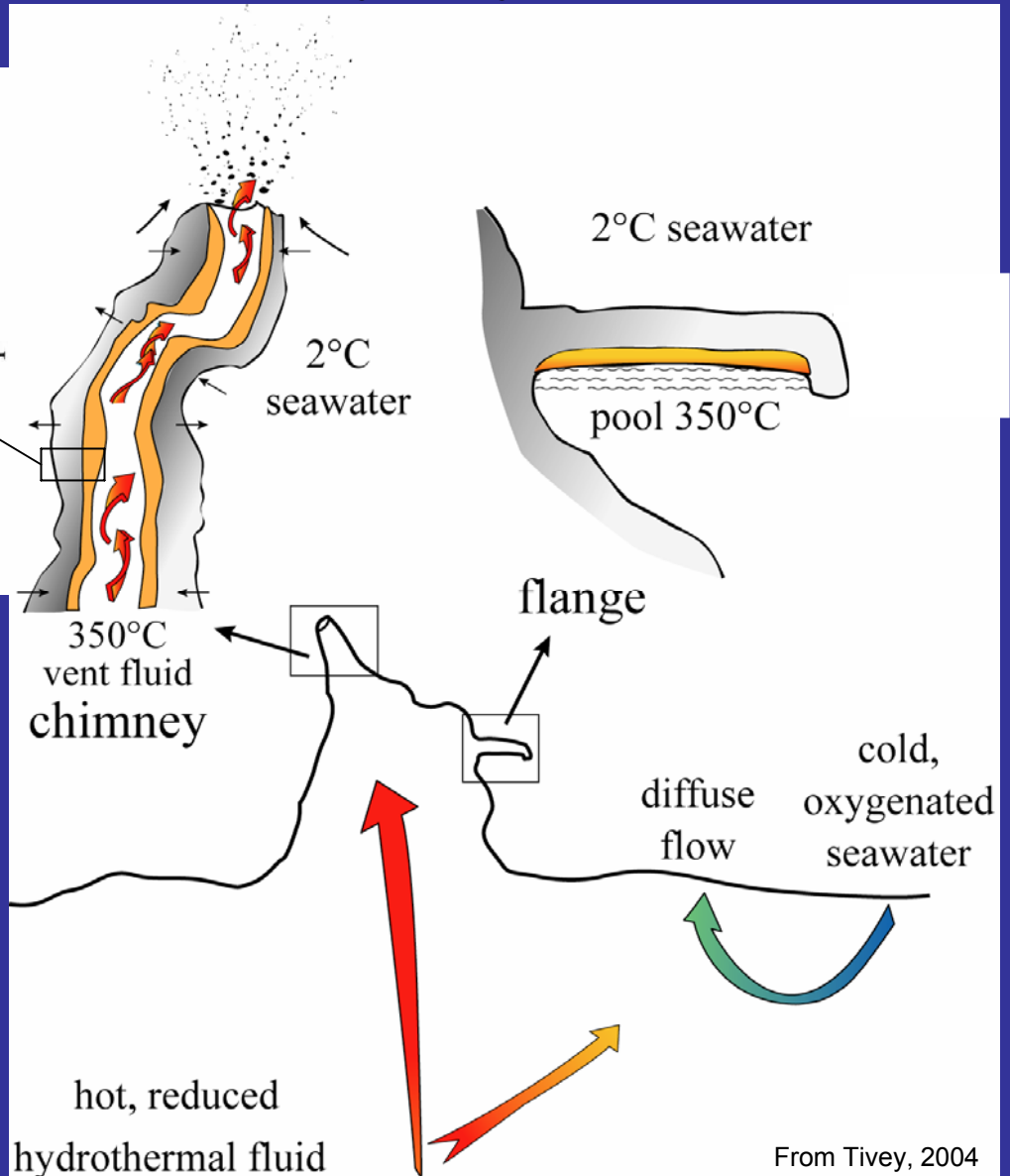
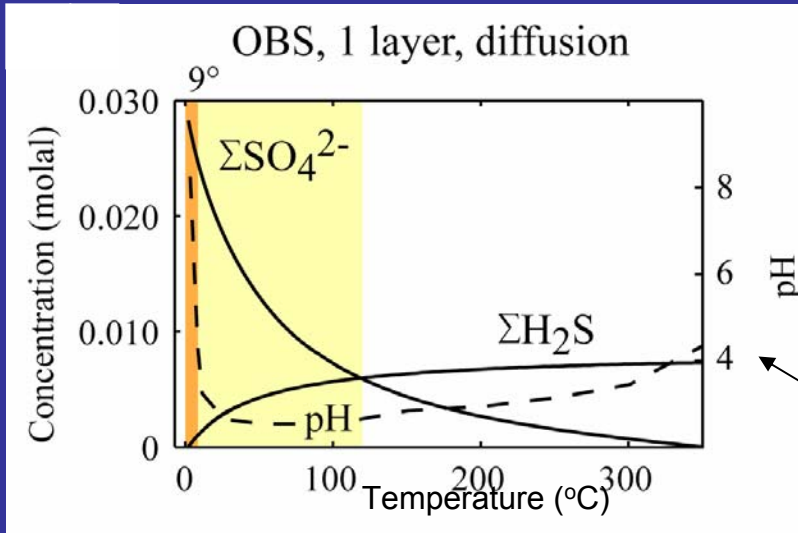
$$- \phi u \frac{\partial C_i}{\partial x} + \phi \Sigma R_i = \phi \frac{\partial C_i}{\partial t} = 0$$

advection

reaction

Because activity coefficients change with T, must consider the gradient in activity coefficients as well as the gradient in concentration of each species

Assumes reaction rates are slow relative to transport (e.g., steady-state gradients are established in hours to at most 1 day; Tivey and McDuff, 1990)



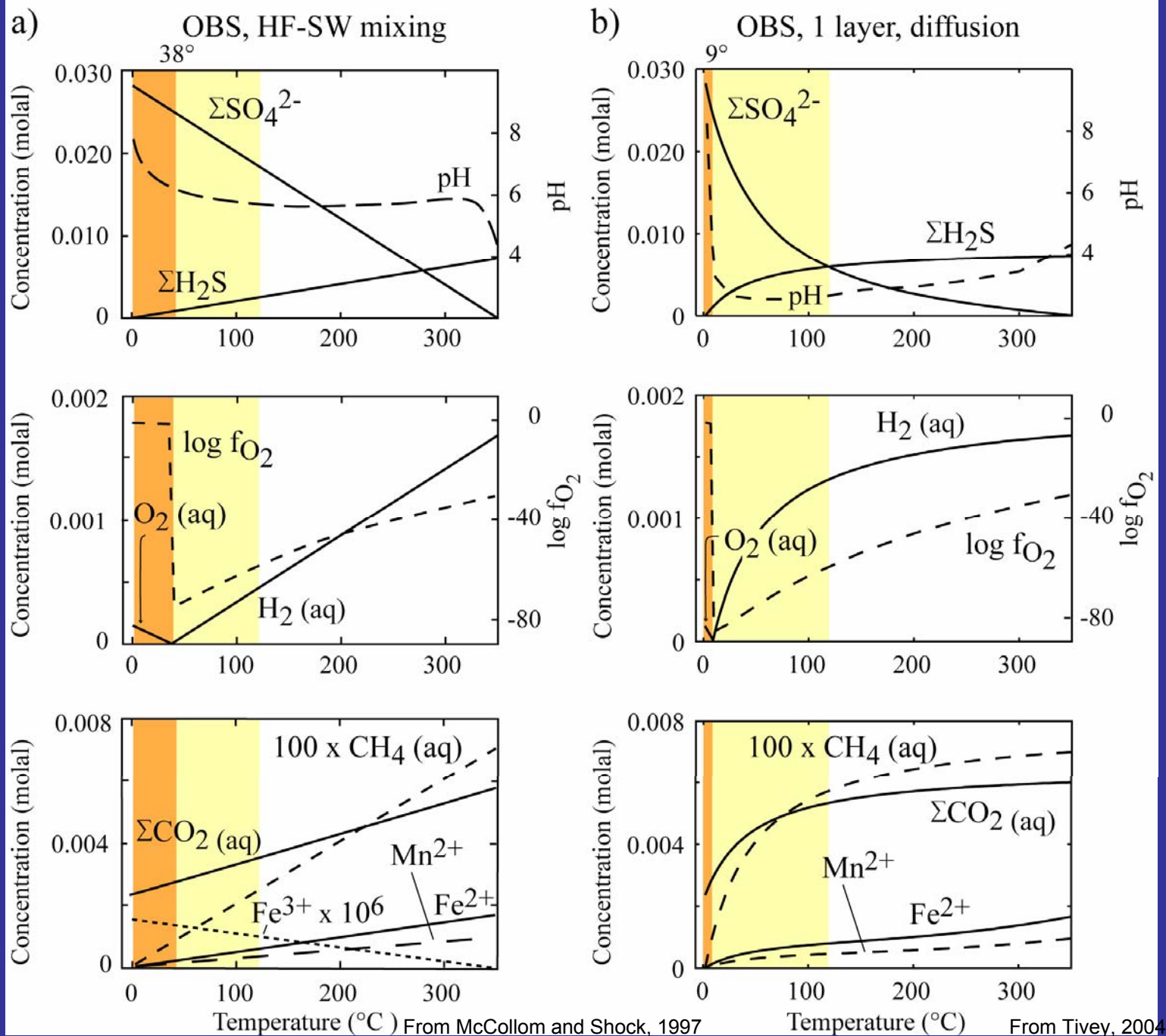
Concentration:

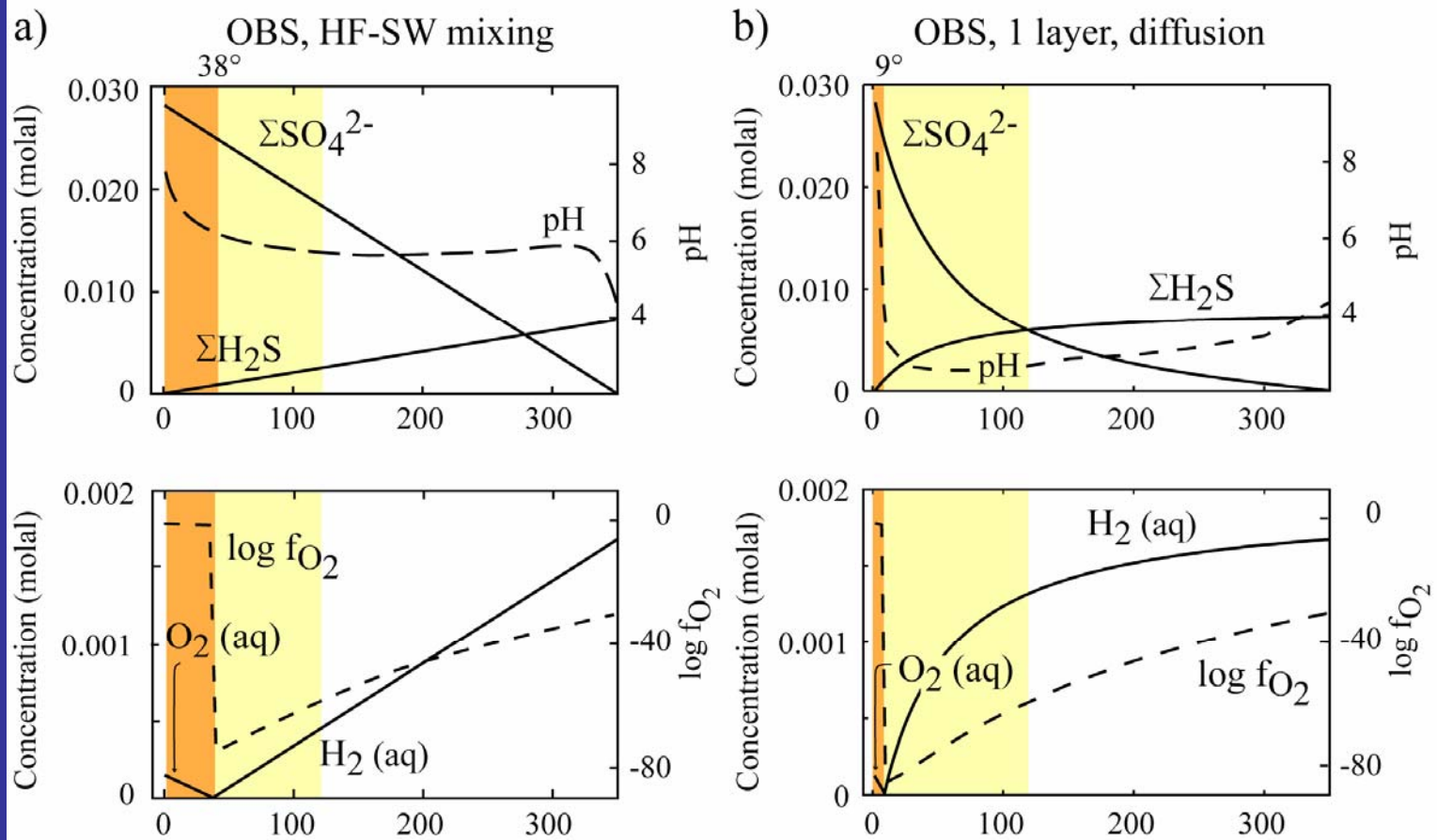
$$\frac{\partial}{\partial x} \left(D_i'' \frac{\partial C_i}{\partial x} \right) + \frac{\partial}{\partial x} \left(D_i'' C_i \frac{\partial \ln y_i}{\partial x} \right)$$

diffusion

$$- \phi u \frac{\partial C_i}{\partial x} + \phi \sum R_i = \phi \frac{\partial C_i}{\partial t} = 0$$

advection 0 reaction



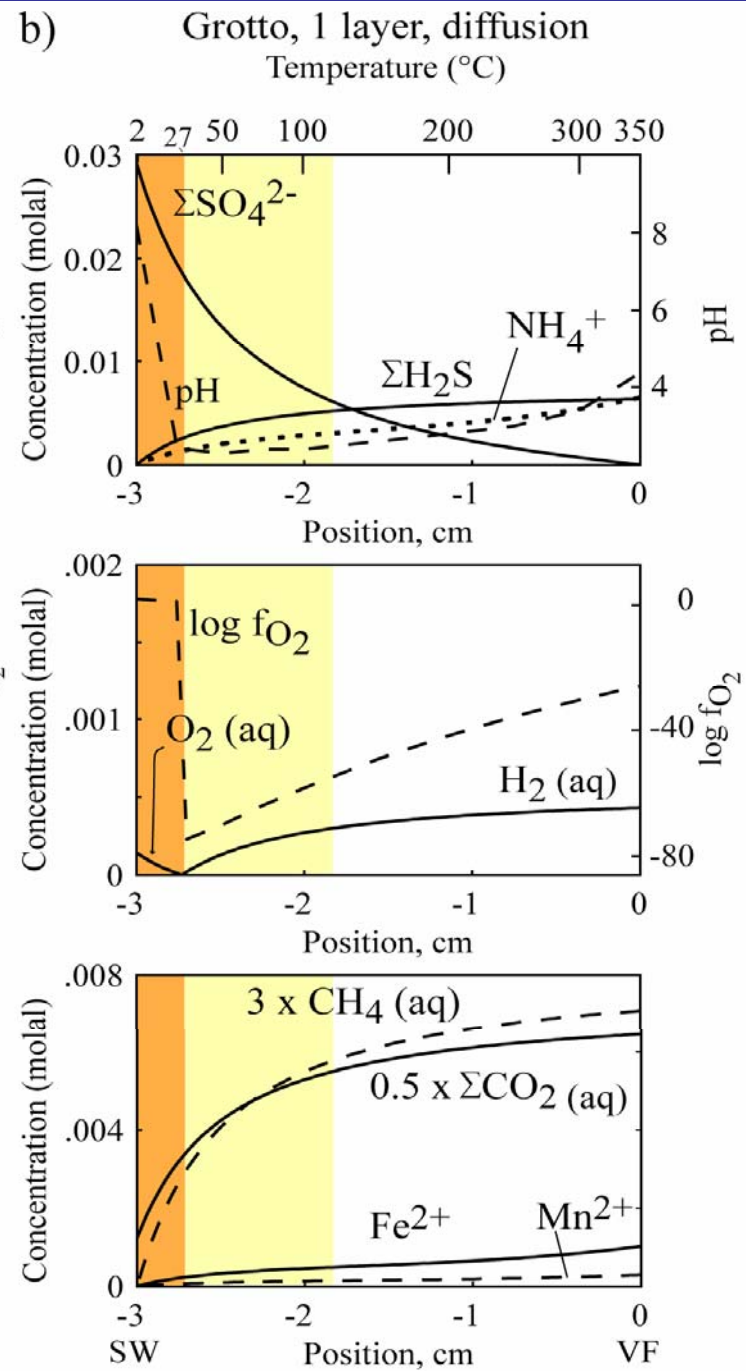
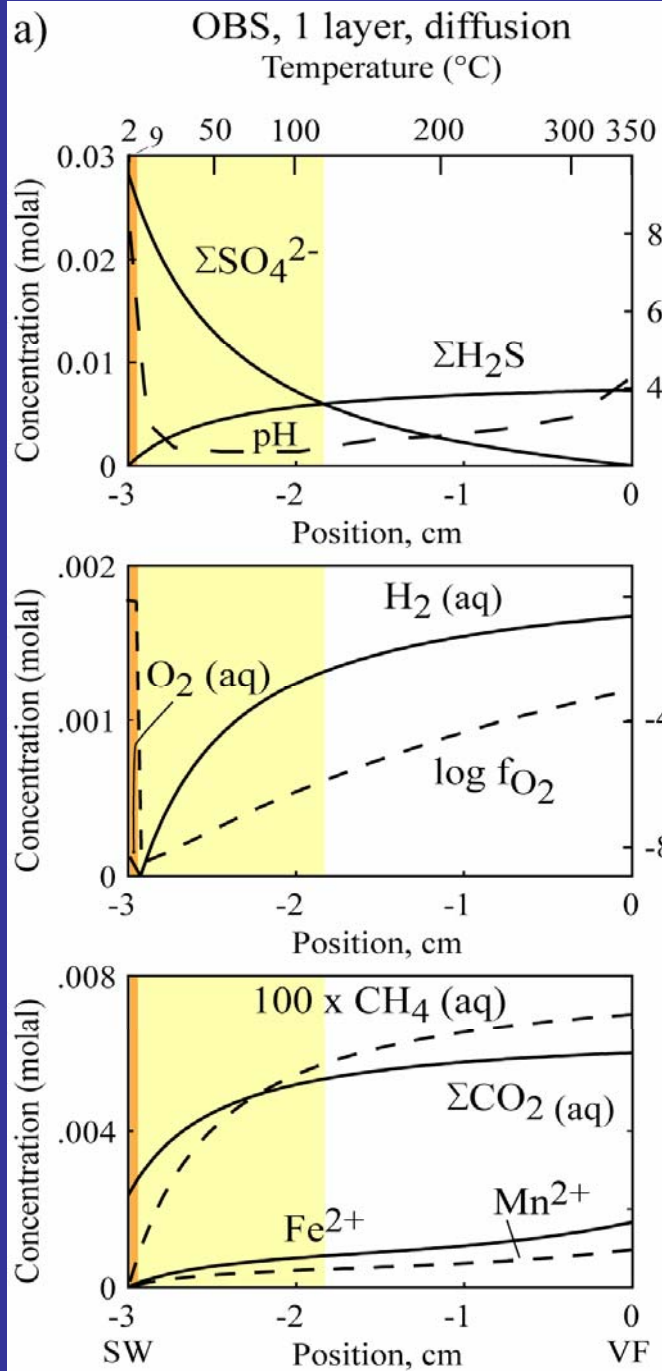


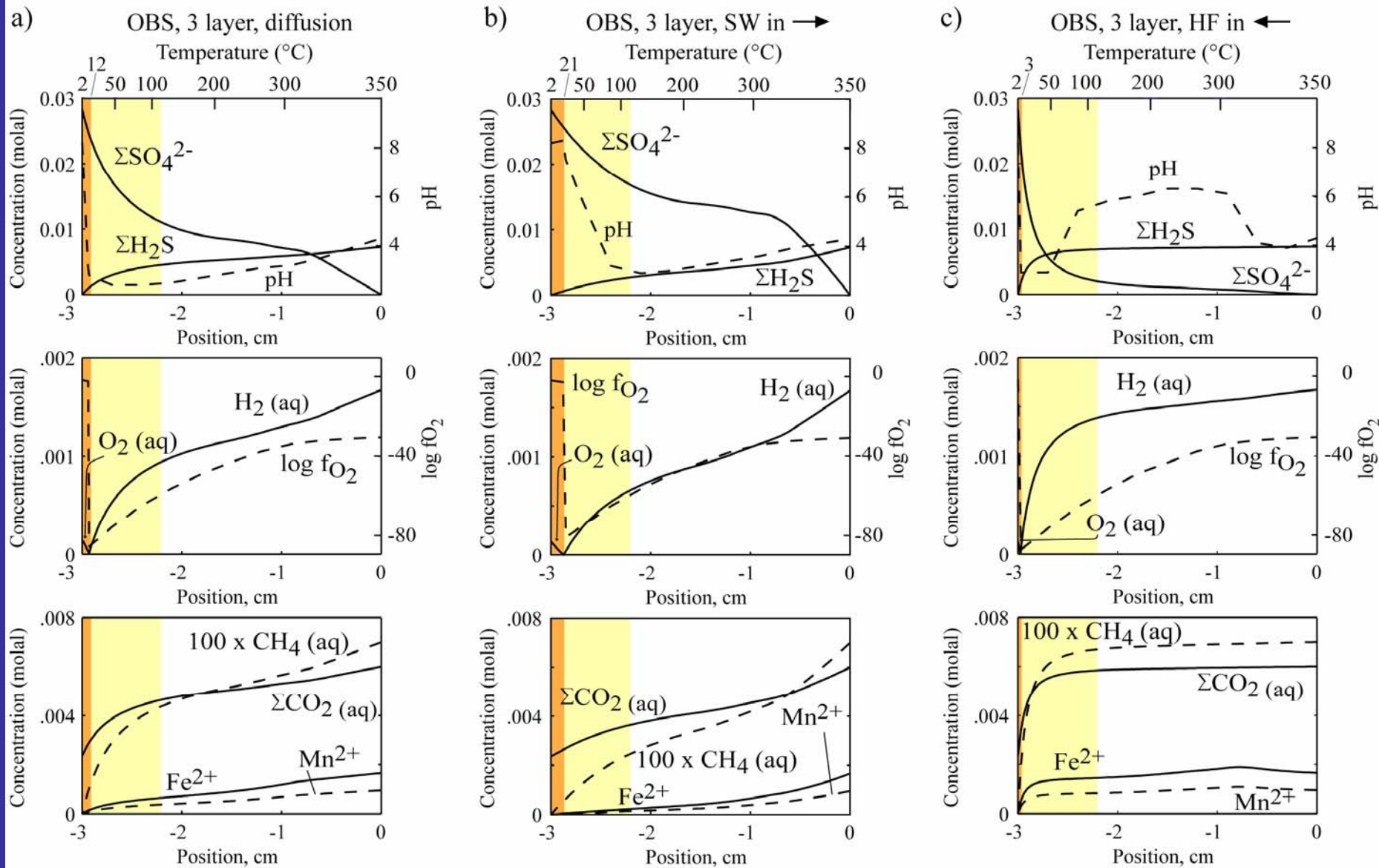
$$\Delta G = \Delta G^\circ + 2.303RT \log Q$$

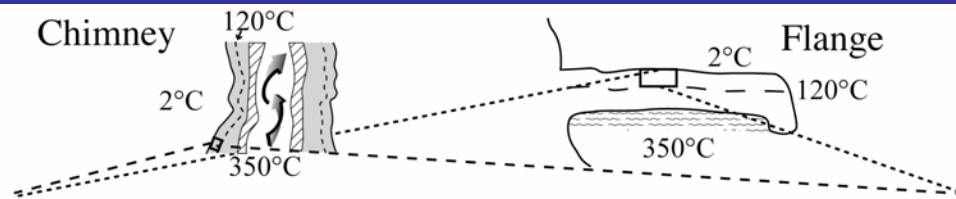
$$Q = \frac{a_{\text{H}_2\text{S}}}{[a_{\text{SO}_4^{2-}}(a_{\text{H}^+})^2(a_{\text{H}_2})^4]}$$

$$Q = \frac{[a_{\text{SO}_4^{2-}}(a_{\text{H}^+})^2]}{[a_{\text{O}_2}]^2 a_{\text{H}_2\text{S}}]}$$

Note: log activity is important, so minor differences in activity do not greatly affect energy available; pH and T of redox transition have much greater effect.







Mixing style	<45°C	45°C to 80°	80°C to 120°C
OBS-SW mix	pH~6-7 38°C ≤-8.0 ^{SO} , ≤-1.9 ^M	pH~6 ≤-7.5 ^{SR}	pH~5.5-6 ≤-6.5 ^M
OBS-SW diff	pH~3-7 9°C ≤-7.0 ^{SO} ≤-1.6 ^M	pH<3 ≤-15.4 ^{SR}	pH<3 ≤-9.3 ^M
OBS-SW sw in	pH~7-8 21°C ≤-0.9 ^{SO} ≤-1.0 ^M	pH~6.5-7 ≤-6.5 ^{SR}	pH~3.5-4 ≤-4.0 ^M
OBS-SW vf in	3°C pH~3 ≤-13.8 ^{SR} , ≤-10.2 ^M	pH~6	pH~5.5 to 6
OBS cond cool	pH~3.4	pH~3.4 ≤-16.5 ^M	pH~3.4
Grotto-SW diff	pH~3-8 27°C ≤-10.7 ^{SO} , ≤-11.7 ^M	pH<3 ≤-3.0 ^{SR}	pH<3 ≤-1.5 ^M
Grotto-SW sw in	pH~7-8 ≤-4.2 ^{SO} , ≤-8.9 ^M	pH~4-7	pH~4 92°C pH~3.5-4 ≤-0.7 ^{SR} , ≤-0.2 ^M
Grotto-SW vf in	pH<3-8 13°C ≤-6.6 ^{SO} ≤-7.2 ^M	pH<3 ≤-3.7 ^{SR} ≤-1.9 ^M	pH<3
Grotto cond cool	pH~4.2	pH~4.2 ≤-3.5 ^M	pH~4.2

Note sensitivities of results (e.g., pH and T of redox transition) to fluid compositions and transport styles.

Yellow, highly reduced; orange, relatively oxidized; sulfate reduction, SR; sulfide oxidation, SO; methanogenesis, M (yellow); methanotrophy, M (orange). OBS-SW mix data are from McCollom and Shock [1997].

From Tivey, 2004

Tools available

I. Distribution of species as fn of T (MINEQL, EQ3, REACT)

Sensitivity to input

A. thermodynamic data

B. fluid composition data

C. temperature data

II. Path reaction (EQ6, REACT)

A. assumptions about kinetics

B. assumptions about whether T is conservative

III. Transport-reaction

A. small scale across steep gradients

▶ B. large scale at low transport rates

C. assumptions – kinetics, boundary conditions, steady-state

More complicated 1-D and 2-D coupled transport-reaction models that consider conservation of fluid mass in the system:

$$\frac{\partial \phi}{\partial t} = -\nabla \cdot \mathbf{q}$$

where ϕ is porosity, \mathbf{q} the velocity vector

And conservation of solute mass:

$$\frac{\partial(\phi C_i)}{\partial t} + \nabla \cdot (\mathbf{J}_{\text{disp}} + \mathbf{J}_{\text{adv}} + \mathbf{J}_{\text{diff}}) = R_i$$

where C is moles/m³ fluid, R is net rate (moles i/m³ rock/s) for all chemical reactions, \mathbf{J} is flux (dispersive (disp), diffusive (diff), and advective (adv)); Steefel and Lasaga, 1990.

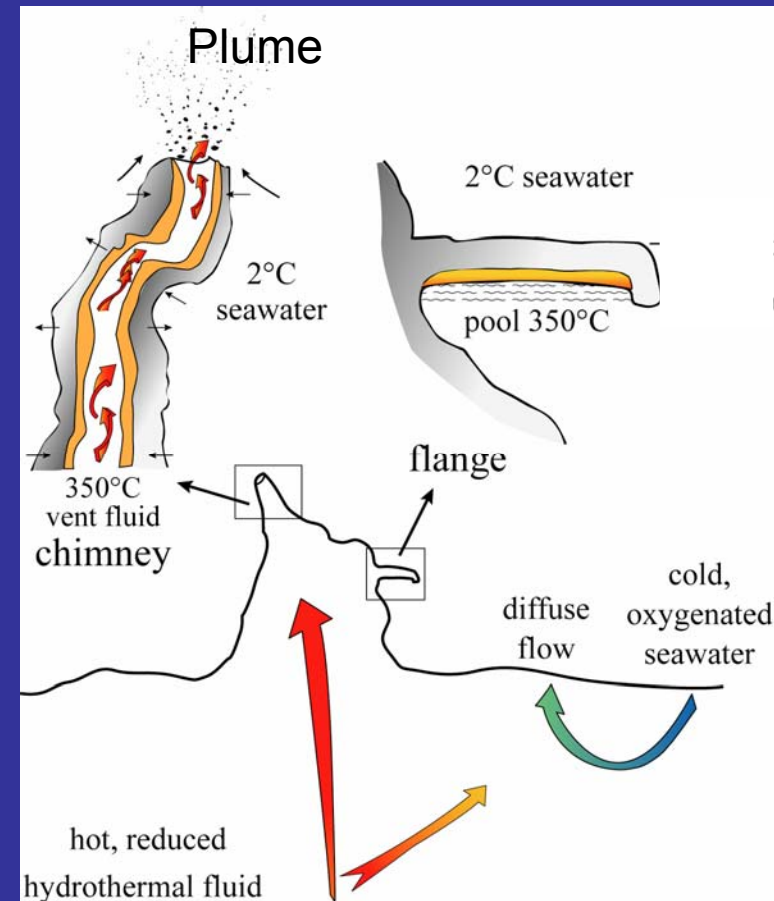
Need information on kinetics of various reactions, on how changes in porosity affect permeability. If fluid flow (advection) is rapid, it is not possible to fully couple the equations.

IV. Best tools for specific environments

Diffuse flow – Mixing using path reaction model

Plumes – Path reaction model with precipitation allowed
and hydrogen oxidation inhibited

Chimney walls – Transport through
porous/permeable media



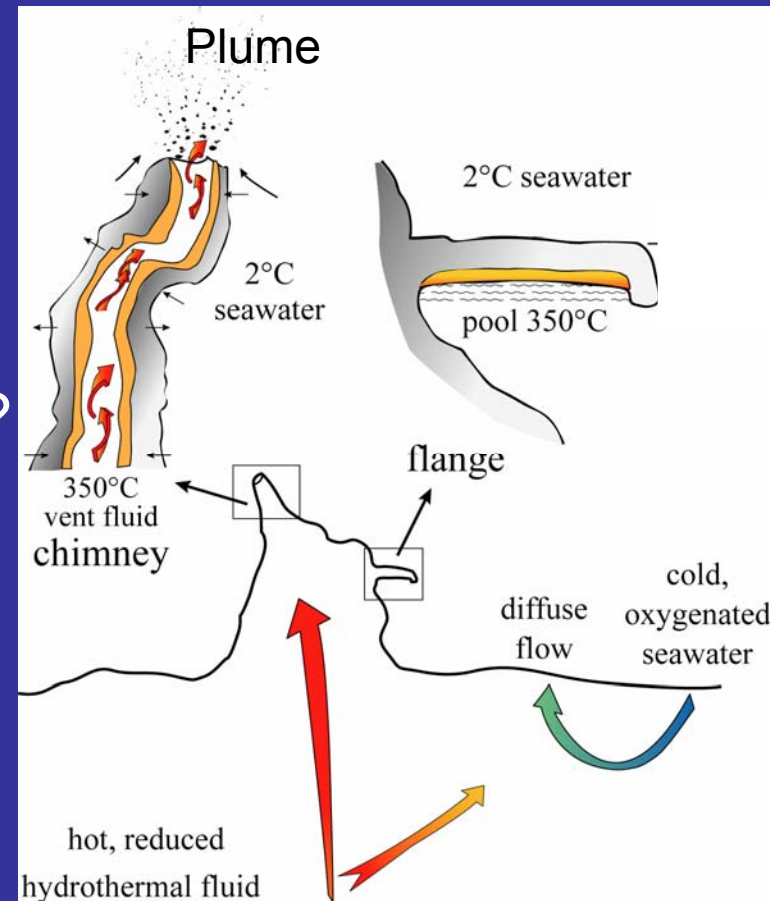
V. Sensitivity of results to assumptions made

Is temperature conservative?

Should some reactions be inhibited?

Is mixing a good approximation for question being asked?

Are boundaries really at steady-state?





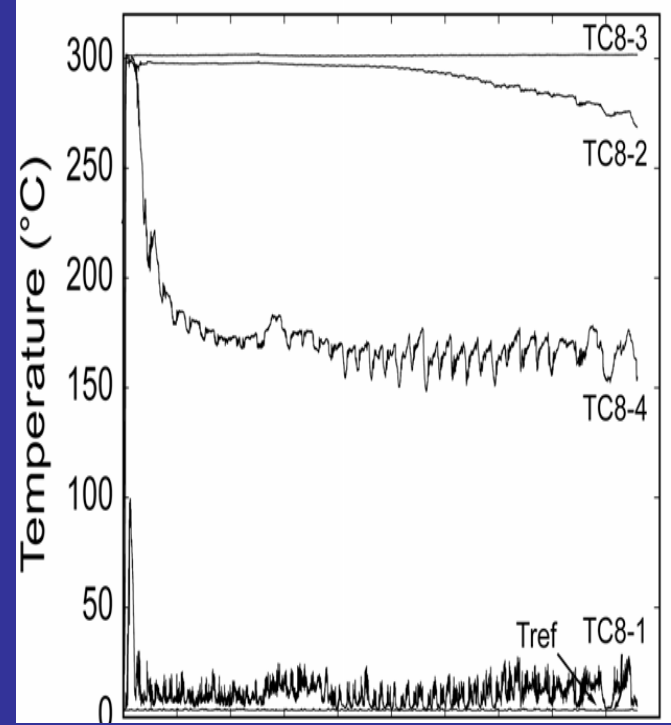
Copyright 2003 Monterey Bay Aquarium Research Institute
Miburch/2003/138/05_43_35_19.rgb (AUX)
Sun May 18 21:44:36 2003 GMT (local +7)
[stationary]

TC8-4=middle of chimney wall.
TC8-1=outside chimney wall

So the temperature, and likely the fluid composition, at the exterior of the deposit varies on ~12 hr time-scale.

Boundary conditions (e.g., T and maybe composition) at chimney exteriors can vary periodically due to tidally driven bottom currents and wafting of warm fluids

BM72



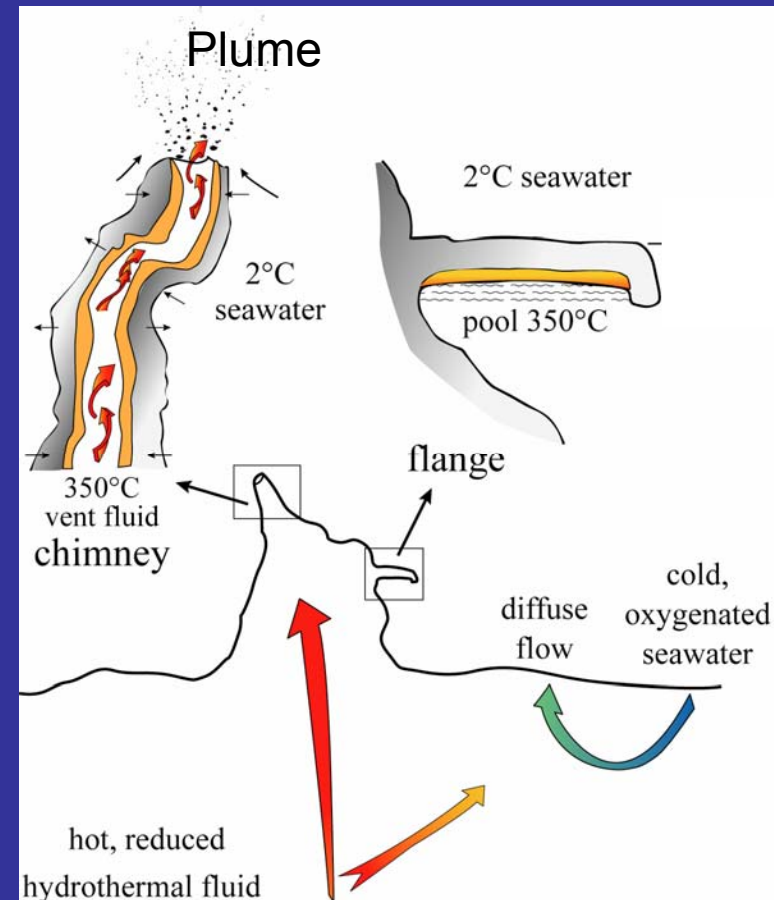
(Pagé et al., submitted)

VI. Limitations in current ability to quantify processes

Models assume steady-state.

Need information on reaction rates.

If flow rates are very high, problems occur, cannot converge on solution.

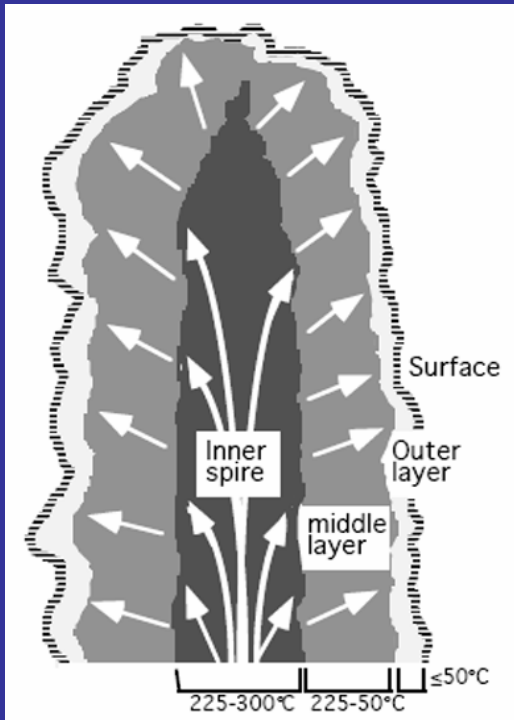


VI. Limitations in current ability to quantify processes

Models assume steady-state.

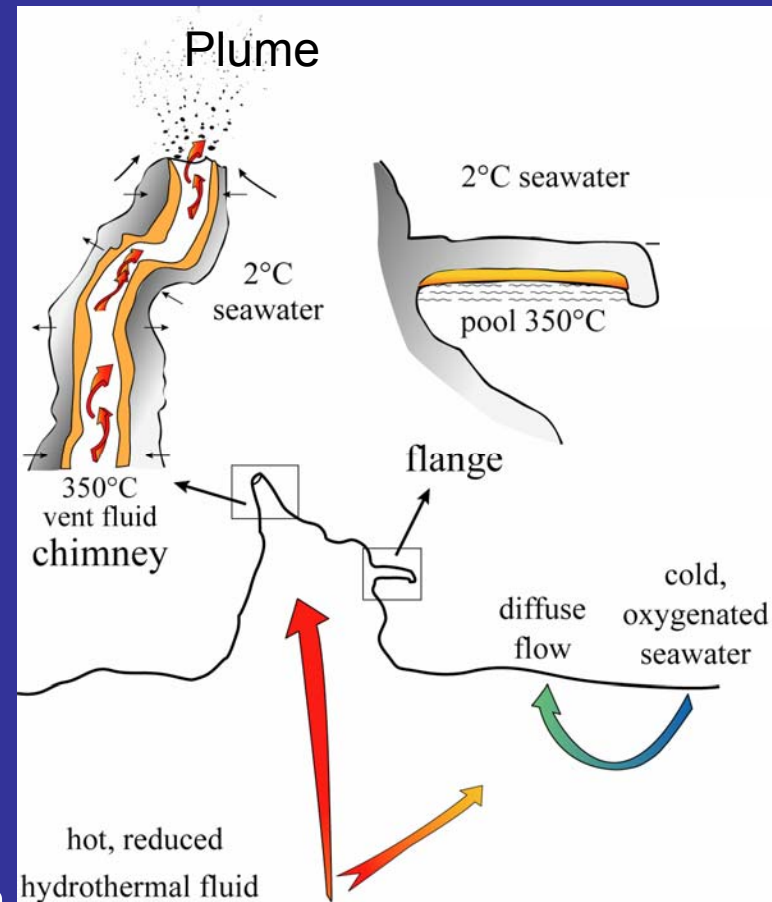
Need information on reaction rates.

If flow rates are very high, problems occur, cannot converge on solution.



For example with diffusers, flow rates are large enough so that transport by diffusion and advection cannot be calculated.

Instead, assume advection across a thermal gradient dominates, and model as a conductively cooled fluid. Need to know actual flow rates! Measure in the field.



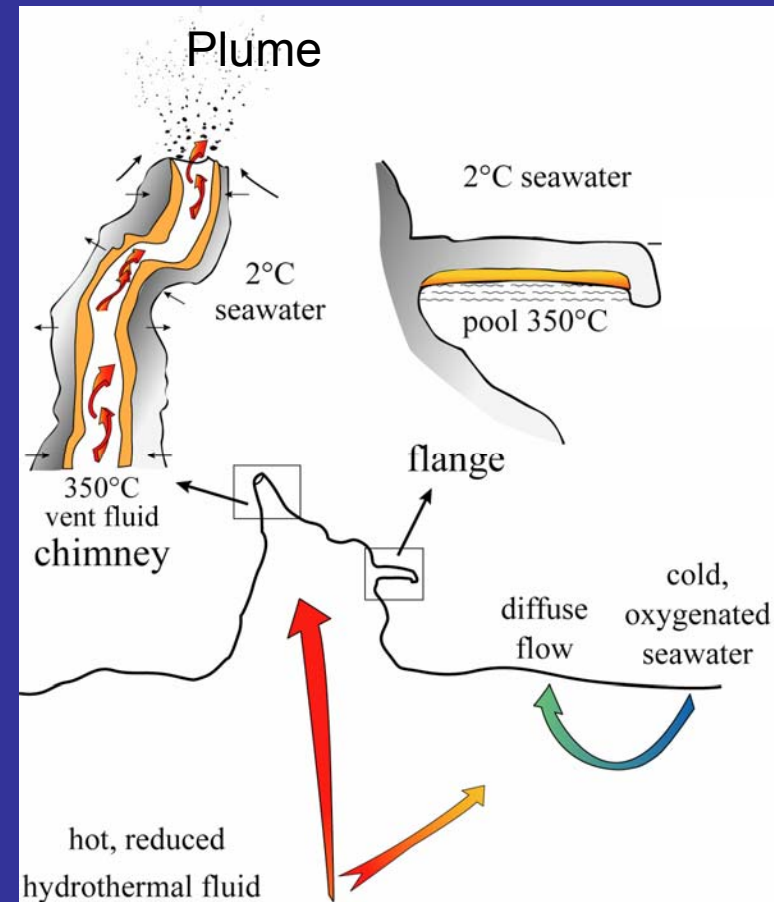
Key points to remember:

Models are tools dependent on quality of input

Can be used very effectively to test significance of various parameters/assumptions

- change 1 piece of input and run again
- match observed field data

In most vent environments, transport dominates, so reactants are not limiting, and products are carried away



Models are best used coupled to collection of field/laboratory data.