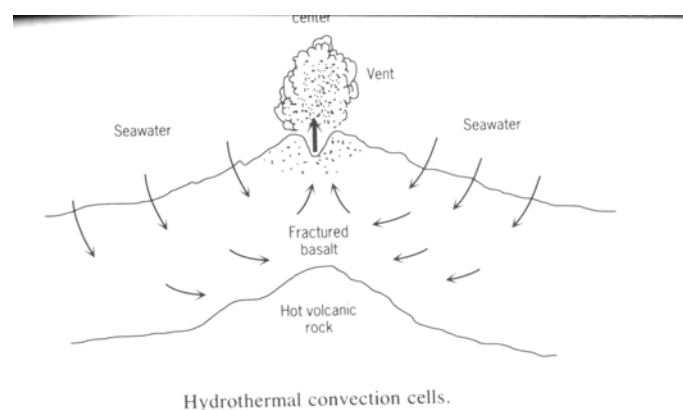**Lecture 13. Hydrothermal Circulation**

The discovery of hot springs on the ocean floor during the 1970s was one of the most exciting events in the history of oceanography. Although hydrothermal activity at mid oceanic ridges (MOR) was predicted as part of the plate tectonics theory, it took more than two decades before hydrothermal vents were actually found. First indications for the existence of such systems came in the late 60s when the ocean floor was dredged in the East Pacific and sediments rich in Fe, Mn and other metals were found. As some more samples and short cores were recovered, it was evident from the type of minerals found in cracks in the rocks that these deposits must have been formed through some high temperature reactions. Temperature anomalies were detected (only a few degrees above ambient) along the EPR that supported these conclusions and in the mid 70s, when undersea navigation systems, better cameras, and a manned submarine were utilized for this purpose, the vents were finally discovered.

Giant tubeworms and clams, clouds of bacteria and strange shrimp were discovered. A whole ecosystem whose metabolic energy is derived at least partially from the Earth's internal heat rather than from the sun was described. The primary producers in this system are the wide variety of chemoautotrophic bacteria and Archaea that utilize sulfur, hydrogen, methane and other compounds released by the reaction of seawater with the newly formed oceanic crust.

When newly formed oceanic crust cools, it contracts and "cracks" are formed in the basaltic complex. Seawater percolates into the oceanic crust through these fractures, is gradually heated, and reacts at high temperatures (~350º C) with the crustal rock. In these reactions, Mg from seawater is removed into the rock, acid (H^+) is produced and major (Ca, Ba) and transition metals (Fe, Mn, Zn, Cu) are leached from the rock into the fluid. Some sulfate is reduced to H_2S and bicarbonate is converted to CO_2. Along the way (at lower temperatures), sulfate is removed from solution by precipitation as anhydrite. These hot, acidic, anoxic fluids become buoyant and rise towards the ocean floor, continuing to react with the rock through which they flow. The hydrothermal fluids cool by loss of heat to the surrounding rock (conductive cooling) and through mixing with cold seawater as they get close to the sea floor. The cooling and mixing causes precipitation of secondary minerals (metal sulfides, quartz, and sulfates) and the metals that expel to the oxic seawater oxidize and precipitate as metal rich sediments. Of specific interest is the ^3He discharge ("primordial") from the vents. This gas is non-reactive (noble gas) and can be used to map patterns of oceanic circulation and mixing.
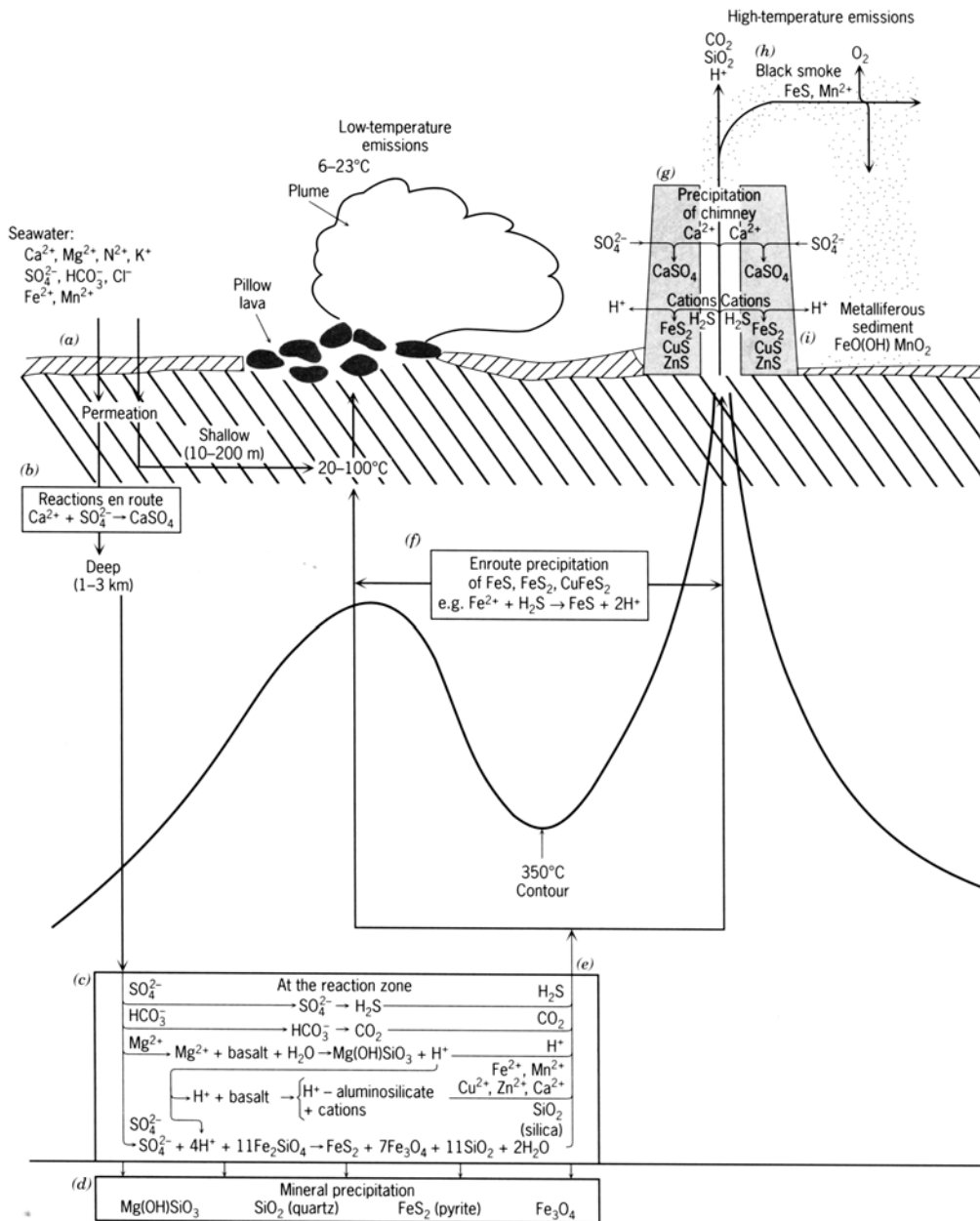
Important parameters that determine the high temperature fluid composition are: pressure, temperature, water/rock ratio, rock composition, recharge fluid composition and reaction time.

Hydrothermal convection cells.

Mass Balance and Hydrothermal Activity

To know the importance of hydrothermal circulation in ocean chemistry, one must determine the reactions that occur in these areas and the rate of flow of water through the hot rocks. The "missing" sink or source for river- born Mg^{2+}, K^+, H_4SiO_4, and HCO^{3-} may be found in reactions that occur in active hydrothermal areas of the ocean floor.

A Schematic Diagram Hydrothermal Circulation and Related Processes

High-temperature emissions
CO_2
SiO_2 (h) O_2
H^+ Black smoke
FeS, Mn^{2+}

Low-temperature
emissions
6–23°C

Plume

(g)
Precipitation
of chimney
Ca^{2+} | Ca^{2+}
SO_4^{2-} SO_4^{2-}
$CaSO_4$ $CaSO_4$

Seawater:
Ca^{2+}, Mg^{2+}, N^{2+}, K^+
SO_4^{2-}, HCO_3^-, Cl^-
Fe^{2+}, Mn^{2+}

Pillow
lava

H^+ Cations Cations H^+ Metalliferous
          FeS_2 H_2S|H_2S FeS_2 (i) sediment
          CuS   CuS   FeO(OH) MnO_2
          ZnS   ZnS

(a)

Permeation

Shallow
(10–200 m)   20–100°C

(b)

Reactions en route
$Ca^{2+} + SO_4^{2-} \rightarrow CaSO_4$

(f)

Enroute precipitation
of FeS, FeS_2, $CuFeS_2$
e.g. $Fe^{2+} + H_2S \rightarrow FeS + 2H^+$

Deep
(1–3 km)

350°C
Contour

(e)

(c)

SO_4^{2-}	At the reaction zone	H_2S
HCO_3^-	$SO_4^{2-} \rightarrow H_2S$	CO_2
Mg^{2+}	$HCO_3^- \rightarrow CO_2$	H^+

$Mg^{2+} + basalt + H_2O \rightarrow Mg(OH)SiO_3 + H^+$

Fe^{2+}, Mn^{2+}
Cu^{2+}, Zn^{2+}, Ca^{2+}

$H^+ + basalt \rightarrow$ {$H^+ -$ aluminosilicate + cations}

SiO_2
(silica)

SO_4^{2-}
$SO_4^{2-} + 4H^+ + 11Fe_2SiO_4 \rightarrow FeS_2 + 7Fe_3O_4 + 11SiO_2 + 2H_2O$

(d)
Mineral precipitation
$Mg(OH)SiO_3$ SiO_2 (quartz) FeS_2 (pyrite) Fe_3O_4

The Hydrothermal Heat Flow
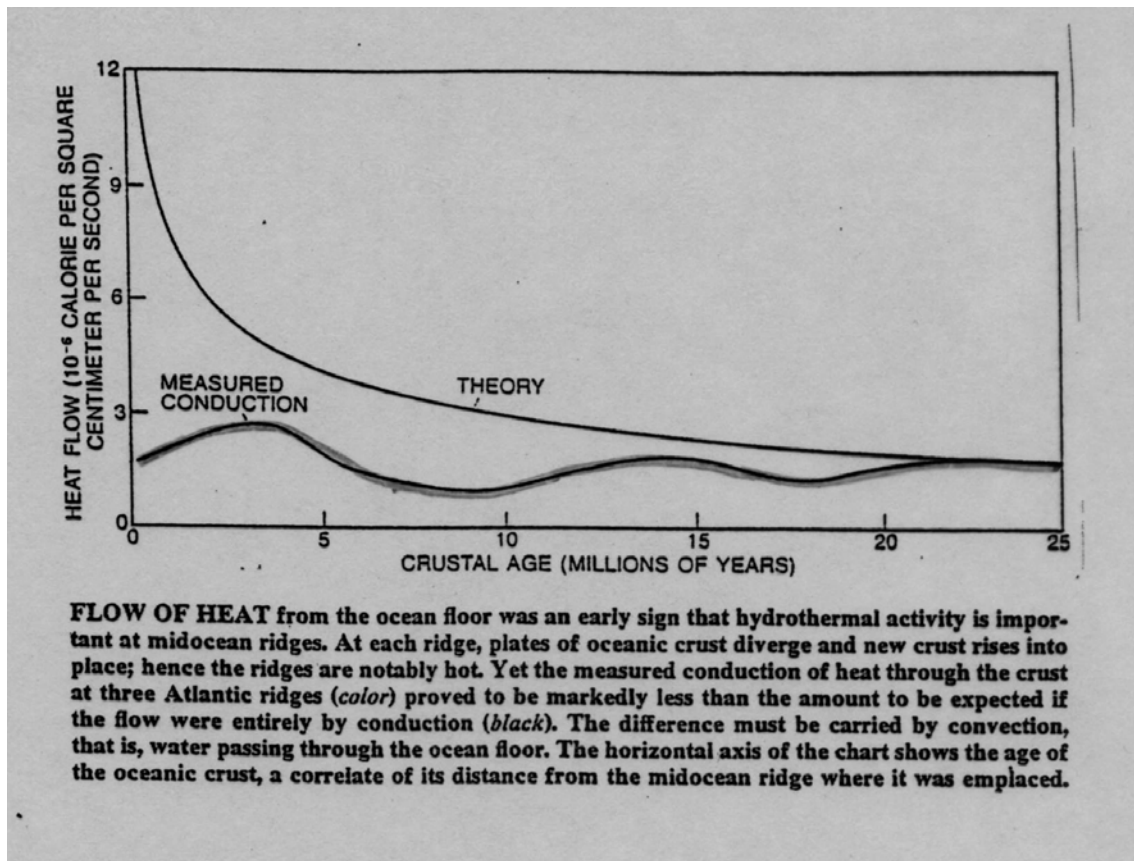How much seawater is circulated through hydrothermal vents every year?
One way to do this calculation is to calculate the amount of heat lost by convection at the ridges each year, and find out how much water is needed to absorb this heat using the heat capacity of water. The necessity for convection (advective flow) of seawater through the crust and sediments near hydrothermal areas was discovered by heat-flow measurements which were made by attaching thermometers to piston cores and determining the thermal gradient in sediments. Temperature in sediments increases with depth due to heat transport from the crustal plate. The diffusive (conductive) heat loss is determined by calculating the Heat Flux, q:

$$q = K(dT/dz) \, C_p \, \rho$$

     K   = thermal diffusivity ($\cong 10^3$ cm^2 s^{-1})
     C_p = heat capacity ($\cong 1$ cal g^{-1} deg^{-1} or ≈ 4 J g^{-1} °K^{-1}; It is temperature dependent.)
     ρ = density (g cm^3)
     T   = temperature (deg C)

Observations indicate that the actual heat flow measured using temperature gradients is much less than predicted by using the above relations (see figure below). This suggests that the difference must be lost be convection.

The theoretical relationship between heat flow, q, and crustal temperature T : $q = A / t^{1/2}$, where A is a constant to be determined in the model of a cooling slab

FLOW OF HEAT from the ocean floor was an early sign that hydrothermal activity is important at midocean ridges. At each ridge, plates of oceanic crust diverge and new crust rises into place; hence the ridges are notably hot. Yet the measured conduction of heat through the crust at three Atlantic ridges (*color*) proved to be markedly less than the amount to be expected if the flow were entirely by conduction (*black*). The difference must be carried by convection, that is, water passing through the ocean floor. The horizontal axis of the chart shows the age of the oceanic crust, a correlate of its distance from the midocean ridge where it was emplaced.

Recent estimates of the total predicted global oceanic heat flux is 32×10^{12} W, 240×10^{18} cal yr^{-1} (Elderfield and Schultz, 1996). Temperature measurements and the calculated conductive (diffusive) heat flow can account for about 66% of this flux. The difference between these estimates is caused by seawater circulation through fractured hot crust, causing heat flow by advection (convection); i.e., about 34% of the heat flux (11×10^{12} W) must be lost by hydrothermal flow.

Hydrothermal Water Flow
The flow of water, F, associated with the convective heat flow, H, is related through the temperature change, ΔT, and the heat capacity of seawater, c_p:

$$F = H / \Delta T \, c_p$$

Where $c_p = 4.0$ J g^{-1} K^{-1} at 5.0 °C and 350 bar and 5.8 J g^{-1} K^{-1} at 350 °C and 350 bar

Axial flow: If all the heat released at the axis is via black smokers at 350ºC (H= 11×10^{12} W).

$$F = 11 \times 10^{12} \text{ W} / (350 \times 5.8) = 5.4 \times 10^9 \text{ g s}^{-1} = 1.7 \times 10^{14} \text{ kg yr}^{-1}$$

This is an upper limit because much of the axial flow is probably not exiting at 350ºC, assuming ~60% is off axis we can calculate:

Off Axis flow: (H = 7×10^{12} W, exiting at 10ºC):

$$F = 7 \times 10^{12} / (10 \times 4.0) = 1.75 \times 10^{11} \text{ g s}^{-1} = 5.5 \times 10^{15} \text{ kg yr}^{-1}$$

The water flow off axis is about 10 times that on axis!

The residence time for water with respect to cycling through hydrothermal vents can be calculated:
$$\tau = 1.4 \times 10^{21} \text{ kg of seawater} / 1.7 \times 10^{14} \text{ kg yr}^{-1} = 8.2 \times 10^6 \text{ yr}$$
$$\tau = 1.4 \times 10^{21} \text{ kg of seawater} / 5.5 \times 10^{15} \text{ kg yr}^{-1} = 0.25 \times 10^6 \text{ yr}$$

Chemical Changes During Hydrothermal Circulation

The reactions at hydrothermal vents profoundly affect the composition of seawater. Practically all the Mg and much of the S output today is through these processes, and about 70% of K, 20% of Ca up to 50% of Si as well as significant proportions of the Li, Rb, Ba and transition metal inputs are from this system. These values are not easy to get at. When the vent waters are sampled, they are already mixed with seawater and the end member hydrothermal composition can only be inferred through calculations and assumptions regarding the temperature of reaction and/or type of reactions occurring. For example, the composition could be derived from

extrapolating temperature to 350° C or Mg to zero. These are the expected end member temperature and composition of the hydrothermal fluids.
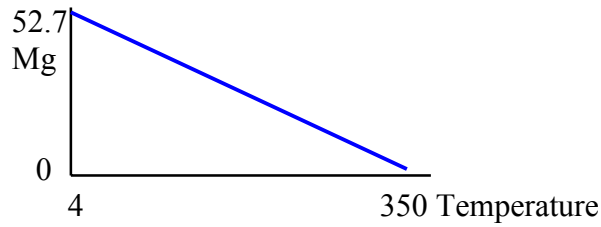
There are a few lines of evidence that support this temperature range:
- $\delta^{18}O$ of the minerals precipitated suggest that this is the temperature of reaction, as the fractionation is temperature dependent.
- Using some thermodynamic principles, this can be calculated from the chemistry of the discharged waters and the mineral composition of the rocks (phase separation).
- Lab experiments in pressure chambers at different temperatures indicate that these are the right conditions to produce observed products (strip all the Mg out, etc).

Our knowledge of chemical transformations at hydrothermal areas derives from:
    A. Laboratory studies,
    B. Water column measurements
    C. Actual measurements of the hydrothermal water.

*A. Laboratory Experiments*
Laboratory studies of seawater-rock interaction at high temperature and pressure (200 – 500 °C and 500 bars) reveal the types of changes one might expect in nature. Bishoff and Dickson (1975) squeezed 300 g seawater and 30 g basalt and observed the following changes in the liquid phase: Lower pH, Mg, Ca, and SO_4 concentrations drop. In the solid phase changes include:
    1. Basaltic glass => Mg-rich clay mineral (Montmorillonite) Exchange of Ca for Mg.
    2. Formation of quartz (Si was leached from the basalt and a much more insoluble silicate phase, quartz, forms, releasing H_4SiO_4 to solution).
    3. Formation of $CaSO_4$ (anhydrite).

B. *Water column tracers of hydrothermal activity*
A few elements are so enriched in hydrothermal waters they can be detected even after the water is thousands of times diluted with ambient seawater. Such elements include ^3He, or more precisely, the $^3He / ^4He$ ratio. ^3He is primordial (i.e., formed during element synthesis in the sun) and is now degassing from the mantle. ^4He originates from radioactive decay. Since hydrothermal areas (and volcanoes) are conduits to the earth's mantle, these regions are rich in ^3He (Craig and Lupton, 1981). A plume of elevated $^3He / ^4He$ ratios is observed above active vents.
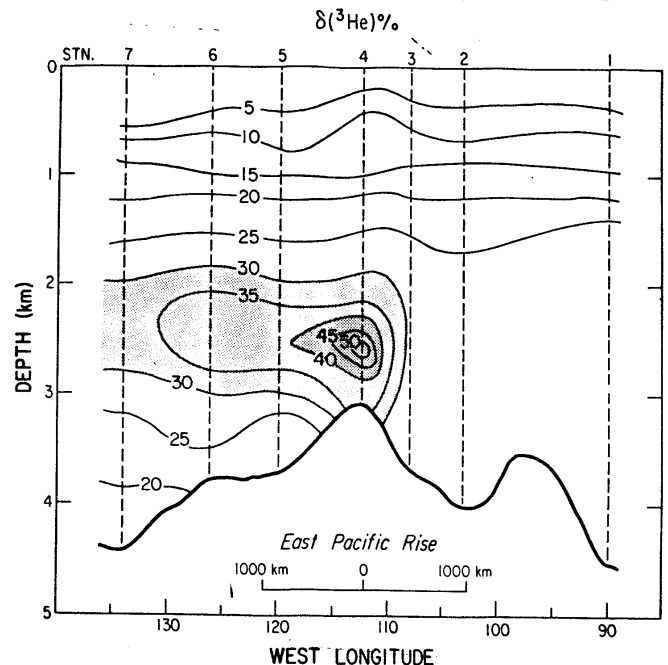
A similar tracer is Mn^{2+}. Hydrothermal waters are very reducing (oxygen poor) they are thus rich in the reduced form of many chemicals. Manganese is abundant in rocks and is relatively easily reduced. Mn has a long oxidation time, so it is observed in waters surrounding hydrothermal activity sites. (Chester, 1990)
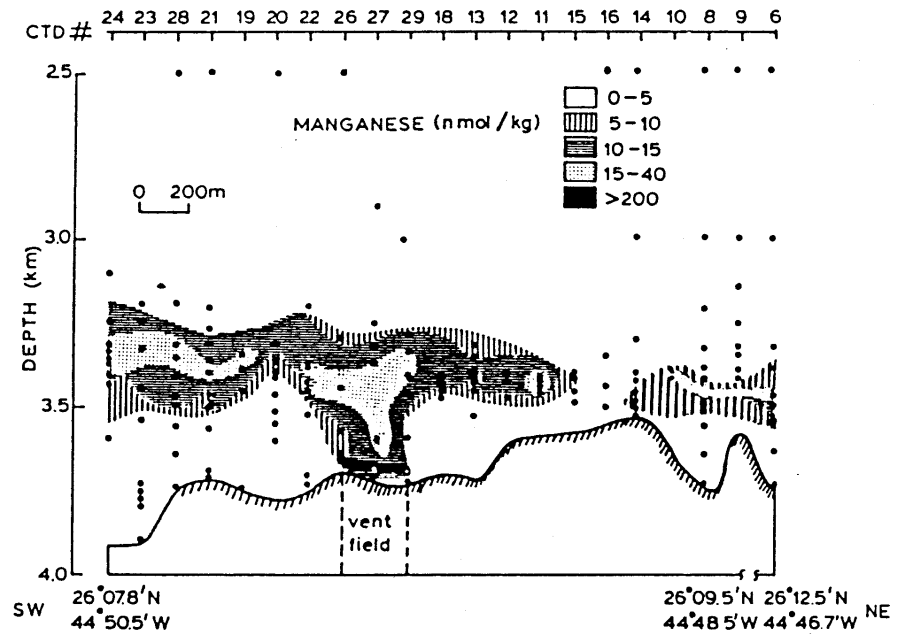

Figure 5.2 SW-NE transect for total reactive Mn at the TAG hydrothermal system on the Mid-Atlantic Ridge (from Klinkhammer *et al*. 1986). Total reactive Mn is the Mn extracted from unacidified seawater samples by oxine after adjustment of the pH to 9, and represents mainly the dissolved fraction of the element.

Germanium, (Ge) is a trace element in seawater that exhibits a constant ratio to H_4SiO_4 (Ge/Si = 0.7 x 10^{-6}). Since H_4SiO_4 is enriched in hydrothermal waters, so is Ge; but the Ge signal is more detectable in the surrounding waters because of the very low concentration of Ge in ambient seawater. (Froelich et al., 1985)


$$Ge/Si)_{ocean} = 0.7 \times 10^{-6}$$
$$Ge/Si)_{hydrothermal} = 16 \times 10^{-6}$$
$$Ge/Si)_{rivers} = 0.7 \times 10^{-6}$$
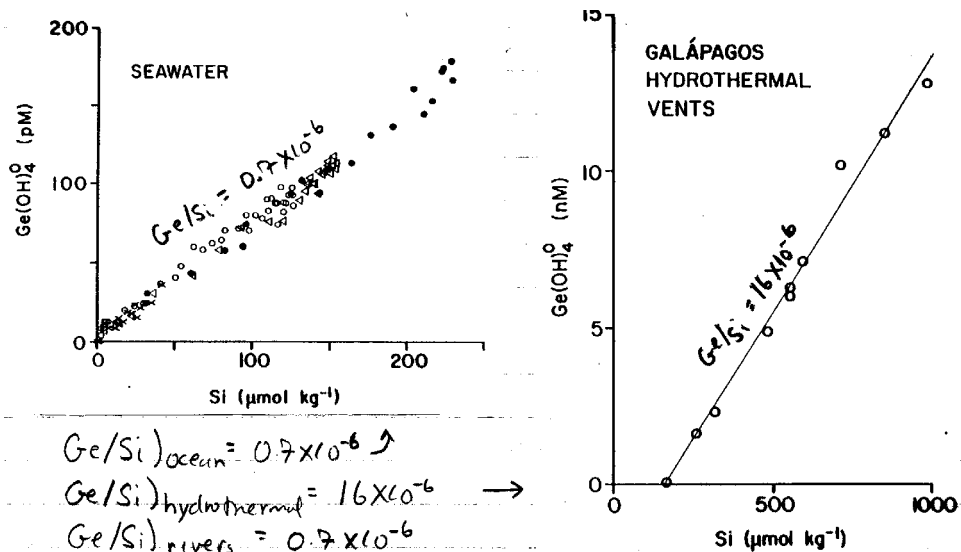
C. *Chemistry of Hydrothermal Vents*

This depends on the location of circulation; we can divide the vent chemistry into that represented by – axial-low temperature, axial-high temperature and off-axis circulation.

Results from the Galapagos (axial-low temperature) revealed dramatic increases in H_4SiO_4 and decreases in Mg. (Edmond et al., 1979). The temperature of the pure hydrothermal water was estimated to be about 350°C based on the solubility of quartz at those temperatures and pressures; and, extrapolation of the Mg/T relationship to zero concentration.

Sampling the black smokers at 12 °N EPR (axial-high temperature) detected temperatures in the range of 350°C and confirmed the above estimates. Von Damm et al. (1985) compiled the hydrothermal end-member concentrations for many of the elements in seawater.
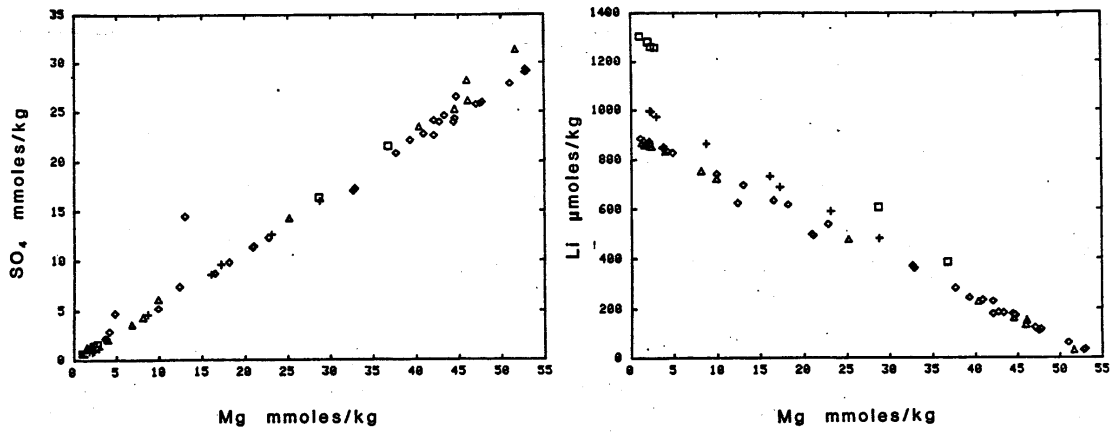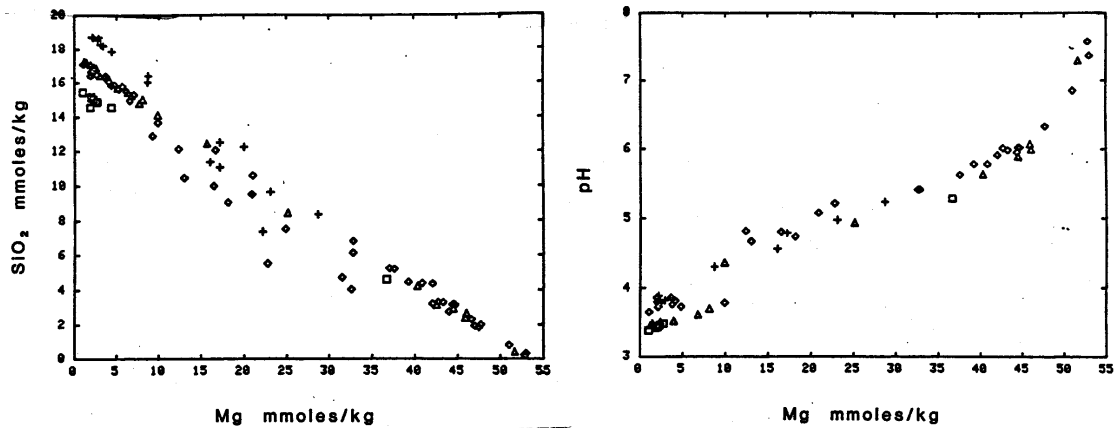

data of Von Damm et al (1985)

TABLE 3: ENDMEMBER CONCENTRATIONS

	NGS	21° OBS	NORTH SW	HG	GSC[1]	SEAWATER
The Alkalis						
Li μ[2]	1033	891	899	1322	689→1142	26
Na[3] m	510	432	439	443	+,-[4]	464
K m	25.8	23.2	23.2	23.9	18.7→18.8	9.79
Rb μ	31	28	27	33	13.4→21.2	1.3
NH$_4$ m	<0.01	<0.01	<0.01	<0.01	n.a.	<0.01
The Alkaline Earths						
Be n	37	15	10	13	11→37	0.02
Mg m	0	0	0	0	0	52.7
Ca m	20.8	15.6	16.6	11.7	24.6→40.2	10.2
Sr μ	97	81	83	65	87	87
Ba μ	>15	>7	>9	>10	17.2→42.6	0.14
ΣBa[5] μ	>16	>8	>10	>11		
$^{87}Sr/^{86}Sr$[6]	.703019	.703171	.703345	.703026	n.a.	.7091
	±68	±32	±103	±120		
pH	3.8	3.4	3.6	3.3		7.8
Alk meq	-0.19	-0.40	-0.30	-0.50	0	2.3
Cl m	579	489	496	496	+,-	541
SiO$_2$ m	19.5	17.6	17.3	15.6	21.9	0.16
Al μ	4.0	5.2	4.7	4.5	n.a.	0.005
Trace Metals						
Mn μ	1002	960	699	878	360→1140	<0.001[7]
Fe μ	871	1664	750	2429	+	<0.001
Fe/Mn	0.9	1.8	1.0	2.9		
Co n	22	213	66	227	n.a.	0.03
Cu μ	<0.02	35	9.7	44	0	0.007
Zn μ	40	106	89	104	n.a.	0.01
Ag n	<1	38	26	37	n.a.	0.02
Cd n	17	155	144	180	0	1
Pb n	183	308	194	359	n.a.	0.01

[1]GSC data is from Edmond et al. (1979a,b) and is /liter.
[2]Units: m = millimoles/kilogram, μ = micromoles/kilogram, n = nanomoles/kilogram, meq = milliequivalents/kilogram.
[3]Sodium is calculated from the charge balance.
[4]+ = gain, - = loss, n.a. = not analyzed.
[5]ΣBa includes barium from the dissolved and the particulate phase and is a lower limit.
[6]The strontium isotopes were measured by T. Trull on the mass spectrometer at M.I.T.
[7]Trace element data for seawater are as compiled in Quinby-Hunt and Turekian (1983).

Geochemical Budgets

The Magnesium Flux
 If we assume that all Mg is lost at the ridge axis, then what flow is necessary to accomplish this?
   Flux Mg from rivers = Flux at hyrothermal axis x concentration difference
   8×10^{12} mol yr^{-1} = F_{hydro} x 53×10^{-3} mol /kg (seawater - hydrothermal)
   F_{hydro} = 15×10^{13} kg yr^{-1}

This flux would corresponds to a heat flow of: $H = 9 \times 10^{12}$ W

This value is about three times too high when compared to measured heat flux estimates. This may imply that one can remove maybe 1/3 of the Mg inflow from rivers at high temperature ridge axes.

Can hydrothermal circulation off axis account for the rest of the sink?

This is very difficult to know because we know little about the chemical changes in this area. There are two lines of evidence indicating that Mg is removed from solution by off axis circulation. These inferences come form measurements in pore waters of sediments.
Mg concentrations in basement fluids (Pore water in contact with the crust) are temperature dependent (Mottl and Wheat, 1994). The fraction of heat lost by advection decreases away from the ridge crest and so do Mg concentrations. The depletion in pore waters does not have to be very large to make a significant Mg sink. A 1% concentration change (nearly immeasurable) would result in a flux of:
$$F = (.01) \times 53 \times 10^3 \text{ mol / kg } (5.5 \times 10^{15} \text{ kg } yr^{-1}) = 2.8 \times 10^{12} \text{ mol / yr}$$

This can account for another 1/3 of the river inflow. The rest is taken out with carbonate deposition and clay formation (reverse weathering).

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