Alkaline Seafloor Hydrothermal Systems: Experimental Simulation of CO$_2$-Peridotite-Seawater Reactions

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Alkaline Seafloor Hydrothermal Systems

Lost City Field (Kelley et al., 2001) is a prime example

- 15km off axis
- 1.5 Ma oceanic crust
Lost City Field

- Carbonate vent chimneys
- Fluids vented at 40°-75°C, pH 9.0 to 9.8
- “driven by heat of exothermic serpentinization reactions between seawater and mantle rocks”

(Kelley et al., 2001)
Today’s Talk

Could alkalinity of these systems be explained by peridotite-seawater reaction in the presence of (magmatic) CO$_2$?

Could these hydrothermal systems serve as analogues for geologic carbon sequestration in oceanic crust?

Experimental perspective of CO$_2$-peridotite-seawater reactions

- Published experimental studies as baseline
- Aqueous geochemical effects
- Mineralogic and petrologic effects
Experimental Approach

- Rocking autoclave with flexible cell hydrothermal apparatus
- 300°C and 500 bars
- Rock = Lherzolite
- Fluid = Synthetic Seawater
- Brine:Rock ≅ 10:1
- Experiment procedure
  - Brine + rock for 38 hours
  - Inject 2 mol% CO₂ into ongoing reaction, react additional 530 hours
Experimental Apparatus

Operating Conditions:
500 bars (7350 psi) @ 300°C

Maximum Conditions:
565 bars (8200 psi) @ 425°C
Experimental Approach

- Supercritical CO$_2$ fluid
- Seawater Solution
- Peridotite Minerals
- Valve
Peridotite

- dunite
- harzburgite
- lherzolite
- olivine orthopyroxenite
- olivine clinopyroxenite
- orthopyroxenite
- olivine websterite
- clinopyroxenite
- websterite
## Mineral Compositions

<table>
<thead>
<tr>
<th>Phase</th>
<th>Mass %</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Olivine</td>
<td>71.4%</td>
<td>Forsterite 89%, Fayalite 11%</td>
</tr>
<tr>
<td>Enstatite</td>
<td>18.4%</td>
<td>wollasonite 4%, Enstatite 77%, Ferrosilite 19%</td>
</tr>
<tr>
<td>Diopside</td>
<td>10.2%</td>
<td>wollasonite 52%, Enstatite 45%, Ferrosilite 3%</td>
</tr>
</tbody>
</table>

*All compositional values represent the mean of five separate analyses*
Powdered Peridotite as Reactant
Mineral Reactants (Fragments)

Olivine

Enstatite
Reaction Textures (Dissolution/Precipitation)

Olivine

Enstatite
Reaction Textures (Dissolution)
Euhedral Magnesite Precipitation
Euhedral Anhydrite Precipitation
Aqueous Fluid Chemistry – pH

- Measured pH
- Calculated in-situ pH
- Inject CO₂
Conclusions

1. Talc, not serpentine, is principal alteration product
2. Magnesite crystallizes
3. Anhydrite crystallizes (and dissolves)
4. Did not “match” pH observed at Lost City
   a) More CO₂ (to generate alkalinity) in experiment?
5. Ongoing calculations to understand this experiment and plan the next suite
   a) Alkalinity
   b) Mg vs SiO₂ activity (why talc?)
   c) Mass balance & sequestering reactions
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Experimental Simulation of Alkaline Seafloor Hydrothermal Systems

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Flow of seawater through hydrothermal systems exhibiting "black smoker" chimneys has previously been shown to alter peridotite to serpentinite (Janecky and Seyfried 1986). The Lost City hydrothermal field (Kelley et al. 2001) shows that certain seafloor hydrothermal systems can also vent alkaline fluids from "white smokers." Experiments were conducted in a flexible cell hydrothermal apparatus on seawater-lherzolite-CO2 systems to simulate alkaline hydrothermal systems and determine the extent of brine-rock reaction. The synthetic lherzolite was comprised of 71.4% forsteritic olivine, 18.4% diopside, and 10.2% enstatite. The lherzolite was reacted at 300°C and 500 bar in a synthetic seawater solution with an ionic strength of 0.69 to approach steady state, then injected with supercritical CO2 and reacted for ~550 hours.

Brine-rock reaction decreases pH from 7.4 to ~5, consumes ~50 mMol of aqueous magnesium and nearly all of the aqueous sodium and potassium. Approximately 2 to 4 mol percent CO2 was injected into these experiments after achieving brine-rock equilibrium. Calcium concentrations decrease (~1 to 2 mMol) following CO2 injection, whereas magnesium concentrations rebound (~1 mMol), as do the silica concentrations (3 to 7 mMol), both likely a result of increased brine acidity. Significant dissolution of olivine and pyroxenes occurred, as shown by surface pits and etching. The powdered solid reactants have been extensively serpentinitized, and mineral fragments developed serpentine overgrowths. Needle-like laths of calcium sulfate and rhombs of magnesium carbonate were extensively precipitated on the reactants and the inner surfaces of the reaction cell. The experiments experienced a gradual pressure decrease following CO2 injection (27 bars); this pressure decrease is a result of dissolution and mineralization of CO2.

These reactions provide initial constraints as to the extent and rate of reactions occurring in alkaline hydrothermal systems. Additionally, the extensive formation of magnesium carbonate minerals indicates that direct injection of carbon dioxide into magnesium silicate rich terranes, as such peridotite hosted hydrothermal systems may be a viable means of sequestering anthropogenic CO2.

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Input received from discussions and Q&A

1) Immiscible CO$_2$ phase as ultimate source for alkalinity is novel hypothesis but requires much work

2) Heat of serpentinization hypothesis for alkaline vents is contentious

3) A 3$^{rd}$ hypothesis for source of alkalinity: seawater reacts with gabbros at depth to generate Ca(OH)$_2$(aq), which generates both carbonates and alkalinity with release to ocean floor
Extra Slides
Quantitative X-Ray Analysis:
-Reaction Products

- Talc
- Magnesite
- Anhydrite
- Lizardite

%H of products

% of products
Change in Pressure after Injection of CO$_2$
Relevance for Other Geologic Environments?

Temperature (C)

Pressure (MPa)

Depth (km)

CO₂ critical point

Diagenesis Begins

Metamorphism Begins

Carbonate Veins

H₂O critical point

Deep Saline Aquifers

Decarbonation Reactions

Deep Natural Gas Resources

CO₂-H₂O Saddle Point

XCO₂ = 20%

XCO₂ = 5%

20°C/km

60°C/km

after Kaszuba et al., 2006