Interaction between seawater and oceanic basement is important for:

1. Heat removal from the solid Earth
2. Evolution of the oceanic crust:
   changes in mineralogy, chemistry, and physical properties with age
3. Geochemical mass balances
4. Deposition of metalliferous deposits,
   including ferromanganese nodules and crusts and polymetallic sulfides
5. Support of biological communities,
   including both microbes and macrofauna
6. Concentrations and distribution of minor and trace chemical species in the oceans
7. Vertical mixing of mid-depth waters, and possibly deep-ocean circulation itself.
CHEMICAL MASS BALANCE BETWEEN RIVERS AND OCEANS

Mackenzie and Garrels (1966) simplified:

<table>
<thead>
<tr>
<th>Avg. River Water (meq/l)</th>
<th>After removing:</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>SO$_4^-$</td>
</tr>
<tr>
<td>Ca$^{2+}$</td>
<td>0.750</td>
</tr>
<tr>
<td>Mg$^{2+}$</td>
<td>0.342</td>
</tr>
<tr>
<td>SO$_4^-$</td>
<td>0.234</td>
</tr>
<tr>
<td>HCO$_3^-$</td>
<td>0.958</td>
</tr>
<tr>
<td>Na$^+$</td>
<td>0.274</td>
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<tr>
<td>K$^+$</td>
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REMOVING THE RIVER INPUT OF SULFATE AND Ca²⁺, as:

1. CaSO₄ (gypsum or anhydrite)

2. H₂S or Fe-sulfide: by reduction with organic C:

\[
SO_4^{2-} + 2 \text{CH}_2\text{O} = H_2\text{S} + 2 \text{HCO}_3^- \]

\[
\text{Ca}^{2+} + 2 \text{HCO}_3^- = \text{CaCO}_3 + \text{H}_2\text{O} + \text{CO}_2
\]

In both cases there is a mole-for-mole loss of Ca²⁺ with sulfate.
**Chemical Mass Balance Between Rivers and Oceans**

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Conversion of Limestone to Dolomite

2CaCO$_3$ + Mg$^{2+}$ = CaMg(CO$_3$)$_2$ + Ca$^{2+}$

(calcite) dolomite

Precipitation of calcium carbonate (limestone):

Ca$^{2+}$ + 2HCO$_3^-$ = CaCO$_3$ + H$_2$O + CO$_2$

(calcite or aragonite)

Problem:

Dolomite is not common in younger rocks, nor is it forming rapidly anywhere today!
Weathering: e.g., of plagioclase feldspar
(most abundant mineral group in crust):

\[
\text{CaAl}_2\text{Si}_2\text{O}_8 + 3\text{H}_2\text{O} + 2\text{CO}_2 = \text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 + \text{Ca}^{2+} + 2\text{HCO}_3^-
\]

Kaolinite = clay mineral = shale

\[
2\text{NaAlSi}_3\text{O}_8 + 3\text{H}_2\text{O} + 2\text{CO}_2 = \text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 + 2\text{Na}^{2+} + 2\text{HCO}_3^- + 4\text{SiO}_2
\]

Kaolinite = clay mineral = shale

Cation-Al-silicate + \text{H}_2\text{O} + \text{CO}_2 =
clay mineral + cations + 2\text{HCO}_3^- + silica

Reverse Weathering:

Degraded Al-silicate + cations + \text{HCO}_3^- + silica
= cation-Al-silicate + \text{H}_2\text{O} + \text{CO}_2
Cross-section of a fast-spreading mid-ocean ridge (Lister, 1976)
### CHEMICAL MASS BALANCE BETWEEN RIVERS AND OCEANS

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Heat flow on young crust
1) is much lower than predicted
2) is highly scattered
3) eventually reaches the predicted value.

Wolery and Sleep (1976)
The global “heat flow anomaly” through the seafloor results from advective loss of heat by flow of seawater through the oceanic crust, at the ridge axis (~30% of the total) and through the ridge flanks (~70%).
**Sclater et al. (1976)**

**Axis**  
-- magmatic heat source  
-- bare rock seafloor  
-- hot (350°C) springs

**Young flanks**  
-- sediment ponds;  
mostly bare rock  
-- may be reheating

**Older flanks**  
-- mostly sedimented;  
isolated rock outcrops

**Abyssal plains**  
-- continuous thick (>160 m) sediment  
-- continued circulation but no exchange
3 sources of data on basalt-seawater interaction

1. Laboratory experiments
2. Solutions from natural systems
3. Solid products:
   -- altered rocks
   -- chemical precipitates
MOR hot (350°C) springs, discovered in 1979, were immediately christened “black smoker chimneys”.

Both the smoke and the chimneys are composed of polymetallic sulfide minerals, chiefly pyrrhotite (FeS), pyrite (FeS$_2$), chalcopyrite (CuFeS$_2$), chalcocyprite (CuFeS$_2$) and sphalerite or wurtzite (ZnS).
On heating, seawater precipitates $\text{CaSO}_4$ (anhydrite) and then $\text{Mg-OH-SO}_4$ (caminite).

Heated seawater is **self-acidifying**.

When rock is added, Mg-OH-silicate is precipitated instead!


---

**Fig. 1.** pH and molality of Mg, Ca, and SO$_4$ in Point Hueneme seawater from 25$^\circ$ to 350$^\circ$C at 500 bars.
Water-Rock Reaction

As seawater penetrates young, hot oceanic crust, the entire chemical system is initially wildly out of equilibrium. The primary igneous phases are unstable and tend to dissolve. Reaction ensues, the primary rock recrystallizes to a secondary (alteration) mineral assemblage, and the aqueous solution tends toward equilibrium with this secondary assemblage.

The degree of equilibration achieved depends on:
1. the reaction rate for: a) primary phases (dissolution) 
   b) secondary (alteration) phases
2. the flow rate of the solution through the system.
Seawater Mg\textsuperscript{2+} is lost to the altered rock.

- Open symbols = basaltic glass
- Closed symbols = diabase (~coarsely crystalline basalt)
Basalt-Seawater reaction at 200-400°C:

1) Rapid exchange of Mg$^{2+}$ for Ca$^{2+}$

2) Slower exchange of Na$^{+}$ for Ca$^{2+}$

3) Half of Ca$^{2+}$ leached precipitates as CaSO$_4$ (anhydrite), removing sulfate.

Seawater is converted to a Na-Ca-K-Cl solution.

Mottl and Holland (1978, GCA)
Typical seafloor hot springs fall in the supercritical field, at least for P if not T.

Where magmatic activity is present at shallow levels (Low P) the supercritical solution can separate into vapor and brine phases.

This phase separation will look more like condensation of a brine phase than boiling.

Where separation has occurred, individual vents tend to emit either vapor or brine for periods of months to years.

System NaCl-H2O at 350-600°C
Chemical changes: **hot spring waters** relative to **seawater**:

Mg is almost completely taken up by the rock. Ca, K, Si, Fe, Mn, and CO$_2$ are leached from the rock. Na and chloride can go either way.

Sulfate is precipitated as anhydrite (CaSO$_4$) and reduced to H$_2$S by reaction with Fe$^{2+}$.

Seawater is converted to a Na-K-Ca-Cl solution that is saturated with quartz (SiO$_2$) and Fe-sulfide minerals.

**Warm springs** along mid-ocean ridge flanks:

Major element changes are similar to those above, but generally less extreme. Few have been discovered and sampled.
Seawater vs. Hot Springs

• Seawater:
  --cold (2°C)
  --alkaline (pH ~8)
  --oxidizing
  --sulfate-rich
  --metal deficient
  --Mg-rich

• Hot Springs:
  --hot (350°C)
  --acid (pH ~4)
  --reducing
  --H₂S-rich
  --metal-rich
  --Mg-free
Solution to the mass balance problem?

• Qualitatively, yes: trade Mg for Ca (as in dolomitization) and precipitate Ca along with excess bicarbonate alkalinity as CaCO$_3$.

• Quantitatively: let’s see!

( Remember, this is where both dolomitization and reverse weathering appeared to fail.)
Concentrations of K, Rb, Cs, B, and Ba depend on the water/rock ratio. At a mass ratio of 1:1, altered rock will gain 0.2 wt.% Mg, which constrains the amount of crust that must be altered to dispose of the river input of Mg.
“Magmatic heat”: latent heat vs. heat of cooling

Latent heat (676 J/g) 8.7 1.15
Heat of cooling to 350°C 12.7 1.68
Heat of cooling to 0°C 5.3 0.71
TOTAL: 26.7 3.54

vs. total advective anomaly 74.6 9.9

Magmatic heat supplies 1/3 of advected heat.
ADVECTIVE HEAT LOSS AT THE AXIS

Alteration and Mg uptake for \( w/r = 1 \)

- % of crust altered
- % of river Mg taken up

% vs. \( 10^{18} \) cal/y
Conclusions

• Reaction of seawater with basalt at high $T$ along the MOR axis is qualitatively adequate to complete mass balances, but quantitatively can account for at most 40% of the river input of Mg.

• Whether reaction along MOR flanks can solve the Mg problem is still an open question.