

Lecture 13 - Hydrothermal Processes

(1) The rate of removal of dissolved Mn from seawater to deep-sea sediments is an order of magnitude greater than the rate of supply of dissolved Mn from rivers. Which of these two rates would give the shorter residence time? What additional source of Mn could supply the shortfall between the rivers source and the sediment sink?

The greater the input or output rate the shorter the residence time, thus using the removal rate of Mn which is greater than the river input will result in shorter residence time. Hydrothermal input of Mn is the source needed to balance the output.

(2) Cycling of fluids at hydrothermal vents removes which of the following components from seawater:

- (a) sulfate and magnesium
- (b) silicon and sodium
- (c) nitrate and chlorine
- (d) iron and manganese
- (e) nutrients
- (f) magnesium and barium

What characterizes hydrothermal vent fluids?

- Mn = 0
- Mg = 0
- alkaline
- enrichment of ^4H
- enrichment of primordial ^3He

Please complete:

(3) At hydrothermal vents in the mid oceanic ridges seawater percolates into the oceanic crust. As it descends calcium sulfate precipitates. At deeper levels the seawater reacts with hot basalt to produce mineral precipitates of magnesium silicates, quartz and pyrite. These reactions result in seawater being an important sink for sulfate and magnesium. A hot fluid with low pH that is rich in metals such as iron, manganese, cobalt, and zinc, as well as in other elements leached from the basalt such as calcium, barium, lithium, and silica rises back towards the ocean floor. In some vent systems these fluids encounter cold seawater and sulfide minerals precipitate enroute, other minerals such as anhydrite, and barite precipitate in chimneys as these fluids contact and mix with seawater. These vents are rich in the following gases CO_2 , H_2S , and ^3He some of which support unique communities of chemosynthetic organisms. Some of the metal in the emerging fluids get oxidized in seawater and precipitate as metal-oxides in the vicinity. The vent activity and deepwater flow around the vents could be traced by the primordial ^3He anomaly in seawater.

(4) Using your knowledge of the Mg mass balance in the ocean and assuming that uptake in hydrothermal processes is the only sink for Mg can you calculate how long will it take for all the water in the oceans to pass through the vents (residence time of the water with respect to the vents)? Is this an upper or lower limit?

Mg river input flux is 5.7×10^{12} moles/year and the oceanic concentration is 53×10^{-3} moles/kg. The mass of seawater is 1.37×10^{21} kg.

Total Mg in seawater is 7.26×10^{19} moles. If we need to remove is 5.7×10^{12} moles/year for mass balance and assuming Mg is removed completely from seawater at the vents it would take $7.26 \times 10^{19} / 5.7 \times 10^{12} = 12.7$ Ma to recycle all the seawater through hydrothermal vents note that this is much longer than the residence time of water with respect to river input.

This is probably a lower limit because there are other sinks for Mg thus only part of the 5.7×10^{12} moles/year of Mg are actually removed at the vents.

(5) An accurate estimate of elemental fluxes through hydrothermal vent systems is essential to determine the oceanic mass balance for many elements. Using He-3 as a tracer for the axial hydrothermal heat flux we know that the amount of heat produced at a typical vent is 36×10^8 cal/cm²; about 3×10^{10} cm²/yr of new crust is made each year.

- Using these data, calculate the heat flux out of hydrothermal vents, assuming that 35% of the heat is lost by convection and the remainder by conduction.
- Calculate the global water flux out of vent sites. Remember that the heat capacity of water is 1 cal/g/°C. Now calculate the cycling rate of seawater through vents.
- What additional information is needed to calculate the chemical fluxes? Calculate the flux of Mg and Mn from hydrothermal vents. [Mg] sw = 53 mmol/kg and [Mg] vent fluid = 0; [Mn] sw = 0.002 μmol/kg and [Mn] vent fluid = 610 μmol/kg
- How will this additional flux affect the mass balance and residence time for Mn and Mg in seawater? is this an important source/sink? would it effect oceanic distribution of these elements?

Heat flux = $(36 \times 10^8 \text{ cal/cm}^2)(0.35)(3 \times 10^{10} \text{ cm}^2/\text{yr}) = 37 \times 10^{18}$ cal/yr (the actual range is 35-45 since the fraction lost to convection is 0.32-0.42)

Water flux = $(37 \times 10^{18} \text{ cal/yr}) / (1000 \text{ cal /kg/}^\circ\text{C}) / 350^\circ\text{C} = 1.08 \times 10^{14}$ kg/yr

Cycling rate of seawater: 1.37×10^{21} kg of seawater / 1.08×10^{14} kg /yr = 12.7 Ma

To calculate the chemical fluxes we need to compare the concentration of the vent fluid with seawater in addition to the water flux through the vents

- flux for Mg = $(1.08 \times 10^{14} \text{ kg/yr})(-53 \times 10^{-3} \text{ mol/kg}) = -5.7 \times 10^{12} \text{ mol Mg/yr}$
since $[\text{Mg}]_{\text{sw}} = 53 \text{ mmol/kg}$ and $[\text{Mg}]_{\text{vent fluid}} = 0$; the change is $-53 \times 10^{-3} \text{ mol/kg}$.
Note that this is a negative flux so it's a sink for Mg.
- flux for Mn = $(1.08 \times 10^{14} \text{ kg/yr})(610 \times 10^{-6} \text{ mol/kg}) = 6.6 \times 10^{10} \text{ mol Mn/yr}$
since $[\text{Mn}]_{\text{sw}} = 0.002 \text{ } \mu\text{mol/kg}$ and $[\text{Mn}]_{\text{vent fluid}} = 610 \text{ } \mu\text{mol/kg}$
- This is a significant and important flux for Mg and is roughly equal to the source for Mg, which is rivers. This results does not change the residence time of Mg but resolves the mass balance problem ("missing sink").

for Mn = $6.6 \times 10^{10} \text{ mol Mn /yr}$ is a significant source of Mn to the ocean compared to the other sources. BUT, since Mn^{+2} produced at the vents is reduced, it is thermodynamically unstable and would be expected to be oxidized in seawater relatively quickly and form Mn oxide particles that fall out of solution. Thus Mn produced at vents would not be expected to alter the $[\text{Mn}]$ in the ocean significantly. At and near vent sites metalliferous sediments are enriched in Mn and other metals (Fe, V, Zn, Cu, Ni, Co, etc.)

(6) Hydrothermal vents have been sampled at 21°N along the East Pacific Rise.

a) When the thermometer was placed into the hot fluids of a black smoker, it melted the thermocouple housing; how could they determine the temperature a different way? What is the approximate temperature of the end member hydrothermal fluids?

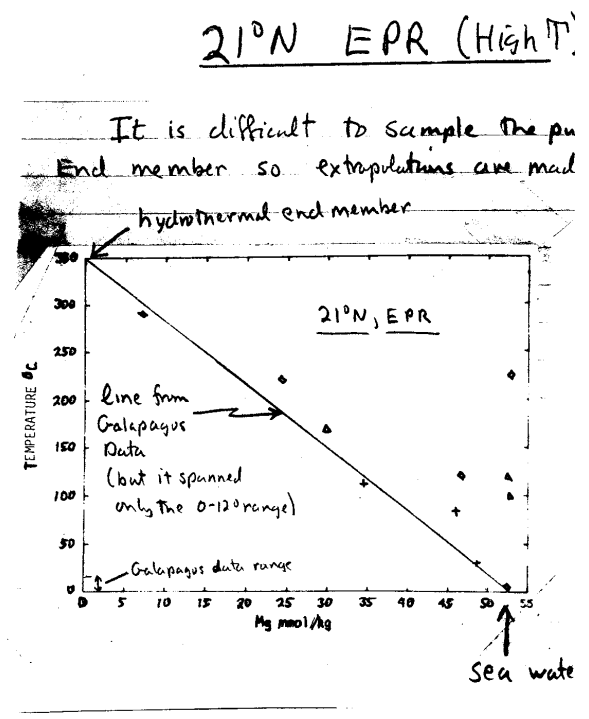
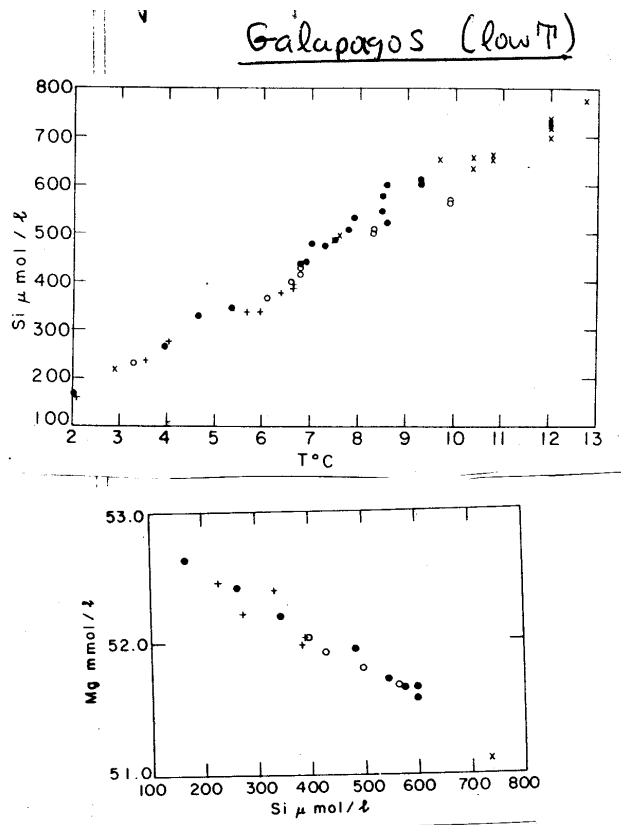
b) Describe the ways in which vent solution differs from average seawater and the chemical changes that occur as a result of seawater/hot basalt interactions.

There are several lines of evidence to constrain the vent temperature the simple one is constructing a mixing line for Mg versus temperature and extrapolating to zero Mg the approximate temperature of the end member hydrothermal fluids is 350°C. Other constraints include lab experiments at high pressure and temperature and determining the temperature at which quartz is soluble at the appropriate pressure.

Vent solution have a lower pH than seawater, higher temperatures and are low in Mg and SO_4 , relative to seawater a few other elements such as Se, F, U, Cd also have lower than seawater concentrations in vent fluids oxygen and nitrate are also consumed by hydrothermal activity. On the other hand these fluids are rich in Li, K, Rb, Ca, Ba, Si Fe Mn and other metals as well as methane, CO_2 , H_2S and ^3He .

(7) The following relation between vent fluid temperature and Si and Mg and Si have been observed in hydrothermal fluids. Are the hydrothermal reactions at the ridges a source or a sink for Si and Mg? Can you give a more quantitative estimate for the magnitude of this source/sink?

The vents are a source for Si and a sink for Mg. When plotting Si vs. Mg and extrapolating to zero Mg we get an end member Si of $\sim 20 \text{ mmol/kg}$. The flux is therefore: $1.08 \times 10^{14} \text{ kg/yr} \times 20 \text{ mmol/kg} = 2.16 \times 10^{12} \text{ moles/yr}$.



(8) John Edmond calculated that the K flux to the ocean from hydrothermal vents is about 1.25×10^{12} mol/yr, the K concentration in basalt is 1160 ppm can you use this information to estimate the Rb flux from the vents the Rb concentration in basalts is 1.11 ppm. What are you assuming in your calculation? Can you justify this assumption? Could you use the same argument to estimate the Ba flux? Can you suggest a way to prove your point?

Assuming that Rb and K are leached from basalt in proportion to their concentration in the rock because they are chemically similar elements (same column in the periodic table) we can calculate the Rb flux as follows: $1.11 \times 1.25 \times 10^{12} / 1160 = 1.2 \times 10^9$ mol/yr. We cannot use the same argument for Ba because it is not an element that would behave like Rb and K. To prove this we can plot the Ba to K fluxes relative to their concentration in basalt and see if the flux is indeed a function of the basalt concentration only.

(9) Give at least two methods that were used or could be used to estimate the end member temperature of vent fluids.

Si solubility, high pressure experiments, mineral assemblages, oxygen 18 data, phase separation of Cl, extrapolation of Mg or other conservative upon mixing elements and temperature measurements in black smokers.