

## Seafloor Hydrothermal Systems

### I. Introduction

The mid-ocean ridge system is the largest continuous feature on the surface of the earth. It extends the length of the Atlantic and Indian Oceans and continues through the southern and northeastern Pacific (Figure 1). It has been the object of extensive study in recent years as the major surface connection with the Earth's mantle. It is the location where new oceanic crust, which is both the material for seafloor spreading and an important source of heat to the Earth's surface, is formed.

At mid-ocean ridges, new crust forms and cracks as it cools and as it spreads away from the ridge crest. Cold seawater penetrates the warm crust. The sub-seafloor heat source (either magma or newly solidified hot rock) exchanges heat with the fluid, resulting in a plume of buoyant fluid that rises rapidly, to be discharged at the sea floor through hydrothermal vents. This fluid is replaced by seawater "recharge", creating a circulation cell. The recharge seawater reacts with crustal rocks as it travels towards the heat source. The reaction of seawater with basaltic rocks at elevated temperatures results in a fluid with a changed composition. Hydrothermal circulation therefore leads to net fluxes of chemicals into and out of the ocean (Figure 2).

Our study of the importance of seafloor hydrothermal processes to ocean chemistry will proceed with:

- An examination of seafloor hydrothermal activity as a source of heat to Earth's surface. Patterns of the Earth's heat flow are used to estimate the location and temperature of fluid convection and seawater-rock interactions. As will be explained, there are important differences between the reactions occurring at low and high temperatures.
- Description of the reactions occurring at and near mid-ocean ridges between seawater and basalt as the seawater is warmed, as well as those occurring in the hydrothermal fluid as it interacts with seawater as it exits the sea floor.
- Estimation of hydrothermal fluxes resulting from reactions near the axis of the mid-ocean ridge system, using measured compositions of hydrothermal fluids; and estimation of fluxes resulting from low-temperature reactions occurring off the ridge axis.
- Description of the composition of hydrothermal fluids present at vent sites, their significance to ocean chemistry, and their influence on chemical, physical, and biological processes occurring in the water column in the vicinity of vent sites.

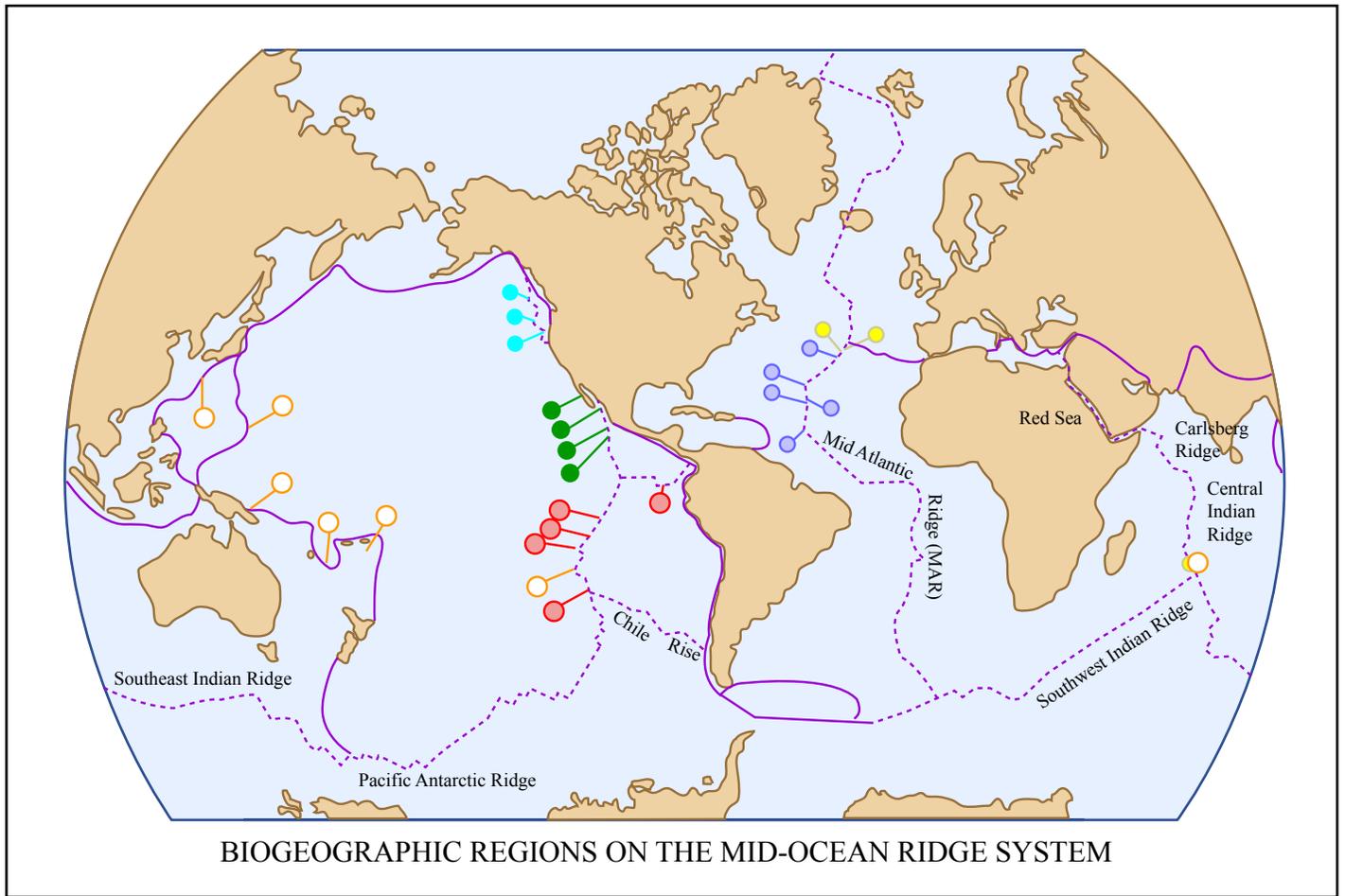
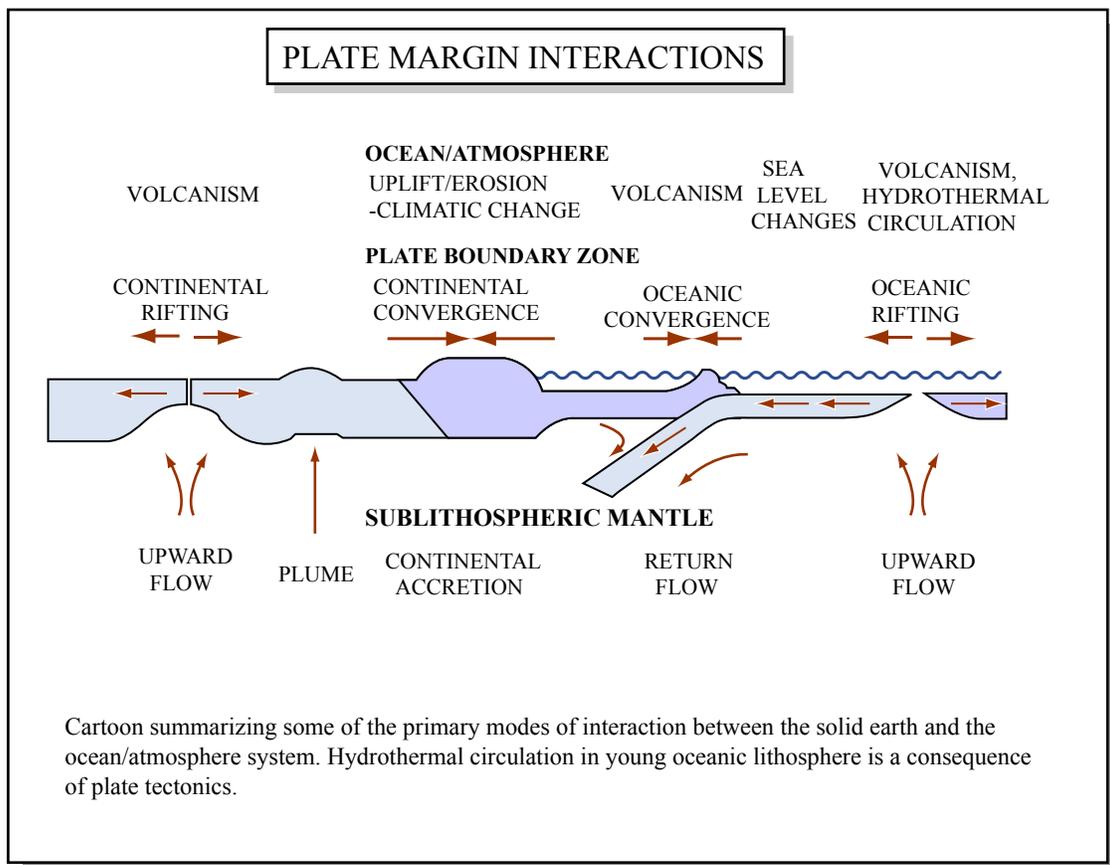
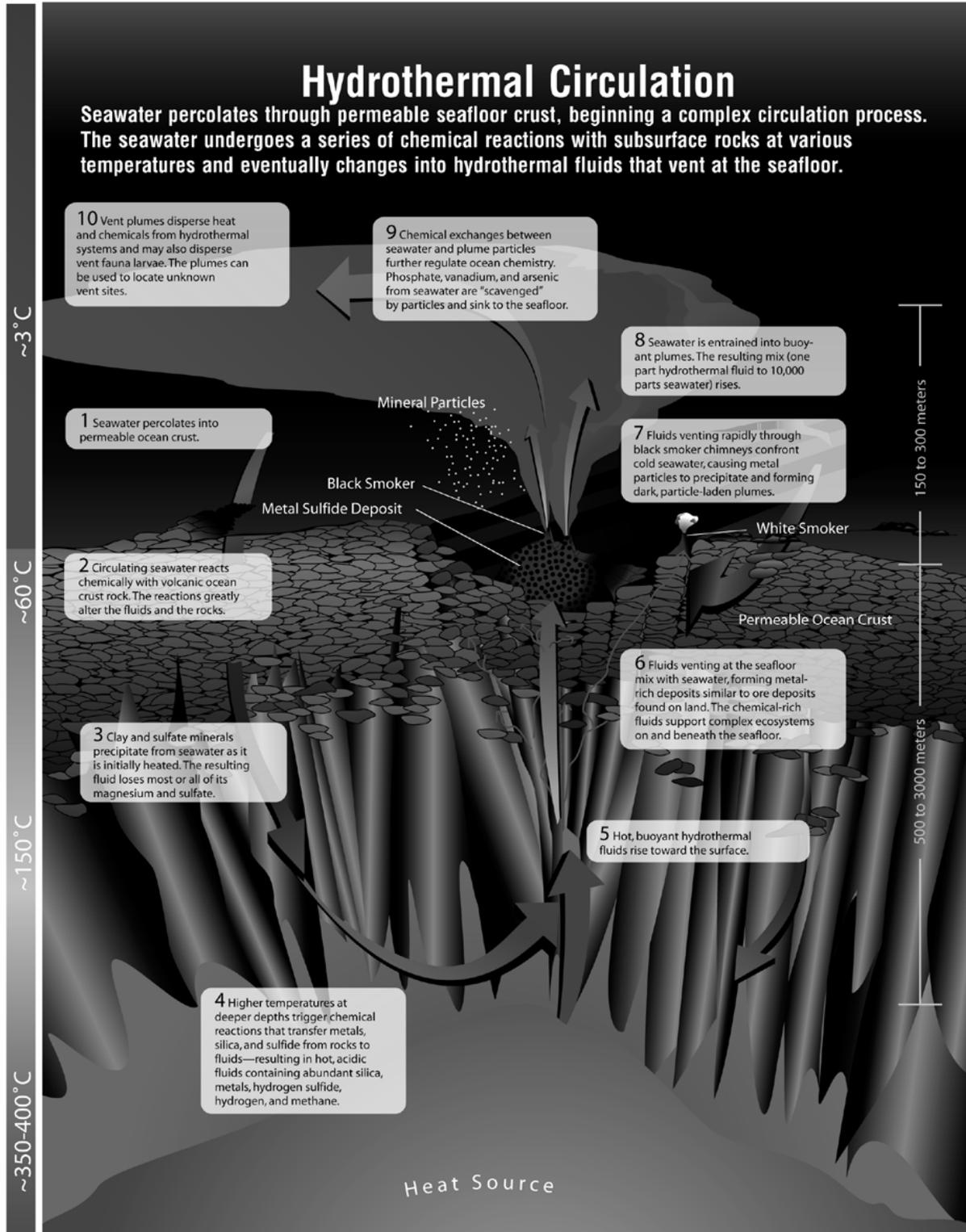


Figure by MIT OCW.





□ Figure 2 (from Tivey, 2004, *Oceanus* 42, no. 2, 60-65)

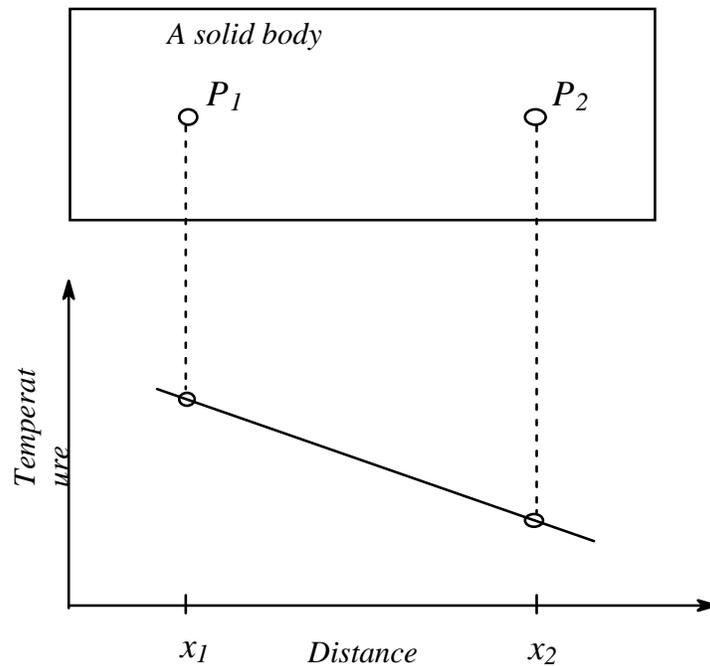
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## II. The heat flux from the mantle

### II.1 Geophysical models and measurements

Freshly formed oceanic crust and the underlying lithosphere are hot. Over time, the new crust moves away from the mid-oceanic ridge as more new crust is formed; as the crust and lithosphere move away, they cool and contract. Theoretical models can be constructed to predict this heat loss and contraction, assuming that all cooling occurs by upward heat transfer solely by conduction in the rock. These model predictions of heat loss solely by conduction can then be compared to actual measurements of the conductive heat flux, with discrepancies the result of fluid circulation, or heat loss from convection.

Before discussing the results of these comparisons, we will take a quick look at the two ways in which heat is transferred from crust to seawater. One transport mechanism is *conduction*. Think of a solid body in which two points,  $P_1$  and  $P_2$ , are maintained at different temperatures.



In this situation, there will be a flow of heat from the warmer to the cooler point that is proportional to the temperature gradient between the two:

$$\text{Heat Flux} \cong -K \frac{T(P_2) - T(P_1)}{x_2 - x_1}$$

with  $K$  being the "thermal conductivity" in  $\text{W m}^{-1} \text{K}^{-1}$ , a property of the solid. The transport of heat is accomplished without large scale motion within the body. The second important means of heat loss from the crust is *convection*. Convective heat transport is accomplished by the relative motion of portions of the heated body. In the case of the oceanic crust, convective heat loss occurs when water circulates through the crust, gaining heat from the surrounding rock as it circulates.

Predictions of heat loss from the crust based on theoretical cooling models give the *total* heat loss. Measurements of heat loss (from heat flow probe measurements) yield the amount of heat transported by *conduction*. Comparisons of model predictions and measurements show differences, called the "heat flow anomaly", that vary systematically with crustal age. The data in Figure 3 show that, on average, the predicted heat loss is significantly greater than measured heat loss in young crust; that there is considerable variability in the measured heat flux; and that, in old crust (with age exceeding about 65 million years – see figure 3A), the predicted and measured heat fluxes are about the same. It is concluded that, in young crust, convective transport by hydrothermal circulation accounts for the difference between predicted and measured values.

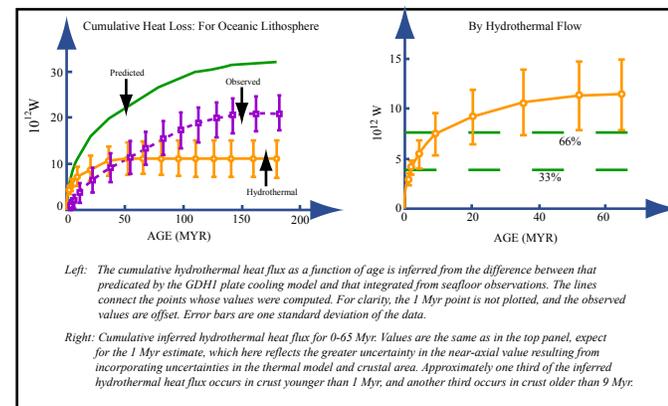
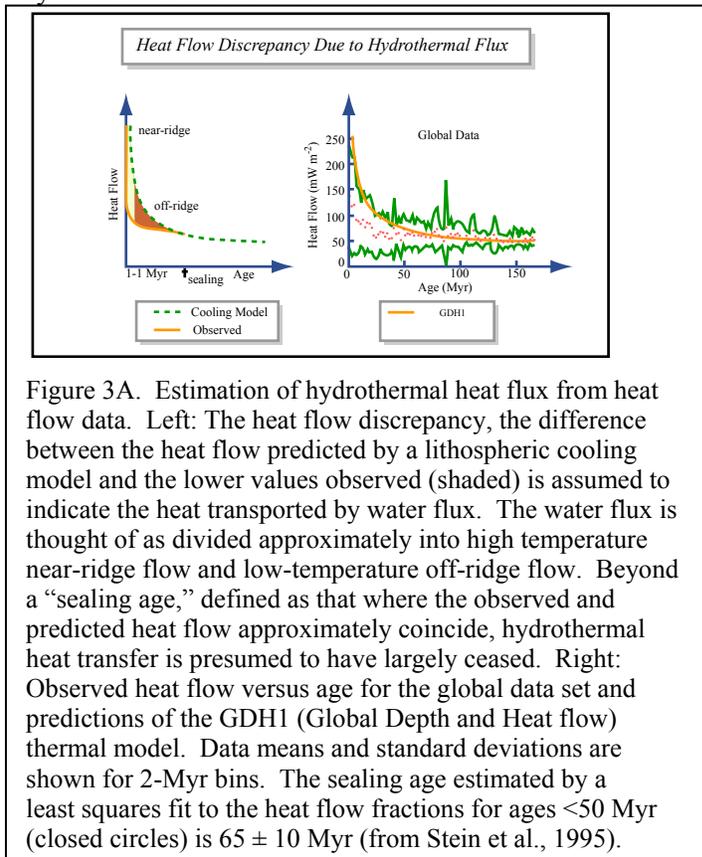


Figure by MIT OCW.

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The total oceanic heat flux predicted by geophysical models is about  $32 \times 10^{12}$  W, or  $240 \times 10^{18}$  cal/yr. The hydrothermal heat flux, obtained by adding up the heat flow anomaly over the age of the crust, is  $11 \times 10^{12}$  W ( $80 \times 10^{18}$  cal/yr), or about 34% of the total. As will be seen later, it is important to note that a fraction of this convective heat flux occurs in very young crust, that is, at the mid-ocean ridge axis ( $\sim 3.2 \times 10^{12}$  W ( $24 \times 10^{18}$  cal/yr), or  $\sim 29\%$  of the total), and  $\sim 70\%$  “off-axis” in crust  $>1$  Myr (Fig. 3).

## *II.2 Crystallization and cooling of magma at ridge crests*

The new crust formed in the mid-ocean ridge system is formed by the cooling of magma. The cooling process involves both crystallization of crustal rocks and subsequent cooling. The amount of heat that must be lost from the crust can be estimated by calculating the heat transferred during these processes.

The rate of formation of new crust is approximated as the product of the crustal formation rate ( $3 \text{ km}^2 / \text{yr}$ ), crustal thickness (5 km), and its density ( $2.8 \text{ g/cm}^3$ ):  $4.2 \times 10^{16}$  g/yr. If we assume a latent heat of crystallization of magma of 161.5 cal/g, then the heat released is  $6.8 \times 10^{18}$  cal/yr. The magma crystallizes at about  $1200^\circ\text{C}$ . Cooling from this temperature to the typical hydrothermal reaction temperature of  $350^\circ\text{C}$  releases about 270 cal/g, or a total of about  $11 \times 10^{18}$  cal/yr. Subsequent cooling to seafloor temperature would release an additional  $4.6 \times 10^{18}$  cal/yr (110 cal/g). The maximum available heat would be the sum of heat released by these 3 steps,  $23 \times 10^{18}$  cal/yr. It has been suggested that a reasonable range of values for heat transported by convection at the ridge axis is that released by crystallization alone or by the sum of crystallization and cooling to  $350^\circ\text{C}$  (Mottl and Wheat, 1994): 6.8 to  $18 \times 10^{18}$  cal/yr. This estimate is consistent with the estimate from geophysical considerations.

## *II.3 The flux of helium from the mantle.*

There are two isotopes of helium:  $^3\text{He}$ , formed at the birth of the solar system, is released steadily from the earth's mantle; and  $^4\text{He}$ . The  $^4\text{He}$  nucleus is the  $\alpha$  particle that is released during  $\alpha$  decay, and it is formed in both the crust and mantle at rates determined by the concentrations of uranium and thorium. The isotopes of helium have been measured in the fluids released from hydrothermal vents, and the ratio of  $^3\text{He}$  to  $^4\text{He}$  confirms that the helium in the fluids has a mantle source (Figure 5a). It is known that  $^3\text{He}$  is supplied to the earth's surface from the mantle at a rate of about  $6.5 \times 10^{26}$  atoms/yr. From this fact and the ratio of heat to  $^3\text{He}$  in hydrothermal emanations, the hydrothermal heat flux can be estimated:

$$\left[ \text{He-3 supply rate} \right] \times \left[ \frac{\text{heat}}{\text{He-3}} \right] = \text{axial hydrothermal heat flux}$$

The heat :  ${}^3\text{He}$  ratio can be estimated from measurements of  ${}^3\text{He}$  and temperature in hydrothermal fluids (Figure 5b); the heat flux calculated from such measurements, carried out at vents near the Galapagos (Jenkins et al. 1978), was  $49 \times 10^{18}$  cal/yr, much larger than the two estimates shown above.

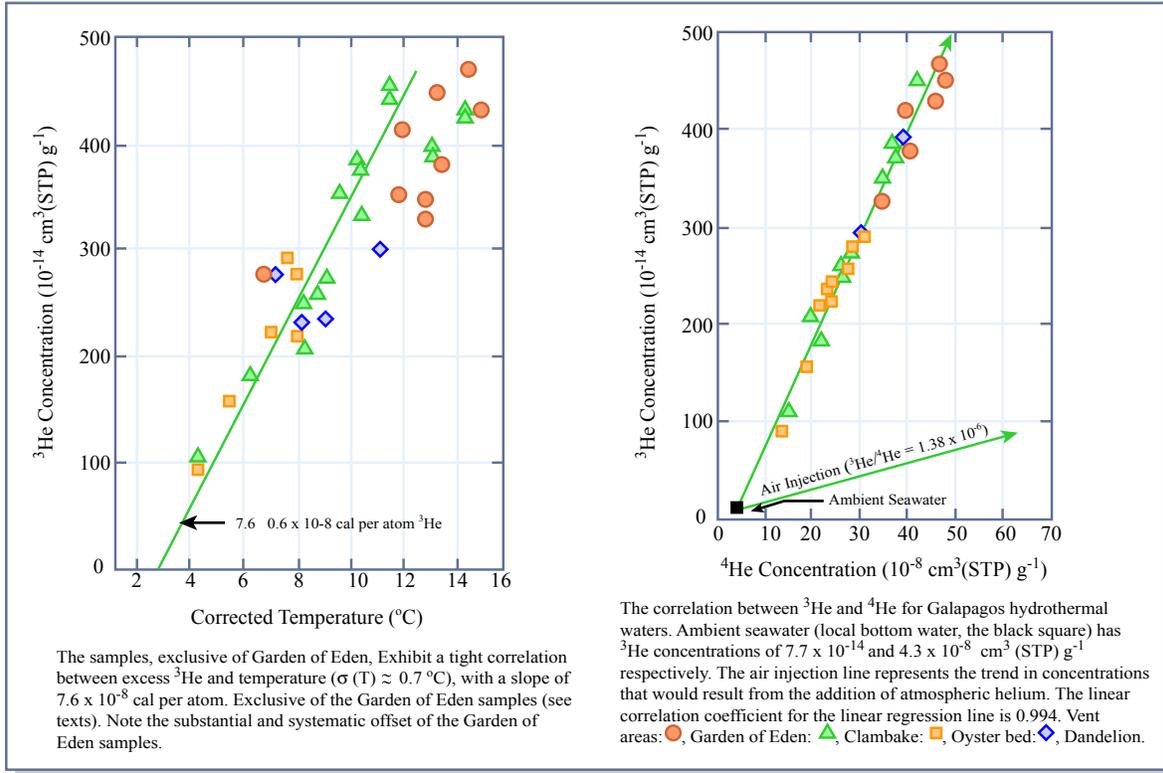


Figure by MIT OCW.

Figure 5A from Jenkins et al., 1978.

Figure 5B from Jenkins et al., 1978.

Subsequent measurements at more hydrothermal vent sites showed that the heat :  ${}^3\text{He}$  ratio varied by about a factor of 10 between sites, so that an estimate of the global heat flux from measurements at a single site is highly uncertain. Lupton et al. (1989) offered a different type of calculation using helium isotopes. They assumed that all the  ${}^4\text{He}$  in the mantle originated from U and Th decay, and that heat and He are removed from the mantle together. They then used estimates of the U and Th contents of the mantle, along with the decay constant, to calculate that  $0.16 \times 10^{-6} \text{ cm}^3(\text{STP})$  of  ${}^4\text{He}$  are produced per calorie of heat. Using an estimated  ${}^3\text{He} / {}^4\text{He}$  ratio of  $1.1 \times 10^{-5}$  in the upper mantle, they calculated:

$$\left[ \frac{{}^3\text{He}}{\text{heat}} \right]_{\text{upper mantle}} = 2 \times 10^{-12} \frac{\text{cm}^3(\text{STP}){}^3\text{He}}{\text{calorie}} = 5.3 \times 10^7 \frac{\text{atoms}{}^3\text{He}}{\text{calorie}}$$

If this number is coupled with a  $^3\text{He}$  supply rate from the mantle of  $6.5 \times 10^{26}$  atoms/yr, then the estimated heat flux is  $12 \times 10^{18}$  cal/yr -- in agreement with geophysical estimates.

A summary of the heat flow estimates is shown below:

Total crustal heat loss from cooling models =  $240 \times 10^{18}$  cal/y

By conduction =  $160 \times 10^{18}$  cal/y

By convection =  $80 \times 10^{18}$  cal/y

Off-axis (lower T) =  $\sim 60 \times 10^{18}$  cal/y

Axial (high T) =  $\sim 20 \times 10^{18}$  cal/y

Crystallization of magma =  $\sim 7 \times 10^{18}$  cal/y

Crystallization of magma + cooling of rock to  $\sim 350\text{C}$  =  $\sim 18 \times 10^{18}$  cal/y

He – initial estimate based on Galapagos data =  $49 \times 10^{18}$  cal/y

He – revised, based on mantle properties =  $12 \times 10^{18}$  cal/y

### III. Seawater / Rock Reactions in the Oceanic Crust

#### III.1 *Description of the System*

The oceanic crust near a mid-ocean ridge is pictured in idealized, layered form in Figure 6 (top 2 cartoons), reasonable for crust formed at medium to fast spreading rates. It consists of a thin layer of sediments overlying a layer of volcanic rocks that is several hundred meters thick. These volcanic rocks cover sheeted dikes that, in turn, overlie gabbros and the axial heat source. There are sharp gradients in porosity and permeability between the volcanics and the sheeted dikes. As a result, water circulation tends to be open in the volcanics, restricted below; and water-rock ratios decrease with increasing depth below the surface. Water-rock reactions can be divided into those that occur while seawater is sinking through the crust and being heated (during "recharge"), those that occur at high temperature, near the axial heat source (in the "reaction zone"), and those that occur during the ascent of the altered seawater (now, the hydrothermal fluid) back to the sea floor ("discharge"). This division is that of Alt (1995). (At slow spreading ridges, the crust is not as simply layered (Fig. 6, bottom cartoon)).

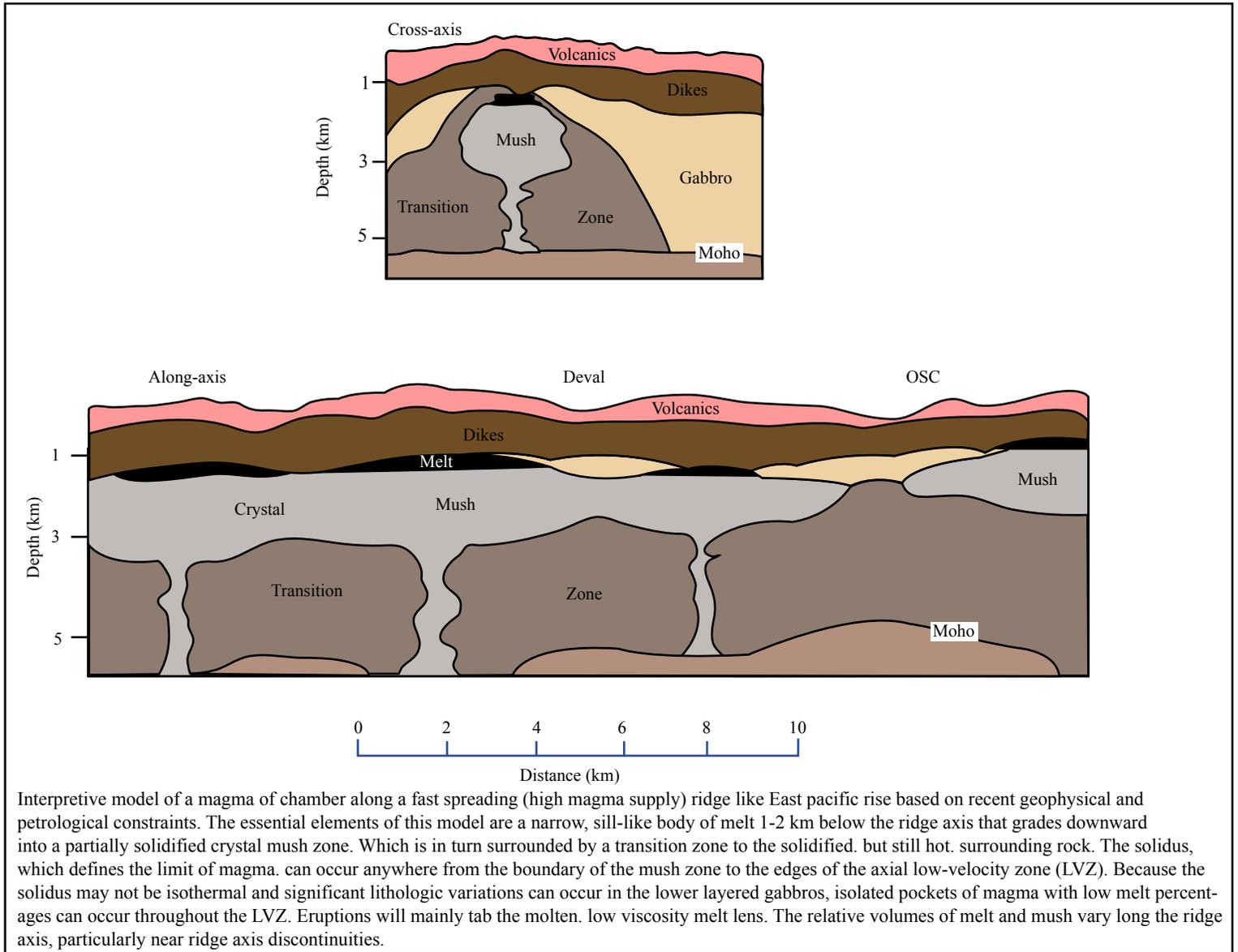
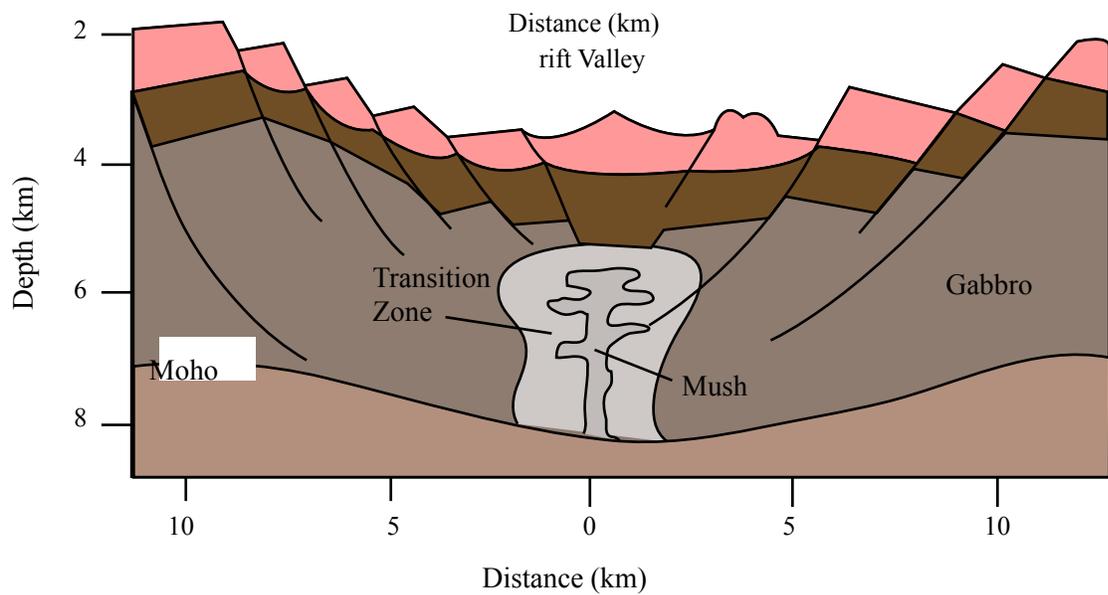


Figure by MIT OCW.



Interpretive model of a magma chamber beneath a slow spreading (low magma supply) ridge like the Mid-Atlantic Ridge, based on recent geophysical and petrologic constraints. Such ridges are unlikely to be underlain by an eruprable magma lens in any steady state sense. A dike-like mush zone is envisioned beneath the rift valley forming small sill-like intrusive bodies which progressively crystallize to form oceanic crust. Eruptions will be closely coupled in time to injection events of new magma from the mantle. Faults bordering the rift valley may root in the brittle-ductile transition within the partially molten magma chamber.

Figure by MIT OCW.

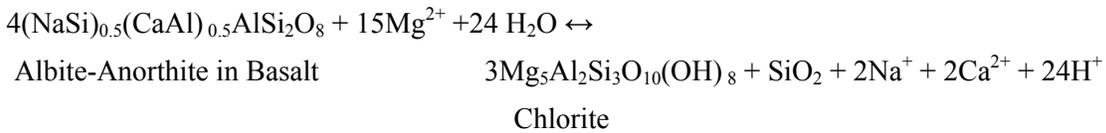
Figure 6 showing differences in layering of the crust at fast (fig. 9) and slow (fig. 10) spreading ridges (from Sinton and Detrick, 1992).

### III.2 Water-Rock Reactions in the Sinking Seawater.

Low temperature reaction, at temperatures up to about 40°C, of seawater with basalt results in the alteration of basaltic glass, olivine, and plagioclase by oxidation to ferric micas and smectite, Mg-rich smectite, and Fe oxyhydroxides. During these reactions, alkali metals (K, Rb, Cs), B and H<sub>2</sub>O are removed from seawater to the altered minerals. Si, S and, in some cases, Mg, may be lost from the minerals. When the low temperature reactions occur at depths where sulfide is present, the sulfur may be oxidized and lost from the minerals. The reactions are more extensive, the more open the seawater circulation through the crust. They occur not only in young crust at mid-ocean ridges, but also in older crust. Since, as we will see later, these low temperature reactions may have opposite effects on seawater composition from high temperature reactions, it is important to take into account their occurrence in off-axis crust.

When seawater is heated to temperatures above 150°C, two reactions occur: the precipitation of Mg hydroxides (fixation of seawater Mg in the crust) and anhydrite (CaSO<sub>4</sub>).

Precipitation of Mg into various clays can be represented by the following reaction, showing chlorite formation:

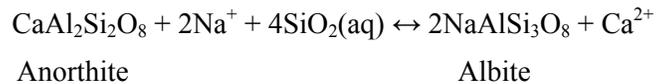


In general, the products of Mg hydroxide formation are smectites when the temperature is below 200°C and chlorites above 200°C. The reactions are important, in addition to their effect on the seawater Mg budget, because they can make the recharge seawater more acidic. However, H<sup>+</sup> is also consumed by silicate hydrolysis reactions that moderate the acidity of the altered seawater. For example, results of experimental reaction of seawater with basalt demonstrates that uptake of Mg is roughly balanced by release of Ca from the basalts (Mottl, 1983). The sum of all reactions results in an altered fluid that is slightly more acid than heated seawater. At temperatures above 150°C, Mg uptake is accompanied by leaching of alkali metals and B from rocks: reactions that are opposite in direction from the lower temperature reactions, important in off-axis crust, that remove these elements from seawater.

Anhydrite formation, occurring at temperatures in excess of 150°C, removes essentially all of the Ca from seawater; in so doing, it also removes about one-third of seawater sulfate. (Anhydrite exhibits retrograde solubility; if seawater is heated, anhydrite becomes saturated at ~150°C). Additional anhydrite precipitation can occur following release of Ca from basalt. Sulfur isotope data from vent fluids indicate that some of the seawater sulfate is reduced. This likely occurs at temperatures in excess of 250°C, with seawater sulfate reduced through reaction with igneous pyrrhotite to secondary pyrite. A combination of this seawater-derived sulfide with basaltic sulfide (0‰), results in the observed slightly elevated δ<sup>34</sup>S values of hydrothermal sulfide

in altered sheeted dykes and in fluids venting at the seafloor (>1‰). (In terms of mass balance, it is important to recognize that much of the anhydrite formed in the down-welling limb of the hydrothermal system may be dissolved or replaced by other phases as the crust ages).

Other elements are affected by ion exchange reactions. One that occurs at temperatures in excess of 250°C, and that affects the concentrations of Ca and Na in the resulting vent fluid, is albitization, or the alteration of basaltic anorthite to albite:



The set of reactions occurring in the "recharge" zone (Figure 2) results in a fluid that is slightly acidic, anoxic, and alkali-rich and Mg-poor relative to the starting seawater.

### *III.3 Reactions Near the Axial Heat Source*

The final steps in the formation of hydrothermal fluids take place in the "reaction zone" near the axial heat source. The acidic, anoxic fluid reaching this region reacts, at low water-rock ratios, with the gabbros present. Most importantly, the fluid attacks magmatic sulfide minerals, adding S and heavy metals (e.g., Cu, Fe, Mn, Zn) to solution. In some cases, the fluid may separate into a low salinity vapor phase and a brine phase; intermittent contact between the circulating fluid and the brine would then result in varying salinity (and Na and Cl content) of the hydrothermal fluid. In addition, magmatic volatiles are added to the circulating fluid: <sup>3</sup>He, CO<sub>2</sub> with a mantle stable carbon isotopic signature, CH<sub>4</sub>, H<sub>2</sub>.

### *III.4 Processes Occurring during Ascent to the Sea Floor*

Heating in the reaction zone results in a very buoyant fluid that rises at a rapid rate to the seafloor; the difference in density of seawater as a function of temperature and pressure is shown in Figure 7. It is unclear the extent to which this fluid reacts with the surrounding rock as it rises to the seafloor. Within ophiolites (slices of ocean crust that have been obducted and are exposed on land), the deep part of the focused upflow zones (within the lower sheeted dikes) are characterized by epidote zones (epidote + quartz ± chlorite). However, only one sample exhibiting these alteration phases has been recovered from the ocean crust. A well developed "stockwork" consisting of an alteration pipe with zones of quartz and sulfide veins, and with alteration haloes, has been revealed beneath the TAG active hydrothermal mound at 26°N on the Mid-Atlantic Ridge, by recovering drillcore from depths of up to 125 meters below seafloor. The rock record, however, integrates the effects of water-rock interaction over long periods of time. Thermodynamic calculations considering the measured compositions of fluids sampled at vents indicate that the fluids are supersaturated with respect to quartz, undersaturated with respect to many other phases, and close to saturation with chalcopyrite at the temperatures and pressures of

the vents. In general it has been assumed that 1) quartz becomes saturated as the fluid rises (due to decreasing pressure), but is kinetically inhibited from precipitating (and is not observed within actively forming chimneys), 2) there may be minor amounts of precipitation and/or dissolution of sulfide phases as the fluid rises, thus 3) the fluids rise rapidly enough so that their fluid composition is not greatly affected during upflow.

Fluids exit the seafloor at vent sites rapidly, as high temperature focused flow, and also slowly through cracks and surfaces as lower temperature diffuse flow. Analysis of diffuse fluid compositions indicate that the lower temperature fluids are mixtures of seawater and vent fluid, though some fluids show evidence for there having been conductive cooling of vent fluid, or conductive heating of seawater, and/or reaction (precipitation/dissolution) as the vent fluid and seawater mixed. Comparison of the high temperature and low temperature vent fluid compositions indicate that the mixing, cooling, heating, and/or reaction takes place in the shallow subsurface.

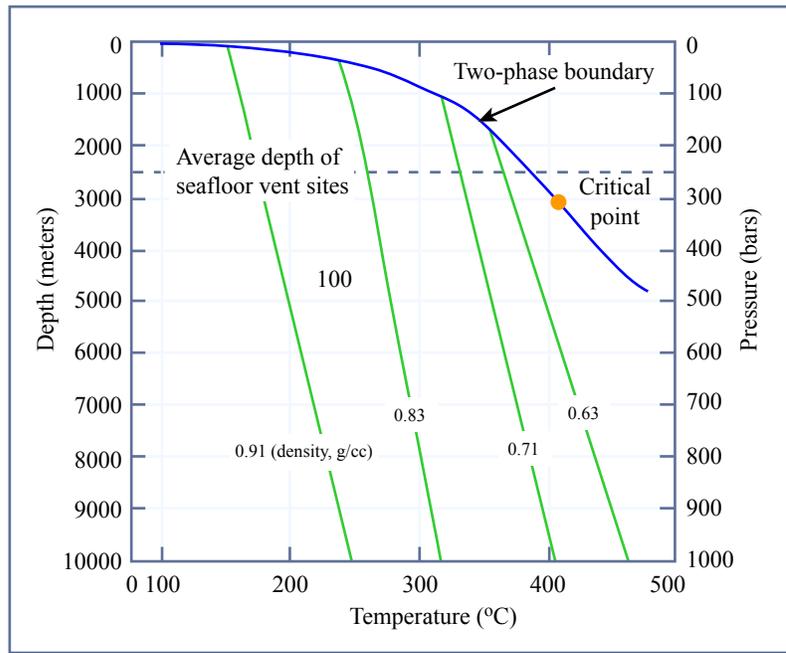


Figure 7

Figure by MIT OCW.

### III.5. Sampling hydrothermal fluids

Hydrothermal fluids from within the crust cannot be sampled directly. Rather, fluid is sampled as it exits hydrothermal vents. Inevitably, the fluid is mixed with varying amounts of seawater. Thus, the concentration of the element of interest in hydrothermal fluid must be estimated from an extrapolation to the pure hydrothermal fluid endmember. The extrapolation is accomplished using the assumption that pure hydrothermal fluids contain no Mg. The concentration of the element in the suite of samples, consisting of varying mixtures of seawater and hydrothermal fluid, is plotted vs. the Mg concentration in the samples; the resulting line is

extrapolated to zero Mg concentration to determine the hydrothermal end member. Obviously, the calculation assumes conservative mixing, and fails if the element undergoes reactions during mixing with seawater. Some examples of hydrothermal end member calculation are shown in Figure 8. Note that non-conservative behavior of Cu prevents calculation of an accurate endmember (Mg concentration in seawater is ~52.7 mmol/kg).

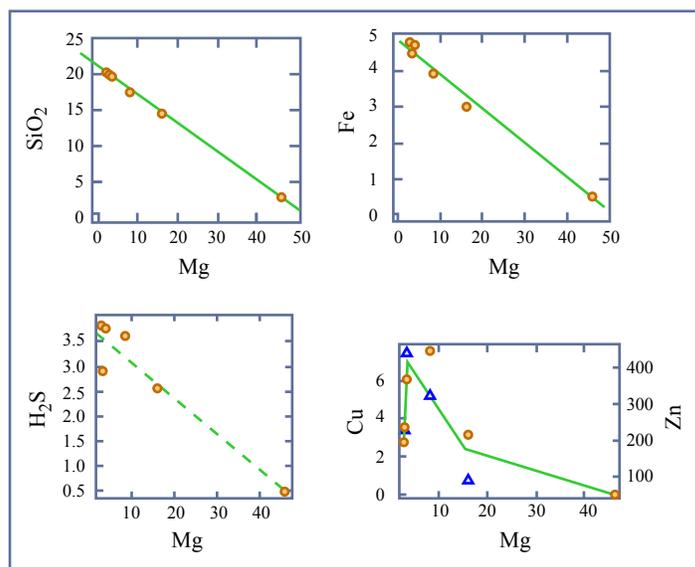


Figure by MIT OCW.

Figure 8

A summary of concentrations of the major elements of seawater in some mid-ocean ridge hydrothermal fluids is shown below. The ranges of concentrations for different vents illustrates the variability in processes that may affect hydrothermal reactions.

Chemical composition of vent fluids (from Von Damm, 1995; Von Damm et al., 1997)				
	TAG 1990	EPR 9°N, 1991	EPR 9°N, 1994	Seawater
T (°C)	360-365	388	351	2
pH (25°C)	3.35	2.8	2.6	7.8
Si(OH) <sub>4</sub> (mmol/kg)	20.75	5.9	20	0.2
H <sub>2</sub> S (mmol/kg)	2.3-3.5	41	8.7	0
Cl (mmol/kg)	636	46.5	846	540
Na (mmol/kg)	537	38.4	683	464
K (mmol/kg)	17.1	1.2	41.5	10.1
Ca (mmol/kg)	30.8	0	0	9.9
Mn (μmol/kg)	680	0.2	3.3	0
Fe (μmol/kg)	5590	1.5	12.1	0
Cu (μmol/kg)	98-120	-	-	0

Zn ( $\mu\text{mol/kg}$ )	47-53	-	-	0
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#### IV. Hydrothermal Fluxes

##### *IV.1. Heat flux and hydrothermal circulation*

As chemical oceanographers, a major interest is to estimate the net inputs and outputs of various chemical elements to and from the oceans due to seafloor hydrothermal activity. The best estimates of these fluxes due to hydrothermal activity at the axis of the mid-ocean ridge come from measurements of concentrations of elements in hydrothermal fluids. In order to translate these measurements into net inputs and outputs, the rate of circulation of seawater through hydrothermal systems must be estimated.

Heat flow estimates, with the heat capacity of seawater over the 0-350°C temperature range, have been used to estimate the circulation rate. It takes about 367 cal/g to heat seawater from 0° to 350°. If, for example, the *axial* heat loss is  $15 \times 10^{18}$  cal/yr, then the seawater circulation rate is

$$\frac{15 \times 10^{18} \text{ cal}_{\text{yr}}}{367 \text{ cal}_{\text{g}}} \times \frac{1 \text{ l seawater}}{1026 \text{ g}} = 4 \times 10^{13} \text{ l}_{\text{yr}}$$

This rate is about 0.1% of the rate of input of water to the oceans from rivers. Therefore, for an elemental flux due to axial hydrothermal activity to be as large as river input, the concentration difference for the element between the hydrothermal fluid and seawater must be about 1000 times its concentration in river water.

Heat is also lost from older crust, along the flanks of the mid-ocean ridge system. Mid-ocean ridge flanks are much less well characterized than axial hydrothermal systems; seawater flow through the crust is diffuse and patchy, therefore difficult to quantify. If, however, the effective temperature of the circulating seawater is 20°C (Mottl and Wheat, 1994), and  $50 \times 10^{18}$  cal/yr are removed by seawater circulation along ridge flanks, then the implied seawater circulation rate is  $2.4 \times 10^{15}$  l/yr, or about 7% of the river input rate. Low-temperature basalt-seawater reactions can be significant compared to river fluxes even if they produce fluids with much smaller concentration differences from seawater than are present in axial hydrothermal fluids.

##### *IV.2 Fluxes Due to Discharge from Hydrothermal Vents*

Fluxes from hydrothermal vents can be calculated by

$$Flux^i = (C_{hf}^i - C_{sw}^i) \times V_{sw}$$

where  $C_{hf}^i$  is the average concentration of element  $i$  in hydrothermal fluids,  $C_{sw}^i$  is its concentration in seawater, and  $V_{sw}$  is the volume of seawater discharged from hydrothermal vents per year. We have discussed the estimation of  $V_{sw}$ , and its uncertainty, above. In this section, we will illustrate the estimation of concentrations in hydrothermal fluids, discuss their variability, and show the results of flux calculations.

As shown in the table above, concentrations of various elements differ from vent to vent. Some generalizations about the major elements in hydrothermal fluids can be made. Na tends to follow Cl (as it must to maintain electrical neutrality, since these elements are the most concentrated in seawater) but can be somewhat depleted; the depletion is believed to be due to the exchange of Na for Ca in the Ca-rich plagioclase present in basalts and gabbros (albitization). Ca and K are enriched in hydrothermal fluids due to similar exchange reactions involving primarily  $Na^+$ ,  $Mg^{2+}$ , and  $H^+$ . Mg is quantitatively removed due to the precipitation of Mg hydroxides from seawater as it is heated. Sulfate is essentially quantitatively removed from seawater by anhydrite precipitation and sulfate reduction, with some seawater sulfate returned as  $H_2S$ . Cl concentration can differ slightly ( $\pm 10\%$ ) from that of seawater if the rock is hydrated (and  $H_2O$  is lost from the seawater, enriching it in Cl), or if minerals precipitate that incorporate Cl (e.g., amphiboles). However in general Cl is not involved to any significant extent in mineral alteration reactions; large variations in its concentration reflect effects from sub-critical boiling, super-critical phase separation, and segregation of the resulting vapor and brine phases. The high salinity fluids contain elevated Cl, Na, Ca, and K, while volatiles (e.g.,  $H_2S$ ) are enriched in the vapor phase. Finally, in most cases, hydrothermal processes represent a sink for seawater alkalinity. The exceptions are the sediment-covered sites, where reactions of the fluids with sediments result in solutions with alkalinity and pH near those of seawater.

Species that are very highly enriched in hydrothermal fluids relative to seawater include Li, an example of the alkali metals;  $SiO_2$ , enriched due to the equilibration of hydrothermal fluids with quartz at high temperature and pressure; Mn and Fe, leached from rocks by the high temperature, high pressure, slightly acidic hydrothermal fluids.

Fluxes into and out of the oceans due to hydrothermal activity were summarized by the RIDGE/VENTS Workshop of September, 1994 (Kadko et al., 1994) (Figure 9). Concentration ranges derived from a large data set were used. Two values of the heat flux were used: a low-end estimate equivalent to the latent heat of crystallization of the magma ( $6.8 \times 10^{18}$  cal/yr); and a high end that adds to this value the heat of cooling to  $350^\circ C$  ( $11.5 \times 10^{18}$  cal/yr). This range of heat fluxes gives a range of  $V_{sw}$  of  $1.8$ - $4.9 \times 10^{16}$  g/yr. Two elements appear to be lost from the oceans at rates exceeding 20% of the riverine flux to the oceans: Mg and S. The elements added to the

oceans in significant quantity by axial hydrothermal activity are the alkali metals (except Na), for which the fluxes may exceed riverine fluxes. Mn and Fe are also added in significant amounts; as we will see later, these elements (especially Fe) oxidize in seawater and fall out into the sediments near the ridge system. As they oxidize, they can affect other elements: for instance, P, As, V, and rare earth elements are removed by sorption onto the newly precipitated oxide particles.

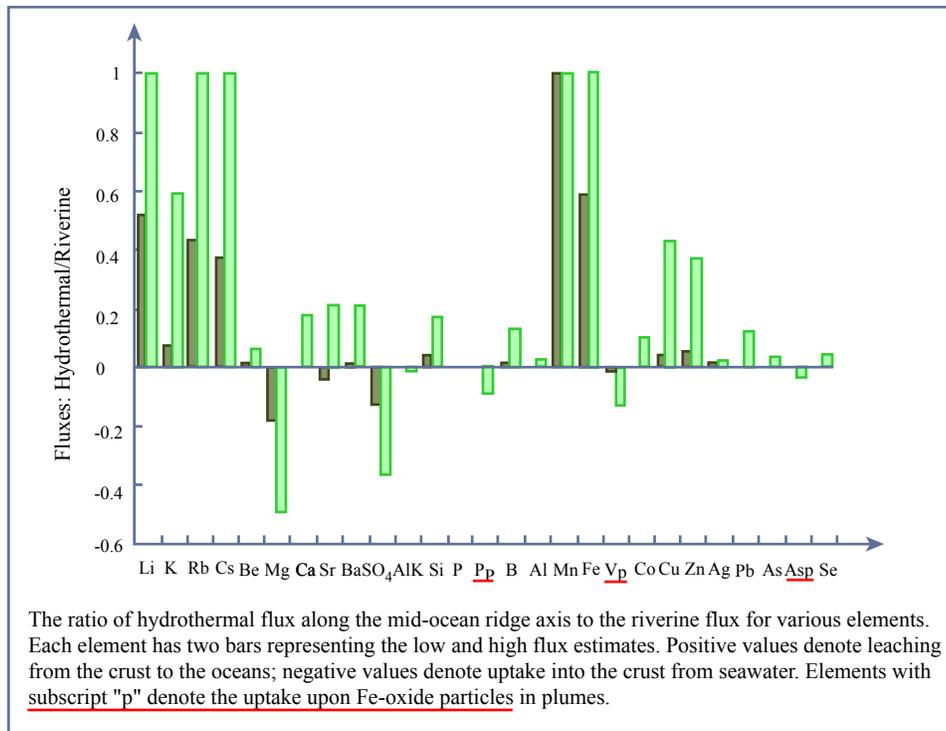


Figure by MIT OCW.

Figure 9

#### IV.3 Fluxes on the Ridge Flanks

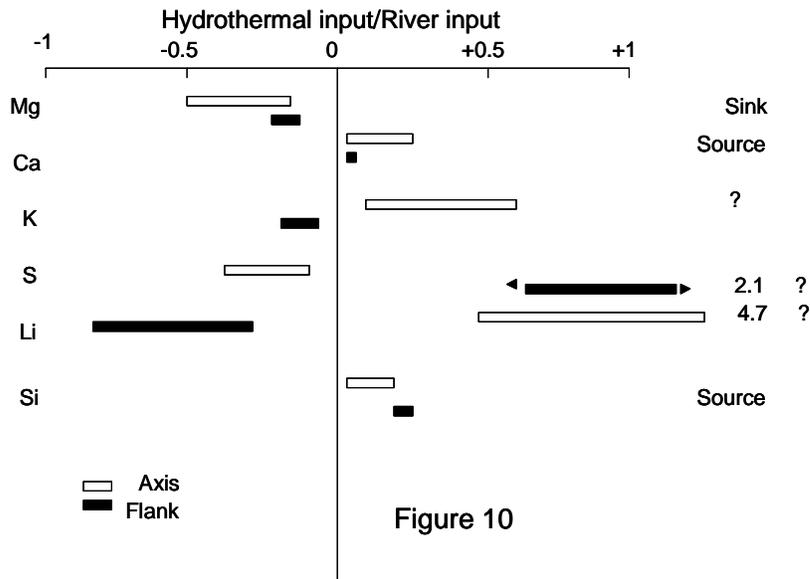
Most of the heat carried from crust to ocean by hydrothermal activity is lost, not from the ridge axis, but from the older crust on the ridge flanks. Circulation in these areas is relatively shallow, and the water is not heated to high temperatures. Because more heat is carried by the circulation than at the ridge axis, and the water is not as hot, the volume of water involved is much greater than on the axis. Therefore, significant fluxes to and from the oceans would require only small concentration changes in the circulating seawater; this fact, and the diffuse nature of the discharge, make it impossible to evaluate fluxes by measuring concentration changes in the circulating seawater. Instead, fluxes are estimated by comparing the concentrations of elements of interest in altered basalts and basaltic glass to their concentrations in fresh rock. For example (Table below), Hart and Staudigel measured enrichment factors for several alkali metals in

altered, compared to unaltered, basalts. When they combined these data with an estimate of the rate of alteration of basalt by low-temperature hydrothermal activity, they found that low temperature alteration was a significant sink from the ocean for these elements.

Upper crust alkali fluxes (after Hart and Staudigel, 1982)

	K (μg/g)	Rb (μg/g)	Cs (μg/g)
418A whole rocks	2666	4.995	0.1125
418A smectites/palagonites	<b>7955</b>	<b>22.20</b>	<b>0.387</b>
Average, 75% WR, 25% sm/pg	3990	9.3	0.18
Average unaltered basalt [24]	1064	1.02	0.0131
Net addition to upper crust	2925	8.30	0.167
Flux into upper 600 m (g/yr) SINK	$1.5 \times 10^{13}$ *	$4.2 \times 10^{10}$	$8.6 \times 10^8$
River flux (g/yr) SOURCE	$7.4 \times 10^{13}$	$3.5 \times 10^{10}$	$6.4 \times 10^8$

\*calculated assuming crustal production rate =  $5.6 \times 10^{16}$  g/yr  
 crustal thickness = 6.4 km, depth of alteration = 0.6 km  
 $2925 \times 10^{-6}$  g/g  $\times [(0.6/6.4) \times 5.6 \times 10^{16}$  g/yr] =  $1.5 \times 10^{13}$  g/yr



A few results showing the influence of low temperature processes on oceanic budgets are shown in Figure 10. The most striking result is that the large fluxes of the alkali metals occurring at the ridge axis, which are due to high temperature reactions deep in the crust, are essentially neutralized by consumption of the elements during low temperature alteration on the ridge flanks (see Li and K in Figure 10). A similar situation appears for sulfur: S is lost largely as a result of precipitation of anhydrite; this anhydrite redissolves as the crust is cooled. The amount of S returned to the ocean in this way is uncertain, but it surely reduces significantly the loss of S from

the oceans due to hydrothermal activity. In the cases of Mg, Ca, and Si, the low temperature reactions add to the fluxes due to high-temperature reactions, thus fluxes on the ridge flanks add to axial fluxes.

**Suggested References:**

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