Seafloor eruption and hydrothermal fluid chemistry

Tina Lin
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Components/processes involved in generating reduced fluid

- Initial fluid (e.g., seawater)
- Mixing of two fluids - chemical rxns - mineral precipitation/dissolution
- Modified fluid
- Porous media composition (e.g., basalt, peridotite, andesite, rhyolite, dacite ± sediment) and structure
- Volcanic eruption-heat source
  (temperature-pressure of fluid-rock interaction; geometry of heat source)

Tivey (2007)
Outline

• What can chemical compositions of fluids tell us?

• Sampling methods

• Generic hydrothermal vent system
  • Generic answers to the question → eruption event

• Data interpretation
  • Mixing curve
  • Time series → changes after eruption
  • Phase separation

• Future study

What can chemical compositions of fluids tell us?

• Sample quality

• Elemental cycle
  • Major sink
  • Major source

• Biology
  • Nutrients
  • Chemical energy
  • pH

• Geology
  • Water-rock ratio
  • Reaction temperature
  • Reaction depth
Fluid sampling-1

CTD- Rosette
Niskin/Go-Flo water sampler

Fluid sampling-2

UH-GeoMicrobe Sled
"long-term monitoring"

UH-MPS system
"Large volume fluid & particle sampling"
Fluid sampling-3

<table>
<thead>
<tr>
<th>MBARY-&quot;OSMO&quot;</th>
<th>PMEL-&quot;Beast&quot;</th>
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</thead>
<tbody>
<tr>
<td>Long term, very small volume fluid</td>
<td>~300mL fluid and particle sampling</td>
</tr>
</tbody>
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http://www.pmel.noaa.gov/vents/nemo2006/logbook/images/sep04img2.html

Fluid sampling-4

- Ti Major
- Gas tight sampler

http://oceanexplorer.noaa.gov/explorations/05lostcity/background/sampling/media/gastights3.html
Hydrothermal vents → plumes

- [http://www.divediscover.whoi.edu/vents/vent-chemistry.html](http://www.divediscover.whoi.edu/vents/vent-chemistry.html)
What can chemical compositions tell?

- $[\text{Mg}^{2+}] \rightarrow$ sample integrity
- $[\text{Cl}^-] \rightarrow$ phase separation $\rightarrow$ reaction depth
- $[\text{SO}_4^{2+}] \rightarrow$ biological activity (sulfate reduction) & mineral precipitation
- $[\text{H}_2\text{S}] \rightarrow$ biological activity (sulfate reduction)
- $[\text{NH}_3] \rightarrow$ biological activity (sulfate reduction)
- $[\text{Fe}^{2+}], [\text{Mn}^{2+}], [\text{Si}], [\text{Li}^+] \rightarrow$ water/rock reaction
- $[\text{Li}^+] \rightarrow$ water-rock ratio

Redox status

- Reduction-Oxidation state

<table>
<thead>
<tr>
<th></th>
<th>Reduced species (e-donors)</th>
<th>Oxidized species (e-acceptors)</th>
</tr>
</thead>
<tbody>
<tr>
<td># Electron</td>
<td>Rich</td>
<td>Depleted</td>
</tr>
<tr>
<td>S</td>
<td>$\text{H}_2\text{S}$</td>
<td>$\text{SO}_4^{2-}$</td>
</tr>
<tr>
<td>C</td>
<td>$\text{CH}_4$</td>
<td>$\text{CO}_2$</td>
</tr>
<tr>
<td>N</td>
<td>$\text{NH}_3$</td>
<td>$\text{NO}_3^-$</td>
</tr>
<tr>
<td>Fe</td>
<td>$\text{Fe}^{2+}$</td>
<td>$\text{Fe}^{3+}$: Fe-oxide, brownish particles</td>
</tr>
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</table>
Mixing curve

- **End member, Mg=0 mM**
- **Additional source**
- **Conservative mixing**
- **Extra removal**

Element/Compound vs. Mg

**SO₄²⁻ v.s. Mg²⁺**

- Straight line – conservative mixing line
- Data **above** the line \( \rightarrow \) **addition** of \( SO₄²⁻ \)
- Oxidation of sulfide to form sulfate
- Dissolution of sulfate bearing mineral
**H₂S v.s. Mg²⁺**

- Straight line – conservative mixing line
- Data below the line → removal of H₂S
  - Oxidation of sulfide
  - Precipitation of sulfide bearing mineral

**Element/Heat**

- Heat is calculated as

\[
H(J) = C(J/Kg/°C) \cdot M(Kg) \cdot \Delta T(°C) = 4200(J/Kg/°C) \cdot M(Kg) \cdot \Delta T(°C)
\]

Butterfield (1997)
Cl⁻ v.s. Mg²⁺

- Flow and Floc vents (low T diffuse)
- Source vents (high T)

Butterfield (1997)

Phase separation

- T, P below critical point (407°C, 298 bars)
  - Sub-critical
  - Boil of H₂O
  - Form low [Cl] vapor

- T, P above critical point
  - Super-critical
  - Condensation of H₂O
  - Form high [Cl] brine

Larson et al. (2009)
Vapor dominate → brine dominate

- Endeavor Main Field
- N. Cleft segment
- Co-Axial

![Graph showing relative intensity over time for various elements including brine, decay, vapour, event, time, heat flux, Cl, Fe, H₂S.

Butterfield (1997)

[Cl⁻] v.s. time after eruption

![Graphs showing [Cl⁻] over time, critical temperature, and critical pressure over time.

Von Damm (2004)
East Pacific Rise: 9°50’N

Von Damm (2004)

Larson et al. (2009)
Future study

• Precisely/accurately measure the flux → heat budget

• Look for “finger-print” signature b.w. vents and plumes

• Compare the fluid data with the “precipitates”

• Time-series sampling at various sites to test the phase separation hypothesis.